Chapter 26

VANADIUM

The wide distribution of vanadium throughout the earth's crust has been clearly established, not only in ores and coals but in clays, limestones, sandstones, and igneous rocks.[1] Vanadium occurs in appreciable amounts in the more basic igneous and metamorphic rocks, up to 0.08 per cent or more of V_2O_3, but it seems to be absent or nearly so from the highly siliceous rocks. Some of their ferric aluminous silicate constituents carry still higher percentages—up to 0.13 per cent V_2O_3 in a biotite separated from a pyroxenic gneiss. Hence the quantitative search for vanadium will usually be limited to rocks with less than 60 per cent of silica. The search for it even then will perhaps not often warrant the necessary expenditure of time, but in this connection it should be remembered that neglect to determine it introduces an error in the figures for alumina, and for both ferrous and ferric oxides, which in extreme cases may be of considerable moment in the last two cases.

The relation of vanadium to the ferric aluminous silicates of rocks, taken in connection with the existence of the mineral roscoelite, classed as a vanadium mica, indicates that the vanadium corresponds in condition to aluminum and ferric iron, and that it is to be regarded as replacing one or both of these elements. Hence in these cases it should be reported as V_2O_3 and not V_2O_5.

What its condition may be in matter of secondary origin, like clays, limestones, sandstones, coals, and ores of iron, is yet open to discussion. It was the opinion of one of us (W.F.H.) at one time that it should be regarded as in the pentavalent state (V_2O_5), but work on certain remarkable vanadiferous sandstones[2] of Western Colorado, in which it unquestionably occurs as trivalent vanadium (V_2O_3), led to a decided unsettling of this view.

I. GENERAL CONSIDERATIONS

In analyses of rocks by the usual method, vanadium is reduced to the quadrivalent state during the removal of silica by repeated evaporation with hydrochloric acid. Practically all of the small amount of vanadium in rocks will be found in the ammonia precipitate when R_2O_3 is high, with Fe_2O_3 preponderating. When Al_2O_3 preponderates, the precipitation is less complete. When the precipitate is ignited, the vanadium is oxidized to the quinquevalent state and therefore weighed as V_2O_5. If vanadium is not removed before the determination of iron by volumetric methods, its effect will depend on the method of reduction. Hydrogen sulfide, sulfur dioxide, and stannous chloride all reduce it to the quadrivalent stage in which 1 mg $V_2O_5 = 0.878$ mg Fe_2O_3. Zinc reduces the element to the bivalent stage in which 1 mg $V_2O_5 = 2.63$ mg Fe_2O_3. It is evident that, if vanadium is ignored, plus errors for both iron and aluminum will result when reduction to the quadrivalent compound takes place, whereas high results for iron and low results for aluminum will ensue when reduction goes to the bivalent stage. Bivalent vanadium is so unstable under the conditions that usually obtain that its effect in the determination of iron cannot be calculated unless the reduced solution has been caught in an excess of ferric sulfate. In addition to the effects already noted, vanadium interferes in the colorimetric determination of titanium and in the determination of phosphorus.

II. ATTACK OF VANADIUM MINERALS

The complete analysis of vanadium minerals is best made by working with several portions of material, the different analyses being combined as convenient.

Most vanadium minerals readily yield to acids, an initial treatment with hydrochloric acid followed by nitric acid usually sufficing to give complete extraction of vanadium. For complete decomposition of the ore, any insoluble residue is fused with sodium carbonate, dissolved in hydrochloric acid, and added to the main solution. If silica is not to be determined, the insoluble matter can be digested with hydrofluoric acid and the latter then eliminated by evaporation with sulfuric acid or by repeated evaporation with the acid that is desired. The customary treatment with hydrofluoric and sulfuric acids, followed by evaporation and ignition to remove silica, is not desirable with residues bearing vanadium, for there is danger of forming volatile fluorides or oxyfluorides of vanadium at red heat.

Vanadium minerals also respond readily to fusion with sodium or potassium carbonate or sodium peroxide. When the carbonates are used, it is desirable to add a little niter; if sodium peroxide is used, it is not necessary to heat to complete fusion, the reaction being complete when the mixture sinters together.

Fusion with pyrosulfate is not often employed except for the recovery of small amounts of vanadium in residues obtained in the course of an analysis.

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[1] W. F. Hillebrand, *Am. J. Sci.,* [4] **6,** 209 (1898); *Chem. News,* 78, 216 (1898); *U. S. Geol. Survey Bull.* 700, 184 (1924).

[2] W. F. Hillebrand and F. L. Ransome, *Am. J. Sci.,* [4] **10,** 120 (1900).

With regard to solution methods having to do with the determination of the condition of vanadium, as in roscoelite, one of us (W.F.H.)[3] effected decomposition by heating the air-free powder with dilute sulfuric acid in a tube sealed during the passage of a current of carbon dioxide through it.

It is sometimes stated that losses of vanadium occur when solutions containing the element are heated above 100° C. We have been unable to detect any loss when hydrochloric acid solutions were evaporated to dryness and baked at 175° C, nor when sulfuric acid solutions of quinquevalent or quadrivalent vanadium were heated for 5 hours at the same temperature. That no volatilization occurs is explained by the fact that the volatile chlorides of vanadium are unstable in the presence of moisture.

Small amounts of vanadium, approximating 1 part of vanadium per 1000 parts of tungsten, are carried down by tungstic acid and must be recovered if the tungstic acid precipitate is large.[4]

III. METHODS OF SEPARATION

Most methods for the separation of vanadium can be classed as they serve to gather the element in a precipitate or in a filtrate. Among the former can be mentioned the gathering of vanadium in the ammonia precipitate, in the ammonium phosphomolybdate precipitate, in the residue obtained by evaporation with nitric acid, and in the precipitates produced by mercurous nitrate, lead acetate, or cupferron. The second class include fusions with sodium peroxide or sodium carbonate and niter, followed by extraction with water, and precipitations with sodium hydroxide or with hydrogen sulfide in acid solution. Entirely different methods are such as electrolysis with a mercury cathode, the separation of iron and molybdenum from vanadium by extraction with ether in cold dilute hydrochloric acid solution (1 + 1), and the volatilization of vanadium in a current of dry hydrochloric acid gas.

When by itself, vanadium is not precipitated by ammonium hydroxide. Its presence in the ammonia precipitate depends on the formation of insoluble compounds with bases such as iron and aluminum. As complete retention is uncertain and the percentage of vanadium is ordinarily based on its determination in a separate sample, the precipitation of it by ammonium hydroxide is chiefly of interest in that it necessitates precautions in the analysis of the ammonia precipitate.[5]

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[3] *Am. J. Sci.*, 7, 451 (1899).

[4] According to H. H. Willard and P. Young [*Ind. Eng. Chem.*, 20, 764 (1928)], small amounts of vanadium in tungstic acid can be determined colorimetrically as yellow vanadotungstic acid as follows: Dissolve the tungstic acid in 15 ml of a 4 per cent solution of sodium hydroxide, filter if necessary, dilute to 75 to 100 ml, acidify with 5 ml of phosphoric acid (sp. gr. 1.37), and match the color within 1 to 2 hours with that obtained by adding a standard solution of vanadotungstic acid to a like volume of water. Ammonium salts must be absent. The standard solution conveniently contains 0.1 mg of vanadium and 5 mg of tungsten per ml and is prepared by dissolving the required amounts of sodium vanadate and sodium tungstate in water, adding 25 ml of phosphoric acid (sp. gr. 1.37), and diluting to 500 ml.

That ammonium phosphomolybdate precipitates carry down quinquevalent vanadium and become orange or brick red in color has long been known. Cain and Hostetter[6] showed that the precipitation can be made quantitative if the amount of phosphorus is five to ten times that of the vanadium. If, however, vanadium is in the quadrivalent state and precipitation is made at room temperature, none of it comes down with the phosphomolybdate precipitate.[7] Coprecipitation of vanadium with phosphorus gives the same separation from other elements as that of phosphorus alone (p. 696). In a few tests made by us, the separation of 5 mg of quinquevalent vanadium from 100 mg of sexivalent uranium was very satisfactory. To make the separation, prepare the solution as for a precipitation of ammonium phosphomolybdate, add ten times as much phosphorus as there is vanadium present and then a slightly greater excess of ammonium nitrate than usual, render nearly neutral by the addition of ammonium hydroxide, heat to boiling, add the usual excess of molybdate reagent, and shake for a few minutes. Filter, and wash by decantation with a hot (80° C) solution of acid ammonium sulfate (1000 ml of water, 15 ml of ammonium hydroxide, and 25 ml of sulfuric acid).

Evaporation of a nitric acid solution[8] to dryness, followed by extraction with water, filtration, and washing of the residue with a dilute solution of ammonium nitrate, yields a fair separation of vanadium as pyrovanadic acid, $H_4V_2O_7$, together with such elements as iron and aluminum, from others such as alkalies and uranium which are dissolved. The separation is not quantitative,[9] as it is impossible to prevent a little of the vanadium, iron, and aluminum from going into solution, and more or less uranium, especially when phosphorus is present, from staying with vanadium.

Precipitation with mercurous nitrate in a solution containing a slight amount of sodium carbonate was long used[10] for the group separation

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[5] Tests made by H. B. Knowles indicated that 1 mg of either quinquevalent or quadrivalent vanadium is quantitatively held by 100 mg of aluminum. Ten milligrams of vanadium in either valency were not held by this amount of aluminum. Retention by iron was slightly better, 100 mg retaining 10 mg of vanadium quantitatively when in the quinquevalent and almost quantitatively when in the quadrivalent state.

[6] J. R. Cain and J. C. Hostetter, *J. Ind. Eng. Chem.*, 4, 250 (1912); *J. Am. Chem. Soc.*, 43, 2552 (1921).

[7] J. R. Cain and F. H. Tucker, *J. Ind. Eng. Chem.*, 5, 647 (1913).

[8] C. Friedel and E. Cumenge, *Compt. rend.*, 128, 532 (1899).

[9] W. F. Hillebrand and F. L. Ransome, *op. cit.*, 136.

[10] W. F. Hillebrand, *J. Am. Chem. Soc.*, 20, 454 (1898); *U. S. Geol. Survey Bull.* 700, 185.

of the small amounts of vanadium, chromium, molybdenum, tungsten, phosphorus, and arsenic that occur in rocks. The separation is applied after fusion with carbonate and niter as follows: Thoroughly fuse 5 g of the powdered rock with 20 g of sodium carbonate and 3 g of sodium nitrate. Extract the melt with water, reduce manganese with alcohol, and filter. In case fusion was incomplete or much vanadium is present, ignite the residue, repeat the operation, and combine the filtrates. Nearly neutralize with dilute nitric acid (1 + 1), the amount to be used having been determined by a blank test on the amount of fusion mixture employed. Do not overrun neutrality, lest chromium and vanadium be reduced by nitrous acid set free from nitrite produced during fusion. Evaporate until the solution is nearly dry. Dilute with 100 ml of water, warm to dissolve soluble salts, and filter. Evaporate the silica and alumina precipitate with hydrofluoric and sulfuric acids, fuse the residue with sodium carbonate, dissolve the melt in 100 ml of water, again nearly neutralize with nitric acid, boil for a few minutes, filter, and add the filtrate to the main one. Add a nearly neutral solution of mercurous nitrate, drop by drop, to the cold alkaline solution until a further addition causes no precipitation after the precipitate has settled. If this does not occur by the time a fair precipitate has been formed, too much sodium carbonate was left in solution. In this event add dilute nitric acid (1 + 1), drop by drop, until an added drop of mercurous nitrate no longer produces a cloud. Heat to boiling, let settle, filter, and wash moderately with hot water containing a few drops of mercurous nitrate solution. Dry and remove from the paper to obviate possible loss of molybdenum and injury to the crucible by reduction of arsenic. Heat gently in a platinum crucible under a good hood until mercury is expelled, and then ignite at not over 400 to 500° C. Fuse the residue with a little sodium carbonate under oxidizing conditions, extract the melt with water, and test the solution for vanadium as directed in Section IV, bearing in mind that the solution should contain chromium and molybdenum quantitatively and that more or less phosphorus, arsenic, and tungsten may also be present.

Precipitation of vanadium as lead vanadate is but a preliminary separation at best and usually no more than a group separation, for the precipitate cannot be weighed directly, and other elements such as molybdenum, tungsten and sexivalent chromium are also precipitated. As carried out, the vanadium is obtained in alkaline vanadate solution, which is then made faintly acid with nitric acid, treated with a slight excess of lead acetate, heated to boiling, and stirred until the precipitate has coagulated. The precipitate is washed with very dilute acetic acid and dissolved in nitric acid, and lead separated as sulfate after evaporation with sulfuric acid.

Precipitation of quinquevalent vanadium by cupferron (p. 119) furnishes an excellent separation of vanadium from a number of elements, particularly sexivalent uranium, chromium, arsenic, phosphorus, and aluminum.[11] This precipitation can be applied directly to the complete solution of a rock when the amount of vanadium, iron, zirconium, and titanium is small. If the last three are present in large amount, the precipitation can be made in the combined and acidified water extracts of carbonate-niter fusions obtained as in the separation with mercurous nitrate. In the latter case, chromium should be reduced to the trivalent condition by hydrogen peroxide and the excess peroxide removed by boiling.

Fusions with sodium peroxide or sodium carbonate and niter, followed by extraction with water, serve the same purpose: namely, to separate elements such as iron, titanium, and zirconium from vanadium, phosphorus, arsenic, molybdenum, chromium, uranium, and most of any aluminum or silicon. These separations are therefore group separations and ordinarily necessitate further separations. The same is true in the main of precipitations with sodium hydroxide.

The precipitation of uranium as phosphate in alkaline solution furnishes a good separation of uranium from vanadium according to Finn[12] and is done by adding approximately 0.5 g of ammonium phosphate per 0.25 g of U_3O_8 in dilute sulfuric acid solution, heating to boiling, and making alkaline with ammonium hydroxide. After boiling for a few minutes, the solution is filtered, and the precipitate washed with hot water containing a little ammonium sulfate.

Vanadium by itself is not precipitated by hydrogen sulfide in acid solution. It shows, however, a tendency to accompany other members of the group unless tartaric acid is also present.

A very satisfactory method, which should be borne in mind for the separation of various elements from vanadium, consists in electrolysis with a mercury cathode in dilute sulfuric acid solution[13] (p. 138). By this operation, elements such as iron, chromium, cobalt, nickel, copper, and molybdenum are deposited and separated from vanadium and such other elements as uranium, aluminum, and phosphorus. Arsenic is partially volatilized; the remainder stays with the vanadium.

Separation of iron and molybdenum from vanadium by extraction with ether in cold dilute hydrochloric acid solution (p. 134) is not often applied outside of the analysis of ferrovanadium or alloy steels. Quinquevalent vanadium is appreciably soluble in ether; quadrivalent vanadium is very

[11] According to S. G. Clarke [*Analyst*, **52**, 466, 527 (1927)], vanadium can also be separated from tungsten if precipitation is made in the presence of hydrofluoric acid.

[12] A. N. Finn, *J. Am. Chem. Soc.*, **28**, 1443 (1906).

[13] J. R. Cain, *J. Ind. Eng. Chem.*, **3**, 476 (1911).

much less so, the solubility being inappreciable when a few milligrams are in question.[14]

Volatilization in a current of dry hydrochloric acid gas is a desirable method for the removal of the major part of vanadium prior to the determination of certain other elements in material rich in the element.[15] In this method, a current of dry hydrochloric acid gas is passed over the dry material contained in a boat in a glass tube, which may be heated gently, if need be, for better expulsion of vanadium. The volatilized vanadium oxychloride can be caught in water and its amount determined. As some vanadium is reduced during the passage of the gas and does not then volatilize, better separations are had if the contents of the boat are oxidized by evaporation with nitric acid and again distilled and the operation repeated until no further evidence of a brown distillate appears. Molybdenum and arsenic accompany vanadium, as will iron also if the tube is heated too highly. The method can be combined with the nitric acid evaporation; in this case, the dried residue and the evaporated and dried nitric acid solution are best treated separately with hydrochloric acid gas.[16]

IV. METHODS OF DETERMINATION

Numerous methods, both gravimetric and volumetric, have been proposed for the determination of vanadium. The gravimetric methods are subject to so many interfering elements, and their applications are so limited that final recourse must generally be had to the volumetric methods. When gravimetric methods are employed, vanadium is usually weighed as the pentoxide (V_2O_5). This is a reddish-brown crystalline solid that melts at 658° C and does not volatilize at this temperature. It may, however, suffer slight reduction to V_2O_4 if organic matter was present and had therefore better be treated with a few drops of nitric acid and reignited.

A. BY REDUCTION WITH SULFUR DIOXIDE

The reduction of vanadium to the quadrivalent state by sulfur dioxide, followed by the expulsion of the gas by carbon dioxide and titration in hot solution with a standard solution of permanganate, furnishes one of the most satisfactory methods for the determination of large or small amounts of the element. The reduced compound is quite stable in hydrochloric or sulfuric acid solution.[17] Elements that interfere, such as iron, arsenic, and antimony, are not numerous and are usually easily separated. Chromium is an undesirable accompanying element, for its presence necessitates titration in cool solution, which is not quite so attractive because of the slower oxidation of vanadium and less sharp end point, or else correction for the partial oxidation of chromium that takes place during titration in hot solution.[18] Platinum should be excluded, for it leads to marked plus errors, caused in part by the formation of platinous compounds, and also because these prevent complete expulsion of sulfur dioxide. If hydrogen sulfide has been used to separate platinum or other metals, the solution must be thoroughly boiled to expel *all* hydrogen sulfide and then treated with permanganate to a pink tint in order to destroy polythionic compounds. Sodium sulfate does not interfere as is stated in some texts.

PROCEDURE. Prepare a dilute sulfuric acid solution (2 + 98) of vanadium which is free from other substances that are oxidized by permanganate after reduction by sulfur dioxide. Heat to boiling, add a strong solution of potassium permanganate until the solution is pink, and then pass sulfur dioxide[19] through the solution for 5 to 10 minutes. Next pass a rapid stream of carbon dioxide (free from oxygen and hydrogen sulfide) through the solution until it is free from sulfur dioxide, as tested by bubbling the stream through an acidified and very dilute solution of permanganate. Cool the solution to 60 to 80° C, and titrate with a standard solution of potassium permanganate which has been standardized against sodium oxalate. 1 ml of 0.1 *N* solution = 0.0051 g of vanadium. If chromium is present, it is better to titrate in cool solution, until the color produced by a drop of the permanganate does not fade upon continued stirring for 1 minute. The reduction and titration can be repeated once or twice if desired; if it is carried out too many times, the accumulation of manganous sulfate renders the end point uncertain. In case very little vanadium is indicated, its presence should be verified by evaporation to small volume and testing with hydrogen peroxide as in E, after the removal of interfering elements such as molybdenum or titanium if these are present.

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[14] In tests made by H. A. Bright with 2.25 g of iron and 24 mg of vanadium, 2 mg of the latter was extracted by ether when the element was quinquevalent and less than 0.03 mg when it was quadrivalent. However, when 0.67 g of iron and 0.33 g of quadrivalent vanadium were used, 1.6 mg of the latter was found in the ether extract.

[15] E. F. Smith and J. G. Hibbs, *J. Am. Chem. Soc.*, **16**, 578 (1894).

[16] For the volatilization of vanadium in a current of CO_2—CCl_4, see P. Jannasch, *Z. prakt. Chem.*, **97**, 93, 141, 154 (1918).

[17] For example, L. E. Stout and G. C. Whitaker [*Ind. Eng. Chem.*, 20, 210 (1928)] stated that a sulfuric acid solution of vanadyl sulfate underwent no change in 6 months.

[18] W. F. Hillebrand, *U. S. Geol. Survey Bull.* 700, 199.

[19] The direct use of a solution of sulfur dioxide or of an alkali sulfite is inadmissible unless these have been freshly prepared, for, after a lapse of time, they contain other oxidizable bodies than sulfurous acid or sulfite. Sulfur dioxide is most conveniently used from a cylinder of the liquefied gas, or it may be obtained as wanted by heating a flask containing a solution of the gas, or of a sulfite to which sulfuric acid is added drop by drop.

B. BY THE FERROUS SULFATE-PERSULFATE METHOD[20]

In cool acid solution containing no silver nitrate, ammonium persulfate oxidizes ferrous sulfate but does not react rapidly with quadrivalent vanadium, permanganate, bivalent manganese, or trivalent chromium. This behavior furnishes the basis for an excellent method for the rapid determination of vanadium, in that it is possible to reduce the element by adding an excess of ferrous sulfate, to destroy the excess with persulfate, and then to titrate the reduced vanadium with permanganate. Tungsten interferes; chromium, nickel, cobalt, molybdenum, arsenic, and uranium are without effect. The method is not so accurate, particularly with small amounts of vanadium as the foregoing method, but is a good substitute for it when rapid results of reasonable accuracy are wanted. Other points in its favor are the noninterference of iron, and the fact that it can be applied after the determination of chromium as described under Chromium (p. 527).

PROCEDURE. Prepare a dilute sulfuric acid solution (1 + 9) which is free from tungsten and the substances other than vanadium that are oxidized by permanganate after treatment with ferrous sulfate and ammonium persulfate. If iron is present, add enough phosphoric acid to decolorize it, and render the solution permanently pink by the addition of permanganate. Add, with constant stirring, approximately 0.1 *N* ferrous sulfate solution (1 ml of 0.1 *N* solution = 5.1 mg of V)[21] until a drop of the solution gives an immediate blue color with potassium ferricyanide, and then 3 to 5 ml in excess. Stir the cool solution for 1 minute, add 8 ml of ammonium persulfate solution (freshly made 15% solution of the 95% salt), and stir vigorously for 1 minute. Titrate with standard 0.03 *N* or stronger permanganate solution to a definite pink color which does not fade upon continued stirring for 30 seconds.

C. PRECIPITATION BY CUPFERRON

Quinquevalent vanadium is quantitatively precipitated by cupferron in cold dilute sulfuric acid solution (1 + 9), (p. 119). The reaction is not often applied for the determination of vanadium, however, for the necessity of previously separating other elements such as iron, titanium, and zirconium renders other methods more attractive. The method finds its chief application for group separations where the precipitable elements are present in minor amounts.[22]

D. POTENTIOMETRIC

Potentiometric methods for the determination of vanadium are capable of yielding excellent results, and are especially suitable for routine work. In the usual case, the titration depends on the reduction of quinquevalent vanadium to the quadrivalent condition by the measured addition of ferrous sulfate solution.[23] Other reducible substances must be absent or their effect deducted. Of these, chromium is the most common troublemaker, as complete oxidation of vanadium at the start of the analysis is apt to cause some formation of chromate. Kelley[24] and his coworkers showed that the oxidation of vanadium by nitric acid is only 99 per cent complete at the concentrations that give no oxidation of chromium. Willard and Fenwick[25] insured complete oxidation of vanadium by boiling with nitric acid, then treating with a slight excess of permanganate, and finally boiling with sodium perborate in acetic acid solution to destroy chromate.[26]

E. COLORIMETRIC

Oxidation by hydrogen peroxide in acid solution is not so satisfactory for the colorimetric determination of vanadium as it is for titanium, be-

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[20] H. L. Hamner, *Met. Chem. Eng.*, **17**, 206 (1917).

[21] Prepared by dissolving 39.2 g of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in 1000 ml of cool dilute H_2SO_4 (1 + 19).

[22] The accuracy of the procedure is illustrated by an average value of 0.2564 g of V_2O_5, obtained by precipitating with cupferron and carefully igniting the precipitate at about 800° C, as compared with 0.2560 obtained by potentiometric titration of aliquot portions of the same solution. In such ignitions, carbon should be burned completely under good oxidizing conditions *before* fusion takes place and the oxide then heated just above the melting point.

[23] For example, with an apparatus such as that developed by Kelley (p. 203), the calomel and platinum electrodes are immersed in a cold dilute nitric-sulfuric acid solution of quinquevalent vanadium and the solution titrated with a standard solution of ferrous sulfate until the beam of light from the reflecting galvanometer begins to move again after a period of rest. A standard solution of potassium chromate of equivalent strength is then added until the beam shifts to its former position at the period of rest, whereupon the ferrous sulfate solution is again added until a marked displacement occurs. The volume of chromate used is then subtracted from the volume of ferrous sulfate required and the amount of vanadium calculated on the basis that 1 V = 1 Fe. Chromium and tungsten do not interfere.

[24] G. L. Kelley, J. A. Wiley, R. T. Bohn, and W. C. Wright, *Ind. Eng. Chem.*, **11**, 632 (1919).

[25] H. H. Willard and F. Fenwick, *J. Am. Chem. Soc.*, **45**, 84 (1923).

[26] According to H. H. Willard and P. Young [*Ind. Eng. Chem.*, 20, 764 (1928)], vanadium can also be quantitatively oxidized to the quinquevalent state by the action of potassium bromate in a solution containing ammonium salts and a definite concentration of hydrochloric acid. Under such conditions, tungsten, molybdenum, and chromium remain sexivalent and manganese bivalent. In 200 ml of a dilute sulfuric acid solution containing 4 g of iron, 10 mg of vanadium, and 40 mg of chromium, 6 ml of hydrochloric acid, 5 g of ammonium sulfate, and 2 g of potassium bromate are needed. The solution is heated from 25 to 60° C in the course of 15 minutes, then boiled for 10 minutes to destroy the excess of bromate, treated with 25 ml of sulfuric acid (sp. gr. 1.5), and cooled to 5° C before titrating potentiometrically with ferrous sulfate. Tungstic acid can be kept in solution by dissolving it in sodium hydroxide and pouring it back into the original solution, to which sufficient ferric sulfate to give 5 g of iron has been added, before the oxidation of the vanadium is carried out.

cause the color, reddish yellow to a brown red depending on the amount of vanadium, is harder to match against a standard. The reaction is used chiefly for the verification of the presence of vanadium, although it serves fairly well for its determination in solutions containing 15 to 20 per cent of sulfuric acid, not more than 0.1 mg of vanadium per ml, and preferably no other elements that give a color. Quinquevalent vanadium should be used, as the color is only slowly developed with the element in its lower valences. The color is intensified by strong acids and is not destroyed by hydrofluoric acid; the use of the latter therefore permits the detection of vanadium in the presence of titanium which is bleached (p. 581). Iron can be decolorized by the addition of either phosphoric or hydrofluoric acids. Molybdenum also yields a color and must be separated before the test is made.

PROCEDURE. Prepare a dilute sulfuric acid solution (about 1 + 4) which has been freed from molybdenum, titanium, and elements that give colored solutions. Add 1 to 2 ml of 30 per cent hydrogen peroxide, dilute with sulfuric acid (about 1 + 4) to a definite volume, and compare with the color produced in a standard solution of vanadium by the method outlined under Titanium (p. 583).[27]

F. OTHER METHODS

Most of the other methods for the determination of vanadium are volumetric ones, based on titration with permanganate after the vanadium has been reduced by various reagents. Such are: (1) Campagne's method,[28] in which vanadium is reduced to the quadrivalent state by evaporation with hydrochloric acid, preferably in the presence of ferric iron and sulfuric acid, and then finally titrated in sulfuric acid solution after evaporation to fumes of that acid[29] and diluting; (2) the Jones reductor method, in which vanadium is reduced to the bivalent state and caught in a solution of ferric sulfate (p. 111);[30] (3) the reduction by hydrogen sulfide method in which vanadium is reduced to the quadrivalent state by the gas, which is then

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[27] According to J. Meyer and A. Pawletta [*Z. anal. Chem.*, **69**, 15 (1926)], the test works best in a solution containing 15 to 20 per cent H_2SO_4 and a ratio of V to H_2O_2 of about 1 to 1. An excess of H_2O_2 (by dilution of the acid) gives a yellow instead of the red-brown color. J. Lukas and A. Jílek [*ibid.*, **76**, 348 (1929)] stated that vanadium can be detected in the presence of moderate amounts of tungstates or molybdates by adding solid boric and oxalic acids to the alkaline solution until it is acid, and then 30 per cent hydrogen peroxide.

[28] Em. Campagne, *Compt. rend.*, **137**, 570 (1903).

[29] The temperature should be no higher than is required to fume the acid, and the fuming should not be continued longer than 10 minutes.

[30] The bivalent compound is very easily oxidized under ordinary conditions. According to A. S. Russell [*J. Chem. Soc.*, **129**, 497 (1926)], it is quite stable in cool 10 *N* H_2SO_4.

expelled by boiling as carbon dioxide is blown through the solution;[31] (4) reduction to the quadrivalent state by shaking with mercury in dilute hydrochloric or sulfuric acid solution, containing enough sodium chloride to react with the mercurous compound formed, followed by filtration and titration with permanganate;[32] and (5) reduction to the quadrivalent state by hydrogen peroxide in hot sulfuric acid solution.[33] Other interesting methods are those perfected by Johnson[34] and by Furman.[35] In the former, quinquevalent vanadium is reduced to the quadrivalent state by titration with a standard solution of ferrous ammonium sulfate and the use of potassium ferricyanide as internal indicator. In the latter, diphenylamine (p. 397) is used as an internal indicator. This is a sensitive indicator of the end point of the reaction between vanadic acid and ferrous iron in solutions containing hydrochloric or sulfuric acid and, in the presence of iron, phosphoric acid. Ferric iron, quinquevalent arsenic, and hexavalent uranium do not interfere; but a slight correction must be made for the vanadic acid consumed in oxidizing the indicator.

All of the foregoing methods are subject to various interfering elements, and none of them should be applied unless the analyst knows what elements are present in solution and what their reactions will be.

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[31] G. E. F. Lundell and H. B. Knowles [*J. Am. Chem. Soc.*, **43**, 1566 (1921)], showed that the reduction gives rise to polythionic acids which cause slightly high results.

[32] L. W. McCay and W. T. Anderson, Jr., *J. Am. Chem. Soc.*, **43**, 2372 (1911); **44**, 1018 (1922). In such reductions iron, antimony, and molybdenum interfere, while titanium, arsenic and uranium do not.

[33] J. R. Cain and J. C. Hostetter, *Ind. Eng. Chem.*, **4**, 250 (1912).

[34] C. M. Johnson, *Chemical Analysis of Special Steels*, 3d ed., p. 6 (1920).

[35] N. H. Furman, *Ind. Eng. Chem.*, **17**, 314 (1925).

Chapter 27

URANIUM [1]

Uranium is a rare element that is found as an essential constituent of but few minerals, chief of which are uraninite, carnotite, and samarskite. Its occurrence in rocks is confined almost exclusively to the very siliceous ones; thus the phosphates, autunite and torbenite, are not uncommon in granite; the same is true of uraninite, whereas carnotite occurs with sedimentary sandstones. Uranium occurs sparingly in a number of minerals, especially those containing columbium, tantalum, thorium, zirconium, and some of the rare earths.[2]

Uraninite is the proper name for a crystalline uranium mineral, varieties of which were given the names of bröggerite, cleveite, and nivenite before their relationship to uraninite was known. This mineral occurs in certain pegmatite veins, so far as known chiefly in Norway and North America. All of these are characterized by a high content of uranium in both the quadrivalent and sexivalent state, by a content of rare earths, usually mainly thoria, and of lead. The least altered mineral found at Branchville, Conn., contained 72 per cent of UO_2 and 13 per cent of UO_3. The varieties that are most altered, cleveite and nivenite, show a much lower content of UO_2, even below that of UO_3. It is probable that the original mineral had originally the formula UO_2, corresponding to the ThO_2 of thorianite.

Pitchblende, often wrongly called uraninite, is an amorphous uranium compound found in a few mineral veins in association with sulfide minerals and nearly free from thoria and other rare earths and helium.

Both of these minerals dissolve readily in nitric acid with oxidation of their UO_2 content. Given sufficient time, they all dissolve with widely varying readiness in warm dilute sulfuric acid and with evolution of helium and nitrogen if present. Uraninites are decomposed completely by hydrofluoric acid, uranous fluoride separating with the fluorides of lead and the rare earths.

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[1] A comprehensive review of the methods developed during World War II on the determination of uranium is given by C. J. Rodden, *Analytical Chemistry of the Manhattan Project*, pp. 3–159, McGraw-Hill Book Co. (1950).

[2] For a critical study of a fluorescent sodium fluoride bead test for uranium applied directly to minerals containing over 1 per cent of uranium, consult M. A. Northrup, *Ind. Eng. Chem. Anal. Ed.*, **17**, 664 (1945).

I. GENERAL CONSIDERATIONS

In the analysis of rocks by usual procedures, the behavior of uranium will depend to a considerable extent on the presence or nonpresence of carbon dioxide and vanadium, both of which interfere in its normal reactions. If these are absent, uranium will be quantitatively present in the ammonia precipitate. If correction is not made for it, the errors in the analysis will then depend on the method that is used for the determination of iron. Most of the error will fall on iron if this element is determined by titration with permanganate after reduction by zinc, for uranium is reduced by zinc to a state somewhat below the quadrivalent. As the Fe_2O_3 titer of a 0.1 N solution of permanganate is less than the U_3O_8 titer, the result for aluminum will also be in error and a little high. If, however, iron is reduced by sulfur dioxide, hydrogen sulfide, or stannous chloride, all of the error will fall on alumina, for uranium is not reduced by these reagents.

II. ATTACK OF URANIUM MINERALS

Most ores of uranium are decomposed by attack with nitric acid, with the aid of hydrochloric acid in certain cases. With ores containing much siliceous matter, final treatment with a mixture of hydrochloric and hydrofluoric acids is desirable unless silica is also to be determined, in which case the insoluble matter is fused with sodium carbonate.

Swedish kolm can be broken up by treating with concentrated sulfuric and hydrofluoric acids, and heating to fumes of the former. If a residue remains after a second treatment with hydrofluoric acid, the solution is diluted and filtered, the residue ignited and fused with potassium pyrosulfate, and the melt dissolved in the original solution. Uraninite can be decomposed by attack with nitric and sulfuric acids.[3]

Titanocolumbates and similar minerals are decomposed by fusion with sodium pyrosulfate.

For the solution of carnotite, see Vanadium (p. 453), and, for a discussion of methods of attack in the analysis of uraninite, see an article by one of us (W.F.H.) in *U. S. Geol. Survey Bull.* 78 (1889–90), and *Am. J. Sci.*, **40**, 384 (1890).

For the determination of nitrogen one of us (W.F.H.) dissolved the mineral by continued boiling at 100° C with dilute sulfuric acid (1 + 6), and also by mixing the mineral with sodium-potassium carbonate in a porcelain boat enclosed in a cylinder of platinum foil, open at both ends and heated in a combustion tube as in a determination of absolute nitrogen.

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[3] W. R. Bennett, *J. Am. Chem. Soc.*, **56**, 277 (1934).

III. METHODS OF SEPARATION

It should be borne in mind that carbon dioxide and vanadium interfere seriously in the usual separations of uranium. Thus uranium is precipitated completely by ammonium hydroxide that is free from carbon dioxide, incompletely by ammonium hydroxide that has absorbed some carbon dioxide from the air, and not at all by solutions of ammonium carbonate. Similarly, uranium is quantitatively precipitated by sodium hydroxide that is free from carbonate if vanadium is absent, but incompletely if at all when this element is present. Most separations of uranium had best be repeated two or three times.

Perhaps the most important separations of uranium are those based on the use of the alkaline carbonates; thus elements such as iron and aluminum are separated from uranium by precipitation with ammonium carbonate. All such precipitations are done in hot solutions, care being taken in the case of ammonium carbonate lest it be entirely decomposed and uranium then precipitated. When sodium or potassium carbonates are used, better separations are possible if sodium peroxide is also employed.

Uranium can be separated from the members of the hydrogen sulfide group by precipitation of the latter in acid solution containing tartaric acid (p. 63), and from the members of the arsenic group of sulfides by precipitation with ammonium sulfide. If ammonium carbonate is present, uranium is not precipitated by ammonium sulfide, and the precipitation serves to separate iron, aluminum, titanium, and the like from uranium. Uranium is not precipitated as sulfide in ammonium tartrate-sulfide solution and can thus be separated from iron, cobalt, and the like.[4]

Interesting separations of certain elements from sexivalent uranium and of quadrivalent uranium from other elements are those based on the use of cupferron (p. 116). For example, vanadium, iron, titanium, and zirconium can be easily separated from sexivalent uranium by precipitation with cupferron in sulfuric acid solution (p. 119), and then uranium can be reduced to the quadrivalent state, precipitated by this same reagent (p. 119), and separated in turn from such elements as aluminum, chromium, manganese, and phosphorus.

Uranium can be quantitatively separated from tantalum, columbium, and titanium by precipitating these elements with tannin in a feebly acid oxalate solution which is half-saturated with ammonium chloride,[5] filtering, and then precipitating the uranium by adding more tannin and rendering the solution ammoniacal.

Uranium can be separated from large amounts of iron by extraction of the latter by ether in hydrochloric acid solution[6] (p. 134), and from both iron and chromium by electrolysis with a mercury cathode in dilute sulfuric acid solution (p. 138).

Quadrivalent uranium yields an insoluble fluoride and can thus be separated from sexivalent uranium that does not (p. 551). F. Hecht and H. Krafft-Ebing[7] state that precipitation with hypophosphoric acid, $H_4P_2O_6$, in mineral acid solution serves the same purpose.

Methods for the separation of uranium from vanadium are discussed under Vanadium (p. 457), from rare earths on page 551 and from the earth acids on page 591.

For the separation of beryllium from uranium, Brinton and Ellestad[8] proposed the use of both ammonium carbonate and hydroxylamine hydrochloride as follows: To the hydrochloric acid solution of the beryllium and uranium, add 5 g of ammonium chloride, 5 g of hydroxylamine hydrochloride, and then a concentrated solution of ammonium carbonate until the precipitate which at first forms has entirely dissolved. Heat the solution to boiling, and continue the boiling for from one-half to one minute after the appearance of the heavy white precipitate of basic carbonate. Avoid excessive boiling. Filter without delay, and wash thoroughly with cold water. Reserve this precipitate, which is free from uranium, and combine it with the small recovery of beryllium hydroxide obtained in the filtrate. Acidify the filtrate with hydrochloric acid, and boil to remove carbon dioxide. Add 1 g of hydroxylamine hydrochloride, cool, and then add ammonium hydroxide in slight excess. Filter the cool solution to recover any beryllium hydroxide, wash the precipitate with a 2 per cent solution of ammonium nitrate to which have been added a few crystals of hydroxylamine hydrochloride and enough ammonium hydroxide to insure alkalinity. If the precipitate has a tinge of yellow, dissolve it in hydro-

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[4] R. Fresenius and E. Huntz [Z. *anal. Chem.*, **34**, 437 (1895)] separated uranium from phosphates and arsenates as follows: Separate silica as usual by evaporation with hydrochloric acid, add potassium ferrocyanide in excess to the slightly acid solution, and saturate with sodium chloride. Wash the impure ferrocyanides by decantation with a solution of sodium chloride, filter, and wash thoroughly. Without heating, decompose the ferrocyanides by treating with a dilute solution of potassium hydroxide. Wash once by decantation with water, filter, and wash the hydroxides uninterruptedly with water containing a little ammonium hydroxide and ammonium chloride until no test for ferrocyanide can be obtained in the acidified washings. Dissolve the hydroxides, which are now free from phosphorus and arsenic, in hydrochloric acid, concentrate if need be, nearly neutralize with ammonium hydroxide, and add ammonium carbonate in moderate excess. Let stand, filter, and wash the precipitate with water containing ammonium carbonate. Heat the filtrate and washings to free most of the carbon dioxide, acidify, and boil to expel all of the gas. Precipitate with hydrogen sulfide in boiling solution, filter, and precipitate uranium in the filtrate by usual procedures.

[5] W. R. Schoeller and H. W. Webb, *Analyst*, **58**, 143 (1933).

[6] E. F. Kern, *J. Am. Chem. Soc.*, **23**, 689 (1901).

[7] *Z. anal. Chem.*, **106**, 321 (1936).

[8] P. H. M.-P. Brinton and R. B. Ellestad, *J. Am. Chem. Soc.*, **45**, 395 (1923).

chloric acid, and reprecipitate as before. Combine the beryllium precipitates, and ignite to BeO. For the precipitation of uranium, combine the filtrates if two precipitations of beryllium hydroxide were made, slightly acidify with hydrochloric acid, and oxidize the hydroxylamine by adding 75 to 100 ml of 3 per cent hydrogen peroxide and boiling until the evolution of oxygen ceases and the solution has been concentrated to about one third of its volume. In case a precipitate is formed, dissolve it in hydrochloric acid. The oxidation of the hydroxylamine can also be done by adding solid sodium or potassium bromate until free bromine is evident and then boiling to expel the bromine. Precipitate uranium by ammonium hydroxide as described in IV, A.

Uranium can be separated from almost all other elements by extracting the dried nitrate with ethyl ether or certain other organic solvents.[9]

IV. METHODS OF DETERMINATION

The gravimetric method in which uranium is precipitated as diammonium uranate $(NH_4)_2U_2O_7$, and weighed as uranous uranate, U_3O_8, and the volumetric method in which it is reduced by zinc and titrated by permanganate are both accurate procedures if simple precautions are observed. The chief concern when these methods are used in the analysis of mixed materials lies in the removal of such elements as interfere, as for example vanadium and iron which interfere in either method.

Obviously the most rapid method of determining uranium or thorium is to make use of the natural radioactivity of these elements, but, unfortunately, it is necessary that only uranium or only thorium be present. Furthermore, the element in question must be in equilibrium with its radioactive dissociation by-products. Whereas, in some ores and minerals, equilibrium has been reached, in others, such as the carnotite-bearing sandstones of Colorado, this is not true, and radioactive methods are therefore unreliable. For these reasons and because expensive equipment and trained personnel are required, methods depending on natural radioactivity will not be disscussed here.[10]

A. GRAVIMETRIC BY PRECIPITATION WITH AMMONIUM HYDROXIDE

Notwithstanding many researches to the contrary, the determination of uranium by weighing as U_3O_8 following precipitation by ammonium hydroxide is an accurate procedure. The chief objection to the method is

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[9] E. Peligot, *Ann. chim. phys.*, [3] **5**, 5 (1842); W. F. Hillebrand, *U. S. Geol. Survey Bull.* **78**, 47 (1891); R. C. Wells, *J. Wash. Acad. Sci.*, **20**, 146 (1930); J. I. Hoffman, *ibid.*, **38**, 233 (1948).

[10] See C. J. Rodden, Determination of Naturally Occurring Radioactive Elements, *Anal. Chem.*, **21**, 331 (1949).

that it can rarely be applied directly because of the presence of other elements that are precipitated by ammonium hydroxide.[11] The chief precautions lie in the elimination of organic matter and of carbonates, both of which prevent precipitation. Ignition of the precipitate under good oxidizing conditions suffices, and there is no need for final ignition in oxygen or reduction of the precipitate to UO_2 in a stream of hydrogen; in fact complete reduction to UO_2 is almost impossible in a crucible.[12]

PROCEDURE. Prepare a dilute sulfuric acid solution containing 1 per cent or less of uranyl sulfate and no carbon dioxide, organic compounds, or elements other than uranium that are precipitated by ammonium hydroxide or that unite with uranium in the presence of this reagent. Add a few drops of methyl red indicator, heat to boiling, and then add dilute ammonium hydroxide that is free from carbonate, until the indicator just changes to a distinct yellow. Stir in macerated paper in amount equal to one-half of a 9-cm filter, filter, and wash the precipitate with a hot 2 per cent solution of ammonium nitrate.[13] Dry the wet paper and precipitate in a platinum crucible, ignite under good oxidizing conditions at as low a temperature as possible until carbon is destroyed, and then continue the ignition with the crucible in a slanting position over a full Tirrill burner or its equivalent (1000° C). Finally cover, and continue the heating for a minute. Cool in a desiccator, and weigh as U_3O_8.

Theoretically, the weighed U_3O_8 residue should have the composition $UO_2 \cdot 2UO_3$. Determinations of its UO_2 and total uranium contents are desirable checks on a determination, especially if the uranium was originally associated with elements that might escape complete separation and finally

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[11] The oft-repeated statement that uranium is prone to carry down sodium has no basis in fact. For example, H. B. Knowles obtained 0.2386 g of U_3O_8 after single, 0.2386 after double, and 0.2387 after triple precipitations with NH_4OH in three 100-ml solutions, each originally containing 5 g of NaCl and uranium nitrate equivalent to 0.2389 g of U_3O_8.

[12] In some tests of ignition procedures by Lundell and Knowles [G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, **47**, 2637 (1925)], ignited residues obtained by precipitation of aliquot portions of a standard solution weighed 0.1138 and 0.1138 when ignited in air, 0.1136 and 0.1136 when ignited in oxygen, and 0.1137 and 0.1136 when those ignited in oxygen were dissolved in nitric acid, evaporated to dryness, and again ignited in air. Tests of the weighed U_3O_8 residues for UO_2 showed that this might vary by as much as 1 mg from the theoretical. Such differences cause less than 0.1 mg variation in the weight of U_3O_8 and are without significance in ordinary weighings. Careful ignition in an atmosphere of hydrogen gave 0.1118 and 0.1115, representing about two-thirds reduction to UO_2.

[13] According to Kin'ichi Someya [*Science Repts. Tôhoku Imp. Univ.*, **15** [1], 411 (1926); *Z. anorg. Chem.*, **152**, 378 (1926)], a crystalline precipitate can be obtained and the use of macerated paper avoided by adding ammonium hydroxide until the indicator turns orange red, boiling for 10 minutes, and then adding ammonium hydroxide until the indicator changes to a distinct yellow.

contaminate the precipitate. These determinations can be easily made as follows:

Treat the weighed residue, contained in a platinum crucible, with 10 ml of hydrofluoric acid, crush any small lumps with a platinum or Bakelite rod, and stir for 3 to 5 minutes. Do not heat. The material will not go into complete solution because of the insolubility of uranous fluoride. Treat the solution with 10 to 20 ml of dilute sulfuric acid (1 + 1), stir for a few moments, and transfer to a beaker containing 100 ml of a cool, saturated solution of boric acid. Stir until the salts are in solution, titrate with standard permanganate solution, subtract the volume required for the end-point color, and calculate the UO_2 content on the basis of oxidation from UO_2 to UO_3.

Transfer the titrated solution to a platinum dish, evaporate to fumes of sulfuric acid, dilute so that the solution contains 5 per cent by volume of sulfuric acid, and proceed as in the volumetric method, B. If ferrous sulfate solution was added to obtain an end-point correction in the preceding determination, its permanganate equivalent must be deducted from the permanganate reading in addition to the correction for reagents and for end-point color. Calculate the total uranium content on the basis of oxidation from UO_2 to UO_3. Theoretically, the volume of permanganate required in this titration should be three times that of the first.

Because of the high uranium titer of the permanganate solution, it is essential in accurate analyses that the first titration be corrected by the volume of permanganate solution required to produce the end-point color and that the second titration be corrected for the end-point color as well as for the volume of permanganate required in a blank run. The corrections for the second titration are discussed in B. The correction for the end-point color in the first titration is somewhat different, and usually less than that in the second, and can be found as in the second titration except that the small amount of ferrous sulfate solution must be carefully measured. This is necessary so that the permanganate equivalent may be subtracted in the second titration in addition to the corrections there made for the reagents and the end-point color.

The UO_2 content of a U_3O_8 residue can also be determined by titration with permanganate after decomposition of the material at 150 to 175° C in a sealed tube containing dilute sulfuric acid (1 + 6) and an atmosphere of carbon dioxide.[14]

In the above tests of the purity of a weighed U_3O_8, it is quite likely that the result for UO_2 will represent the true UO_2 content. The value for total uranium will also be correct if the contaminants are not reduced in the reduction, as for example aluminum or zirconium. If, however, any contaminating substance is reduced and afterwards reoxidized by permanganate, the result for total uranium will be too high and will exceed the theoretical content if the reducible compound is the only contaminant; such are vanadium and titanium. In any event, it is quite certain that contaminants will have a distinct effect on the U^{IV} to U^{VI} ratio, for it is not likely that uranium will be reduced during ignition in the same fashion, if elements such as aluminum or titanium are present.

B. VOLUMETRIC BY REDUCTION WITH ZINC AND TITRATION WITH PERMANGANATE

A proper reduction of uranium by amalgamated zinc in acid solution always proceeds below the quadrivalent stage, never reaches the trivalent, and rarely proceeds to exactly the same point.[15] Fortunately, the reduced compound can be oxidized to the quadrivalent state by exposure to the air. Stirring for 5 minutes or bubbling of air through the solution for an equal period suffices in determinations involving as much as 0.25 g of uranium; 1 to 2 minutes are enough for amounts less than 0.1 g. Quadrivalent uranium is quite stable in cool sulfuric acid solutions but is slowly oxidized in warm solutions.[16] In cool solutions, no oxidation of the quadrivalent compound occurs, even though the solution is exposed for 4 hours and occasionally stirred, or agitated with bubbled air for as long as 25 minutes. If, then, uranium is reduced in sulfuric acid solution at room temperature, and the reduced solution is given sufficient exposure to the air, the volumetric method becomes as accurate as the corresponding ones for vanadium, titanium, iron, and molybdenum.

PROCEDURE. Prepare a solution containing 1 per cent or less of uranium, 5 per cent by volume of sulfuric acid, and no compounds other than uranium that are reduced in the Jones reductor.[17] Add enough permanganate

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[14] W. F. Hillebrand, *op. cit.*

[15] According to Kin'ichi Someya (*loc. cit.*), uranium is easily reduced to the trivalent condition by treatment with zinc amalgam in 2 to 6 *N* hydrochloric acid solution, and to exactly the quadrivalent state by reduction with bismuth amalgam in 6 to 10 *N* HCl or 10 to 12 *N* H_2SO_4. With aluminum in dilute sulfuric acid solution, reduction also proceeds to the quadrivalent state [H. V. Churchill, R. W. Bridges, and A. L. Miller, *Ind. Eng. Chem. Anal. Ed.*, **8**, 348 (1936)].

[16] G. E. F. Lundell and H. B. Knowles (*loc. cit.*). According to G. Vortmann and F. Binder [*Z. anal. Chem.*, **67**, 269 (1925)], a sulfuric acid solution of $U(SO_4)_2$ is sufficiently stable to permit its use as a standard reducing solution.

[17] Nitric acid must be entirely expelled as it yields reduced compounds in the reductor that afterwards consume permanganate. According to J. A. Holladay and T. R. Cunningham [*Trans. Am. Electrochem. Soc.*, **43**, 329 (1923)], nitric acid is obstinately retained by uranium and is not entirely expelled by repeated evaporation to fumes with sulfuric acid. They recommended that nitric acid be avoided and that the uranium compound be dissolved in sulfuric acid alone or after fusion with pyrosulfate. Possibly all nitric acid can be expelled by cautious addition of permanganate to a hot concentrated sulfuric acid solution as recommended under Molybdenum (p. 308).

to produce a permanent pink tint, cool the solution to 20 to 25° C, and pass it through a Jones reductor (p. 108) at a rate of 50 to 100 ml per minute. Blow clean air through the reduced solution for 5 minutes, or pour the solution into a casserole, and stir it for an equal period. Titrate with a solution of potassium permanganate that has been standardized against pure sodium oxalate (p. 185), and correct the titration reading for the volume of permanganate required by the reagents, as well as the volume required to obtain an end-point color in the yellow solution. One milliliter of 0.1 *N* permanganate solution corresponds to 0.01191 g of uranium.

To obtain the volume of permanganate required by the reagents, pass a solution of the reagents through the reductor, titrate with the permanganate solution, and then subtract the small volume of permanganate required to reproduce the end-point color in the same volume of solution. To obtain the correction for the end-point color, treat the titrated solution of uranium with a few drops of 0.1 *N* solution of ferrous sulfate, add 0.5 to 1 g of ammonium persulfate, stir for 1 minute, and then titrate with the permanganate solution until the original end point is reproduced. For the titration of uranium in ores by dichromate see reference in footnote 1.

C. GRAVIMETRIC BY PRECIPITATION WITH CUPFERRON

As has already been stated in Section III, cupferron in hydrochloric or sulfuric acid solution precipitates quadrivalent but not sexivalent uranium. An attractive procedure in certain cases therefore lies in first precipitating with cupferron while uranium is sexivalent (p. 119), filtering, and then again precipitating with cupferron (p. 119), after the cupferron in the first filtrate has been destroyed and the uranium reduced by zinc as in B. In this manner, iron, vanadium, titanium, and zirconium can be quantitatively separated from uranium and then uranium in turn separated from such other elements as aluminum and phosphorus. Bivalent chromium is partly precipitated. Its interference can be overcome partially, if not entirely, by exposure of the reduced solution to air as in B.

D. OTHER METHODS

Among other methods for the determination of uranium may be mentioned its determination by weighing as $Na_2U_2O_7$, as $(UO_2)_2P_2O_7$ and as $V_2O_5 \cdot 2UO_3$. Precipitation of uranium by sodium hydroxide should only be employed as a separation, for the determination of uranium by weighing as sodium biuranate is an inaccurate procedure that normally yields high results.[18] The determination of uranium as phosphate offers no advantages over weighing as U_3O_8, save in routine analyses where no prior separation of vanadium is contemplated.[19] The same can be said of precipitation as ammonium uranyl vanadate and ignition to $V_2O_5 \cdot 2UO_3$.

The yellow fluorescence of uranium in fused sodium fluoride under ultraviolet light is intense and reproducible. Methods based on this fluorescence are quite useful for determining traces of uranium in low-grade ores, sands, soils, and other materials. Because of the interference of ions such as iron, copper, chromium, and manganese, which inhibit the fluorescence, the uranium is usually first separated from the other constituents of the material by extracting it as uranyl nitrate with a suitable organic solvent which is then evaporated and the residue fused with sodium fluoride and potassium carbonate in a gold dish. The solid is removed from the dish and brought under an ultraviolet light, and the fluorescent intensity is measured with a photovolt electronic photometer.[20]

Uranyl salts, when activated by wave energies below 3000 A, exhibit intense fluorescence in solution. Sill and Peterson[21] have developed a quantitative method based on this phenomenon.

Small amounts of uranium can be determined colorimetrically in somewhat the same fashion as with chromium (p. 530) by developing the color with sodium hydroxide and sodium peroxide and comparing the color with known amounts of uranium treated similarly,[22] or photometrically by measuring the transmittancy of the solution at 425 mμ.[1]

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[18] According to H. T. S. Britton [*J. Chem. Soc.*, **127**, 2110 (1925)], the precipitate obtained with sodium hydroxide consists chiefly of the hydroxide and not sodium biuranate.

[19] The separation of uranium from vanadium is not complete, even though the precipitation of the phosphate is repeated. For example, after double precipitations, 0.3052, 0.3056, and 0.3058 g of $(UO_2)_2P_2O_7$ were obtained from three aliquot portions of a solution containing uranium nitrate alone, and 0.3081, 0.3102, and 0.3147 from three other portions to which 0.2-g portions of vanadium as sulfate had been added.

[20] M. A. Northrup, *Ind. Eng. Chem. Anal. Ed.*, **17**, 664 (1945); C. E. White, *Anal. Chem.*, **21**, 104 (1949).

[21] C. W. Sill and H. E. Peterson, *ibid.*, **19**, 646 (1947).

[22] For interfering elements, see G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis*, p. 172 (1938).

Chapter 28

THALLIUM

Thallium occurs in the rare minerals: crookesite, $(CuTlAg)_2Se$; lorandite, $TlAsS_2$; vrbaite, $TlAs_2SbS_5$; and hutchinsonite, a sulfide of thallium, silver, copper, lead, and arsenic. Thallium is also found in minute quantity, associated with the alkali metals, iron, zinc, lead, copper, and manganese in certain rocks and minerals, as for example in carnallite, alunite, copper and iron pyrites, zinc blende [1] and braunite. When such minerals are used in manufactures, their thallium contents may be concentrated and give rise to determinable amounts, as in chamber mud and flue dust from sulfuric acid plants; in zinc, copper, and tellurium; and occasionally in commercial sulfuric and hydrochloric acids.

I. GENERAL CONSIDERATIONS

The behavior of thallium in an ordinary analysis will depend upon its valency. If it is monovalent and present in small amount, it will probably escape precipitation and detection unless the filtrate from the ammonia precipitation is treated with ammonium sulfide before the separation of calcium. If it is present in large amount, thallous chloride, TlCl,[2] may separate during the dehydration of silica with hydrochloric acid, and probably be noted because of its appearance or its melting during the ignition of the silica. In the usual ignition, some of the thallium might be fixed as silicate, but considerable would no doubt be lost by volatilization. In case the attack of the material has been such as to give thallic salts, most of the thallium will be found in the ammonia precipitate. Some, if not all of it, will be converted to the monovalent state during any strong ignition of the precipitate. It will then be counted as aluminum unless iron is determined by titration with permanganate after treatment with a reducing agent, such as hydrogen sulfide or sulfur dioxide, that reduces thallium to the monovalent state. In this event, part of the thallium would be counted as iron and part as aluminum.

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[1] W. N. Hartley and H. Ramage, *Chem. Soc.*, **71**, 533 (1897).

[2] According to M. Randall and K. S. Chang [*J. Am. Chem. Soc.*, **50**, 1535 (1928)], 1 liter of water will dissolve 3.863 g of TlCl at 25° C.

Thallium can be detected in a mineral spectroscopically by crushing the ore to a very fine powder in an agate mortar, moistening with hydrochloric acid, and taking up in a platinum loop which is then gradually introduced into the outer edge of a Bunsen flame. The characteristic green line appears as a glow that continues for at least several seconds. If the glare of the sodium line is cut out, as little as 0.0002 per cent of thallium can be detected in 0.03 g of material.[3]

II. ATTACK OF THALLIUM MINERALS

Thallium minerals are easily broken up as follows: Finely powder 1 g of the mineral, transfer to a 250- to 500-ml Erlenmeyer flask, and add 2 g of potassium sulfate and 10 ml of sulfuric acid. Heat over a free flame until completely decomposed, allow to cool, add 100 ml of water, boil, and again cool. Filter, neutralize the filtrate with sodium carbonate, and add 2 g in excess. Dilute to 200 ml, add 3 g of sodium cyanide that is free from sulfide, heat to boiling, and set aside for 12 hours. Filter, wash the residue with a 1 per cent solution of sodium carbonate, and treat the filtrate with colorless ammonium sulfide until no more black sulfide is precipitated. Cool, filter, and wash the precipitate with diluted colorless ammonium sulfide, taking care not to let the filter run dry. Dissolve the sulfide in dilute sulfuric acid (1 + 4), boil to expel hydrogen sulfide, and add a few drops of sulfurous acid. Make nearly neutral with sodium carbonate, filter if necessary, and precipitate the thallium as in Section IV.

For the determination of thallium in minerals such as pyrite or blende, treat 25 to 100 g of the finely ground material with hydrochloric acid, boil, and add nitric acid at intervals until decomposition is complete. Add dilute sulfuric acid (1 + 1) in excess, heat to fumes of the acid, cool, dilute, and filter. Reduce the thallium, copper, cadmium, and the like to metal by adding an excess of zinc to the filtrate and letting the solution stand overnight. If the acid is spent, add enough more to start reaction with the zinc, filter through a paper containing a few pieces of zinc, and quickly wash the residue with a little hot water. Extract the thallium with hot dilute sulfuric acid, and treat the extract with sodium carbonate and cyanide as above.[4]

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[3] R. Berg and W. Roebling [*Ber.*, **68**, B, 403 (1935)], and R. Berg and E. S. Fahrenkamp [*Z. anal. Chem.*, **109**, 305 (1937)], maintain that thioglycolic acid β-aminonaphthalide ("thionalide") is specific for the detection or determination of thallium in sodium hydroxide-sodium cyanide solution, with or without tartrate, and that it is especially suitable for macro- or microtoxicological work.

[4] In examinations of organic matter, the sample had better be decomposed by wet oxidation, as with sulfuric and nitric acids, for ignition, even at low temperatures, may lead to losses of thallium.

III. METHODS OF SEPARATION

Thallium is monovalent or trivalent in its compounds, the former resembling the alkali metals in its reactions, the latter the heavy metals. Thallic salts are easily reduced to the monovalent state by the action of sulfurous acid or hydrogen sulfide in acid solution. Thallous salts are oxidized by chlorine, bromine,[5] or aqua regia but not by nitric acid alone.

When by itself, thallium is not precipitated by hydrogen sulfide in strong acid solution. Separations based on this fact, however, are as a rule worthless, for thallium forms compounds with members of the hydrogen sulfide group, such as arsenic, antimony, tin, or copper. Thallium is incompletely precipitated by hydrogen sulfide in the presence of dilute mineral acids, and completely precipitated as thallous sulfide, Tl_2S, in acetic acid solution, or by ammonium sulfide. As thallous sulfide is rapidly oxidized by air, filtrations must be done as rapidly as possible without letting the paper run dry, and the final washing must be carried out with dilute colorless ammonium sulfide.

Lead can be readily separated from thallium by repeated precipitation as the sulfate (p. 227). For the separation of silver the best method is that based on the precipitation of silver chloride in a dilute nitric acid solution of either thallous or thallic salts. The latter are somewhat more desirable, and, to make sure of their presence, the chloride precipitate can be boiled with aqua regia and the solution diluted, or the precipitation can be made with hydrochloric acid saturated with chlorine.

Thallium can be precipitated as thallous iodide and separated from elements such as cadmium, iron, aluminum, chromium, cobalt, nickel, zinc, manganese, alkaline earths, magnesium, and the alkalies by treating a cold, feebly acid solution of the sulfates with sulfur dioxide, adding potassium iodide in moderate excess, and filtering. Under these conditions, copper and silver are also precipitated; the former can afterwards be dissolved by digesting the precipitate with dilute ammonium hydroxide. Mercury is at first precipitated as the red iodide but can be dissolved by adding iodide until the thallous iodide is pure yellow.

L. Moser and A. Brukl[6] stated that manganese and lead can be separated

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[5] P. E. Browning, *Ind. Eng. Chem. Anal. Ed.*, **4**, 417 (1932).

[6] *Monatsh.*, **47**, 709 (1926). In a later communication [*ibid.*, **52**, 343 (1929)], L. Moser and W. Reif described a method for separating aluminum, chromium, and ferric iron from monovalent thallium which is based on treating an acid solution of the sulfates with sodium carbonate until nearly neutral, heating to 40° C, adding 20 ml of a 7 per cent solution of ammonium nitrite and 20 ml of methyl alcohol, and boiling gently for 20 minutes. After adding more reagents and boiling to make sure that precipitation is complete, the solution is filtered, the precipitate washed with 2 per cent solution of ammonium nitrate, and the thallium precipitated as the chromate in the filtrate after evaporating to 100 to 200 ml and rendering ammoniacal.

from monovalent thallium by precipitating with diammonium phosphate in an ammoniacal solution containing sulfosalicylate, and that thallium can be precipitated in the filtrate by adding chromate. This last reaction serves to separate thallium from iron, aluminum, and chromium which are not precipitated by chromate in an alkaline sulfosalicylate solution. The chromate reaction also serves to separate thallium from selenium, cadmium, zinc, nickel, and cobalt, provided enough ammonia is first added to hold these in solution; from copper, mercury, and silver, if cyanide is also used; and from arsenic and antimony, if these are first oxidized to the quinquevalent condition by treating with hydrogen peroxide in ammoniacal solution. Moser and Brukl assert that bismuth can be separated from monovalent thallium by precipitating with diammonium phosphate in a solution of the neutral salts.

Gallium can be separated from thallium by precipitating with ammonium hydroxide in boiling solution after prior reduction of the thallium by sulfur dioxide in nearly neutral solution.

An interesting separation of thallium from a number of elements is that based on the repeated extraction of thallic chloride from 6 *N* hydrochloric acid solution by means of ether[7] (p. 134). Thallium can also be quantitatively precipitated as the metal and separated from many elements by reducing with zinc[8] or magnesium in dilute hydrochloric or sulfuric acid solution. The thallium sponge that is obtained is easily oxidized by air or dissolved oxygen and must be compressed into a lump by means of a glass rod, most of the solution decanted, and the residue washed quickly by decantation with recently boiled water.

A possible method of depositing thallium and separating it from elements such as vanadium, aluminum, and zirconium lies in electrolysis with a zinc amalgam cathode in dilute sulfuric acid solution.[9]

IV. METHODS OF DETERMINATION

Practically all methods for the determination of thallium call for its prior reduction to the monovalent state. Reduction is easily accomplished in acid solution by treating with an excess of sulfur dioxide, which is then expelled by boiling. Probably the most satisfactory method of analysis for general use is that in which thallium is weighed as thallous chromate, Tl_2CrO_4. Weighing as thallic oxide, Tl_2O_3, is also satisfactory, but is more

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[7] A. A. Noyes, W. C. Bray, and E. B. Spear, *J. Am. Chem. Soc.*, 30, 489, 515, 559 (1908).

[8] See H. B. Knowles, Analysis of Thallium Halide Crystals, *Anal. Chem.*, 21, 1539 (1949).

[9] G. W. Morden, *J. Am. Chem. Soc.*, 31, 1045 (1909).

troublesome, especially when small amounts of thallium are in question. Determinations based on the precipitation of the iodide, TlI, are usually low because of the solubility of the salt.[10]

A. BY WEIGHING AS THE CHROMATE

The following method is a modification of that proposed by Browning and Hutchins.[11] Prepare a solution containing approximately 0.001 g of monovalent thallium per milliliter, no excessive amounts of ammonium salts, and no substances that form precipitates with ammonium hydroxide, reduce chromate, or react with thallium or potassium chromate in ammoniacal solutions. Neutralize with dilute ammonium hydroxide (2 + 1), and add 3 ml in excess per 100 ml of solution. Heat to 70 to 80° C, add a 10 per cent solution of potassium chromate, slowly and with stirring, until the solution contains approximately 2 g of the chromate per 100 ml. Let cool and stand for at least 12 hours. Filter through a Gooch crucible, and wash first with a 1 per cent solution of potassium chromate and then moderately with a 50 per cent solution of alcohol. Dry for 1 hour at 120 to 130° C, and weigh as Tl_2CrO_4.

B. BY WEIGHING AS THALLIC OXIDE

Thallous salts when treated with potassium hydroxide and potassium ferricyanide are oxidized and the thallium precipitated as thallic hydroxide. This reaction was utilized by Browning and Palmer[12] for the determination of thallium and modified by F. Mach and W. Lepper[13] as follows: Prepare 50 to 100 ml of an acid solution containing thallium in the monovalent state, no reducing substances, no compounds other than thallium that are precipitated by potassium ferricyanide or ferrocyanide in a solution containing potassium hydroxide, and no other compounds, such as iodide, that would react with thallium. Neutralize with a 5 per cent solution of potassium hydroxide, and add 25 ml in excess, and then 25 ml of an 8 per cent solution of potassium ferricyanide. Let stand for 18 hours, filter through a Gooch crucible, and wash the precipitate with hot water. Dry for 1 hour (no longer) at 200° C and preferably in an atmosphere free from carbon dioxide. Weigh as Tl_2O_3.[14]

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[10] For a discussion of methods for the determination of thallium, consult W. Strecker and P. de la Peña, Z. *anal. Chem.*, **67**, 256 (1925–26).

[11] P. E. Browning and G. P. Hutchins, *Am. J. Sci.*, [4] **8**, 460 (1899); F. Mach and W. Lepper, Z. *anal. Chem.*, **68**, 36 (1926); and L. Moser and A. Brukl, *loc. cit.*

[12] P. E. Browning and H. E. Palmer, *Am. J. Sci.*, [4] **27**, 380 (1909).

[13] F. Mach and W. Lepper, *op. cit.*, **41**.

[14] By this procedure, Mach and Lepper obtained 0.4203, 0.1122, and 0.0278 g of thallium in solutions containing 0.4206, 0.1120, and 0.0280 g of thallium, respectively. If very little thallium is present, the precipitate is very finely divided and difficult to filter. The ignited residue is prone to pick up carbon dioxide and breaks down to form thallous oxide at temperatures above 800° C.

C. BY WEIGHING AS THALLOUS IODIDE

The determination of thallium as iodide[15] is not so satisfactory as the foregoing because of the solubility of the precipitate.[16]

PROCEDURE. Prepare 50 to 100 ml of a solution containing not over 0.5 g of thallium as the sulfate or nitrate and free from chlorides and from substances such as lead or silver that are precipitated by iodide or substances such as titanium that hydrolyze in acetic acid solution. If there is any possibility that thallic salts are present, treat the solution with sulfur dioxide, and boil to expel the excess. Render the solution neutral, add 2 ml of acetic acid in excess, heat to boiling, and add a solution of potassium iodide until an excess of 1 g per 100 ml is present. Let stand 12 to 18 hours, filter through a Gooch crucible, and wash with a solution containing 1 per cent of potassium iodide and 1 per cent of acetic acid until free from soluble salts, and finally with 80 per cent acetone to remove the wash water. Dry at 120 to 130° C, and weigh as TlI.[17]

D. OTHER METHODS

Among other gravimetric methods that have been proposed are those in which thallium is weighed as thallous sulfostannate,[18] Tl_4SnS_4; as thallous acid sulfate, $TlHSO_4$, or the neutral sulfate, Tl_2SO_4,[19] and as the chloroplatinate, Tl_2PtCl_6,[20] which is the least soluble of the chloroplatinates.

Volumetric methods that might be mentioned are those based on the oxidation of thallous to thallic sulfate in hydrochloric acid solution by potassium permanganate,[21] potassium bromate,[22] or ceric sulfate.[23]

For the determination of from 0.005 to 0.2 mg of thallium in the presence of 0.5 to 1 g of silver, copper, cadmium, antimony, chromium, and iron,

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[15] G. Werther, Z. *anal. Chem.*, **3**, 1 (1864); H. Baubigny, *Compt. rend.*, **113**, 544 (1891); J. H. Long, Z. *anal. Chem.*, **30**, 342 (1891).

[16] According to F. Kohlrausch [Z. *phys. Chem.*, **64**, 168 (1908)], 1 liter of water dissolves 0.0847 g of thallous iodide at 26° C. It is less soluble in solutions containing potassium iodide, alcohol, or a little acetic acid, and is nearly insoluble in solutions containing ammonium hydroxide or sodium thiosulfate.

[17] By this method, Mach and Lepper (*loc. cit.*) obtained 0.4185, 0.1113, and 0.0277 g of thallium in solutions containing 0.4206, 0.1120, and 0.0280 g of thallium, respectively.

[18] L. F. Hawley, *J. Phys. Chem.*, **10**, 654 (1906); *J. Am. Chem. Soc.*, **29**, 1011 (1907).

[19] P. E. Browning, *Am. J. Sci.*, [4] **9**, 137 (1900).

[20] G. Neumann, *Ann.*, **244**, 349 (1888); A. S. Cushman, *Am. Chem. J.*, **24**, 222 (1900).

[21] L. F. Hawley, *J. Am. Chem. Soc.*, **29**, 300 (1907). See also R. S. Beale, A. W. Hutchison, and G. C. Chandlee, *Ind. Eng. Chem. Anal. Ed.*, **13**, 240 (1941).

[22] H. Marshall, *J. Soc. Chem. Ind.*, **19**, 994 (1900); E. Zintl and G. Rienäcker, Z. *anorg. Chem.*, 153, 276 (1926).

[23] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **52**, 36 (1930).

Haddock[24] recommends the extraction of monovalent thallium with a solution of diphenylthiocarbazone (dithizone) in chloroform, followed by conversion of the thallium to the trivalent state, reduction with potassium iodide in an acid solution containing starch-glycerin, and comparison of the starch-iodine color with samples similarly treated.

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[24] L. A. Haddock, *Analyst*, **60**, 394 (1935).

Chapter 29

INDIUM

Indium, like gallium, has never been found as the predominating metallic constituent of a mineral. It occurs, however, in traces in most zinc blendes and tin ores. It is also found in many samples of pyrites, galena, smithsonite, and siderite,[1] and in manganese, iron, and tungsten ores. It is sometimes present in small amounts in commercial zinc and, together with gallium, in residues from zinc retorts.

I. GENERAL CONSIDERATIONS

In the ordinary course of analysis, indium will be caught in the ammonia precipitate. Some of the indium may be volatilized during the ignition of the precipitate. That which remains will be counted as aluminum if it is not detected and its amount deducted. Indium can be detected, after concentration, by the bright blue color imparted to a flame by the chloride. The finding of the two bright blue lines λ 4511.55 and λ 4101.95 when the spark spectrum is viewed through the spectroscope is more conclusive, whereas an examination of the photographed arc spectra is the most satisfactory of all.

For the concentration and detection of indium, obtain the material in hydrochloric acid solution, and digest with an excess of zinc to precipitate the indium, together with such other reducible elements as copper and lead that may be present. Filter, dissolve the residue in nitric acid, add sulfuric acid, and evaporate to fumes of the latter in order to precipitate lead. Dilute so that the solution contains 10 per cent by volume of sulfuric acid, filter, and wash moderately with sulfuric acid of the same strength. Heat to boiling, add ammonium hydroxide in slight excess, filter, and wash the precipitate with a 2 per cent solution of ammonium nitrate. Dissolve the precipitate in as little hydrochloric acid as possible, nearly neutralize with ammonium hydroxide, and add 5 g of sodium bisulfite. Boil for 15 minutes, filter, and wash the precipitate with cold water. Dissolve the precipitate in hydrochloric acid, evaporate to small volume, and test the solution on a platinum wire in a Bunsen flame.

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[1] W. N. Hartley and H. Ramage, *J. Chem. Soc.*, **71**, 533 (1897).

II. DECOMPOSITION OF MINERALS CONTAINING INDIUM

Methods for the decomposition of minerals that contain indium vary according to the mineral in question; thus, zinc blendes are broken up by attack with hydrochloric acid followed by nitric acid (p. 425), pyrites require solution in aqua regia, while tin ores must be fused, as for example with sodium peroxide (p. 286). There is no danger of loss of indium through volatilization upon evaporation with hydrochloric acid.

For the concentration of indium, use is made of such reactions as reduction by an excess of zinc in acid solution, or precipitation with sodium acetate, barium carbonate, or sodium bisulfite.

III. METHODS OF SEPARATION

Indium forms monovalent, bivalent, and trivalent salts, but only the trivalent salts are stable in aqueous solutions.

Hydrogen sulfide does not precipitate indium when alone in strong acid solutions. It is, however, carried down by certain members of the hydrogen sulfide group in moderately acid, as for example 0.5 *N* sulfuric acid, solution. Unlike thallium, complete separations can be had by precipitating other sulfides in 3.6 *N* or stronger solutions. The yellow sulfide, In_2S_3, is precipitated by hydrogen sulfide in acetic acid or weak (approximately 0.02 *N*) sulfuric acid solution, the latter serving for the separation of indium from iron and aluminum. A white precipitate is formed when hydrogen sulfide is led into alkaline solutions containing indium, or when ammonium sulfide is added to neutral solutions. In cool solutions, precipitation by NH_4HS is very incomplete, and by $(NH_4)_2S$ almost complete. Little, if any, indium is precipitated by these reagents in boiling solutions.

Indium can be quantitatively separated from elements such as zinc, manganese, nickel, or cobalt by precipitation with freshly precipitated barium carbonate (p. 82), or in an ammonium acetate-acetic acid solution (p. 79). Good separations of indium from moderate amounts of copper, zinc, and nickel can be had by double precipitation with ammonium hydroxide in the presence of ammonium chloride as follows: Obtain the elements as the chlorides, dilute to 200 ml, add 5 g of ammonium chloride if not already present, and heat to 60 to 80° C. Add ammonium hydroxide until the copper hydroxide redissolves. Avoid a large excess. Digest for a few minutes, filter, and wash the filter, and precipitate with a hot 1 per cent solution of ammonium chloride. Dissolve the precipitate in hot dilute hydrochloric acid (1 + 10), and then wash the paper thoroughly with hot acid of 1 + 100 strength. Dilute the solution to 200 ml, and repeat the precipitation, filtration and washing.[2]

Precipitation by potassium cyanate[3] is said to give good separations of indium from zinc, nickel, sexivalent chromium, and, with slight modifications, from cobalt. For the simplest case, prepare 200 to 400 ml of feebly acid solution, treat with six times as much ammonium chloride as there is zinc present, add a few drops of methyl orange, and then enough potassium cyanate to produce a yellow coloration. Gradually heat to boiling, filter, wash with hot water, and, if much zinc or nickel is present, dissolve the precipitate in acid, and reprecipitate. If the precipitate is to be ignited, it must be washed until free from chlorides.

Indium salts are easily reduced to the metal by the action of an excess of zinc in dilute sulfuric acid solution, and so the element can be conveniently separated from other elements such as gallium, aluminum, and zirconium that are not reduced. The reaction serves only as a preliminary separation in the presence of reducible compounds such as those of copper, cadmium, tin, and thallium. Electrodeposition of indium from a solution of the sulfate in dilute sulfuric acid solution (1 + 4) provides an excellent method of separating indium from iron, but complete deposition is difficult.[4]

The separation of lead from indium is done by precipitation of the former as sulfate (p. 227).

An insoluble basic sulfite, $In_2(SO_3)_3 \cdot 2In(OH)_3 \cdot 5H_2O$ is formed when a nearly neutral solution of an indium salt is boiled with an excess of sodium bisulfite. This reaction does not serve as a final separation in the presence of other precipitable elements such as tin, titanium, or zirconium.

The separation of indium from gallium by precipitation in boiling alkali hydroxide solution is not entirely satisfactory, for a little indium remains unprecipitated and a little gallium is caught in the precipitate, the latter in spite of double precipitations. For this separation, Dennis and Bridgman[5] neutralized a solution containing approximately 100 mg each of the elements in 200 ml, with sodium hydroxide, then added 1.5 g in excess and boiled the solution for several minutes. The solution was then filtered and the precipitate dissolved in hydrochloric acid and reprecipitated, before proceeding with determinations as in Section IV. The same authors found that precipitation with potassium mercuric thiocyanate (p. 433) does not furnish a satisfactory separation of zinc from indium.

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[2] R. Gilchrist, *J. Research NBS*, **20**, 745 (1938).

[3] L. Moser and F. Siegmann, *Monatsh.*, **55**, 14 (1930).

[4] L. M. Dennis and W. C. Geer, *J. Am. Chem. Soc.*, **26**, 437 (1904); F. C. Mathers, *ibid.*, **29**, 485 (1907); and U. B. Bray and H. D. Kirschman, *ibid.*, **49**, 2739 (1927).

[5] L. M. Dennis and J. A. Bridgman, *ibid.*, **40**, 1552 (1918).

Hydrogen sulfide does not give a precipitate in mineral or organic acid solutions containing gallic salts alone. On the other hand, gallium can be completely precipitated in feebly acid, such as acetic acid-acetate, solutions that contain precipitable elements such as zinc, silver, copper, manganese, iron, or arsenic. In fact, such elements, particularly arsenic, are sometimes added for the purpose of gathering very small amounts of gallium. In this case, the arsenic can then be volatilized as described under Arsenic (p. 260), after dissolving the sulfides in aqua regia and evaporating to fumes with sulfuric acid. Separations by the use of hydrogen sulfide had best be confined to those that can be done in solutions that are appreciably acid.[11]

Like aluminum, gallium can be separated from nickel, manganese, the alkaline earths, magnesium, and the alkalies by precipitation with ammonium hydroxide in the presence of an excess of ammonium chloride. An excess of ammonium hydroxide is to be avoided, for the precipitate is appreciably soluble.

For the separation of gallium from zinc, nickel, cobalt, manganese, cadmium, beryllium, and thallium, as well as for its precipitation preparatory to final ignition and weighing as Ga_2O_3, Moser and Brukl[12] recommended precipitation by tannin in a boiling 1 to 2 per cent acetic acid solution containing 2 per cent of ammonium nitrate. The boiling solution is stirred as a 10 per cent solution of tannin is added, drop by drop, until precipitation is complete. A ten-fold excess should suffice unless the amount of gallium is small, when at least 5 ml should be used. The precipitate is washed with hot water containing a little ammonium nitrate and a drop or two of acetic acid. As a rule, the precipitate had better be dissolved in hot diluted hydrochloric acid, and the precipitation with tannin repeated after the acid is neutralized with ammonium hydroxide and acetic acid added. The final precipitate is ignited in quartz or porcelain. As the precipitate is quite voluminous, more than 0.1 g of Ga_2O_3 is handled with difficulty. In such case, most of the gallium had better be separated by double precipitations by the basic acetate method and the rest recovered by precipitation with tannin in the combined filtrates.

Gallium, together with aluminum, beryllium, and the like, can be separated from indium, iron, titanium, and similar elements by precipitation of the latter by means of sodium hydroxide. The separation is not entirely satisfactory, for the precipitation of indium may be incomplete, and the precipitate tends to retain gallium. According to E. H. Swift,[7] the separation of iron from gallium is complete in one operation, if the final concentration of the sodium hydroxide is not less than 0.3 *N*. For the separation of indium from gallium Dennis and Bridgman[3, 13] preferred a solution that is approximately 0.2 *N*.

Precipitation by barium carbonate (p. 82) serves satisfactorily for the separation of gallium from manganese but is worthless in the presence of zinc, nickel, or cobalt.

A separation for which much is claimed[14] is that based on precipitation of gallium by boiling with cupric hydrate. This is declared to give satisfactory separations from such elements as lead, cadmium, cobalt, nickel, manganese, zinc, iron, thallium (in presence of SO_2), beryllium, uranium, and the rare earths.

The precipitation of gallium by potassium ferrocyanide is a distinctive reaction that is used both for the detection of the element and for its separation from other elements.[15] Other elements such as zinc, zirconium, or indium that also give precipitates must be absent, as must also nitrates or other oxidizing agents. The reaction serves for the separation of gallium from aluminum, chromium, manganese, cadmium, mercury, lead, bismuth, and thallium if the ferrocyanide is added in slight excess to a dilute hydrochloric acid solution $(1 + 3)$ of the chlorides which is then heated to 60 to 70° C, digested at this temperature for 30 minutes, and then allowed to cool and stand for several hours, or days if the amount of gallium is very small. The precipitate is washed with cool dilute hydrochloric acid $(1 + 3)$. According to Browning and Porter, the decomposition of gallium ferrocyanide is done best by fusion with ammonium nitrate and subsequent treatment with sodium hydroxide to remove the iron.

J. Papish and L. E. Hoag[16] stated that a quantitative separation of gallium from iron can be obtained by precipitation of the latter as follows: To a hydrochloric acid solution of the chlorides, add ammonium hydroxide until a slight permanent precipitate is obtained which dissolves on the addition of a drop of hydrochloric acid. Add 2 or 3 drops more of hydrochloric acid and then add enough ammonium acetate to react with the acid. Add an excess of reagent (1 g of α-nitroso-β-naphthol dissolved in 50 ml of a 50% solution of acetic acid and filtered), and let stand several hours. Filter,

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[11] No gallium, for example, is carried down by copper, arsenic, or antimony in 0.36 *N* sulfuric acid solution.

[12] L. Moser and A. Brukl, *Monatsh.*, **50**, 181 (1928).

[13] See under Indium (p. 483).

[14] W. Crookes, *Select Methods in Chemical Analysis*, Longmans, Green & Co., London and New York (1894).

[15] For example, P. E. Browning and L. E. Porter [*Am. J. Sci.*, [4] **44**, 222 (1917)] stated that ferrocyanide gave a positive test for gallium in a dilute hydrochloric acid solution $(1 + 3)$ containing as little as 0.1 mg per 10 ml, provided the solution was allowed to stand for 1 hour. For the application of the reaction to the potentiometric titration of gallium, see H. D. Kirschman and J. B. Ramsey, *J. Am. Chem. Soc.*, **50**, 1632 (1928), and Sunao Ato, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **10**, 1 (1929).

[16] *J. Am. Chem. Soc.*, **50**, 2118 (1928).

and wash the precipitate first with a cold 50 per cent solution of acetic acid and then with water. Dry, ignite very cautiously in porcelain, and weigh as Fe_2O_3. Evaporate the filtrate to dryness, add dilute ammonium hydroxide until alkaline, and boil until a moistened piece of red litmus paper does not turn blue in the vapor. Cool, filter, wash with a 1 per cent solution of ammonium nitrate until free from chlorides, ignite, and weigh as Ga_2O_3 which is hygroscopic.

Aluminum can be separated from gallium by precipitation with gaseous hydrochloric acid in a solution containing equal parts of concentrated hydrochloric acid and ether (p. 134).[8,17] The chief consideration in this separation is to make sure by repeated treatments that all of the aluminum has been precipitated.

Precipitation by cupferron in dilute sulfuric acid (7 + 93) solution as described in IV, B provides an excellent method of gathering any gallium that may be present in a material such as aluminum,[18] and of separating it from elements such as indium, which are not precipitated under the conditions (see p. 493). Solution of the precipitate (p. 118) and reprecipitation are desirable if elements such as aluminum or indium are present in large amount.

Brukl[19] stated that gallium can be separated from (1) titanium, zirconium, and thorium, by precipitating with cupferron in a *N* solution of oxalic acid containing ammonium oxalate, (2) zirconium, by precipitating with phenylarsonic acid (p. 567) in hot 2 *N* sulfuric acid solution, (3) thorium, by precipitating with oxalic acid in a hydrochloric acid solution free from sulfate ion, and (4) vanadium, molybdenum, and tungsten, by precipitating most of the gallium by 8-hydroxyquinoline in hot diluted ammonium hydroxide (5 + 95) and filtering, and then recovering the remainder by rendering just acid with acetic acid, adding 1 ml of a saturated solution of ammonium carbonate, boiling until neutral to litmus, allowing to digest for 2 or 3 hours, and filtering. This last precipitate is usually impure and had better be dissolved and reprecipitated, before the combined precipitates are dissolved in 2 *N* sulfuric acid and the gallium precipitated by cupferron. Precipitation with cupferron in 2 *N* acid serves for the precipitation of the gallium in the phenylarsonic acid filtrate, and in the filtrates obtained in 1 and 3 after evaporating with sulfuric acid to destroy the oxalic acid.

Gallium can be separated from many elements by repeated extraction, at 20° C, of a cold solution of the trichloride in 5 to 6 *N* hydrochloric acid with ether that is free from alcohol and that has previously been shaken

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[17] Browning and Porter, *loc. cit.*

[18] J. A. Scherrer, *J. Research NBS*, **15**, 585 (1935).

[19] A. Brukl, *Monatsh.*, **52**, 253 (1929).

two to three times with acid of the same concentration (p. 134).[20] But traces of indium are extracted under the same conditions.[21]

Gallium chloride can be separated from chlorides that are not volatile or that volatilize at appreciably higher temperatures by heating in a current of chlorine. Thus Dennis and Bridgman[3] separated gallium trichloride (b.p. 215 to 220° C) from indium trichloride (volatilizes slowly at 600° C), and zinc chloride (b.p. 730° C) by distillation of the anhydrous chlorides in a current of dry chlorine at a temperature of about 230 to 255° C.

Zinc can be precipitated in a dilute sulfuric or nitric acid solution by means of potassium mercuric thiocyanate[22] and separated from gallium.[8] The gallium in the filtrate can then be precipitated by ammonium hydroxide after the removal of mercury by precipitation with hydrogen sulfide in a solution containing 5 to 7 per cent by volume of hydrochloric acid. To make sure that no gallium is carried down by the mercuric sulfide, the precipitate had better be dried and ignited to expel mercury, and any residue recovered by fusion with sodium carbonate and solution of the melt in acid. Zinc is precipitated as follows: Prepare a clear solution of the precipitant by dissolving 27 g of mercuric chloride and 39 g of potassium thiocyanate in 1000 ml of water, and then prepare a sulfuric or nitric acid solution of gallium and zinc containing no more than 0.05 g of zinc and 1 ml of either acid per 100 ml of solution. Cool to room temperature, add the precipitant, drop by drop and with constant stirring, until a precipitate begins to form, and then add 20 ml for every 0.1 g of zinc that is present. Let stand for 2 hours or more, filter through asbestos, and wash with a solution containing 20 ml of the reagent per liter. If much zinc is present, set the filtrate aside, treat the precipitate on the asbestos mat alternately with a few drops of a strong solution of sodium hydroxide and of hydrochloric acid, and finally rinse the pad with hot water. Neutralize the solution with sodium hydroxide, make acid as before, reprecipitate, and finally combine the filtrates, which should now contain all of the gallium.

IV. METHODS OF DETERMINATION

Gallium is always weighed as the oxide, Ga_2O_3, after precipitation by ammonium hydroxide, cupferron, ammonium sulfite, or the like in solutions of its trivalent salts. As the chloride, $GaCl_3$, is volatile, precipitation had

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[20] E. H. Swift [*J. Am. Chem. Soc.*, **46**, 2375 (1924)] stated that about 97 per cent of the gallium can be extracted by shaking 50 ml of a 4.9 to 5.0 *N* solution of hydrochloric acid containing 0.1 g of gallium with 50 ml of ether, and that three extractions should leave less than 0.1 mg. See also J. A. Scherrer, *J. Research NBS*, **15**, 588 (1935), who prefers to allow the separatory funnel to stand at room temperature for 1 hour before the acid layer is drawn off after the last extraction.

[21] I. Wada and Sunao Ato, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **1**, 70 (1922).

[22] G. E. F. Lundell and Nai Kim Bee, *Trans. Am. Inst. Metals*, **8**, 146 (1914).

best be made in solutions that are free from the chloride ion. If it is ignited at temperatures below 1000° C, the oxide is hygroscopic and must be handled accordingly. If a proper oxidizing atmosphere is maintained, the oxide can be ignited without loss at temperatures as high as 1300° C, and is then nonhygroscopic.[23] Gallic oxide is pure white. A tinted oxide indicates impurities; indium oxide, for example, causes a yellowish tint.

A. PRECIPITATION BY AMMONIUM HYDROXIDE

An excess of ammonium hydroxide must be avoided in the precipitation of gallium, and care must be taken to recover all of the precipitate, which has a tendency to stick to the vessel.

PROCEDURE. Prepare a sulfuric acid solution of trivalent gallium that is free from organic matter and excessive amounts of ammonium salts and contains no other compounds that are precipitable by ammonium hydroxide. Dilute to 200 ml, add a few drops of methyl red, and heat to boiling. Add dilute ammonium hydroxide, free from carbonate, slowly until a precipitate begins to form, and then cease until further precipitation stops. Again add a little ammonium hydroxide, boil, and so continue until the indicator has just turned yellow.[24] Add a little macerated paper, boil for 1 to 2 minutes longer, filter, and transfer as much of the precipitate as possible to the filter by scrubbing and washing with a hot neutral 2 per cent solution of ammonium nitrate. Cover the funnel, quickly dissolve any precipitate still clinging to the beaker in as little hot dilute sulfuric acid as possible, again precipitate with ammonium hydroxide as before, and filter. Finally wash thoroughly with a hot 2 per cent solution of ammonium nitrate. Transfer the wet paper and precipitate to a platinum crucible weighed with tightly fitting cover, and heat gently (uncovered) until dry and then at as low a temperature as possible until carbon has been destroyed. Ignite under good oxidizing conditions at approximately 1000° C, cover, and resume the heating for a few minutes. Cool over sulfuric acid or phosphorus pentoxide in a desiccator, and weigh while tightly covered. Again heat, cool as before, place weights on the balance, and then quickly weigh. Repeat to constant weight. The weighed residue should be examined for other oxides, and, in accurate analyses, it should always be corrected for impurities such as silica introduced through the reagents or by attack of the glassware.

B. PRECIPITATION BY CUPFERRON

Gallium can be quantitatively precipitated by cupferron in diluted sulfuric acid solution (7 + 93), provided a fair excess of the reagent is used and the solution is allowed to stand for a while before it is filtered. As much as 1 g of tartaric acid is without effect on the precipitation. The precipitation of gallium can, therefore, follow preliminary separations of the elements that are precipitated by hydrogen sulfide in acid solution, and of the elements that are precipitated by ammonium sulfide in ammoniacal solutions containing ammonium tartrate (see p. 65). In this case the method is as follows:

PROCEDURE. Add dilute sulfuric acid (1 + 1) to the ammonium sulfide filtrate until it is acid, and then boil to expel hydrogen sulfide. Filter if a residue remains, and dilute the solution to 375 ml. Neutralize with ammonium hydroxide, stir, and cautiously add 30 ml of sulfuric acid. Chill the solution in ice water, and add enough of a chilled aqueous 6 per cent solution of cupferron to precipitate the gallium and to provide an excess of 15 to 20 ml of the reagent. Add a little ashless paper pulp, stir well, and let stand for 1 hour in the ice water. Filter, and wash the precipitate with cold dilute sulfuric acid (7 + 93) containing 1.5 g of cupferron per liter. Place the paper and precipitate in a platinum crucible. Dry carefully, then char and burn off carbon cautiously, and finally ignite at 1000 to 1300° C, always under *good* oxidizing conditions. Cool in a desiccator and weigh.

The treatment that is indicated removes hydrogen sulfide group elements such as tin, and ammonium sulfide group members such as iron. It does not take care of elements such as titanium, zirconium, or vanadium which are also precipitated by cupferron in acid solution. Unless it is known that these elements are not present in the materials under test, or that additional treatments have insured their removal, the ignited residue must always be examined, and the weight of any accompanying oxides deducted.

C. BY PRECIPITATION WITH AMMONIUM BISULFITE

Dennis and Bridgman[8] stated that precipitation of gallium hydroxide by ammonium bisulfite is complete and that the precipitate does not stick to the walls of the vessel as does the one thrown out by ammonium hydroxide.

PROCEDURE. Prepare 100 to 200 ml of a hydrochloric or, preferably, sulfuric acid solution that contains no more than 0.1 g of trivalent gallium, and no other compounds that are precipitated by ammonium hydroxide or ammonium bisulfite. Add ammonium hydroxide until the solution is faintly alkaline to litmus, then 5 ml of a solution of ammonium bisulfite (prepared by saturating ammonium hydroxide with sulfur dioxide), and finally dilute hydrochloric acid until the solution is just acid to litmus. Dilute the solution to 200 ml, cover, and boil vigorously for 5 minutes. Filter, and proceed as in A. To make sure that precipitation is complete, the filtrate had better be treated with a drop or two of methyl red and then with ammonium hydroxide until the solution just turns yellow.

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[23] G. E. F. Lundell and J. I. Hoffman, *J. Research NBS*, **15**, 409 (1935).

[24] If the amount of gallium is of the order of a few tenths of a milligram, the solution should be allowed to stand at the side of the steam bath overnight.

II. ELEMENTS THAT FORM HYDROXIDES OR BASIC COMPOUNDS

Aluminum, Beryllium, Chromium, Thorium, Scandium, Rare
Earths, Zirconium, Titanium, Columbium, and Tantalum

Chapter 31

ALUMINUM

Aluminum is the most abundant metal and is an essential constituent of nearly all important rocks except the peridotites, sandstones, and limestones. Even in these its compounds are common impurities. It does not occur native for it is easily oxidized, and it always occurs trivalent in nature. Aluminum is found chiefly in silicates, such as the feldspars, micas, and clays, but also as the oxide corundum, the hydroxide bauxite, as fluoride in cryolite, and in various phosphates and sulfates.

I. GENERAL CONSIDERATIONS

The determination of aluminum in pure salts is a comparatively simple matter. Its correct determination in materials such as rocks, minerals and ceramic or metallurgical products is one of the analyst's most difficult problems. In ordinary analyses, aluminum is found in the ammonia precipitate, together with a number of other elements such as iron, titanium, zirconium, vanadium, phosphorus, and silicon. To report such a mixture as "Percentage of R_2O_3," as is often done, is obviously misleading. Unless the analyst knows the composition of the precipitate, it should be reported as "Percentage of Mixed Oxides." Equally misleading is the practice of determining iron, and perhaps titanium, in the ammonia precipitate and reporting the remainder as alumina. In most analyses the percentage of aluminum is best obtained by difference after determinations of each of the other components of the weighed residue. The task can usually be simplified by determining some of the components in groups, as for example the percentage of Fe_2O_3, TiO_2, ZrO_2, and V_2O_5 by precipitation with cupferron (p. 116).

II. ATTACK ON MINERALS CONTAINING ALUMINUM

The attack by fusion of minerals containing aluminum is covered in the chapter on Fluxes (p. 836).

Bauxite can be almost entirely decomposed by a mixture of hydrofluoric, nitric, and sulfuric acids. Such an attack is more attractive than a fusion procedure because the introduction of foreign salts is avoided and silica is eliminated. Hydrofluoric acid must afterwards be *entirely* expelled by fuming with sulfuric acid, lest the subsequent precipitation of alumina by ammonium hydroxide be incomplete; and any insoluble residue must be recovered, fused, and put into solution.

For the decomposition of certain aluminous materials of a refractory nature, such as calcined alumina, Churchill, Bridges, and Miller[1] recommend the following attack: Treat 1 g of sample with 20 ml of hydrofluoric acid, 20 ml of water, and 50 ml of dilute ammonium hydroxide (1 + 1). Evaporate, and heat until almost dry, but still moist and fuming. Repeat two or three times if necessary, then add 5 ml of sulfuric acid. Heat until fuming ceases, and ignite at dull red heat. Add 5 ml of sulfuric acid, and heat until fuming ceases. Take up in 2 ml of sulfuric acid, heat to incipient fuming, cool, and take up in water. This method of attack is attractive in that nonvolatile salts are not introduced, and the solution can be used for the determination of the alkalies, as by the triple acetate method for sodium (p. 666).

Some burned refractories of high alumina content do not respond to a wet attack. For these, as well as for bauxite when silica is to be determined, recourse must be had to a fusion method. Sodium carbonate, sodium peroxide,[2] or alkali pyrosulfate are all satisfactory. With some refractories 7 to 10 g of sodium carbonate are needed for the fusion of a 1-g sample, and the full temperature of a Meker burner must be maintained for at least 1 hour. According to M. O. Lamar,[3] satisfactory fusions of calcined bauxite are obtained through the use of equal parts of sodium carbonate and fused borax.[4] The melt can be dissolved in dilute hydrochloric or sulfuric acid, depending upon which reagent is preferred for the dehydration of silica. If there is any evidence of incomplete decomposition of the sample, after either wet or fusion attack, much trouble can be avoided by filtering off the insoluble matter, igniting, fusing with pyrosulfate, and dissolving the melt in the original solution before proceeding with the analysis.

Alumina (and beryllia) can be decomposed by heating with hydrochloric acid, either alone or with an oxidizing agent such as nitric acid or chlorine,

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[1] H. V. Churchill, R. W. Bridges, and A. L. Miller, *Ind. Eng. Chem. Anal. Ed.*, **8**, 348 (1936).

[2] Preferably by explosion with sugar carbon as described under Fluxes (p. 839).

[3] Chief chemist, Norton Co. (private communication).

[4] If borax is used, it must be removed before determinations of silica or alumina are attempted, for otherwise part of the boron is carried down by silica and finally volatilized as the fluoride, BF_3, while part is carried down by the ammonia precipitate in spite of reprecipitations. The removal of boron is carried out as described under Silicon (p. 672).

Chapter 30

GALLIUM

No mineral is known in which gallium is the predominating constituent. It is, however, widely distributed in nature and is found in minute quantities associated with the elements aluminum, iron, manganese, zinc, lead, and indium. Thus, it occurs in traces in many zinc blendes, iron ores,[1] and kaolin. According to Clarke[2] it is always present in spectroscopic traces in bauxite and in nearly all aluminous materials. As much as 0.02 per cent of gallium has been found in commercial aluminum.

I. GENERAL CONSIDERATIONS

Analytically, gallium belongs in the aluminum group, and so in the ordinary course of analysis gallium will be caught in the ammonia precipitate and counted as aluminum unless it is detected and its amount deducted. Preliminary tests for gallium are usually made by the spark-spectrum method after some preliminary concentration has been done.

Dennis and Bridgman[3] state that as little as 0.0046 mg of gallium and 0.0013 mg of indium can be detected by ocular observation of the spark spectra of hydrochloric acid solutions of their chlorides, and that relatively large amounts of one element do not materially affect the delicacy of the test for the other. For the preliminary concentration and qualitative detection, the precipitation of gallium by potassium ferrocyanide in moderately strong hydrochloric acid solution, as described in Section III, is by far the best.

As little as 0.02 mg of gallium per liter can be detected or determined colorimetrically by the use of quinalizarin, with which it forms a pink- to amethyst-colored lake.[4] The best results are obtained in a solution that contains 0.02 to 0.2 mg of gallium and 0.5 g of sodium fluoride per liter, has a *p*H of 5.0, and is 1 *N* in ammonium acetate and 0.5 *N* in ammonium chloride. Elements that are known to interfere and that must be separated before the test is applied are lead, copper, tin, antimony, indium, platinum, germanium, vanadium, molybdenum, and more than 1 mg of iron or 10 mg of aluminum.

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[1] According to W. N. Hartley and H. Ramage [*Trans. Chem. Soc.*, **71**, 533 (1897)], gallium was found in 35 out of 91 iron ores. Its presence is particularly remarked in all magnetites, and its absence in siderites.

[2] F. W. Clarke, The Data of Geochemistry, *U. S. Geol. Survey Bull.* **770**, 16 (1924).

[3] L. M. Dennis and J. A. Bridgman, *J. Am. Chem. Soc.*, **40**, 1534 (1918).

[4] H. H. Willard and H. C. Fogg, *ibid.*, **59**, 40 (1937).

The detection of as little as 0.1 μg of gallium per 10 ml of solution in the presence of iron (ferrous) and aluminum by a fluorescence reaction following precipitation with 8-hydroxyquinoline at *p*H 2.6 and extraction with chloroform is described by E. B. Sandell.[5] Ferric iron, cupric copper, vanadate, molybdate, fluorine, lithium, beryllium, scandium, indium, and zinc interfere and require special treatments.

II. ATTACK OF MATERIALS CONTAINING GALLIUM

The statement that gallic chloride is lost by volatilization when hydrochloric acid solutions of its salts are evaporated[6] was disproved by E. H. Swift,[7] who found that such solutions can be evaporated to dryness on the steam bath with no loss of the element whatever. Gallium is not volatilized during distillations at 200 to 220° C in which hydrochloric or hydrobromic acids are dropped into solutions of gallium in sulfuric or perchloric acids.[8] The attack of materials containing gallium can therefore proceed along the lines usually adopted for the material in question. Hydrochloric acid or volatile chlorides should never be left in gallium-bearing compounds that are to be ignited.[9]

Metallic gallium can be quite readily dissolved by heating with a mixture of two-thirds concentrated sulfuric acid and one-third perchloric acid (72%).[10]

III. METHODS OF SEPARATION

Gallium is either bivalent or trivalent in its compounds. The gallous compounds, which have reducing properties, are unstable and hence only the gallic compounds are encountered in the usual course of analysis.

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[5] E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, **13**, 844 (1941).

[6] Fresenius-Mitchell, *Introduction to Qualitative Chemical Analysis*, p. 269, John Wiley & Sons (1921).

[7] *J. Am. Chem. Soc.*, **46**, 2377 (1924).

[8] J. I. Hoffman and G. E. F. Lundell, *J. Research NBS*, **22**, 467 (1939).

[9] For the rapid concentration of gallium (and germanium) from zinc oxide by dissolving the oxide in acid, rendering the solution basic by slowly adding some of the original zinc oxide, and filtering, see C. James and H. C. Fogg, *J. Am. Chem. Soc.*, **51**, 1459 (1929). F. Sebba and W. Pugh [*J. Chem. Soc.*, 1371 (1937)] state that all of the gallium in germanite can be obtained in solution by fusing the finely ground ore with sodium hydroxide in an iron crucible, extracting the melt with water, and filtering.

[10] L. S. Foster, *ibid.*, **61**, 3122 (1939).

IV. METHODS OF DETERMINATION

Indium is generally weighed as the oxide, In_2O_3, after ignition at 1100 to 1200° C.[6] The oxide is reddish brown when hot, and light yellow when cold. It dissolves readily in hot acids. As the oxide is quite easily reduced to metal, care must be taken to preserve good oxidizing conditions throughout ignition.

The final precipitation of indium is usually done by precipitation of the hydroxide, $In(OH)_3$, by ammonium hydroxide in a solution containing ammonium nitrate. Ammonium chloride is to be avoided, lest indium chloride be formed and volatilized during subsequent ignition of the precipitate.[7]

Among other methods that may be mentioned are those based on titration with potassium ferrocyanide[8] and on the electrolytic microdeposition of small amounts of indium (2 mg) in a feebly ammoniacal solution containing ammonium oxalate.[9]

The use of dithizone for the determination of small amounts of indium and the effect of copper, lead, iron, nickel, cobalt, zinc, gallium, tin, aluminum, manganese, cadmium, and thallium on the determination is described by I. May and J. I. Hoffman.[10]

A. BY PRECIPITATION WITH AMMONIUM HYDROXIDE

In this precipitation, all other elements that are precipitable by ammonium hydroxide must be absent, and a large excess of ammonium hydroxide must be avoided because of its solvent action on the precipitate. Tartaric acid inhibits the precipitation.

PROCEDURE. Prepare an acid, preferably nitric acid, solution of indium, free from organic compounds and excessive amounts of ammonium salts and containing no other elements that are precipitable by ammonium hydroxide when alone or, like phosphorus, when in combination with indium. Dilute in accordance with the amount of indium present, but avoid a concentration greater than 0.1 g of indium per 200 ml of solution. If not already present, add 1 ml of nitric acid, heat to boiling, and add dilute

ammonium hydroxide (1 + 1) slowly until in *slight* excess. Boil for 1 minute, cool to approximately 60° C, add a little macerated paper, and filter. Wash with a warm, *faintly* ammoniacal 1 per cent solution of ammonium nitrate, and place paper and precipitate in a tared platinum crucible. Carefully dry, char the paper without inflaming, and burn the carbon under *good* oxidizing conditions at as low a temperature as possible. The heating of the crucible is done best in a muffle. If the crucible is heated over a direct flame, it had better be inserted in an asbestos shield to make sure of the exclusion of reducing gases from the flame. When the carbon has been destroyed, increase the heat to 1100 to 1200° C, and heat for 15 minutes. Cover the crucible, heat for a few minutes longer, cool in a desiccator, and weigh. Repeat the ignition to constant weight.

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[6] According to L. Moser and F. Siegmann [*Monatsh.*, 55, 14 (1930)], In_2O_3 is not volatile at the temperature of the blast lamp and is not hygroscopic after this strong ignition.

[7] A. Thiel and H. Koelsch, *Z. anorg. Chem.*, 66, 288 (1910).

[8] See U. B. Bray and H. D. Kirschman [*J. Am. Chem. Soc.*, 49, 2739 (1927)] who recommended potentiometric titration, and H. B. Hope, M. Ross, and J. F. Skelly [*Ind. Eng. Chem. Anal. Ed.*, 8, 51 (1936)], who use diphenylbenzidine as an internal oxidation-reduction indicator.

[9] G. L. Royer, *ibid.*, 12, 439 (1940).

[10] *J. Wash. Acad. Sci.*, 38, 329 (1948).

at 250 to 300° C in a sealed glass tube (p. 347). This permits solution of the material without addition of any foreign substance except the pure acid.

Aluminum dissolves readily in certain acids and alkalies. Solution is rapid in hydrochloric acid, concentrated or moderately dilute; the same is true of hydrofluoric and other binary halogen acids. Reaction with dilute sulfuric acid (2 + 1) starts rapidly but slows up considerably unless a small amount of a salt of mercury is added. The action of nitric acid is slow, but can also be accelerated by mercury. Mixed acids, such as nitric-hydrochloric-sulfuric, are often used. Solutions of fixed alkali hydroxides dissolve aluminum readily.[5]

III. METHODS OF SEPARATION

Although there are satisfactory methods for the separation of aluminum when it is present in simple combinations, there are no simple procedures for its isolation from the complex mixtures in which it usually occurs. Thus, the precipitation of aluminum by phenylhydrazine (p. 128), which serves as an excellent separation from bivalent iron, is but a preliminary step when other elements such as titanium, zirconium, phosphorus, or vanadium are present, as is usually the case.

Aluminum can be separated from the alkalies (including lithium), alkaline earths, magnesium, and moderate amounts of certain elements such as nickel and manganese, by precipitation with ammonium hydroxide in the presence of ammonium chloride (p. 77). Complete precipitation of aluminum and good separations from manganese and nickel depend on neutralizing slowly from *p*H 3 on, and finally holding the *p*H slightly lower than 7 (preferably 6.6 to 6.7). Separations from cobalt, zinc, and copper are not satisfactory.[6]

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[5] H. V. Churchill and associates, *Chemical Analysis of Aluminum*, 3d ed., Aluminum Research Laboratories, New Kensington, Pa. (1950).

[6] W. Blum, *Bur. Standards Sci. Paper* 286; *J. Am. Chem. Soc.*, 38, 1282 (1916); G. E. F. Lundell and H. B. Knowles, *ibid.*, 45, 676 (1923).

The separations that can be expected when aluminum is precipitated as described in IV, A are indicated by the following data:

Aluminum, g	Accompanying Element, g	Amount of Accompanying Element Found in $Al(OH)_3$ after Single Precipitation, g	Double Precipitation, g
0.1	1.0 Mn	0.0017	0.00002
0.1	0.05 Ni	0.0006	None found
0.1	0.05 Co	0.0041	0.0012
0.1	0.05 Cu	0.0211	0.0077
0.1	0.05 Zn	0.0216	0.0108

So many other elements are also precipitated by ammonium hydroxide that the reaction ordinarily serves only as a preliminary separation.

More dense precipitates of aluminum hydroxide can be obtained by the use of sodium thiosulfate,[7] potassium iodide and potassium iodate,[8] or sodium or ammonium nitrite.[9] The reagents are added to feebly acid solutions, and the precipitates can, in general, be expected to contain the same elements as are carried down by ammonium hydroxide. In the first method, the solution is treated with an excess of sodium thiosulfate, boiled until sulfur dioxide is expelled, and then treated with a faint excess of ammonium hydroxide in order to precipitate the small amount of aluminum still in solution. The precipitate always contains sulfur. Its iron content depends on the treatment; very little will be found if thiosulfate alone is used, whereas more or less will be present if ammonium hydroxide has been added. In the second method a *p*H value of approximately 7.5 is obtained by adding equal volumes of a 25 per cent solution of the iodide and a saturated solution of the iodate (about 7%), letting the solution stand for 5 minutes, and then decolorizing with a 20 per cent solution of sodium thiosulfate. A little more iodate and iodide is next added, this is followed by thiosulfate if iodine is liberated, and the solution is heated for about 30 minutes on the steam bath. The precipitate is less prone to carry down alkali salts, and separation from boron is said to be complete. In the nitrite method, the solution is diluted to about 250 ml, treated with an excess (20 ml) of a 6 per cent solution of pure ammonium nitrite,[10] covered, boiled until the evolution of oxides of nitrogen ceases (about 20 minutes) and heated for 15 to 30 minutes on the steam bath. Ammonium hydroxide must then be added in slight excess if more than 1 per cent of ammonium salts were originally present.

Aluminum can be quantitatively precipitated as basic succinate and separated from a number of elements by adding urea and succinic acid to a feebly acid solution of the elements and boiling.[11] The excellence of the

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[7] G. Chancel, *Compt. rend.*, 46, 987 (1858); W. Gibbs, *Z. anal. Chem.*, 3, 391 (1864).

[8] A. Stock, *Ber.*, 33, 548 (1900).

[9] G. Wyncoop, *J. Am. Chem. Soc.*, 19, 434 (1897); E. Schirm, *Chem. Ztg.*, 33, 877 (1909).

[10] Ammonium nitrite occasionally contains barium. If the solution of aluminum contains sulfates, the solution of the reagent must be treated with ammonium sulfate and filtered before use.

[11] H. H. Willard and N. K. Tang, *Ind. Eng. Chem. Anal. Ed.*, 9, 357 (1937); see also p. 389. The procedure is as follows: Prepare 50 to 100 ml of a dilute hydrochloric acid solution containing approximately 0.1 g of aluminum in a 600-ml tall-form beaker, and add dilute ammonium hydroxide until the solution becomes slightly turbid. Add dilute hydrochloric acid (1 + 1) dropwise until the precipitate redissolves, and then add 1 drop in excess. Dilute to 400 ml, add 5 g of succinic acid dissolved in 100 ml of water, and then add 10 g of ammonium chloride and 4 g of urea. Heat to boiling, and boil until the solution begins to become turbid (40 to 45 minutes). The pre-

separation is attributed to a combination of four factors: a dense precipitate, a slow and uniform increase in *p*H (through the hydrolysis of urea with formation of ammonia), a homogeneous solution, and a low final *p*H. By this method, a single precipitation will efficiently separate 0.1 g of aluminum from an equal amount of nickel or cobalt, or from 1 g of calcium, barium, magnesium, manganese, and cadmium, or a few milligrams of aluminum from 1 g of cobalt or nickel. Special treatments are required for zinc, copper, and iron.[12]

Separations based on precipitation by ammonium carbonate or ammonium sulfide are not so satisfactory, for the precipitation of aluminum is incomplete in the excess of these reagents that must usually be employed. There is also danger of incomplete precipitation in the basic acetate method (p. 79), particularly when aluminum is preponderant.

The separation of aluminum based on its precipitation by barium carbonate (p. 82) is a useful procedure but can rarely be applied in cases where aluminum alone is precipitated.

It should be borne in mind that barium, and probably also lead, sulfate carries down appreciable amounts of aluminum.[13]

Iron, titanium, zirconium, rare earths, and manganese can be separated from aluminum by precipitation with sodium hydroxide (p. 84). This separation fails in the presence of magnesium or nickel which carry down aluminum; also when titanium is greatly preponderant, in which case the latter is not completely precipitated. Calcium does not interfere. Phosphorus, vanadium, tungsten, molybdenum, and the like accompany alumi-

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liminary boiling period can be shortened, with but little effect on the separation, by adding dilute ammonium hydroxide to the *hot* solution until it shows a very faint opalescence. Continue the boiling for 2 hours. At this stage, the *p*H of the solution should be within the range *p*H 4.2 to 4.6. Let settle, add a little paper pulp, and filter. Wash the beaker, paper, and precipitate ten times with a 1 per cent solution of succinic acid, made neutral to methyl red with ammonium hydroxide. Scrub the inside of the beaker with pieces of filter paper to remove as much as possible of the precipitate, and add to the paper containing the main precipitate. To recover all of the adhering precipitate, dissolve it in dilute hydrochloric acid, and reprecipitate with ammonium hydroxide as in IV, A. Catch the precipitate on a separate paper, and then ignite both papers and precipitates to constant weight in a platinum crucible at 1200° C.

Slightly less satisfactory separations of nickel, cobalt, zinc, and copper are obtained if 1 g of ammonium sulfate is substituted for succinic acid, which yields a final *p*H of 6.5 to 7.5. For the precipitation of aluminum with ammonium benzoate in magnesium alloys, see V. A. Stenger, W. R. Kramer, and A. W. Beshgetor, *Ind. Eng. Chem. Anal. Ed.*, **14**, 797 (1942).

[12] See also A. J. Boyle and D. F. Musser, *Ind. Eng. Chem. Anal. Ed.*, 15, 621 (1943).

[13] For example, 0.14 per cent instead of the correct content 0.18 per cent of Al_2O_3 was obtained when no attention was paid to the aluminum carried down by $BaSO_4$—$PbSO_4$ in analyses in which 10-g portions of a glass containing 17.5 per cent PbO and 1.4 per cent BaO were dissolved in H_2SO_4—HF and evaporated to fumes of H_2SO_4.

num. Calcium does not interfere in separations based on the use of sodium hydroxide and sodium carbonate, whereas magnesium and manganese do.

Members of the hydrogen sulfide group are separated from aluminum by precipitation with hydrogen sulfide in acid solution (p. 60); precipitation by ammonium sulfide in an ammoniacal solution containing tartrate (p. 89) serves satisfactorily for the separation of iron.

Silica separates in a much more compact and filterable form from sulfuric acid solutions containing considerable aluminum if the hot fuming acid is cooled somewhat, a little cool water is quickly poured into the still warm solution, and the solution is then diluted with warm water, warmed, and treated with macerated paper before filtering.

Precipitation by cupferron (p. 116) affords a clear-cut separation of a number of elements from aluminum and is especially useful when small amounts of elements such as iron, titanium, zirconium, vanadium, tin, columbium, or tantalum must be separated from large amounts of aluminum, as in bauxite or metallic aluminum. If desired, aluminum can be precipitated in the filtrate by adding more cupferron and rendering the solution feebly acid, about *p*H 5. It can also be precipitated in the filtrate by rendering it ammoniacal, warming to 70° C, adding 8-hydroxyquinoline, and proceeding as described on page 508.

Iron, nickel, cobalt, chromium, zinc, gallium, copper, tin, and certain other elements are conveniently separated from aluminum by electrolytic deposition in a mercury cathode in dilute sulfuric acid solution (p. 138).[14] Still another separation of iron from aluminum is that based on the extraction of the former by ether in cold dilute hydrochloric acid solution (p. 134). No doubt an excellent separation of aluminum from chromium can be obtained by oxidizing the latter to the chromate by heating to strong fumes with perchloric acid (see Reagents, p. 39), cooling, diluting, and then precipitating the aluminum with ammonium hydroxide.

So far as we know, the only method that furnishes, in one operation, a reasonably good separation of aluminum from elements such as iron, titanium, the rare earths, and beryllium is that of Gooch and Havens.[15] In this procedure, aluminum is precipitated as the hydrated chloride, $AlCl_3 \cdot 6H_2O$, by passing gaseous hydrochloric acid into a cold, *concentrated* solution of aluminum chloride in a mixture of hydrochloric acid and ether. The solubility of the aluminum chloride amounts to approximately 5 parts of $AlCl_3 \cdot 6H_2O$, corresponding to 1 part of Al_2O_3, in 125,000 parts of the mixture. The authors show that good separations of aluminum from iron, zinc, copper, mercury, and bismuth are also possible. A good separation

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[14] For an application of the method to solutions containing aluminum, copper, iron, nickel, manganese, and chromium, consult D. H. Brophy, *Ind. Eng. Chem.*, 16, 963 (1924).

[15] F. A. Gooch and F. S. Havens, *Am. J. Sci.*, [4] **2**, 416 (1896).

can also be had from phosphorus and presumably from a number of other elements. Alkali chlorides are insoluble and must be avoided.

The procedure is as follows: Obtain the aluminum in hydrochloric acid solution and free from alkali salts. Evaporate the solution to as small a volume as will still keep the salts in solution, say, 5 to 10 ml. Cool, add enough hydrochloric acid to bring the volume to 12 to 25 ml, and saturate the solution with gaseous hydrochloric acid while cooled to a temperature not exceeding 15° C. Add a volume of ether equal to the volume of the liquid, and again pass gaseous hydrochloric acid into the cooled solution until it is saturated. At the same time, or while the solution is kept cold, prepare a washing solution composed of equal parts of hydrochloric acid and ether and saturated with hydrochloric acid gas at 15° C. Filter on a Gooch or Munroe crucible, preferably the latter, after it has been cooled by the passage of a little of the washing liquid through it. If the precipitate is to be ignited and weighed directly, use a crucible which has been tared after washing and igniting as in the method. Wash the precipitate with the cold washing solution until foreign salts are removed.[16] If the precipitate is not to be ignited directly, dissolve the salt in dilute hydrochloric acid, and treat the solution as may be necessary for reprecipitation, or for precipitation by ammonium hydroxide. If the precipitate is to be converted to Al_2O_3 and weighed, cover the chloride with a thin layer of pure (ashless) mercuric oxide to prevent mechanical loss, heat gently until hydrolysis has taken place, then raise the heat to expel mercuric chloride and excess oxide, and finally ignite at 1000 to 1100° C and weigh as Al_2O_3.

Aluminum can be quantitatively precipitated by 8-hydroxyquinoline and separated from phosphates, arsenates, fluorides, and borates in ammoniacal solution;[17] from vanadium, molybdenum, columbium, tantalum, and titanium in an ammoniacal solution containing hydrogen peroxide;[17] from uranium in a solution containing ammonium carbonate;[17] and from beryllium in an acetic acid solution[18] (see p. 519).

IV. METHODS OF DETERMINATION

A. PRECIPITATION BY AMMONIUM HYDROXIDE

The chief method for the determination of aluminum is that in which it is precipitated by ammonium hydroxide and weighed as the oxide, Al_2O_3. In most cases, other metals accompany the aluminum when so precipitated, and, as it is seldom possible then to obtain it free from one or more of its companions, it is almost always necessary to make one weighing of all as oxides, then determine its associates one after another, and so obtain the aluminum by difference, thus throwing upon it all the errors that may have been incurred in determining the others.

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[16] In analyses of the highest accuracy, the filtrate and washings should be evaporated to small volume and again treated with acid and ether.

[17] G. E. F. Lundell and H. B. Knowles, *Bur. Standards J. Research*, 3, 91 (1929).

[18] I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, **50**, 1900 (1928); H. B. Knowles, *J. Research NBS*, **15**, 87 (1935).

The precipitation of aluminum hydroxide begins at approximately *p*H 3, and is complete when the *p*H lies between 6.5 and 7.5, points approximately defined by the color change of methyl red or of rosolic acid. In more alkaline solutions re-solution of the precipitate takes place and becomes appreciable at *p*H 10.[19]

The presence of ammonium chloride is necessary to prevent precipitation of elements such as magnesium, to limit the alkalinity of the solution, and to aid in coagulating the precipitate. The frequently made assertion that sulfates cause incomplete precipitation of aluminum hydroxide has no basis in fact.[20] The precipitation of aluminum in the presence of large amounts of ammonium phosphate is always incomplete and may not take place at all if very little aluminum is present.

Hot water cannot be used in washing the precipitate, for aluminum hydroxide readily assumes the colloidal state.[21] A 2 per cent solution of either ammonium chloride or ammonium nitrate is satisfactory; the former is to be preferred if the filtrates and washings are to be acidified and evaporated in platinum. If the neutral salts are used, there is no advantage in attempting to render the solution just alkaline to methyl red.

The presence of ammonium chloride in the precipitate causes no volatilization of aluminum during ignition. With precipitates containing much iron a 2 per cent solution of ammonium nitrate had better be used in the final washing. Furthermore, no loss of aluminum results when aluminum hydroxide or oxide is treated with hydrofluoric acid and the residue is carefully ignited after evaporation to dryness.

The chief sources of error in a determination of Al_2O_3 in materials, such as bauxite or refractories, of high alumina content are:

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[19] As a matter of fact, in ordinary analyses, the loss of aluminum caused by moderate overstepping of the proper hydrogen ion concentration causes greater errors in the determinations of calcium and magnesium than of aluminum, for, with aluminum, the loss tends to compensate for the usual plus error caused by the analyst's failure to correct for all of the coprecipitated substances, whereas, with calcium and magnesium, the aluminum that is left in solution is precipitated in small part with the former and in larger part with the latter, and adds to the plus errors that are usually made in determinations of these elements.

[20] For example, in the analysis of four aliquot portions of a solution of $AlCl_3$, 0.0969 and 0.0968 g of Al_2O_3 were obtained in two portions by precipitation as usual in the presence of NH_4Cl, and 0.0968 and 0.0970 in the two others by precipitation after adding 5 ml of H_2SO_4, evaporating to fumes of the acid, and diluting with water.

[21] For example, W. Blum (*loc. cit.*) found 0.5 to 2 mg of Al_2O_3 in the washings after washing precipitates equivalent to 0.1 g Al_2O_3 with only 75 ml of hot water.

1. Failure to decompose the material completely. Whenever there is doubt as to the completeness of decomposition, the residue left after dissolving the melt should be fused, dissolved, and added to the original solution.

2. Failure to fuse the nonvolatile residue left after the treatment of the silica with hydrofluoric and sulfuric acids. This residue must be fused, the melt dissolved, and the solution added to the filtrate from the silica.

3. Failure to detect the compounds that are normally carried down in the ammonia precipitate, as for example alkaline earths carried down as phosphates when phosphorus is in excess of what can be taken care of by iron or aluminum, as well as faulty determinations of the compounds that are detected and deducted. The following list of such compounds that are contained in the Bureau of Standards sample of bauxite no. 69 illustrates the extent of the errors that can be made if any or all of such corrections are omitted: Fe_2O_3, 5.66 per cent; TiO_2, 3.07 per cent; ZrO_2, 0.08 per cent; P_2O_5, 0.11 per cent; V_2O_3, 0.03 per cent; and Cr_2O_3, 0.04 per cent.[22]

4. Coprecipitation of hydroxides that require an appreciable excess of ammonium hydroxide for resolution, as for example those of zinc, copper, and cobalt. These cannot be completely removed by repeated precipitation, as the alkalinity required for resolution of their oxides is such as to cause appreciable solution of aluminum as well.[17,23]

5. Precipitation of the alkaline earths as carbonates. Precipitation of the alkaline earths as carbonates through absorption of carbon dioxide during boiling is not likely if the *p*H of the solution is kept at 6.5 to 7.5, but will take place if an ammonium hydroxide containing carbonate is used.

6. Failure to remove the alkali salts carried down by the ammonia precipitate. For example, after fusion of 0.5 g of bauxite with 7 to 10 g of sodium carbonate and elimination of silica, the alkali salts in the ignited mixed oxides as determined by the J. Lawrence Smith method, amounted to 0.7 mg after careful double, and 0.1 mg after triple precipitations by ammonia. The error caused by the retention of alkalies may therefore be as high as 0.14 per cent Al_2O_3 (on a 0.5-g sample) in spite of double precipitations and will be much greater if only a single precipitation is made.

7. Incomplete solution of the hydroxide when resolution and reprecipitation is made. Complete removal of aluminum hydroxide from filter paper by extraction with acid is difficult, and the thoroughly washed paper must either be reserved and ignited with the final precipitate or else added to the solution and macerated just before the filtration of the second precipitate.

8. Improper ignition of the ammonia precipitate. W. Blum[23] showed that Al_2O_3 which has been heated over the blast lamp to constant weight undergoes no further loss upon heating to 1440 to 1460° C. As a result of his tests, he stated that ignition for 5 to 10 minutes over a blast lamp is sufficient to bring Al_2O_3 to constant weight. This statement is correct for small precipitates obtained from pure solutions. In ignitions of the large mixed precipitate obtained from bauxite or refractories, the analyst must be sure that he is igniting at not less than 1200° C and that constant weight has been obtained. For example, a precipitate containing 0.35 g of Al_2O_3 lost but 0.1 mg when heated in a muffle for 1 hour at 900° C, after a preliminary heating for a like period at 800° C. When heated for 1 hour at 1050° C, it lost 1.4 mg, and, upon being heated over the blast, it lost 1.5 mg more, both corrected for the loss of weight of the platinum crucible. The error caused by the retention of water would therefore have been 0.58 per cent of Al_2O_3 (on a 0.5-g sample) if heating had been stopped at 900° and 0.30 per cent if it had been stopped at 1050° C.

9. Failure to protect the ignited residue from moisture before or during weighing. Alumina that has been ignited at moderate temperatures (900 to 1000° C) absorbs water readily and takes up in the first few minutes a large proportion of the water that it will absorb in 24 hours. This is important, as the atmosphere in a desiccator immediately after opening is not much different from that of the room. Fortunately, the rate of absorption is very slow if the crucible is covered with a well-fitting lid during cooling and weighing, and errors are negligible if a good desiccant is used in the desiccator and weighings are made rapidly. For example, a well-covered crucible containing 0.1 g of ignited Al_2O_3 showed no appreciable change in weight in 5 minutes on the balance pan, but gained 1 mg in 5 minutes when uncovered. An oxide ignited at 1200° C is less hygroscopic than one ignited at 1000° C.

10. Failure to correct for silica carried down by the ammonia precipitate. Silica is always carried down by the ammonia precipitate, and the amount depends on the completeness of the recovery of silica at the start of the analysis and the amount afterwards introduced with the reagents, chiefly through ammonium hydroxide. Silica is always left in solution, even after double dehydration with hydrochloric or sulfuric acid. In careful analyses, the amount (on a 0.5-g sample) may represent as little as 0.05 per cent of Al_2O_3 and as much as 0.3 per cent.

11. Misleading corrections for impurities derived from the reagents or through attack on the vessels used. The small precipitate obtained by precipitation with ammonium hydroxide in a solution of reagents alone does not, as a rule, carry down impurities, such as SiO_2 or P_2O_5 introduced through the reagents or during the analysis, as completely as does the much larger precipitate obtained from the material under analysis. For example, in analyses of 0.5-g portions of bauxite, an average correction of 0.25 mg was indicated by the reagents alone, 1.8 mg when 0.25 g of Al_2O_3 as pure aluminum chloride was added to the reagents and no correction for SiO_2

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[22] For a discussion of the analysis of the ammonia precipitate, see p. 92.

[23] W. Blum, *loc. cit.*

was made, and 0.9 mg when aluminum chloride was added and correction for silica was made. If the correction was based on reagents alone, the result for Al_2O_3 in the bauxite would therefore be high and differ by 0.13 from the true percentage. On the other hand, if no correction was made for the silica carried down by the added Al_2O_3, the result would be low and differ by 0.18 per cent from the true value.

PROCEDURE. To the solution containing at least 5 g of ammonium chloride per 200 ml of solution, or an equivalent amount of hydrochloric acid, add a few drops of methyl red (0.2% alcoholic solution), and heat just to boiling. Carefully add dilute ammonium hydroxide, drop by drop until the color of the solution changes to a distinct yellow.[24] Boil the solution for 1 to 2 minutes, and filter at once on paper. Wash the precipitate thoroughly with hot ammonium chloride or nitrate solution (2%). If the nature or amounts of other elements present call for it, dissolve the precipitate in dilute hydrochloric acid (1 + 3), and reprecipitate as before. After the reprecipitation, macerated paper can be stirred in if desired.

Wrap the moist precipitate in its paper, dry, char, and ignite, finally for 5 to 10 minutes at 1200° C.[25] Cool in a desiccator, weigh, and repeat the ignition until constant weight is obtained. The full heat of the ordinary Bunsen flame is insufficient to effect complete dehydration of aluminum oxide unless the quantity is small. If the precipitate is a composite one, containing large amounts of ferric or other oxides that are reducible by the charring paper or that tend to lose oxygen on very strong heating, the final heating must be so conducted as to insure access of air to the interior of the crucible. For ignitions of that kind an electric furnace is well adapted on account of its nonreducing atmosphere.

The weighed oxide almost always contains silica. The amount will vary, depending on whether the determination follows a separation of silica or the precipitation was made in porcelain, glass, or platinum, and on the char-

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[24] The end point would be difficult to determine in presence of much iron, were it not for the fact that ferric iron precipitates before the solution is alkaline to methyl red; hence it is easy to obtain the correct end point by adding at first only enough ammonium hydroxide to precipitate the iron upon short boiling, and allowing the ferric hydroxide to settle; after this, the color of the indicator can be recognized readily in the supernatant liquid, and more ammonium hydroxide added if necessary, or any large excess can be neutralized with dilute acid. If bromthymol blue is used as indicator, ammonium hydroxide is added to the hot acid solution until the color changes to blue green. The solution is then boiled until the color changes to pure green with aluminum alone, or yellowish green when appreciable iron is present. With bromcresol purple, the purple end point (pH 6.8) is taken.

[25] The presence in the precipitate of a little ammonium chloride, derived from the wash fluid, does not lead to loss of aluminum by volatilization during the ignition, nor indeed of iron if its amount is below 1 per cent [Daudt, *J. Ind. Eng. Chem.*, 7, 847 (1915)].

acter of the reagents. If but little oxide is present, it can be treated directly with a drop of dilute sulfuric acid (1 + 1) and 2 to 5 ml of hydrofluoric acid, evaporated to dryness, very slowly brought to the temperature used before, and weighed. If the precipitate weighs more than 50 mg, use more sulfuric acid, evaporate slowly, and ignite very gradually.[26] Silica can also be recovered in any case by fusing with pyrosulfate and evaporating with sulfuric acid as described in Part III (p. 874).

B. PRECIPITATION AS PHOSPHATE

The determination of aluminum by weighing it as the phosphate is not entirely satisfactory, for the precipitate always contains an excess of P_2O_5 if the precipitation has been properly performed, and it is impossible to judge, by a test for phosphate, when the excess has been removed by washing, for $AlPO_4$ hydrolyzes with either water or water containing an electrolyte like ammonium nitrate. Lundell and Knowles[27] found that the washing is facilitated by the use of macerated paper and that the elimination of excess P_2O_5 is indicated by the disappearance of chlorides, which are added at the start of the analysis. With these modifications, the method is quite exact if but a few milligrams of Al_2O_3 alone are in question and is accurate to 1 or 2 parts in 100 with larger amounts.

Aluminum phosphate is precipitated in dilute acetic acid-sodium acetate solution (pH 5 to 5.4), and at least a five-fold excess of the phosphate precipitate, preferably $(NH_4)_2HPO_4$, must be added. Precipitation in alkaline solution or with less precipitant leads to low results. Trivalent iron, titanium, zirconium, and various other elements are also quantitatively precipitated, while others like manganese, zinc, and calcium are precipitated in part. When iron is present, difficulties arise, regardless of whether it is reduced by thiosulfate before the precipitation or precipitated with the aluminum and deducted after separate determination and calculation as $FePO_4$. The former generally causes low results for aluminum because of the presence of sulfurous acid which has a solvent action on aluminum phosphate; this difficulty can possibly be avoided by reduction with some other agent, as for example hydrogen sulfide. Deduction of calculated $FePO_4$ leads to high results, because the washed ferric phosphate usually contains an excess of P_2O_5. Iron had therefore better be removed before the precipitation of aluminum, and this is also true of the other interfering elements.

The interference of calcium can be prevented by keeping the pH value under 6, using a large excess of ammonium chloride, and repeating the

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[26] The precision of the method is indicated by the results 0.0970, 0.0969, and 0.0968 g of Al_2O_3 obtained in three successive determinations in which double precipitations were made, macerated paper added after the second precipitations, and silica volatilized by direct treatment with $HF—H_2SO_4$.

[27] *Ind. Eng. Chem.*, 14, 1136 (1922).

precipitation when much calcium is present. Sodium salts or chromates do not interfere seriously, even when present in considerable amount. Vanadium precipitates partially, but double precipitation gives a good separation if the amount of aluminum does not exceed 50 mg. Many of the interfering elements can be separated from aluminum by precipitation in sodium hydroxide solution, with the addition of sodium carbonate when calcium is present. The most satisfactory procedure in this case lies in nearly neutralizing the solution with sodium hydroxide (free from aluminum), pouring this solution into a solution providing a 5 to 10 per cent excess of sodium hydroxide, diluting to a definite volume, and then taking a filtered half. This separation fails in the presence of magnesium or nickel.

The washing of the phosphate precipitate can be done with hot water or, better, a hot 5 per cent solution of ammonium nitrate. Washing with a dilute acid like acetic or with ammoniacal solutions leads to low results. The ignition must be done cautiously, for the precipitate tends to decrepitate, less so when macerated paper is used. The ignited precipitate is hygroscopic and should be weighed rapidly in a well-covered crucible.

PROCEDURE. Prepare a solution with reference to the foregoing and preferably with hydrochloric as the only acid. Dilute to 400 ml, adjust the acidity so that approximately 10 ml of hydrochloric acid is present, and add 1 g $(NH_4)_2HPO_4$, or more if this does not provide a ten-fold excess. Add macerated paper (one 11-cm no. 40 Whatman or one half of an S. & S. macerated paper tablet no. 292), and then 2 drops of methyl orange. Make just alkaline with ammonium hydroxide, and restore the pink color by the addition of 0.5 ml of hydrochloric acid. Heat the solution to boiling, add 30 ml of a 25 per cent solution of ammonium acetate, and continue the boiling for 5 minutes. Filter, and wash with a hot 5 per cent solution of ammonium nitrate until 5 ml of the washings give an almost indistinguishable opalescence with an acidified solution of silver nitrate. Do not let the precipitate run dry at any time. Dry the paper and precipitate by gentle heating in an open platinum or porcelain crucible, burn off the carbon at a low temperature, and finally cover and ignite at about 1000° C to constant weight. Weigh[28] as $AlPO_4$.

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[28] The accuracy of the method is illustrated by the following data (G. E. F. Lundell and H. B. Knowles, *loc. cit.*):

Al_2O_3 Taken, g	Al_2O_3 Calculated from $AlPO_4$ Obtained, g
0.0019	0.0019
0.0094	0.0096
0.0943	0.0964
0.1886	0.1930

We have never found platinum crucibles to be attacked if carbon is completely destroyed by ignition under good oxidizing conditions and at low temperatures before the final heating at 900 to 1000° C.

C. BY PRECIPITATION WITH 8-HYDROXYQUINOLINE

Aluminum can be precipitated quantitatively by 8-hydroxyquinoline in the range represented by *p*H 4.2 to 9.8.[29] The precipitate has the formula, $Al(C_9H_6NO)_3$, and can be weighed as such, weighed as Al_2O_3 after careful ignition, or titrated after solution in dilute hydrochloric acid.

There is a tendency toward retention of the reagent by the precipitate, and so results are normally somewhat high if the precipitate is weighed as such or is dissolved and titrated on the assumption that it is pure.

a. *Precipitation in Acid Solution.* Precipitation by 8-hydroxyquinoline in feebly acid solution serves admirably for the separation of aluminum from the alkaline earths, magnesium, and beryllium. The reaction has limited application in the determination of aluminum, for numerous other elements are precipitated in acid solution. Determinations are therefore restricted to favorable cases, such as in solutions of feldspars in which interfering elements such as iron, titanium, zirconium, and phosphorus are present in such small amounts that they can be ignored, or in solutions from which the interfering elements have been removed.[30]

PROCEDURE. Prepare 200 ml of an acid solution containing 10 ml of hydrochloric acid, not more than 0.1 g of aluminum, and none of the interfering elements listed on page 122. Add 15 ml of a solution, prepared by dissolving 30 g of ammonium acetate in 75 ml of water, and 8 to 10 drops of a 0.04 per cent solution of bromcresol purple. Add dilute ammonium hydroxide (1 + 1) until the indicator just changes to a distinct purple. While stirring, add slowly from a burette a 2.5 per cent solution of 8-hydroxyquinoline in acetic acid in 15 to 25 per cent excess of the amount called for by the ratio $1\ Al = 3\ C_9H_7NO$.[31] Stir occasionally as the solution and precipitate are heated to boiling, and boil gently for 1 minute. Allow to cool to 60° C. Filter the solution (using moderate suction) through a 35-ml fritted glass crucible of fine porosity (5 to 15 microns such as the Jena glass filter crucible 1bG4).[32] Wash the crucible and precipitate with one or two 10-ml portions of warm water (70 to 75° C), and then with

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[29] H. Gotô, *J. Chem. Soc. Japan*, **54**, 725 (1933).

[30] Interference by small amounts (<1 mg) of iron in precipitations of aluminum by 8-hydroxyquinoline in feebly acid solution (*p*H 4 to 6) can be prevented by reducing the iron to the ferrous state by reductants such as sulfurous acid or hydroxylamine hydrochloride, and adding a complex-forming compound, such as α, α′ bipyridine or orthophenanthroline, which forms a ferrous complex that is stable at the acidity used [E. W. Koenig, *Ind. Eng. Chem. Anal. Ed.*, **11**, 532 (1939)].

[31] To prepare the solution, treat 12.5 g of 8-hydroxyquinoline with 25 ml of glacial acetic acid, and warm gently to effect solution. Pour the resulting solution into 450 ml of water, at 60° C. Cool, filter if necessary, and dilute to 500 ml.

[32] If fritted glass crucibles are not available, the precipitate can be caught on a tight paper, such as a Whatman no. 42.

cool water until the washings are colorless. The volume of wash solutions should not exceed 100 ml.

Determine the aluminum gravimetrically or volumetrically as in c, d, or e.

The neutralization with ammonium hydroxide at the start gives rise to a precipitate of aluminum hydroxide which is subsequently converted to the oxyquinolate. If the final filtrate is to be discarded, or the presence of tartaric acid in it is unobjectionable, the formation of a precipitate can be avoided by adding tartaric acid in amount equal to five times the weight of aluminum present, before the addition of acetate and the neutralization with ammonium hydroxide.[83]

b. *Precipitation in Alkaline Solution.* Precipitation of aluminum by 8-hydroxyquinoline in alkaline solution serves for its separation from phosphorus, arsenic, fluorine, and boron if made in ammoniacal solutions; from tantalum, columbium, titanium, vanadium, chromium, and molybdenum if made in ammoniacal solutions containing hydrogen peroxide; from uranium if made in ammonium carbonate solution; and from elements such as iron, copper, cobalt, and nickel, that form complex ions with cyanide, if made in ammoniacal solutions containing alkali cyanide. The reaction has limited application in the determination of aluminum, for numerous other elements are precipitated in alkaline solution. Determinations are therefore restricted to favorable cases, such as certain filtrates obtained after precipitation with sodium hydroxide, or extractions of alkali hydroxide melts with water.

PROCEDURE. α. *In the presence of phosphorus, arsenic, fluorine, or boron.* Prepare 100 to 200 ml of an acid solution containing not more than 0.1 g of aluminum and free from vanadium, tantalum, columbium, titanium, molybdenum, chromium, or others listed on page 122. Add an excess of a 2.5 per cent solution of 8-hydroxyquinoline in dilute acetic acid (p. 507), then dilute ammonium hydroxide (1 + 1) until alkaline, and finally an excess of 10 ml for each 100 ml of solution. Warm to 60 to 70° C, and digest at this temperature until the precipitate becomes dense and crystalline. Cool, preferably in ice water, filter through a tight paper or fritted glass crucible, and wash the precipitate thoroughly with a cold dilute solution of ammonium hydroxide (1 + 40) containing 25 ml of the reagent, previously neutralized with ammonium hydroxide, in 1 liter. If the precipitate is to be weighed as such or dissolved and titrated, final washing must be with cool water to remove the reagent.

β. *In the presence of tantalum, columbium, titanium, vanadium, chromium, and molybdenum.* The only modification that is needed in the method as described in 1 is to add 10 to 15 ml of a 3 per cent solution of hydrogen peroxide before the 8-hydroxyquinoline.

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[83] For further details, see H. B. Knowles, *J. Research NBS,* **15,** 87 (1935).

γ. *In the presence of uranium.* If uranium is to be separated from aluminum, instead of neutralizing with ammonium hydroxide as in 1, cautiously neutralize with a saturated solution of ammonium carbonate, add an excess of 25 ml per 100 ml of solution, and heat to about 50° C (taking care to avoid excessive effervescence, caused by too rapid heating).[84]

δ. *In the presence of elements such as iron, nickel, cobalt, copper, molybdenum, or chromium that form stable complex cyanides.*[35] Obtain a dilute hydrochloric or perchloric acid solution of the several elements.[86] Dilute to about 250 ml, and add 50 ml of a 20 per cent solution of tartaric acid. If the solution has not been treated for the removal of chromium, add about 20 mg of lead nitrate to aid in the following removal of manganese as sulfide. Add a slight excess of ammonium hydroxide, 10 g of sodium cyanide, and considerable ashless paper pulp. Pass a brisk stream of hydrogen sulfide through the solution for 20 to 25 minutes. Filter on an 11-cm paper containing some ashless paper pulp, and wash 8 to 10 times with ammonium sulfide water containing 2 per cent each of ammonium tartrate, sodium cyanide, and ammonium chloride.

Boil the filtrate 4 to 5 minutes, and slowly add an excess of a 2.5 per cent solution of 8-hydroxyquinoline in dilute acetic acid (p. 507), while stirring vigorously. Add 1 to 2 ml of ammonium hydroxide, and stir with a mechanical stirrer for about 15 minutes. Filter, with moderate suction, through a paper of close texture [or a fritted glass (1bG4) crucible if the precipitate is to be weighed as the quinolate]. Wash 8 to 10 times with a cool aqueous solution containing 2 per cent each of ammonium tartrate, sodium cyanide, and ammonium chloride; then with 5 to 10 ml of hot water (70 to 75° C); and finally with cold water until the washings are colorless.

c. *Titration with Potassium Bromate-Bromide.* Place the crucible with precipitate in a 600-ml beaker, add 200 ml of dilute hydrochloric acid (1 + 4), and warm *gently* until the precipitate has dissolved. In ordinary work the crucible can be left in the beaker. In very accurate determinations, remove the crucible, rinse the adhering solution into the beaker, and recover the solution retained in the frit by replacing the crucible on the filtration apparatus, washing it with warm dilute hydrochloric acid

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[34] For details of the procedures outlined in α, β, and γ, consult G. E. F. Lundell and H. B. Knowles, *Bur. Standards J. Research,* 3, 91 (1929).

[35] T. Heczko, *Chem. Ztg.,* 58, 1032–33 (1934); T. R. Cunningham (private communication).

[36] Chromium tends to retard precipitation of aluminum quinolate in the tartrate-cyanide procedure. Hence, if more than 25 mg of chromium are present, add 20 ml of perchloric acid (if not already present), heat until fumes appear, and then boil for about 5 minutes to convert the chromium to chromic acid. Dilute to 100 ml, and boil for a few minutes. Add a slight excess of a 25 per cent solution of lead nitrate. Cool the solution to 15° C, filter, and wash with cold dilute perchloric acid (1 + 99).

(1 + 9), and adding the wash solution to the beaker. Cool the solution to 20° C ± 3°.

Add a standard solution of potassium bromate-bromide [37] until an excess (about 2 to 3 ml) is present, as determined by the instant fading of the red color when 1 drop of a 2 per cent alcoholic solution of methyl red is added to the solution, or by calculation if the approximate amount of aluminum is known. Stir, and let stand for 30 to 60 seconds to insure complete bromination. Add 15 ml of a 20 per cent solution of potassium iodide, stir thoroughly to make sure that the reaction between the bromine and iodide is complete, and then titrate with a 0.1 *N* solution of sodium thiosulfate until the color of the solution changes to a faint brownish yellow.[38] Add 4 ml of starch solution (p. 191), and titrate until the blue color disappears.

Subtract, from the volume of the potassium bromate-bromide added, the volume of the potassium bromate-bromide solution that is equivalent to the volume of sodium thiosulfate solution that was required. If it was necessary to add more than 2 or 3 drops of the methyl red solution before an excess of bromate-bromide solution has been added, the volume of bromate solution required by the methyl red should be determined and also deducted. To obtain the amount of aluminum, multiply the difference, representing the volume of potassium bromate-bromide solution required in the bromination of the 8-hydroxyquinoline, by the titer of the solution.[39]

The preparation and standardization of the potassium bromate-potassium bromide and sodium thiosulfate solutions are described under Precipitation by 8-hydroxyquinoline (p. 125). For routine determinations of aluminum, the solutions had better be standardized against like materials, which contain amounts of aluminum that are known and approximate those involved in the routine tests, and which are carried through all steps of the method.

d. *Weighing as* $Al(C_9H_6ON)_3$. Dry the precipitate for 1.5 hours at 135 to 140° C, and weigh as $Al(C_9H_6ON)_3$, which contains 5.87 per cent of aluminum.

e. *Weighing as* Al_2O_3. Decomposition of the quinolate and conversion to the oxide, Al_2O_3, is somewhat difficult on account of the volatility of the aluminum compound. If this method is to be used, catch the precipitate on paper, cover with 5 g of anhydrous oxalic acid, fold, and place the

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[37] The solution used in the titration should be of such strength that a reasonable volume is consumed in the titration. Suitable strengths vary from 0.1 *N*, for amounts of aluminum up to 10 mg, to *N*, for amounts such as 50 to 100 mg.

[38] Care in distinguishing between this color and the yellow color caused by the brominated 8-hydroxyquinoline is necessary.

[39] For the direct titration of the hydrochloric acid solution of the precipitate with bromate in the presence of a catalyst such as osmic acid or magnesium chloride, see G. F. Smith and R. L. May, *J. Am. Ceram. Soc.*, 22, 31 (1939).

wet paper and precipitate in a tared crucible. Cover the paper and precipitate with an 11-cm filter paper, followed by an additional 2-g portion of oxalic acid. Heat gradually until the paper begins to char, and then ignite to Al_2O_3 in the customary manner (p. 504). The oxalic acid must be tested and correction made for any nonvolatile residue found.

A more tedious, but a safer, method of converting the precipitate to the oxide lies in destroying all organic matter by digesting the precipitate, or paper and precipitate, with nitric and sulfuric acids (p. 66), diluting, precipitating with ammonium hydroxide, filtering, and igniting as usual. In this method, special attention must be paid to corrections for impurities introduced through reagents or attack on the glass ware.

D. DETERMINATION OF SMALL AMOUNTS (<0.1 Mg) OF ALUMINUM

The detection or determination of very small amounts of aluminum is difficult, for distinctive reactions for aluminum are uncommon. When preliminary operations leave less than 0.1 mg of aluminum in solution, the test or determination is often made with the dye aurintricarboxylic acid,[40] which forms a bright red lake with aluminum in faintly acid solutions, usually regulated with acetic acid-acetate buffers.[41] The aurin dye is not specific for aluminum and a number of cations and anions interfere—in particular iron, beryllium, silicon, copper, chromium, metaphosphates, and fluorides.[42] In general, there is less interference from other ions when the concentration of the aluminum lake is measured in feebly alkaline solution (*p*H 7.1 to 9). There is also less background color of the dye itself, an advantage when very small amounts of aluminum are determined by visual comparison methods. However, the superior photometric properties of the lake developed in a faintly acid solution containing a protective colloid often outweigh the higher specificity of the dye in alkaline solution. Consequently, in most of the recent photometric procedures, the concentration (absorbancy) of the lake is measured photometrically in the slightly acid solution in which the lake is formed.

The intensity and stability of the aluminum lake are affected by a number of factors, such as the *p*H of the solution in which the lake is formed, time and temperature for color development, concentration of aluminum, and the use of protective colloids. It is necessary, therefore, to adhere

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[40] The quality of the dye is an important factor in any aurin method for determining aluminum. The preparation and colorimetric properties of the dye are discussed by W. H. Smith, E. E. Sager, and I. J. Sievers, *Anal. Chem.*, 21, 1334 (1949).

[41] L. P. Hammett and C. T. Sottery, *J. Am. Chem. Soc.*, 47, 142 (1925). These authors stated that the lake is not decomposed in any reasonable time when the solution is made faintly alkaline, although the lake does not form in alkaline solution. See also, G. E. F. Lundell and H. B. Knowles, *Ind. Eng. Chem.*, 18, no. 1, 60 (1926).

[42] J. H. Yoe and W. L. Hill, *J. Am. Chem. Soc.*, 49, 2395 (1927).

strictly to defined operating conditions in order to secure satisfactory reproducibility. It is also important to avoid any contamination by using high-purity reagents and having all apparatus scrupulously clean.[43]

Illustrative applications of the aurin method are those for the determination of aluminum in iron,[44] steel,[45] and water.[46] In the last procedure, the color is developed in a medium of pH 4.4, and the interference of small amounts (up to 100 μg) of iron is eliminated by complexing the iron with thioglycolic acid as described by E. M. Chenery [47] and by C. L. Luke and K. C. Braun.[48]

a. *Photometric Measurement of the Lake in Acid Solution.* The method of Rolfe, Russell, and Wilkinson [46] is carried out as follows:

α. Reagents. 1. *Hydrochloric acid* (5 *N*). Dilute 250 ml of hydrochloric acid (sp. gr. 1.18) with an equal volume of distilled water and redistil in an all-glass distillation apparatus. Standardize, and adjust to 5 *N*.

2. *Starch solution.* Mix 1 g of soluble starch with 5 ml of cold distilled water, add 95 ml of boiling distilled water, and heat to boiling. Prepare fresh every 5 days, and filter before use.

3. *Thioglycolic acid solution.* Dilute 2 ml of thioglycolic acid (90%) to 100 ml with distilled water. Prepare fresh every 5 days.

4. *Ammonium acetate solution* (3.5 *M*). Prepare from glacial acetic acid and redistilled ammonium hydroxide as follows: Determine the normality of the acid by titration with *N* NaOH, using phenolphthalein as indicator. To 10 ml of the ammonium hydroxide, add a measured excess of *N* HCl (150 ml). Titrate the excess of HCl with *N* NaOH. Measure a volume of the glacial acetic acid equivalent to 3500 ml *N*, add about 100 ml distilled water, and then, while stirring, add a volume of redistilled ammonium hydroxide solution equivalent to 3500 ml *N*. Cool, and dilute to 1 liter.

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[43] A. L. Olsen, E. A. Gee, and V. McLendon, *Ind. Eng. Chem. Anal. Ed.*, **16**, 169 (1944).

[44] H. G. Short, *Analyst*, **75**, 420 (1950). In this method iron and other interfering elements are removed by an ether separation, followed by chloroform extraction of cupferron complexes at a pH of 0.5. The aluminum lake is subsequently formed at pH 5 at room temperature for 15 minutes and measured at 530 mμ.

[45] C. H. Craft and G. R. Makepeace, *Ind. Eng. Chem. Anal. Ed.*, **17**, 206 (1945). This procedure is designed for steels containing 0.04 to 1.5 per cent aluminum. Iron is removed with isopropyl ether. The lake is developed in an acetate-acetic acid buffer (pH 5.4), containing Knox gelatin, by heating the solution at 90° to 100° C for 10 minutes. Chromium less than 2 per cent does not interfere.

[46] A. C. Rolfe, F. R. Russell, and N. T. Wilkinson, *J. Applied Chem.*, **1**, 170 (1951).

[47] *Analyst*, **73**, 501 (1948).

[48] See Photometric Determination of Aluminum in Non-ferrous Alloys (i.e., lead and tin-base alloys, manganese bronze, zinc die casting and magnesium alloys, *Anal. Chem.*, **24**, 1120 (1952); *ibid.*, **24**, 1122 (1952).

5. *Ammonium aurintricarboxylate* (*aluminon reagent*). Dissolve 1 g of the salt in about 400 ml of distilled water, filter, and dilute to 500 ml. Let stand 24 hours before use.

PROCEDURE. Measure a suitable volume of the sample of water to contain not more than 20 μg of aluminum into a 50-ml volumetric flask. Add in order, 2 ml of 5 *N* hydrochloric acid, 2 ml of thioglycolic acid solution, 3 ml of filtered starch solution, and 5 ml of ammonium acetate solution. Dilute to about 45 ml, add 3 ml of the aluminon solution, dilute to the mark, and mix. Immerse the unstoppered flask in boiling water for exactly 4 minutes. The flask should be supported in the bath on a stand approximately ½ inch high to avoid local overheating. Remove the flask from the bath, and cool gradually to room temperature for 1 hour, then place in a thermostat, controlled at 20° (±0.1° C) for 30 minutes. Readjust the volume to 50 ml if necessary. Measure the absorbancy in a 4-cm cell, using a 525 mμ filter and distilled water in the comparison cell.

Determine the amount of aluminum from a graph previously prepared from readings obtained with known amounts of aluminum following the procedure used for the sample under analysis. Deduct the aluminum equivalent to the reading obtained on a blank carried through all steps of the procedure.

b. *Measurement of the aluminum lake in alkaline solution* [49] *by visual comparison.* In this method the lake is developed in an acetic acid-ammonium acetate buffer at about pH 4 to 5, and the solution is then made alkaline to approximately pH 8 with ammonium hydroxide or ammonium hydroxide saturated with ammonium carbonate. The final color of the dye alone is a clear light yellow. When aluminum is present, the color ranges from a clear faint pink to a deep red if the amount of aluminum does not exceed 0.1 mg in 100 ml of solution; with larger amounts, the red lake separates. The addition of alkali and acid must be made as specified, and other elements that form precipitates in the alkaline solution should be excluded. A similar lake is produced by beryllium. Iron must be entirely removed.[50]

PROCEDURE. Prepare 40 to 75 ml of clear acid solution containing 0.02 to 0.08 mg of aluminum, not more than 5 ml of sulfuric or hydrochloric

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[49] J. A. Scherrer and W. D. Mogerman, *J. Research NBS*, **21**, 105 (1938).

[50] Zirconium, hafnium, scandium, thorium, yttrium, lanthanum, cerium, neodymium, and erbium give pink or reddish-colored lakes in ammoniacal but not in ammonium carbonate solutions. Gallium in amounts less than 0.1 mg, and iridium and thallium if less than 2 mg, do not interfere. Small amounts (<1 mg) of quinquevalent vanadium have no effect; larger amounts yield a yellow color. Ten milligrams of calcium, strontium, or barium are without effect. Similar amounts of magnesium give a pink color not discharged by ammonium carbonate. Nitric acid, sulfur dioxide, hydrogen sulfide, hydrofluoric acid, and more than 25 mg of phosphoric acid bleach the color of the lake. [A. R. Middleton, *J. Am. Chem. Soc.*, **48**, 2125 (1926); R. B. Corey and H. W. Rogers, *ibid.*, **49**, 216 (1927); and J. H. Yoe, *J. Am. Chem. Soc.*, **54**, 1022 (1932).]

acid, and free of the interfering substances. Add 5 ml of hydrochloric acid if not already present, and then 5 ml of glacial acetic acid and 5 ml of a 0.2 per cent aqueous solution of a suitable grade of ammonium aurintricarboxylate. Mix well, while cautiously adding ammonium hydroxide [51] until the cloudy appearance of the dye disappears and the solution becomes clear, although still acid to litmus and still deeply colored. Place a small piece of litmus paper against the inner surface of the beaker, and, while stirring constantly, add ammonium hydroxide, dropwise, until the litmus paper turns blue. Now add 5 ml of glacial acetic acid, let the solution stand for 10 minutes, and slowly add ammonium hydroxide at a rate of 1 drop every 2 to 3 seconds until the litmus paper just turns blue. Finally, add 5 ml of ammonium hydroxide in excess. When the solution has cooled to room temperature, compare the color obtained with that of solutions of known aluminum content which have been similarly prepared.

If smaller volumes of solution are used throughout, yielding, say, 10 ml of final solution, the test can no doubt be applied to solutions containing as little as 0.001 mg of aluminum.

E. OTHER METHODS

The intensity of the yellow solution of aluminum 8-hydroxyquinolate in chloroform has been utilized by S. E. Wiberley and L. G. Bassett [52] for determining small quantities of aluminum in steel. After removal of iron and the like by a mercury cathode separation, aluminum quinolate is formed in a buffered acetic acid solution at a pH of 6.0 ± 1.0 and extracted with chloroform. The color intensity of the resulting solution is measured at 390 mμ.

The dye, Eriochromecyanine-R, forms a red-violet lake with aluminum in an acetate-buffered solution of pH 5 to 6.[53] Ferric iron causes positive errors in concentrations greater than 2.5 ppm.[54] W. Koch [55] has applied the reaction to the determination of aluminum in steels, subsequent to a mercury cathode separation.

Pontachrome Blue Black R, (4-sulfo-2-hydroxy-α-naphthaleneazo-β-naphthol, color index 202), in an acetate-buffered solution of pH 4.8, forms a lake with aluminum which gives a red fluorescence.[56] The reaction is very sensitive (0.5 μg in a 50-ml volume) and has been applied by A. Weissler and C. E. White to the determination of aluminum in steels, bronzes, and minerals.[57] Ferric iron destroys the fluorescence; titanium interferes slightly, vanadium more so, and zirconium and beryllium not at all.[58]

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[51] If the presence of rare earths, scandium, or zirconium is suspected, ammonium hydroxide saturated with ammonium carbonate should be used throughout.

[52] *Anal. Chem.*, 21, 609 (1949); see also T. Moeller, *Ind. Eng. Chem. Anal. Ed.*, 15, 346 (1943), and C. H. R. Gentry and L. G. Sherrington, *Analyst*, 71, 432 (1946), for a discussion of interfering ions.

[53] R. Fresenius and G. Jander, *Handbuch der Analytischen Chemie*, Part III, Vol. III, p. 310, Springer, Berlin (1942).

[54] W. E. Thrum, *Anal. Chem.*, 20, 1117 (1948).

[55] *Arch. Eisenhüttenw.*, 12, 69 (1938); see also L. C. Ikenberry and Arba Thomas, *Anal. Chem.*, 23, 1806 (1951) for the use of Eriochromecyanine-R in determining aluminum in zinc and steel.

[56] C. E. White and C. S. Lowe, *Ind. Eng. Chem. Anal. Ed.*, 9, 430 (1937); J. A. Radley, *Analyst*, 68, 369 (1943).

[57] *Ind. Eng. Chem. Anal. Ed.*, 18, 530 (1946).

[58] For the determination of aluminum by photometric measurement of the intensity of fluorescent solutions produced by the aluminum-morin reaction, see C. E. White and C. S. Lowe, *ibid.*, 12, 229 (1940).

Chapter 32

BERYLLIUM

Beryllium is a relatively rare element. Its chief occurrence is in beryl, a double silicate of aluminum. Among other minerals containing beryllium are euclase, another double silicate of aluminum; chrysoberyl, an aluminate; phenacite, a silicate; beryllonite, a beryllium sodium phosphate; and hambergite, a borate. It also is associated with yttrium, cerium, and zirconium in the minerals gadolinite, muromontite, and cyrtolite. Washington[1] states that "It has been suggested that in some cases beryllia has been weighed with, and supposed to be, alumina, unidentified beryl being present, thus accounting for an apparent excess of Al_2O_3, which it is difficult to reconcile with the mineral composition of the rock. It has been shown recently that alumina has been mistaken for beryllia in the mineral vesuvianite, in which the presence of beryllium had not been suspected. The need of a closer study of some minerals and rocks as regards this point is obvious."

I. GENERAL CONSIDERATIONS

Beryllium accompanies aluminum in the regular scheme of analysis and will be counted as this element if it is not detected and its amount deducted. In view of the statements just made, it should be the duty of every petrographic analyst to make a special search for beryllium.

If but little material is at hand, qualitative and quantitative tests for beryllium can easily be included in the analysis, as in the method described on page 95. If considerable material is available, the qualitative test for beryllium can be made as follows: Fuse the powdered ore with sodium carbonate, dissolve the melt in hydrochloric acid, and evaporate to dryness. Drench the residue with 5 ml of hydrochloric acid, add warm water, and boil until salts are in solution. Filter immediately to remove silica, and wash the residue with cool dilute hydrochloric acid (1 + 99). Dilute the solution to 200 ml, saturate with hydrogen sulfide, and allow to digest at 40 to 50° C for some time. Filter to remove elements such as tin and most of any germanium, but do not wash the precipitate. Boil the filtrate to expel hydrogen sulfide, add a little nitric acid, and continue the boiling

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[1] H. S. Washington, *The Chemical Analysis of Rocks*, 4th ed., p. 22, John Wiley & Sons (1930). See also *Am. Mineral.*, 16, 37 (1931).

to oxidize iron and to reduce the volume to 25 to 50 ml. Nearly neutralize the solution with a strong solution of sodium hydroxide, heat to boiling, and pour, slowly and with stirring, into sufficient strong sodium hydroxide solution to provide a 10 per cent solution when mixed. Filter to remove titanium, zirconium, and the like. If phosphorus is absent, acidify the filtrate with hydrochloric acid, and precipitate with ammonium hydroxide in slight excess. Filter to remove the excess of accumulated salts, wash the precipitate with a hot 2 per cent solution of ammonium nitrate, and then dissolve it in as little hot dilute hydrochloric acid as possible. If phosphorus is present, acidify the sodium hydroxide filtrate with nitric acid, and precipitate with molybdate reagent as described under Phosphorus (p. 701). Filter to remove phosphorus, boil, and precipitate with ammonia in slight excess. Filter to remove molybdenum and excess of alkali salts. Dissolve the precipitate in hydrochloric acid, reprecipitate with ammonium hydroxide, and again filter. Dissolve the precipitate in as little hot dilute hydrochloric acid as possible. Nearly neutralize the solution with sodium hydroxide, and pour slowly and with stirring into a warm solution containing enough sodium bicarbonate to provide a 10 per cent solution when mixed. Quickly bring to boiling, and boil for 30 seconds. Filter immediately to remove aluminum, acidify the filtrate with hydrochloric acid, boil to expel *all* carbon dioxide, and then add a slight excess of ammonium hydroxide. A white precipitate indicates beryllium. The bicarbonate precipitate should contain all of the aluminum if the work is carefully done and should not retain beryllium unless the amount of aluminum is considerable and that of beryllium very small. Germanium and gallium may be present, and further tests of the final precipitate should be made with these elements in view.

The use of quinalizarin (1,2,5,8-tetrahydroxyanthraquinone alizarin bordeaux) was recommended by H. Fischer[2] for the detection and determination of small amounts of beryllium. In pure solution the qualitative test is made at room temperature as follows: Prepare a solution, preferably free from ammonium salts, and, if acid, neutralize with a solution of pure sodium hydroxide that is free from magnesium. Treat 10 ml of the neutralized solution with 5 ml of 2 *N* sodium hydroxide, and then with 2 to 3 drops of a 0.05 per cent solution of the dye in 0.25 *N* sodium hydroxide or 10 to 15 drops of a 0.01 per cent solution in absolute alcohol. Prepare a

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[2] *Wissenschaftliche Veroffentlichungen aus dem Siemens-Konzern*, Part 2, 99 (1926). This gives a very complete discussion of methods for the detection and determination of beryllium. See also G. Rienäcker, *Z. anal. Chem.*, 88, 29 (1932).

For the detection or determination of 0.0002 to 0.0025 per cent of beryllium in silicate rocks by means of its fluorescence reaction with morin in sodium hydroxide-sodium pyrophosphate solution, consult E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, 12, 674, 762 (1940).

test with 10 ml of water and the reagents alone in exactly the same way, and compare colors by looking down through the solutions held against a white background. Beryllium causes a pure blue solution, whereas the reagents alone give a violet-red color. As little as 0.015 mg of beryllium per ml can thus be detected. Aluminum does not interfere, but phosphates, tartrates, iron, and magnesium do and require modified procedures. Fischer also employed the reagent for the determination of small amounts of beryllium by colorimetric and "colorimetric titration" methods.[3]

II. ATTACK OF BERYLLIUM MINERALS

The attack of beryllium minerals is carried out in the main as described under Aluminum (p. 494), the powdered mineral being fused with sodium carbonate, the melt dissolved in hydrochloric acid, and silica removed by evaporation and filtration before precipitation with ammonium hydroxide or sodium bicarbonate. Beryl can be fused with sodium peroxide in a nickel crucible.

Phosphate minerals can be decomposed by attack with aqua regia and the solution evaporated to dryness several times with nitric acid to destroy chlorides.[4] Any insoluble matter should be separated by filtration, ignited, and fused with sodium carbonate, and the melt extracted with water. The water extract may contain phosphate, while the insoluble residue may consist of titanium or zirconium. The disposition of the extract and residue will depend on the end in view; for example, if phosphorus alone is a consideration, the residue would be discarded and the water solution added to the original filtrate.

III. METHODS OF SEPARATION

The separations of beryllium from other elements closely resemble those for aluminum. Precipitation by ammonium hydroxide requires a slightly higher *p*H than for aluminum. Tartrate prevents the precipitation of the hydroxide under certain conditions, and so beryllium can be separated from

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[3] According to I. M. Kolthoff [*J. Am. Chem. Soc.*, **50**, 393 (1928)], as little as 0.05 mg of Be per liter can be detected by the use of curcumin. This reagent is adsorbed by $Be(OH)_2$ with the formation of an orange-red color. The test is made by adding 1 drop of a 0.1 per cent solution of curcumin in alcohol to 10 ml of a feebly acid solution, then 0.5 ml of 4 *N* NH_4Cl and 6 to 8 drops of 4 *N* NH_4OH. Magnesium decreases the sensitivity of the test, whereas iron and aluminum interfere. Iron can be removed by treatment with NaOH, while aluminum, as well as iron, can be rendered harmless by adding NaF and filtering after 1 hour.

[4] A solution of beryllium chloride can be evaporated to dryness and ignited at 1100° C to chloride-free beryllium oxide without loss of beryllium [L. Fresenius and M. Frommes, *Z. anal. Chem.*, **93**, 275 (1933)].

iron by precipitation of the latter in ammonium sulfide-tartrate solution as described on page 89.

Beryllium, together with aluminum, gallium, germanium, phosphorus, vanadium, and the like, can be separated from iron, zirconium, titanium, and similar elements by precipitation of the latter by an excess of sodium hydroxide as described on page 84.

The best methods for separating beryllium from aluminum are those in which aluminum is precipitated by 8-hydroxyquinoline (p. 122), or by passing hydrochloric acid gas into a cold solution of the chlorides in equal parts of hydrochloric acid and ether as described under Aluminum (p. 500). In the latter, no beryllium is carried down with the aluminum, but there is always danger that the precipitation of aluminum may be incomplete; consequently, the filtrate must be concentrated by evaporation and the process repeated until no more precipitate is obtained. An alternate procedure lies in separating most of the aluminum by the hydrochloric acid-ether method and then removing the remainder by precipitating with 8-hydroxyquinoline in feebly acid solution (p. 124).[5] There is no need for removing the excess of 8-hydroxyquinoline in the filtrate before proceeding to precipitate the beryllium with ammonium hydroxide in hot solution, provided the hot ammoniacal solution is allowed to cool before it is filtered.

The following procedure for separating aluminum from beryllium by precipitating with 8-hydroxyquinoline is that recommended by Knowles:[6] To the acid solution containing not more than 0.1 g of aluminum and 10 ml of hydrochloric acid in a volume of 200 ml, add 15 ml of a solution prepared by dissolving 30 g of ammonium acetate in 75 ml of water, and 8 to 10 drops of a 0.04 per cent solution of bromcresol purple. Add dilute ammonium hydroxide (1 + 1) until the indicator changes to a distinct purple. While stirring, add slowly from a burette a 2.5 per cent solution of 8-hydroxyquinoline in acetic acid[7] until it is in 15 to 25 per cent excess of the amount theoretically necessary to precipitate the aluminum (1 Al = 3 C_9H_7NO). Stir occasionally as the solution and precipitate are heated to boiling, and boil gently for 1 minute. Allow to cool to 60° C. Filter the solution (using moderate suction) through a 35-ml fritted-glass crucible of fine porosity. Wash the precipitate with 100 ml of cool water. In accurate work, and always if much aluminum is present, dissolve the precipitate in dilute hydrochloric acid, (1 + 4), reprecipitate, and combine the filtrates and washings for the determination of beryllium. The determination of

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[5] H. V. Churchill, R. W. Bridges, and M. F. Lee, *Ind. Eng. Chem. Anal. Ed.*, **2**, 405 (1930); J. I. Hoffman and G. E. F. Lundell, *J. Research NBS*, **18**, 8 (1937).

[6] H. B. Knowles, *ibid.*, **15**, 94 (1935).

[7] Prepared as follows: Treat 12.5 g of 8-hydroxyquinoline with 25 ml of glacial acetic acid, and warm gently to effect solution. Pour the resulting solution in 450 ml of water at 60° C. Cool, filter if necessary, and dilute to 500 ml.

aluminum can be completed gravimetrically or volumetrically (p. 509). Beryllium can be precipitated in the filtrate and washings by treating with ammonium hydroxide as described in Section IV (p. 522), except that the solution should be allowed to cool before filtration in order to insure complete precipitation of the beryllium in the presence of the quinolate. It is understood, of course, that the reactions are shared by other elements (see p. 77) and that, if their presence is objectionable, either they must be removed before the separation is attempted, or their effects must be considered in any methods of determination that may be applied after the separation.

For the separation of small amounts of aluminum from beryllium (for example, 1 Al:500 Be), chloroform extraction of the aluminum oxinate is employed by M. S. Richmond and C. J. Rodden.[8]

Stevens and Carron [9] prefer to separate aluminum and beryllium by first forming the phosphates, and then fusing the latter with sodium carbonate and leaching the melt with water for about 15 hours.

Less satisfactory separations of aluminum and beryllium are those based on (1) the precipitation of aluminum in a boiling 10 per cent solution of sodium bicarbonate,[10] (2) the precipitation of aluminum by ammonium carbonate, or (3) the precipitation of beryllium through extensive dilution and boiling of a sodium or potassium hydroxide solution containing the two elements.

Moser and Niessner [11] stated that a satisfactory separation of beryllium from aluminum can be had by precipitating the latter with tannin, as follows: prepare a feebly acid (sulfuric) solution of the sulfates, 500 ml if the amount of alumina is under 0.1 g and 600 to 800 ml for larger amounts. Heat to about 80° C, stir vigorously, and add at one stroke an excess of hot (80° C) clear tannin reagent (3 g of *pure* tannin dissolved in 100 ml of a solution which has been saturated with ammonium acetate at room temperature). Boil for 2 minutes, let settle, and test for complete precipitation by adding more reagent. Cool, filter, and wash with a warm 5 per cent solution of ammonium acetate. If the amount of alumina involved does not exceed 0.06 g, catch the precipitate on paper, and ignite to Al_2O_3, finally after one to three treatments with nitric acid; if larger amounts are present, collect and wash the precipitate in a fritted glass crucible, dissolve in dilute nitric acid (1 + 3), and catch the solution in a tall-form beaker. Cover, boil, treat with fuming nitric acid to destroy tannin, and then precipitate with ammonium hydroxide as usual to obtain a less voluminous precipitate. Boil the filtrate obtained after the original precipitation with tannin, treat with nitric acid to destroy the tannin and volatilize all acetic acid, and precipitate the beryllium with ammonium hydroxide as in Section IV. Alternatively, the beryllium can be precipitated as follows after the removal of tannin and acetic acid: To the feebly acid solution, add 20 to 30 g of ammonium nitrate. Dilute to 300 to 400 ml, and heat to boiling. Add a 10 per cent solution of tannin until the ratio of tannin to beryllium oxide is about 10 to 1. Add ammonium hydroxide, drop by drop, until precipitation is complete. Let settle, filter, and wash with hot water. If alkali salts are present, dissolve the precipitate in a little hot dilute hydrochloric acid, dilute, and repeat the precipitation. Transfer to a platinum or silica crucible, treat with a few drops of nitric acid, evaporate, and ignite to the oxide, BeO. With modifications, the procedure serves for the separation of beryllium from iron, chromium, titanium, zirconium, tungsten, and vanadium.[12]

The separation of beryllium from uranium is described under Uranium (p. 467).

Iron can be separated from beryllium by heating the oxides in a current of dry hydrochloric acid gas containing a little chlorine.[13] The temperature at the start should not exceed 200° C, lest mechanical loss of beryllium be caused by a too rapid volatilization of ferric chloride, and need not exceed 300° C at the end for complete volatilization.

Another separation of beryllium from elements such as iron, chromium, copper, and nickel is that based on electrolysis with a mercury cathode (p. 138).[14]

Beryllium can be separated from the cerium group by precipitation of the latter with sodium sulfate (p. 560), and from the yttrium group by precipitation with oxalic acid in a 0.5 *N* hydrochloric acid solution of the chlorides (p. 551).

A separation of beryllium which we have not tried on mixtures is that based on protracted fusion with sodium carbonate at a high temperature and extraction of the melt with water. It has been maintained that beryllium remains quantitatively in the residue with iron, titanium, and the like, while chromium (as chromate), phosphorus, and most of any silica and alumina go into solution.[15]

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[8] C. J. Rodden, *Analytical Chemistry of the Manhattan Project*, pp. 388-89, McGraw-Hill Book Co. (1950). See also T. Moeller, *Ind. Eng. Chem. Anal. Ed.*, **15**, 346 (1943).

[9] R. E. Stevens and M. K. Carron, Determination of Beryllium in Ores, Contribution to Geochemistry, 1942–45, *U. S. Geol. Survey Bull.* **950**, 91 (1946).

[10] C. L. Parsons and S. K. Barnes, *J. Am. Chem. Soc.*, **28**, 1589 (1906).

[11] L. Moser and M. Niessner, *Monatsh.*, **48**, 113 (1927).

[12] L. Moser and J. Singer, *ibid.*, 671.

[13] F. S. Havens and A. F. Way, *Am. J. Sci.*, [4] **8**, 158, 217 (1899).

[14] R. E. Meyers, *J. Am. Chem. Soc.*, **26**, 1124 (1904).

[15] M. Wunder and P. Wenger, *Z. anal. Chem.*, **51**, 470 (1912). On the other hand, A. Stock, P. Praetorius, and O. Priess [*Ber.*, **58**, 1577 (1925)] had no success with the method. In a single test made by H. B. Knowles with 0.1 g of BeO, 0.6 mg of BeO was found in the water extract after fusion with 6 g of Na_2CO_3 for 3 hours at approximately 1100° C.

Beryllium is incompletely precipitated, if at all, by phenylhydrazine (p. 128). It is not precipitated by cupferron and can be separated by the use of this reagent from elements such as iron, titanium, zirconium, vanadium, and quadrivalent uranium.

IV. METHODS OF DETERMINATION

Beryllium is usually precipitated as the hydroxide $Be(OH)_2$ and weighed as the oxide, BeO. The precipitation must be preceded, of course, by the separation of cations and anions that would be precipitated with beryllium in ammoniacal solution, as well as of organic substances that would prevent its precipitation. Double or triple precipitations of the hydroxide must be made when nonvolatile salts such as sodium chloride are present. The precipitate tends to stick to the walls of the vessel and must be recovered after the removal of the most of the precipitate, by dissolving it in as little acid as possible and reprecipitating with ammonium hydroxide. Beryllium hydroxide is appreciably soluble in pure water and it is therefore necessary to wash it with water containing an electrolyte, preferably ammonium nitrate. The oxide is slightly hygroscopic and should be cooled and weighed as described under Aluminum (p. 504).

Precipitation with ammonium hydroxide can be made in the filtrate which is obtained when aluminum is separated from beryllium by precipitating with 8-hydroxyquinoline in feebly acid solution as described on page 124. In this case, there is no need to remove the 8-hydroxyquinoline if the neutralized solution is allowed to cool before it is filtered. The treatments must, of course, be preceded by the removal of substances that interfere, such as phosphorus[16] in the separation of aluminum from beryllium, or magnesium or tartrates in the precipitation of beryllium.

Beryllium cannot be precipitated as the phosphate and weighed as the pyrophosphate, for the precipitate is not of ideal composition.

PROCEDURE. Prepare a nearly neutral hydrochloric or nitric acid solution containing beryllium as the only substance precipitable by ammonium hydroxide, and at least 5 g of ammonium chloride per 200 ml of solution. Heat to boiling, and add dilute ammonium hydroxide slowly until in very slight excess (*p*H 8 to 9). Boil 1 to 2 minutes, add a little macerated paper, and filter. Transfer as much of the precipitate as possible to the paper by rinsing with a hot 2 per cent solution of ammonium nitrate, and by thorough scrubbing. Cover the funnel, and without delay dissolve any precipitate sticking to the wall of the beaker in a very little hot dilute nitric acid, heat to boiling, and precipitate as before. Filter through the same paper, scrub the beaker, and wash thoroughly with the ammonium nitrate solution. Stir to mix the filtrate and washings, and let stand for several hours to make sure that no further precipitation occurs. Place paper and precipitate in a platinum crucible weighed with cover, dry, heat at a low temperature until carbon has been destroyed, cover, and finally ignite at approximately 1000° C. Cool over sulfuric acid or phosphorus pentoxide in a desiccator, and weigh. Again heat, cool, place the weights required before on the pan, and quickly weigh. Repeat to constant weight. The weighed precipitate should be examined to make sure of the absence of elements such as aluminum, phosphorus, gallium, and germanium.[17]

A. OTHER METHODS

Fluorometric determinations of beryllium in ores can be made by a method described by M. H. Fletcher, C. E. White, and M. S. Sheftel.[18] The sample is fused with a mixture of sodium carbonate and borax, and the melt is dissolved in hydrochloric acid. Sodium citrate and quinizarin are added, and the solution is neutralized with sodium hydroxide. More quinizarin is added, and the fluorescence is compared with standards similarly prepared and treated.[19]

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[16] Phosphorus causes partial precipitation of beryllium as phosphate, at a *p*H as low as 4.2, and contaminates any precipitate of beryllium obtained in the filtrate.

[17] According to A. Craig (private communication), beryllium oxide can be dissolved by fusing with sodium fluoride and a little silica, treating the melt with sulfuric acid, and heating to fumes of the latter.

[18] *Ind. Eng. Chem. Anal. Ed.*, **18**, 179 (1946).

[19] For a photometric method for determining beryllium in aluminum and its alloys with *p*-Nitrobenzeneazoorcinol, see W. Stross and G. H. Osborn, *J. Soc. Chem. Ind.*, 63, 249 (1944).

Chapter 33

CHROMIUM

Chromium is very widely diffused and is almost wholly confined to the femic (ferromagnesian) rocks, especially those that are high in magnesia and low in silica, and consequently contain abundant olivine, such as peridotite and dunite. It occurs as chromite and picotite (chrome spinel) and in some augites, biotites, and olivines. In rocks it may occur up to 0.5 per cent of Cr_2O_3. A few chromates and several silicates containing chromium are also known, but as relatively rare minerals. Chromium is a common constituent of many materials, particularly irons and steels which are rarely entirely free from it, and methods for its determination are of considerable importance.

I. GENERAL CONSIDERATIONS

In the analysis of rocks, chromium is to be found in the ammonia precipitate and tends to cause high values for aluminum, even when the amount of chromium is afterward determined and subtracted as Cr_2O_3 from the weight of the ignited precipitate. This follows because Cr_2O_3 always undergoes some oxidation during ignition. If chromium is ignored, the resultant errors will depend on the manner in which iron is determined. If the solution of the ignited precipitate is reduced by zinc and titrated with permanganate, Cr_2O_3 is reduced to Cr_2O_2 and then reoxidized to Cr_2O_3; as 1 ml 0.1 N permanganate solution is equal to approximately 0.008 g of Fe_2O_3 and 0.0076 g of Cr_2O_3, this procedure would cause high values for iron and slightly low values for aluminum. On the other hand, if iron is reduced by hydrogen sulfide, sulfurous acid or stannous chloride the error falls entirely on aluminum, for these reagents do not reduce Cr_2O_3.

II. ATTACK OF CHROMIUM MINERALS

For the determination of chromium in chromium minerals, attack with sodium peroxide in a porcelain crucible[1] as follows is preferable: Grind the sample to an impalpable powder, dry at 105° C, and mix 0.5 g of the

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[1] Iron or nickel crucibles give rise to oxidized iron or nickel compounds that are difficult to break up by boiling. This may not be true if the "explosion method" (p. 839) is used.

sample with 5 to 6 g of dry, yellow sodium peroxide in a 30- to 50-ml heavy-walled porcelain crucible. Cover the mix with 1 to 2 g of the peroxide, cover the crucible, and carefully fuse the contents by gradual introduction in an electric muffle heated to 600 to 700° C. When the charge melts, slowly whirl the crucible to stir up any unattacked particles. If a flame must be used instead, place the crucible on a triangle, and raise the temperature slowly to the melting point of the flux, using a low flame and holding the burner in the hand. When in quiet fusion, maintain the temperature at low redness for 5 minutes while the melt is occasionally stirred with a platinum wire. Cool the crucible, and place both crucible and cover in a 600-ml beaker. Cover the beaker, add 200 ml of water, and warm until the melt has dissolved. Remove and wash the crucible and cover, boil thoroughly to expel all hydrogen peroxide, nearly neutralize with dilute sulfuric acid, filter through paper, and wash the residue with hot water. Ignite the residue, recover any chromium content of the ash by a second fusion with sodium peroxide, and unite the two filtrates. To make sure that all of the chromium is in the sexivalent state before titration, make acid with sulfuric acid, and oxidize with persulfate as in IV, A. The filtration through paper introduces soluble organic matter, but this is destroyed during the boiling with persulfate.

Fusion with sodium carbonate and potassium nitrate (p. 848) in a platinum crucible is less desirable but can be used when determinations must be made of silica and other elements that might be introduced through fusion in porcelain, nickel, or iron.

Chromite can be decomposed by grinding the sample to an impalpable powder, treating 0.5 g with 50 ml of dilute sulfuric acid (1 + 4) and 5 ml of perchloric acid (sp. gr. 1.54), and heating to fumes of sulfuric acid.[2]

III. METHODS OF SEPARATION

Complete separation of chromium from other elements is rarely necessary as the chief methods for its analysis are applicable in the presence of a number of elements.

The outstanding separation, although a group separation, is based on the oxidation of chromium to soluble sodium or potassium chromate by an oxi-

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[2] T. R. Cunningham and T. R. McNeill, *Ind. Eng. Chem. Anal. Ed.*, **1**, 70 (1929). For the solution of chromite in a mixture of 8 parts of 95 per cent sulfuric acid and 3 parts of 85 per cent phosphoric acid, see G. F. Smith and C. A. Getz, *ibid.*, **9**, 518 (1937). For a method for the complete analysis of chromite following fusion with potassium pyrosulfate in a silica crucible, solution of the melt in acid, filtration, and decomposition of any unattacked matter by fusion with sodium carbonate, see C. F. J. van der Walt, *Analyst*, **63**, 176 (1938); see also F. J. Bryant and P. S. Hardwick, *Analyst*, **75**, 12 (1950), for analysis of chromite.

dizing fusion with alkali or by oxidation in alkaline solution. Thus chromium, together with aluminum, arsenic, molybdenum, tungsten, vanadium, and the like, is easily separated from iron, titanium, zirconium, nickel, cobalt, copper, and many other elements by filtration after precipitation with sodium peroxide (p. 85),[3] or fusion with sodium peroxide or carbonate and niter, followed by extraction with water (p. 839). A separation of chromium from iron and aluminum that is often employed consists in the oxidation of the former to the sexivalent state and then precipitation of aluminum and iron by ammonium hydroxide.

Chromium can also be oxidized to the sexivalent state by heating with perchloric acid at its boiling point. Complete oxidation is difficult.[4] If desired, the oxidized chromium can be volatilized as chromyl chloride, CrO_2Cl_2, by dropwise addition of hydrochloric acid[5] or careful introduction of crystals of sodium chloride to the boiling solution.[6] In either case, the treatment causes partial reduction of the chromium to the trivalent state, which must be corrected by stopping the treatment at intervals and boiling the acid to reoxidize the chromium.

If the presence of lead is not objectionable, chromium can also be removed from solution by oxidizing with perchloric acid, diluting so that the solution is approximately 1.0 M with respect to perchloric acid, rendering it 0.02 M with respect to lead perchlorate, filtering to remove the precipitated lead chromate, and washing with 0.1 M $HClO_4$. The precipitate does not carry down vanadium.[7]

Another group separation that is employed in the analysis of rocks is based on the precipitation of mercurous chromate as described under Vanadium (p. 455).

Precipitation with the sulfide ion in acid solution serves to separate the elements of the sulfide group from chromium, whereas precipitation in alkaline solution serves to separate chromium from elements of the arsenic group of sulfides and from magnesium and the alkaline earths. When the latter reaction is carried out in the presence of ammonium tartrate (p. 89), chromium is not precipitated and can thus be separated from iron, nickel, cobalt, and zinc.

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[3] For the precipitation of trivalent chromium by sodium hydroxide, see Precipitation by Sodium Hydroxide (p. 84).

[4] G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, *Chemical Analysis of Iron and Steel*, p. 298, John Wiley & Sons (1931); G. F. Smith, *Ind. Eng. Chem. Anal. Ed.*, 6, 229 (1934).

[5] J. I. Hoffman and G. E. F. Lundell, *J. Research NBS*, 22, 465 (1939).

[6] F. W. Smith, *Ind. Eng. Chem. Anal. Ed.*, 10, 360 (1938).

[7] For a method in which $chromium^{VI}$ is precipitated as lead chromate by means of lead nitrate in dilute nitric acid solution, and separated from iron, aluminum, cadmium, copper, manganese, and zinc, see D. Tschawdarov and N. Tschawdarowa, *Z. anal. Chem.*, **110**, 348 (1937).

Chromium can be separated almost completely from large amounts of iron by extraction of the latter by ether in a hydrochloric acid solution of the chlorides (p. 134).

An interesting separation of vanadium and such elements as iron, zirconium, titanium, columbium, and tantalum from chromium is that based on the precipitation of the former by cupferron (p. 116).

Another separation that should be borne in mind is that based on electrolysis with a mercury cathode in dilute sulfuric acid solution (p. 138). As here applied, this separation serves to remove large and objectionable amounts of chromium from vanadium, uranium, and a number of other elements.

The separation of small amounts of silica from a solution containing large amounts of chromium is done best by adding an excess of sulfuric acid (20 to 30 ml), evaporating at as low a temperature as possible until fumes of sulfuric acid just appear, cooling slightly, and adding water as the solution is vigorously stirred.

IV. METHODS OF DETERMINATION

The most satisfactory methods for the determination of chromium are the colorimetric method and the method in which chromium is oxidized to chromate and titrated with ferrous sulfate and permanganate. The former is suited for such small amounts of chromium as are usually to be found in rocks; the latter for the determination of such amounts as cannot be handled in the colorimetric method.

A. TITRATION WITH FERROUS SULFATE AND PERMANGANATE

In our experience the most satisfactory method for the determination of chromium lies in its oxidation to chromate, followed by the addition of a measured excess of ferrous sulfate and titration with potassium permanganate or dichromate. The oxidation of chromium can be done either by fusion or by treatment in acid solution—both methods find their application. Of the fusion methods, the use of sodium carbonate and potassium nitrate (p. 848) suffices for small amounts of chromium, whereas the use of sodium peroxide as in Section II is more desirable for large amounts. Oxidation in acid solution can be done by means of lead dioxide, potassium chlorate, potassium permanganate, or potassium or ammonium persulfate in the presence of silver nitrate.[8] Of these the last is by far the best and will be described in detail.

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[8] M. Philips, *Stahl u. Eisen*, 27, 1164 (1907); H. E. Walters, *J. Am. Chem. Soc.*, 27, 1550 (1905); *Met. Chem. Eng.*, 12, 310 (1914).

In this method silver nitrate is essential for complete oxidation and is always added to the hot acid solution before the addition of persulfate and in amount at least equal to that of the chromium.[9] If the solution is too acid complete oxidation is impossible; 5 to 6 ml of sulfuric acid and 1 ml of nitric acid per 100 ml of solution are best. The addition of 3 to 5 ml of syrupy phosphoric acid is desirable when iron or moderate amounts of tungsten are present, for this aids in judging the end point and helps to keep tungsten in solution. The persulfate is employed in freshly prepared solution of a salt that shows 95 per cent purity by test (p. 37). In all cases the solution must be boiled for 8 to 10 minutes to insure complete oxidation and also to destroy the excess of persulfate. Manganese, if present, is oxidized to permanganic acid or manganese dioxide and must also be destroyed before ferrous sulfate is added. This is easily done by adding 5 ml of dilute hydrochloric acid (1 + 3) per 300 ml of solution *after* the persulfate has been destroyed, continuing the boiling until the oxidized manganese compounds have disappeared, and then boiling for 5 minutes more to expel chlorine. No reduction of chromic acid occurs in this treatment if the persulfate has been destroyed *before* the acid is added.[10] If the amount of chromium is large, the reduction is made most conveniently by adding weighed crystals of a uniform grade of ferrous ammonium sulfate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$. With moderate amounts of chromium, and particularly when many determinations are to be run, it is more convenient to use a dilute sulfuric acid solution of the salt. In the presence of considerable chromium, the end point is a little difficult to judge because of the green color, but the proper correction for the end point can be easily determined. All reactions proceed quantitatively, and consequently the theoretical titers as based on sodium oxalate can be used.

Vanadium and arsenic do not interfere, for, although they are reduced by ferrous sulfate, they are again oxidized with the consumption of an equivalent amount of permanganate. Moderate amounts of tungsten cause a change in the character of the end point but do not interfere in the reactions. If the amount of tungsten is so large as to make the end point uncertain, it had better be removed and its chromium content determined separately. Nickel, cobalt, molybdenum, and uranium are without effect.

PROCEDURE. Prepare a solution, by fusion as in Section II or otherwise, which is free from chloride ion and contains approximately 15 to 18 ml of sulfuric acid and 3 ml of nitric acid in 300 ml of solution. Heat to boiling. Add a 2.5 per cent solution of silver nitrate in amount equal to 0.01 g of the salt for each 0.01 g of chromium present. Heat to boiling, and add 20 ml of a freshly prepared 10 per cent solution of ammonium persulfate. Boil the solution for 10 minutes, and then, if permanganic acid or oxides of manganese are present, add 5 ml of a 5 per cent solution of sodium chloride or 5 ml of dilute hydrochloric acid (1 + 3), resume the boiling, and boil for 5 minutes after the manganese compounds are reduced. If complete reduction of manganese does not occur, add more sodium chloride or hydrochloric acid, and repeat the boiling. Cool the solution, add a measured excess of a solution of ferrous ammonium sulfate or of the weighed salt, and then titrate with a solution of permanganate that has been standardized against sodium oxalate. When the end point is reached and the readings have been noted, heat to boiling to destroy the excess of permanganate, cool to room temperature, and resume the titration with permanganate until the same end point is obtained as before, and subtract the volume required from that then required.[11] Multiply this corrected volume by the ferrous ammonium sulfate equivalent of 1 ml of the standard permanganate solution, subtract the product from the amount of ferrous sulfate used, and calculate the amount of chromium on the basis of 3 Fe to 1 Cr. To determine the ferrous ammonium sulfate equivalent, take as much of the ferrous ammonium sulfate as was used in the test, dissolve or dilute in a solution having the same volume and acidity, titrate with the permanganate solution, and subtract the small amount of permanganate required to obtain an end point in this solution.

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[9] D. M. Yost [*J. Am. Chem. Soc.*, 48, 152 (1926)] showed that the rate of the reaction between peroxysulfuric acid and chromic sulfate when catalyzed by silver salts at 25 to 35° C is proportional to the first power of the concentration of peroxysulfate ion and silver ion and that it is independent of the concentration of chromic ion and not greatly affected by that of hydrogen ion. It is also stated that trivalent silver can exist in the form of a solid oxide and as a salt in strongly acid solution, and the results indicate that the silver ion acts as a carrier catalyst through the formation of this trivalent salt as the intermediate compound.

[10] This is shown by the following tests made by W. C. Fedde. In every case, the dichromate was contained in 300 ml of dilute H_2SO_4 (1 + 9) at the start, and the solution was finally titrated potentiometrically.

	$K_2Cr_2O_7$	
	Taken	Found
1. Titrated directly with $FeSO_4$ solution	0.1939	0.1940
2. Same as 1	0.1939	0.1938
3. Added 20 ml HCl (1 + 3). Boiled 30 minutes	0.1939	0.1937
4. Same as 3	0.1939	0.1938
5. Added 10 ml $AgNO_3$ (2.5 g per l) + 1 g $(NH_4)_2S_2O_8$. Boiled 10 minutes. Treated with 5 ml HCl (1 + 3) and boiled 5 minutes more	0.2131	0.2131
6. $MnSO_4$ added and then as in 5	0.2143	0.2142
7. Added 5 ml 0.3 *N* $KMnO_4$, reduced with $FeSO_4$, and then as in 5	0.2143	0.2145
8. Added 5 ml 0.03 *N* $KMnO_4$, 10 ml $AgNO_3$ (2.5 g per l), 2 g $(NH_4)_2S_2O_8$ and 5 ml HCl (1 + 3). Boiled 10 minutes	0.2040	0.1943
9. Same as 8 except solution was boiled 10 minutes before the HCl was added	0.2052	0.2053

[11] The titrated solution can be used for the determination of vanadium as described under Vanadium (p. 460).

In routine analyses, it is not necessary to oxidize with persulfate after a careful peroxide fusion. In such work, dissolve the melt in 200 ml of water, add 1 g of sodium peroxide, boil vigorously until hydrogen peroxide is decomposed (approximately 10 minutes), filter through asbestos, wash with hot water without letting the precipitate run dry, acidify the filtrate and washings with sulfuric acid, and proceed with the addition of ferrous sulfate. In this method, organic matter, derived for example by filtration through paper, must be avoided, for it causes low results for chromium. This error is not caused by a reduction of chromate, as might appear at first thought, but by reduction of permanganate.

The ease with which a potentiometric titration of chromium can be carried out by the use of an apparatus such as that developed by Kelley[12] is indicated by the following outline of the procedure: Prepare a dilute sulfuric acid solution in which all of the chromium has been oxidized to the sexivalent state. Cool to about 20° C, immerse the calomel and platinum electrodes, and bring the beam of light from the reflecting galvanometer near the left end of the scale. Add a standard solution of ferrous sulfate, gradually until the beam has shifted permanently to the right. Now add an equivalent standard solution of potassium chromate until the beam will move no further to the left. Again add ferrous sulfate until the first permanent displacement toward the right occurs. Subtract the volume of chromate from the volume of ferrous sulfate, and calculate the amount of chromium on the basis of $1\text{Cr} = 3\text{Fe}$. In the above titration, vanadium is also reduced by ferrous sulfate and is counted as chromium. Tungsten does not interfere.

B. COLORIMETRIC METHODS

a. *Chromate Method.* Determinations of chromium by the colorimetric method are preferably made by comparing the color of chromates in alkaline solution. In the analysis of rocks, a water extract of a sodium carbonate-potassium nitrate melt of the rock is usually employed, and no ordinary elements interfere. If niter has been used in the fusion in platinum and the crucible has been at all attacked by it, a yellow coloration of the filtrate may be due to dissolved platinum, but neither the proportion of niter nor the temperature of the blast should ever be high enough to permit the crucible to be attacked. If fusion is done with sodium peroxide, a little iron sometimes remains in the solution of the melt and gives a false color; this can be avoided by digesting the solution of the melt on the steam bath for an hour or more before filtration. A false color is also obtained when sodium hydroxide solutions are filtered through paper; this difficulty can be prevented quite satisfactorily by thoroughly washing the paper with alkali solution before use, and entirely avoided by filtration

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[12] G. L. Kelley and others, *J. Ind. Eng. Chem.*, **9**, 780 (1917).

through asbestos in a Büchner funnel or on a Witt plate. Borates do not interfere. In the presence of uranium, the method fails, for this element also gives a yellow color. Comparisons are best made in solutions containing approximately 0.01 to 0.1 mg of Cr_2O_3 per ml.

PROCEDURE. Prepare a standard solution by dissolving recrystallized potassium dichromate, $K_2Cr_2O_7$ (conveniently, NBS Standard Sample 136) in water and diluting to 1000 ml. Each ml of the solution should correspond to 0.1 mg of Cr_2O_3. When this solution is used, it should be made alkaline to compare with the solutions under test.

For the determination of chromium in rocks make a carbonate-niter fusion of 1 to 5 g of rock as described under Vanadium (p. 456). Dissolve the melt in water, add a few drops of ethyl alcohol to destroy the color if sodium manganate is present, and filter through asbestos. If the color of the filtrate is very faint, concentrate the solution by evaporation or by precipitation with mercurous nitrate and treatment as described under Vanadium (p. 455).

In the analysis of other materials, as for example ammonia precipitates, that contain but small amounts of chromium, a desirable substitute oxidation method consists in fusion with sodium peroxide in a porcelain crucible.

In any case, transfer the final solution to a graduated flask of such a capacity that the color of the solution when diluted to the mark will be in the range equivalent to 0.01 to 0.1 mg Cr_2O_3 per ml. Complete the determination by titrating an equal amount of blank solution with the standard dichromate solution until the colors are equivalent, or, alternatively, by any of the usual colorimetric or photometric measurements.

b. *Diphenylcarbazide method.* For microgram quantities of chromium, the determination may be completed by the diphenylcarbazide method,[13] which utilizes the red-violet color formed with the dichromate ion in weak acid solution. Vanadium, if present in appreciable amount, interferes and can be removed by extraction of the 8-hydroxyquinoline compound with chloroform.[14] Uranium does not interfere in this procedure.

C. OTHER METHODS

Chromium can be quantitatively precipitated by ammonium hydroxide as in the method given under Aluminum (p. 504).[15] The precipitate, how-

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[13] C. F. J. van der Walt and A. J. van der Merwe, *Analyst*, **63**, 809 (1938).

[14] E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, **8**, 336 (1936).

[15] In tests made by H. B. Knowles, complete precipitation in a solution containing 0.06 g of Cr^{III} in 350 ml was obtained by boiling and adding methyl red and then ammonium hydroxide to a distinct yellow tint. With 1 ml of NH_4OH in excess, 0.1 mg of Cr was left in solution; with 5 ml of NH_4OH, 0.2 mg; and, when 25 ml of HCl were added and then NH_4OH in 5 ml excess, 0.4 mg of Cr was unprecipitated. 0.1 mg of Cr was dissolved when the precipitate was washed with 200 ml of 2 per cent NH_4Cl solution.

ever, oxidizes during ignition, and results are high unless the ignition is finished in an atmosphere of hydrogen. For this reason, as well as because of the fact that chromium is seldom found unassociated with such other precipitable elements as iron, aluminum, phosphorus, or vanadium, the method is rarely used for the determination of chromium.[16]

Precipitation of chromium as silver chromate, Ag_2CrO_4; mercurous chromate, Hg_2CrO_4; or barium chromate, $BaCrO_4$ are of more interest as methods of group separation and of qualitative test than as quantitative methods, for a number of other elements are also precipitated by these reagents.

An accurate volumetric method for the determination of chromium consists in the reduction of the chromate by hydriodic acid and titration of the liberated iodine by a solution of sodium thiosulfate. This method is not of such general application as that described in A, for elements such as ron, copper, arsenic, vanadium, or molybdenum in their higher valencies that liberate iodine in an acidified solution of potassium iodide must be absent.

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[16] It is of interest that strongly ignited Cr_2O_3 is said to be soluble in warm dilute solutions of potassium bromate, yielding chromate [R. Lydén, *Z. anorg. u. allgem. Chem.*, 223, 28 (1935)].

Chapter 34

THORIUM

Thorium is probably a more common constituent of silicate rocks than has been generally supposed and is seemingly more abundant in highly sodic rocks. It is found associated with uranium, zirconium, titanium, tantalum, columbium, and the rare earths in such minerals as uraninite, titano and tantalocolumbates and monazite sand. Thorium, like uranium, is strongly radioactive, and so are its compounds. The typical thorium mineral is the silicate thorite, $ThSiO_4$, which always occurs more or less altered. Thorianite, a thorium-uranium oxide, is noteworthy for being richer in helium than any other known mineral. The chief source of thoria is monazite sand, in which it occurs in variable amount associated with phosphates of the cerium group. The use of the lead-uranium-thorium ratio in determinations of the ages of rocks and minerals has given added interest and importance to methods for the determination of thorium.

I. GENERAL CONSIDERATIONS

For the detection of thorium, it is desirable that it first be separated as oxalate, together with scandium and the rare earths, from zirconium, titanium, and the other common elements. The separation of thorium from scandium and the rare earths is then accomplished by precipitation with a large excess of potassium iodate in strong nitric acid solution that is free from hydrochloric acid.[1] For this precipitation two solutions are required: (1) a concentrated solution containing 15 g of potassium iodate, 50 ml of nitric acid, and 100 ml of water, and (2) a dilute solution containing 4 g of iodate, 50 ml of nitric acid, and 450 ml of water. To make the test, concentrate a nitric acid solution of the rare earths, boil with a little sulfurous acid to reduce ceric nitrate, and treat 5 ml of the solution with 10 ml of solution 1. Mix thoroughly, add 20 ml of solution 2, and boil. Some ceria and yttria earths may precipitate upon the addition of solution 1, but these are dissolved upon boiling with solution 2. A permanent precipitate indicates thorium, and the test is sensitive to 0.1 mg of thoria per ml of the original solution. Zirconium is also precipitated. Should there be doubt as to its prior separation, filter, wash, sluice the precipitate into a small

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[1] R. J. Meyer, *Z. anorg. Chem.*, **71**, 65 (1911).

beaker, and boil with 50 ml of a 10 per cent solution of oxalic acid. Zirconium is then dissolved while thorium is converted to the insoluble oxalate.

Thorium can also be detected by spectrum analysis and by the "emanation method."[2]

In the course of an ordinary analysis, thorium will fall with the ammonia precipitate and will be counted as aluminum if this element is calculated by difference. If the ammonia precipitate is dissolved and treated with hydrofluoric acid or oxalic acid (p. 551), for the separation of crude rare earths, thorium will be precipitated and, if not otherwise provided for, eventually caught with the cerium or yttrium group, depending on the mode of treatment.

II. ATTACK OF THORIUM MINERALS

Monazite sand is decomposed as follows:[3] Transfer 50 g of sand to a 500-ml porcelain casserole, and add 75 ml of concentrated sulfuric acid. Heat for about 4 hours, maintaining a gentle evolution of fumes and stirring frequently. When the mass has become pasty, cool the mixture, and add the thick mass gradually to about 400 ml of cold water, contained in a large beaker surrounded by ice water. Do not allow the temperature of the solution to rise above 20° C. Decant into a graduated 1000-ml flask. Extract the residue with small portions of cold water, and set the extracts aside. Dry the remaining sand, add 10 ml of concentrated sulfuric acid, heat to copious white fumes, and continue the heating for 1.5 hours. Cool, chill the reserved extracts, and slowly add the pasty mass. Let settle, and decant the solution into the liter flask. Extract the residue thoroughly with dilute sulfuric acid (1 + 10), decanting each time into the flask. Dilute the solution to the mark at room temperature, mix thoroughly, and filter to obtain 200-ml aliquot portions for as many separations as may be planned. Dilute each portion (representing 10 g of sand) to 1000 ml, and feed the solution, drop by drop, from a separatory funnel into 150 ml of a cold saturated solution of oxalic acid which is vigorously agitated by a mechanical stirrer. Let stand overnight. Filter, and wash the precipitate with water, by decantation and on the filter, until free from acid. Dry the paper and precipitate in an air bath, and reserve. Neutralize the filtrate and washings with ammonium hydroxide, render acid with hydrochloric acid, and then add 15 ml in excess. Let the precipitate settle overnight, filter, and wash with dilute (1 + 1000) hydrochloric acid containing 2 per cent of oxalic acid. Ignite the paper and precipitate in a platinum dish, moisten the residue with water, and dissolve by warming with a little

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[2] H. H. Helmick, *J. Am. Chem. Soc.*, 43, 2003 (1921).

[3] *Bur. Mines Bull.* 212, 53 (1923).

hydrochloric acid. Filter, wash with small portions of dilute hydrochloric acid (1 + 99), render just acid to methyl red, and precipitate in a volume of 50 ml with 50 ml of a cold saturated solution of oxalic acid. Warm for a few minutes, let stand for 4 hours, filter and wash with the diluted hydrochloric-oxalic acid solution. Transfer the precipitate to a platinum crucible, and ignite. Separate the reserved dried oxalates from the paper, and burn the paper in the crucible. Finally add the dried oxalates, and cautiously ignite to constant weight. This represents the "total rare earth oxides." Transfer to a 600-ml beaker, moisten with a little water, dissolve in dilute hydrochloric acid (1 + 1), and proceed with the separation of thorium as described in Section III.

Monazite sand and rare earth minerals that contain but little thoria can also be broken up as follows: Intimately mix 0.5 g of the finely ground sample with 0.5 g of sodium fluoride and 10 g of potassium pyrosulfate in a large platinum crucible. Cover, place over a very small flame, and increase the heat very gradually until the melt is in quiet fusion. Cool, digest the melt with dilute hydrochloric acid (1 + 10) until it has disintegrated, let settle, and filter. Sluice the residue back into the beaker, digest with 10 ml of hydrochloric acid, dilute to 100 ml, and again filter. Nearly neutralize the combined filtrates with ammonium hydroxide, and proceed with the precipitation of crude rare earth oxalates by the same general procedure as is described in Section IV.

Thorite and other silicates that are rich in thoria and poor in rare earths can be decomposed by digesting the very finely powdered sample with concentrated hydrochloric acid for 1 to 2 hours at a temperature just short of boiling. The solution is then evaporated to dryness, silica removed as usual, and the siliceous residue fused with pyrosulfate. The melt is extracted with dilute hydrochloric acid (1 + 1), the solution filtered, and the filtrate combined with that first obtained.

III. METHODS OF SEPARATION

The separations of thorium that are of particular interest are those based on (1) precipitation as fluoride or oxalate, whereby thorium is separated from the common metals, including zirconium and titanium, but not from the rare earths; (2) precipitation with peroxide, iodate, hexamine, or thiosulfate, whereby thorium is separated from the rare earths; and (3) precipitation with iodate or an excess of ammonium fluoride, whereby thorium is separated from scandium.

Thorium oxalate is soluble in solutions of alkali oxalates and in strong mineral acids. Precipitation must therefore be made under conditions that insure the absence of alkali oxalates, and are preferably made by the addition of oxalic acid to hydrochloric acid solutions containing less than 4 per cent by volume of the acid. Separations of thorium from the rare earths that are based on the solubility of thorium oxalate in ammonium oxalate are unsatisfactory, no matter whether the mixed oxalates are digested with ammonium oxalate or precipitation is made by adding an excess of ammonium oxalate.[4]

Thorium fluoride is quite insoluble in dilute mineral acids. Separation as the fluoride is used more for the separation of thorium, together with the whole rare earth group, from the other elements in the ammonia precipitate that is obtained in ordinary analysis, than it is for the separation of large amounts of thorium from common metals. The separation is best applied under conditions that insure the absence of acids other than hydrofluoric, as for example by transferring the washed ammonia precipitate to a platinum dish, treating with hydrofluoric acid, and evaporating to small volume (p. 554). More complete precipitation is obtained, particularly in the presence of mineral acids, if ammonium fluoride is added.

Thorium must be separated from phosphorus before the hexamine, thiosulfate or peroxide separations are applied or final precipitation with oxalic acid is made. Fusion with sodium carbonate or precipitation with sodium hydroxide is not satisfactory because of the solubility of the precipitate in alkaline solutions containing carbonate. Separation can be accomplished by the iodate method as described, or by precipitation with oxalic acid in cold, dilute, hydrochloric acid solution. As applied to monazite sand, the most common case, the separation is as follows: Dilute 200 ml of the sulfuric acid solution obtained as in Section II to 1 liter, and pour, very slowly and with constant stirring, into 150 ml of a cold saturated solution of oxalic acid. Let stand for at least 15 hours, filter, wash the precipitate with dilute hydrochloric acid (1 + 99), dry, and set it aside. Neutralize the filtrate and washings with ammonium hydroxide, add an excess of 10 ml of hydrochloric acid, and let stand 15 hours. Filter, and wash with a solution containing 40 ml of hydrochloric acid and 25 g of oxalic acid per liter. Dry, ignite gently in a porcelain dish, moisten with a little water, dissolve the residue in 10 ml of hydrochloric acid, and filter. Dilute to 500 ml, heat to boiling, and slowly add 100 ml of a hot 10 per cent solution of oxalic acid. Let stand for 4 to 5 hours at room temperature, filter, wash with the dilute hydrochloric-oxalic acid solution, and dry. Combine with the reserved precipitate, ignite to oxides, and proceed with the separation of thorium from the rare earths.

Perhaps the simplest method for the separation of thorium from the rare earths lies in precipitation with hexamethylenetetramine (hexamine or urotropine, $C_6H_{12}N_4$) as follows:[5] Prepare 100 ml of a dilute hydrochloric

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[4] E. Benz, Z. *angew Chem.*, **15**, 297 (1902).

[5] A. M. Ismail and H. F. Harwood, *Analyst*, **62**, 185 (1937).

acid solution of the elements (*p*H 2 to 4), warm to 30° C, and add 5 g of ammonium chloride. Add a 10 per cent solution of hexamine, drop by drop and with stirring after each addition, until a slight excess is present. At this point, the *p*H should be approximately 5.8, and no further precipitation of thorium should be observed when the precipitate is allowed to settle and one drop is added to the clear supernatant solution. Decant the solution through a Whatman no. 41, or equivalent paper, then transfer the precipitate, and wash the paper and precipitate with a warm 2 per cent solution of ammonium nitrate. Reserve the filtrate for the determination of the rare earths. Dissolve the precipitate on the paper in hot 2 *N* hydrochloric acid, and thoroughly wash the paper with hot water. Dilute the solution to 100 ml, add a few drops of methyl red, and then dilute ammonium hydroxide (1 + 1), slowly and with stirring, until the indicator just turns yellow. Next add dilute hydrochloric acid (1 + 1) until the solution turns pink. If not already present, add enough ammonium chloride to bring the content in the solution to 5 per cent. Warm to 30° C, precipitate with hexamine, wash as before, and add the filtrate and washings to the reserved filtrate. The washed precipitate can be ignited and weighed as ThO_2,[6] or dissolved in hydrochloric acid and precipitated as oxalate as described on page 542.

An alternative separation of thorium from moderate amounts of cerium and lanthanum is that based on precipitation with hydrogen peroxide.[7] The method has not been tested in the presence of other rare earths, or of scandium. Zirconium and titanium accompany thorium. The precipitation is carried out as follows: Treat the neutral solution of the nitrates of thorium, cerium, and lanthanum[8] with 10 g of ammonium nitrate, dilute to 100 ml, warm to 60 to 80° C and precipitate the thorium by the addition of 20 ml of hydrogen peroxide (3%). Filter, and wash the precipitate with a hot 2 per cent solution of ammonium nitrate. If the precipitate is colored yellow, cerium is still present and must be removed by a second precipitation, after solution of the precipitate in nitric acid, evaporation to dryness, and

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[6] By this procedure, the authors obtained satisfactory separations of thorium from cerium^{III}, lanthanum, neodymium, praseodymium, and yttrium. Scandium accompanies thorium. In analyses of monazite sand, C. J. Rodden obtained a final precipitate in which none of the rare earth elements could be found by spectrochemical test.

[7] G. Wyrouboff and A. Verneuil, *Compt. rend.*, **126**, 340 (1898); E. Benz, Z. *angew. Chem.*, **15**, 297 (1902).

[8] The nitrates can be prepared directly from the oxalates as follows: Sluice the oxalates from the filter to a porcelain dish by the use of as little water as possible, wash the paper alternately with hot dilute nitric acid and hot water, and evaporate the solution nearly to dryness. Add 5 to 10 ml of nitric acid, then 20 ml of fuming nitric acid, and cover with a glass. Place on the steam bath, and heat until evolution of gases ceases. Remove and wash the glass, rinse down the side of the dish, and evaporate the solution to dryness. Moisten with a little water, and again evaporate to dryness.

solution of the nitrates in 100 ml of a 10 per cent solution of ammonium nitrate.[9]

According to R. J. Meyer and M. Speter,[1,10] thorium can be readily separated from cerium^{III}, "didymium," common metals, and phosphoric acid, by precipitating with potassium iodate in strong nitric acid solution. Titanium and zirconium accompany thorium. The procedure is as follows: Dissolve the oxides or hydroxides of thorium and the rare earths in a mixture of 100 ml of water and 50 ml of nitric acid, and cool the solution in ice water.[11] Add a cooled solution of 15 g of potassium iodate in 30 ml of water and 50 ml of nitric acid, and stir occasionally during the course of 30 minutes. Let settle, filter, break up any lumps of precipitate with a rod flattened at one end, wash with 250 ml of a cool solution containing 8 g of iodate and 200 ml of dilute nitric acid (1 + 1) per liter, and let drain. Sluice the precipitate back into the beaker with 100 ml of the wash solution, stir thoroughly, and filter on the same paper. Let drain, and again sluice the precipitate into the beaker, this time with hot water. Heat nearly to boiling and dissolve the precipitate by adding 30 ml of nitric acid, slowly and with stirring. Dilute to 60 ml, add a solution of 4 g of iodate in a little water and dilute nitric acid, and let cool. Filter on the original filter, wash by decantation as before, and transfer the precipitate to the paper. Sluice the precipitate into the beaker, and wash the paper with hot dilute hydrochloric acid containing a little sulfurous acid. Boil the solution, adding more hydrochloric and sulfurous acids if necessary, until the precipitate is dissolved. Dilute, precipitate with ammonium hydroxide, filter, and wash the precipitate with hot water until free of iodides. Finally dissolve in hydrochloric acid, and precipitate with oxalic acid as in Section IV.[12]

A modification of the iodate method described in the detection of thorium in Section I serves for the separation of scandium as well.[13] In this case, separate the rare earths by precipitating with oxalic acid, ignite, dissolve the oxides in hydrochloric acid, and separate thorium and scandium by the

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[9] By this procedure, Benz obtained 0.1468 g of ThO_2, by a single precipitation in a solution containing 0.1470 g of ThO_2, 0.13 g of CeO_2, and 0.2 g of La_2O_3; and 0.0735 g of ThO_2 by double precipitation in a solution containing 0.0735 g of ThO_2 and the same amounts of cerium and lanthanum.

[10] R. J. Meyer and M. Speter, *Chem. Ztg.*, **34**, 306 (1910).

[11] A 100-ml aliquot portion of a sulfuric acid solution of monazite obtained as in Section II can be treated directly with the nitric acid.

[12] By this method, Meyer and Speter obtained 0.4994, 0.4990, and 0.4988 g of ThO_2 in solutions containing 0.4995 g of ThO_2; and 0.4999 g of ThO_2 in a solution containing 0.4995 g of ThO_2 and 10 g of cerium nitrate. Praseodymium and neodymium were also found to be without effect. As applied to monazite sand, 5.54, 5.57, 5.58, and 5.57 per cent ThO_2 were found in a sample that showed 5.53 per cent "by the most refined methods."

[13] R. J. Meyer, *op. cit.*, p. 67.

thiosulfate method (below). Dissolve the final thiosulfate precipitate and recovery in nitric acid, filter, and evaporate the solution to dryness. Take up the residue in 5 ml of water to which a few drops of nitric acid have been added, and add 5 to 10 ml of iodate solution 1 (p. 533), depending on the amount of thorium present. Stir, add 10 to 20 ml of iodate solution 2, digest for 15 minutes at 60 to 80° C, and then set aside until the precipitate has settled. Filter, wash the precipitate with portions of solution 2 reserve the filtrate, and sluice the precipitate back into the beaker. Add ammonium hydroxide in goodly excess, boil to convert the iodate to hydroxide, and, toward the end of the boiling, add the filter paper. Filter, wash thoroughly to remove iodate, dry, and ignite to ThO_2. Heat the reserved filtrate, add ammonium hydroxide in excess, boil, filter, wash as with thorium, ignite, and weigh as Sc_2O_3.

The separation of thorium from scandium by precipitating the thorium as fluoride in a solution containing a large excess of ammonium fluoride is described under Scandium (p. 545).

According to R. J. Carney and E. D. Campbell,[14] a very satisfactory separation of thorium from trivalent cerium, lanthanum, praseodymium, and neodymium can be made by precipitating with sodium pyrophosphate in a solution approximately 0.3 *N* with respect to hydrochloric or sulfuric acid, preferably the former.[15]

The separation of thorium (and scandium) from the rare earths by precipitation with sodium thiosulfate is not entirely satisfactory, for the precipitation of thorium is incomplete and the separation is not sharp. The separation does not work so well with the yttria as with the ceria earths.[16] Another drawback to the method is the impossibility, because of separated sulfur, of telling whether any precipitation has taken place when small amounts of thorium are in question. Precipitations must be repeated until test of the thiosulfate filtrate with ammonium hydroxide indicates that the separation from rare earths is satisfactory. Moreover, thorium must be recovered in the thiosulfate filtrates. Elements such as aluminum, titanium, and zirconium are also precipitated and should be removed before the separation is attempted. The procedure is as follows: [4,17] Dissolve the mixed oxides or hydroxides, obtained after a preliminary separation with oxalic acid, in hydrochloric acid, evaporate the solution to dryness, and moisten

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[14] R. J. Carney and E. D. Campbell, *J. Am. Chem. Soc.*, **36**, 1140 (1914).

[15] According to M. Koss [*Chem. Ztg.*, **36**, 686 (1912)] and F. Wirth [*Z. angew. Chem.*, **25**, 1678 (1912)], a satisfactory separation of thorium from cerium, praseodymium, and neodymium can be had by adding a cool solution of $NaHPO_3$, dropwise and with stirring, to a boiling 15 to 20 per cent H_2SO_4 solution of the elements, letting stand for several hours, and filtering to separate the precipitated $Th(PO_3)_2$.

[16] G. P. Drossbach [*Z. angew. Chem.*, **14**, 655 (1901)] found that appreciable yttrium was retained in spite of four precipitations.

[17] R. Fresenius and E. Hintz, *Z. anal. Chem.*, **35**, 525 (1896).

the residue with 5 to 10 ml of water. Again evaporate to dryness, add 150 ml of water and 2 drops of hydrochloric acid, and heat to boiling. No precipitation should take place if the original precipitation with oxalic acid was properly made. Gradually add a solution of 2 g of sodium thiosulfate in 10 ml of water. Cover, and boil for 15 minutes. Filter, wash the precipitate with hot water, and set the filtrate (A) aside for recovery of its thorium content. Spread the paper on a glass plate, sluice the thiosulfate precipitate into a porcelain dish by means of a jet of hot water, and wash the paper thoroughly with hot dilute hydrochloric acid and then with a little hot water. Add 20 ml of hydrochloric acid to the solution, boil for 5 to 10 minutes, filter, and wash the sulfur residue and the paper with dilute hydrochloric acid and water. Evaporate the solution to dryness, and again precipitate with thiosulfate. Set the second thiosulfate precipitate (B) aside. Boil the filtrate, add ammonium hydroxide in slight excess, filter, wash the precipitate with a little hot water, and set it aside for recovery of its thorium content. The size of this precipitate (C) shows whether B must be dissolved and reprecipitated with thiosulfate. Dissolve the final thiosulfate precipitate in hydrochloric acid as already described, and reserve the solution (D) for the precipitation of thorium as oxalate as described in Section IV. Combine the thiosulfate filtrate (A and any others not already treated with ammonium hydroxide), heat to boiling, add ammonium hydroxide in excess, filter, and dissolve the ammonia precipitate, together with precipitate C and any others obtained with ammonium hydroxide, in hydrochloric acid. Evaporate the solution to dryness, precipitate with thiosulfate as before, filter, wash the precipitate, and reserve the filtrate if rare earths are to be determined. Dissolve the thiosulfate precipitate in hydrochloric acid, and combine the solution with solution D which contains most of the thorium.[18]

T. O. Smith and C. James[19] stated that thorium can be quantitatively precipitated and separated from cerium, lanthanum, praseodymium, neodymium, samarium, and gadolinium by treating a boiling neutral solution of their salts with a slight excess of a hot nearly saturated solution of sebacic acid (added slowly and with constant stirring), filtering at once, washing the precipitate with hot water, and igniting to the oxide, ThO_2. One drawback of the separation is the difficulty of decomposing sebacic acid if the filtrate is to be treated by methods in which the presence of the acid is objectionable.

According to W. B. Giles,[20] a suspension of pure lead carbonate precipitates thorium, zirconium, cerium^{IV}, and iron^{III} completely; uranium,

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[18] By essentially this procedure, Benz obtained 0.0436 g of ThO_2 and 0.2077 g of CeO_2 in a mixture containing 0.0443 g of the former and 0.2086 of the latter.

[19] *J. Am. Chem. Soc.*, **34**, 281 (1912).

[20] *Chem. News*, **92**, 1, 30 (1905).

chromium^{III}, and aluminum incompletely; and cerium^{III}, lanthanum, neodymium, praseodymium, yttrium, samarium, and the yttria group (so far as investigated) not at all. Precipitation is carried out by adding an excess of lead carbonate[21] to the cool solution and letting it stand with occasional stirring for 24 hours.

Precipitation with phenylarsonic acid, $C_6H_5AsO(OH)_2$, in boiling acetic acid-ammonium acetate solution has been suggested for the separation of thorium from the rare earth elements present in monazite sand.[22] Cerium must be in the trivalent state; zirconium is also precipitated.

Treatment with hydrogen sulfide, preferably started in strong acid solution which is afterward diluted (p. 58), serves to separate the members of the hydrogen sulfide group from thorium, whereas precipitation with ammonium hydroxide (free from carbonate) serves to separate thorium from magnesium, the alkaline earths, and the alkalies. The hydroxide is insoluble in an excess of carbonate-free sodium or potassium hydroxide, which permits separation from elements such as aluminum and beryllium. Thorium is not precipitated by ammonium hydroxide or ammonium sulfide in the presence of ammonium tartrate, and so can be separated from iron in sulfide solution.[23]

Thorium is precipitated by a fresh solution of barium carbonate (p. 82), even in the cold, and so separated from elements such as nickel and manganese. The precipitation of thorium by cupferron (p. 116) is incomplete in solutions containing free mineral acids,[23, 24] but complete in solutions containing acetic acid and ammonium acetate.

Thorium can be separated from zirconium by double precipitation of the latter as phosphate in dilute sulfuric acid solution (1 + 10) (see p. 570). Separation from tungsten can be carried out by volatilizing the latter at 700° C in a current of oxygen and dry hydrochloric acid gas, first oxidizing the tungsten in oxygen alone if the metals are involved.[25]

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[21] The lead carbonate is prepared as follows: Dissolve recrystallized pure $Pb(NO_3)_2$ in five times its weight of water, warm to 70° C, stir vigorously, and then add enough resublimed $(NH_4)_2CO_3$ to cause a decided precipitation. From time to time, withdraw some of the turbid liquid, filter, acidify with HNO_3, and test with KCNS. If iron is present, continue the stirring until it is completely precipitated. Cool, filter, and pour the clear filtrate in a thin stream into a clear saturated solution of resublimed ammonium carbonate. Let settle, wash by decantation with distilled water, collect on a filter, and wash until 500 ml of washings show a decided acid reaction when treated with methyl orange and 2 drops of *N* HNO_3. Let drain, heat at 40 to 50° C until pasty, and preserve in a wide-mouth glass-stoppered bottle.

[22] A. C. Rice, H. C. Fogg, and C. James, *J. Am. Chem. Soc.*, **48**, 895 (1926).

[23] W. M. Thornton, Jr., *Am. J. Sci.*, [4] **42**, 151 (1916).

[24] G. E. F. Lundell and H. B. Knowles, *J. Ind. Eng. Chem.*, **12**, 349 (1920).

[25] D. H. Brophy and C. Van Brunt, *Ind. Eng. Chem.*, **19**, 107 (1927).

IV. METHODS OF DETERMINATION

Practically all methods for the determination of thorium call for its final precipitation as the oxalate in order to make sure of the elimination of elements such as zirconium and titanium that are likely to accompany thorium in preliminary treatments. The precipitation with oxalate must ordinarily be preceded by prior separations, such as are described in Section III, for the purpose of removing the common metals, the alkaline earths, the rare earths, and scandium. Precipitation with ammonium hydroxide as described under Aluminum (p. 504), followed by ignition to the oxide, is entirely satisfactory with solutions that are free from other precipitable compounds, but in this case the precipitate had better be washed with ammonium nitrate rather than the chloride because of the volatility of thorium chloride.

PROCEDURE. Obtain the thorium in a hydrochloric acid solution free from phosphates and from the rare earths including scandium, and containing not more than 4 per cent of hydrochloric acid by volume and not over 1 mg of ThO_2 per ml. Heat to boiling, and add slowly and with stirring enough of a boiling 10 per cent solution of oxalic acid to combine with the thorium and to leave an excess of 20 ml for every 100 ml of solution. Let the solution cool and stand overnight. Filter, wash moderately with a solution containing 40 ml of hydrochloric acid and 25 g of oxalic acid per liter, ignite at approximately 1100° C, and weigh as ThO_2.

Chapter 35

SCANDIUM

Although scandium is the predominating basic constituent of only one known mineral, thortveitite, a silicate of scandium and the yttrium earths, it is actually one of the most widely distributed of the elements on the earth.[1] The amounts present are usually so very small, however, that spectral methods are required for their detection. Scandium is found in many rare earth minerals, in certain zirconium minerals, in beryls, titanates, niobates, titanoniobates, micas, and especially in cassiterite and wolframite.[2]

I. GENERAL CONSIDERATIONS

The detection of scandium is usually accomplished by concentrating the oxide as described in Sections II and III, dissolving it in hydrochloric acid, and examining the arc spectrum of the solution for the characteristic scandium lines 3572.72, 3613.98, 3630.90, and 3642.96.

In the course of an ordinary analysis, scandium will come down in the precipitate produced by ammonium hydroxide, and will be counted as aluminum if this element is calculated by difference. If the ammonia precipitate is dissolved in hydrofluoric acid and the solution evaporated for the separation of crude rare earth fluorides (p. 554), scandium will be precipitated and will eventually be caught with thorium, the yttrium metals, or the cerium metals, depending on the mode of treatment.

II. DECOMPOSITION OF MINERALS CONTAINING SCANDIUM

If appreciable amounts of scandium are present, as in thortveitite, fuse 1 g of the powdered mineral with 5 to 6 g of sodium carbonate, and either carry the analysis through the search for rare earths in the ammonia precipitate (p. 554), or else remove silica by dehydration with hydrochloric acid

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[1] G. Eberhard, *Sitzber. kgl. preuss. Akad. Wiss.*, 38, 851 (1908); *Chem. News*, **99**, **32** (1909); **102**, 211 (1910).

[2] H. S. Lukens [*J. Am. Chem. Soc.*, 35, 1470 (1913)] mentioned the occurrence of scandium in a wolframite from Colorado. In spectrochemical determinations of scandium in silicate rocks, A. Kvalheim and L. W. Strock [*Spectrochim. Acta*, **1**, 221 (1939)] found from 0.0056 to 0.0178 per cent of Sc_2O_3 in pyroxenites.

and proceed with the direct separation of scandium, zirconium, titanium, and thorium by precipitating with sodium thiosulfate as in Section III.

Rare earth minerals are decomposed as described under Rare Earths (p. 549), and scandium is accumulated in the yttrium group by the sodium sulfate method of separation.

For the decomposition of wolframite, fuse 10 to 100 g of the finely powdered mineral with two to three times its weight of sodium carbonate, and separate the scandium from most of the tungsten by leaching the melt with hot water and filtering.[3] Dissolve the insoluble residue in hydrochloric acid, remove silica in the usual fashion, and precipitate the scandium as impure fluoride in the hydrochloric acid filtrate from the silica by precipitating with sodium silicofluoride as in Section III. The finely powdered ore can also be digested with aqua regia and tungsten separated as described under Tungsten (p. 690).

Some minerals containing titanium, tantalum, and columbium can be decomposed and scandium separated by moistening the finely ground sample with water, cautiously adding hydrofluoric acid in excess, evaporating to dryness on the steam bath, taking up the residue in dilute hydrofluoric acid, filtering, and washing the crude scandium fluoride with dilute hydrofluoric acid (1 + 99).

III. METHODS OF SEPARATION

Scandium resembles yttrium and lanthanum in some of its properties and thorium and zirconium in others. Like lanthanum it gives an insoluble double salt when treated with a saturated solution of potassium sulfate, and is precipitated by oxalic and hydrofluoric acids. Like thorium, it forms (1) an oxalate that is soluble in ammonium oxalate, (2) a carbonate that is soluble in a cool solution containing an excess of alkali carbonate, and (3) a basic thiosulfate upon boiling with sodium thiosulfate in neutral solution. Like zirconium, its fluoride is soluble in an excess of alkali fluoride.

The most characteristic separation of scandium is that in which the fluoride, ScF_3, is precipitated in boiling dilute hydrochloric acid solution (1 + 10), by the addition of sodium silicofluoride (2 g per 100 ml of solution) in small portions as the solution is vigorously stirred.[4] The solution is then boiled for 30 minutes (as the volume is kept constant by additions of hot water), and allowed to stand until the precipitate has settled, the clear solution is decanted, and the precipitate finally transferred to the filter and washed with dilute hydrochloric acid (1 + 99) containing 1 per cent of sodium silicofluoride. In addition to scandium, the precipitate will contain silica and more or less of any thorium and rare earths originally present. The precipitate is therefore treated with sulfuric acid and evaporated to expel all hydrofluoric acid, before such further treatments as may be necessary.

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[3] R. J. Meyer, *Chem. News*, 99, 86 (1909); *Z. anorg. Chem.*, 60, 134 (1908).

[4] R. J. Meyer, *op. cit.*, 97.

Of the ordinary reactions, precipitation with hydrogen sulfide in a solution containing mineral acid serves to separate the members of the hydrogen sulfide group from scandium,[5] whereas precipitation with ammonium hydroxide serves to separate the latter from magnesium and the alkaline earths.

Scandium is precipitated by oxalic or hydrofluoric acid (p. 551), and can thus be separated from elements other than thorium and the rare earths. Scandium oxalate is the most soluble of the rare earth oxalates, and so precipitations must not be done in the presence of mineral acids or ammonium oxalate. On the other hand, the fluoride is one of the least soluble, provided an excessive amount of hydrofluoric acid, which leads to the formation of soluble complex compounds, is avoided, and 2 to 4 ml of hydrochloric acid per 100 ml of solution are present.

The separation of scandium (and thorium) from the rare earths is made by precipitating with sodium thiosulfate, as described under Thorium (p. 539). The separation from the cerium group can be carried out by precipitating the latter in a saturated solution of sodium sulfate (p. 560).

The separation of scandium from thorium has been studied more for the purpose of purifying scandium than of separating it quantitatively. Among such methods may be mentioned the precipitation of scandium by the slow addition of ammonium hydroxide to a boiling concentrated solution of ammonium tartrate containing the two elements,[6] and the separation of scandium by precipitation in a boiling 20 per cent solution of sodium carbonate and filtration while the solution is still hot.[7] According to Meyer and his associates,[8] a satisfactory method for quantitative purposes consists in pouring the nearly neutralized solution of the chlorides of thorium and scandium, slowly and with vigorous stirring, into a hot solution of ammonium fluoride, containing at least eight times as much fluoride as there is scandia present. The solution, in a hard rubber or Bakelite beaker, is then boiled for 10 minutes and filtered through paper in a hard rubber or Bakelite funnel, and the precipitate is washed with a little hot water. The scandium is then recovered by evaporating the filtrate to fumes with sulfuric acid and precipitating with ammonium hydroxide or oxalic acid.

Thorium can also be separated from scandium by precipitating with potassium iodate in strong nitric acid solution as described under Thorium (p. 538).

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[5] According to R. J. Meyer (*loc. cit.*), lead sulfide carries down scandium, and so separations with hydrogen sulfide had better be started in strongly acid solutions which are then diluted.

[6] R. J. Meyer and H. Goldenberg, *Chem. News*, 106, 13 (1912).

[7] R. J. Meyer and H. Winter, *ibid.*, 102, 176 (1910).

[8] R. J. Meyer, A. Wassjuchnow, N. Drapier, and E. Bodländer, *Z. anorg. Chem.*, 86, 257 (1914).

IV. METHODS OF DETERMINATION

Scandium is preferably ignited and weighed as the oxide, Sc_2O_3, after precipitation with ammonium hydroxide. Precipitation with ammonium hydroxide is carried out as for aluminum (p. 504), and the precipitate is washed with a 2 per cent solution of ammonium nitrate. The wet precipitate is dried in the crucible, carefully ignited to the oxide, and finally heated at approximately 1000° C.

Chapter 36

RARE EARTH METALS

Under the name rare earth metals are grouped a number of elements, nearly all trivalent, whose compounds have in the main great similarity. The more restricted rare earth group includes only the metals having atomic numbers 58 to 71 inclusive, but scandium (21), yttrium (39), and lanthanum (57), have pronounced rare earth characteristics and are regarded as belonging to the group. Because of some of its chemical characteristics and its close association in nature with the trivalent earth metals, thorium is usually treated as a member of the group, which all form earth-like basic oxides. These, except thorium, all have the formula M_2O_3, but certain of them form also higher oxides, of which CeO_2 is the best-known example. In this form, cerium shows relationship with the single oxide of thorium, ThO_2.

The rare earths are widely distributed in nature,[1] and the minerals are numerous and well scattered, but usually found in small deposits or intimately mixed with other minerals. Silicates are the most common form, phosphates are numerous, while halides, carbonates, oxides, titanates, uranates, columbates, tantalates, and zirconates are found in varying degrees of complexity. Several or all of the distinctive acidic elements may occur in one and the same mineral. The minerals are generally found in granite or pegmatite veins in elaeolite syenites, or in gravels derived therefrom.[2] About 150 different rare earth minerals are listed, of which the best known are gadolinite, a silicate of beryllium, iron, and the yttrium group; xenotime, an yttrium orthophosphate containing erbium and members of the cerium group; euxenite, a titanocolumbate containing titanium, uranium, thorium, and members of the yttrium and cerium groups; fergusonite, a tantalocolumbate of yttrium containing thorium, zirconium, uranium, and members of the yttrium and cerium groups; samarskite, a tantalocolumbate containing uranium, thorium, zirconium, and the yttrium and cerium groups; monazite, a phosphate of the cerium metals with thorium silicate; cerite, a hydrated silicate of cerium metals with more or less yttria earths, calcium, and iron; allanite, a hydrated silicate containing members of the

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[1] B. S. Hopkins, *Chemistry of the Rarer Elements*, 1923 ed., p. 96, D. C. Heath and Co., New York.

[2] F. W. Clarke, The Data of Geochemistry, *U. S. Geol. Survey Bull.* 770, 15, 21.

cerium and yttrium groups, in addition to calcium, beryllium, iron, and aluminum; and yttrocerite, an yttrium cerium calcium fluoride. Aside from the common elements, calcium, iron, and aluminum, which are almost always associated with the characteristic ones indicated in the foregoing list, the following are either of frequent or occasional occurrence: uranium, beryllium, fluorine, boron, lead, antimony, arsenic, tin, tungsten, helium, nitrogen, and probably others such as hafnium.

I. GENERAL CONSIDERATIONS

The whole rare earth group forms oxalates, which are insoluble in oxalic acid and in dilute mineral acids, and fluorides, which are insoluble in dilute hydrofluoric acid. These two reactions afford means for effecting group separations from most of the other elements. The further fact that they are all quantitatively precipitable by ammonium hydroxide makes it possible to separate them from the alkali and alkaline earth metals and magnesium. Further, their hydroxides are insoluble in the hydroxides of sodium and potassium, a behavior that the analyst turns to good account on occasion.

Thorium is practically always associated with the rare earth metals in nature, and its oxalate and fluoride comport themselves towards hydrofluoric acid and oxalic acid like those of the rare earths.[3] The behavior of its hydroxide toward the alkali hydroxides is also like that of the rare earth hydroxides. Zirconium occurs also in many rare earth minerals and has to be considered in all analytical procedures that involve rare earths and thorium. Hence it is convenient to treat it analytically in connection with the rare earth group, even though it does not form an insoluble oxalate or fluoride. In certain of its reactions, it follows in a measure quadrivalent cerium and thorium.

In an ordinary analysis, the rare earths are caught in the ammonia precipitate and are counted as aluminum.[4] They give no indication of their presence by distinctive reactions, except for the color of certain of the oxides, as do other uncommon elements such as the earth acids or tungsten. Special tests, as with oxalic or hydrofluoric acid, must be made to make sure of their absence or presence. Certain of the elements yield colored oxides and colored solutions, which should put the analyst on guard in the comparatively uncommon case in which they may occur in appreciable amount and not associated with other colored compounds. The presence of the rare earths can oftentimes be established by examining the spectrum of the light reflected by the hydroxide or other compound or by examining the light transmitted by a solution of these compounds. If bands due to neodymium or praseodymium are observed, the cerium group is indicated; if erbium bands are observed, the yttrium group is generally present.

It should be noted that cerium, praseodymium, and terbium yield higher oxides (R_2O_{3+}) on ignition in air, and will cause high summations if the weight of the ignited ammonia precipitate is corrected on the basis of the trivalent oxides.

II. DECOMPOSITION OF RARE EARTH MINERALS

So varied are the rare earths in character and composition that no rules for analysis can be laid down to cover all cases, even those that fall within the same subgroup. The best that can be done is to sketch broadly some of the most commonly used procedures. The practiced analyst will find greater opportunity for the exercise of judgment and choice of procedure or combinations of procedures here than anywhere else in the field of mineral analysis.

Before a quantitative analysis of a mineral is begun, a most thorough qualitative examination (preferably spectrographic) should be made if the supply of material permits, for knowledge of the qualitative composition is essential, and some idea of the relative amounts of the constituents is desirable. The information may be decisive in indicating the best methods of attack or of separation. Unfortunately it is very often the case that material is lacking for exhaustive preliminary test, in which event the analyst always risks error, sometimes slight, sometimes great. Examination of the light reflected from the surface, by means of a hand spectroscope, yields helpful information in many cases.

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[3] Ammonium oxalate is as good a precipitant as oxalic acid for many of the rare earth metals, but an excess of it redissolves certain of the oxalates, so that its applicability is not general.

[4] The more basic rare earths may be more or less incompletely precipitated at the *p*H 6.5 to 7.5 usually established for the precipitation of aluminum. Under certain conditions, lanthanum may not be precipitated at all. In their presence, it may be better to precipitate and to filter as usual, and then to recover unprecipitated rare earths by adding more ammonium hydroxide to the filtrate and again filtering if a precipitate is obtained. This leads to a better recovery of aluminum, and to less contamination by manganese. Better recoveries of lanthanum, cerium, and yttrium are obtained in this second precipitation if (1) ammonium salts are first destroyed by digesting with acid (p. 133), (2) the excess of acid is removed by evaporating nearly to dryness, (3) the diluted solution is treated with enough ammonium hydroxide to cause malachite green to fade completely ($pH > 14$), (4) the solution is warmed to 50 to 60° C before filtering, and (5) the precipitate is washed with dilute ammonium hydroxide (5 + 95) containing 1 per cent of ammonium nitrate. W. R. Schoeller and E. F. Waterhouse [*Analyst*, 60, 284 (1935)] state that, even so, complete precipitation is difficult, and that a better procedure lies in adding tannin before the boiling solution is treated with ammonium hydroxide in excess. In such case, ammonium salts and even tartrates are said to be without effect.

Although there are rare earth minerals of relatively simple composition and earth acid minerals equally simple, each free perhaps from the most characteristic components of the other class, there is as a rule complexity, often mingling of the components of the two. Then indeed the difficulties of the analyst reach their climax.

Nitric acid alone is very little used for opening up minerals of the kind under consideration. Uraninite, bröggerite, cleveite, nivenite, pitchblende, and thorianite are the only ones perhaps for which it is specifically indicated, because it dissolves them completely and at the same time oxidizes the quadrivalent uranium to the sexivalent state. Some of the minerals, particularly silicates of the rare earths, are decomposed more or less readily by hydrochloric acid. When completely decomposable, the resulting solution is to be treated like the solution of an ordinary silicate (p. 860). Other minerals yield with ease to attack by hydrofluoric acid (samarskite for example) and nearly all to fusion with an acid alkali fluoride. An attack of either kind is usually restricted to the columbates, tantalates, and titanates that are free from silicon. Naturally the boron- or fluorine- or silicon-containing minerals must be opened up by an alkali fusion for the determination of those elements. Most of the minerals yield to sulfuric acid. Some, like monazite and xenotime and cerite, require prolonged treatment at 200° C or over. For their phosphorus content, one or more fusions with an alkali is to be preferred, as also for those minerals that carry boron and usually for those with fluorine.

Probably all the minerals succumb to fusion with an alkali pyrosulfate, but, as with sulfuric acid, this mode of attack is used more for the commercial assay for thorium than for general analysis. When it is used, the sodium salt is to be preferred because of the greater solubility of some of the resulting sulfates. Fusion with an alkali carbonate or hydroxide is usually resorted to for the determination of silicon when acids fail or when fluorine is present, and when boron or fluorine is to be determined. For a general analysis, phosphates also are decomposed by fusion with sodium carbonate. For fluorine, an evolution method may be used when the mineral is soluble in hot concentrated sulfuric acid. Sodium hydroxide or peroxide is sometimes used in commercial assaying, but neither of these is so well suited as sodium carbonate when a general analysis is to be made, because they either are apt to be less pure or attack too strongly the fusion vessels.

III. METHODS OF SEPARATION

The methods of separating the rare earth metals from other elements in mineral analysis vary according to the composition of the mineral and the reagent used for its attack. Rare earth silicates, containing no titanium,

columbium or tantalum, are generally soluble in hydrochloric or nitric acid or are decomposable by an alkali-carbonate fusion. If so, the silica is separated in the usual manner by evaporation and filtration at least once repeated (p. 860). Then, as a rule, a double ammonia precipitation is made (p. 869). If both rare earths and calcium are present in appreciable amounts, three or four precipitations may be needed to insure complete separation of calcium. The precipitate contains the totality of the rare earth metals present, including thorium, also zirconium, titanium, and any other elements that are precipitable by ammonium hydroxide, and should be free from manganese, nickel, the alkaline earth metals, magnesium, and the alkali metals. It is dissolved in hydrochloric acid, the solution evaporated, and the residue taken up with water and just enough hydrochloric acid to give a clear solution. From this solution, the rare earths are precipitated by adding a saturated solution of oxalic acid in excess, the amount of which is gaged mainly by the amount of trivalent iron or sexivalent uranium present.[5] Both ferric iron and sexivalent uranium have a solvent effect on rare earth oxalates, especially those of the more basic metals, an effect that is largely overcome by having more than enough oxalic acid present to form ferric oxalate[6] and uranyloxalic acid,[7] as well as to precipitate the earths.[8]

Columbates and tantalates are for the most part insoluble in hydrochloric or nitric acid, but some yield more or less readily to hydrofluoric acid. If completely decomposable by the last named, the rare earth fluorides, thorium fluoride, and uranous fluoride, precipitate almost completely and can be washed free from nearly all other elements by weak hydrofluoric acid. This is especially advantageous as a means of separating the rare earths and quadrivalent uranium from columbium, tantalum, titanium, zirconium, and sexivalent uranium, whose fluorides are soluble. After conversion of the

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[5] L. A. Sarver and P. H. M.-P. Brinton [*J. Am. Chem. Soc.*, **49**, 943 (1927)] studied the solubilities of the oxalates of lanthanum, cerium, praseodymium, neodymium, samarium, and gadolinium in hydrochloric, nitric, sulfuric, and oxalic acids. They found that the solubilities of the oxalates of these elements in solutions saturated with respect to oxalic acid and containing very little hydrochloric acid decrease in the order given. For pure solutions, they recommend that 0.5 *N* hydrochloric acid be used in all cases, and that the solution be almost saturated with oxalic acid for the precipitation of lanthanum and cerium, and contain 0.5 *N* oxalic acid for the precipitation of the others. Furthermore, that the hot concentrated solution of oxalic acid be added with stirring to the boiling solution of the rare earths in 0.5 *N* hydrochloric acid and that the solution be then allowed to stand overnight before filtering.

[6] M. Dittrich, *Ber.*, **41**, 4373 (1908).

[7] O. Hauser, *Z. anal. Chem.*, **47**, 677 (1908).

[8] The rare earth oxalates can be changed into soluble compounds by (1) igniting the oxalates and dissolving the oxides in acid, (2) treating with H_2O_2 if much CeO_2 is present, (3) boiling with fuming nitric acid, and (4) boiling with NaOH or KOH and dissolving the washed hydroxides in acid.

fluorides to sulfates and solution of these in dilute hydrochloric acid, precipitation by ammonium hydroxide frees the rare earth metals from the alkaline earth metals that may have been also precipitated as fluorides. The washed hydroxides may then be ignited to oxides directly if U^{IV} was not originally present,[9] or they may be dissolved in hydrochloric acid (nitric if U^{IV} is present), the solution evaporated, and the rare earths precipitated by oxalic acid in excess.

The hydrofluoric acid treatment will recommend itself further in one form or another when very small amounts of rare earths are accompanied by large amounts of other elements which ammonium hydroxide precipitates, as in silicate analysis (p. 868). In such cases, the ammonia precipitate can be treated directly with hydrofluoric acid, the solution evaporated nearly to dryness, and the earth fluorides filtered off and washed with dilute hydrofluoric acid and further treated as outlined above. Of course, this treatment of the ammonia precipitate may be employed also with large amounts of rare earths as an alternative to the oxalate precipitation already mentioned, and in general gives more complete precipitation. Protactinium is not precipitated by hydrofluoric acid. Quadrivalent cerium is precipitated by both hydrofluoric and oxalic acid, the latter ultimately yielding the trivalent salt.

Small amounts of the rare earths admixed with the earth acids can be separated as follows:[10] Fuse 0.5 g of the oxides with 6 g of potassium bisulfate in a silica crucible, and dissolve the melt in 60 ml of a 10 per cent solution of tartaric acid. Dilute to 400 ml, add 50 ml of concentrated hydrochloric acid, and boil for 3 minutes. Let settle, and filter under light suction through a filter paper containing a little paper pulp. Return the paper and pulp to the beaker, stir with acidulated water, again filter, and discard the residue. Combine the filtrates, make ammoniacal, heat to boiling, and

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[9] It is difficult to obtain constant weight when certain rare earth oxides are ignited; there is a tendency to descend to a minimum and then gradually to register successive slight, but in the aggregate considerable, gains during subsequent ignitions [Sarver and Brinton, *loc. cit.*]. According to P. H. M.-P. Brinton and H. A. Pagel [*J. Am. Chem. Soc.*, **45**, 1460 (1923)], praseodymium oxide obtained from the oxalate has the formula Pr_6O_{11} when ignition is carried out in air, and Pr_2O_3 when carried out at 900 to 1000° C in hydrogen. Cerium is always weighed as the dioxide, CeO_2, after ignition at approximately 1200° C, and cannot be readily reduced to Ce_2O_3 by ignition in hydrogen. Terbium yields Tb_4O_7 in air, and can be reduced to Tb_2O_3 by ignition in hydrogen. In a later paper, Pagel and Brinton [*J. Am. Chem. Soc.*, **51**, 53 (1929)] stated that they could obtain no higher oxides of lanthanum, neodymium, samarium, gadolinium, erbium, or ytterbium. They found, however, that the composition of the oxide of praseodymium obtained by ignition in air varies with the conditions of ignition and cooling. For summation analyses, cerium must be removed before igniting the remaining rare earth oxides in hydrogen.

[10] W. R. Schoeller and E. F. Waterhouse, *loc. cit.;* W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium*, p. 98, Chapman & Hall, London, England (1937).

add 10 g of ammonium acetate and a fresh solution of 0.7 g of tannin. Let settle, filter, and wash the precipitate with a 5 per cent solution of ammonium nitrate containing a little tannin and ammonium hydroxide. Ignite in a silica crucible, fuse with 2 g of *sodium* bisulfate, and dissolve the melt in 50 ml of a 10 per cent solution of tartaric acid. Dilute to 100 ml, heat to boiling, stir, and slowly add 10 ml of a saturated solution of oxalic acid. Let stand overnight, filter, and wash with a solution containing 1 per cent each of oxalic and tartaric acids. Ignite, to obtain the rare earths as oxides.

The minerals that resist attack by all of the acids named will yield either to sulfuric acid or to fusion with an alkali bi- or pyrosulfate or with potassium-hydrogen fluoride. If the last reagent is used, the rare earth fluorides will not be so insoluble as when precipitated with hydrofluoric acid, because they are somewhat soluble in the alkali fluoride present. It may then be necessary to recover the residual amount held in solution, after evaporating the filtrate and removing the fluorine by sulfuric acid. Solutions obtained after attack by sulfuric acid are evaporated and heated until most of the excess acid is expelled, and the resulting pasty mass is cooled and dissolved by the addition of small portions of cold water (preferably ice cold to lessen the tendency for insoluble sulfates to form). Solution proceeds slowly and must be aided by frequent stirring. When all has dissolved that will dissolve, the solution is filtered. The residue may consist of undissolved mineral, silica, and titanic oxide. If the mineral was impure (monazite sand), the residue may contain also foreign minerals. It is collected on a filter and ignited, and the treatment with sulfuric acid, etc., is repeated as often as the magnifying glass reveals unattacked particles of the mineral.

Solution of a mineral other than a phosphate having been effected by nitric, hydrochloric, or sulfuric acid, silica, if present, is rendered insoluble as in silicate analysis (p. 860) and filtered. If lead is present and sulfuric acid the attacking agent, lead sulfate will accompany the silica and must be separated from it before igniting, by extracting with ammonium acetate solution or hot hydrochloric acid. If it is first ignited, there is danger of formation of lead silicate and incomplete extraction.[11] If tin or antimony is present and nitric acid the attacking agent, stannic and antimonic oxides will contaminate the silica. Titanic, columbic, and tantalic oxides, if present, will also be rendered insoluble wholly or partly upon evaporation, if any one of the acids named above was used for attacking the mineral. After ignition of the mixture, the silica can be volatilized by evaporating with

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[11] Similar difficulties are encountered in many analyses for silica. Trouble can often be avoided by carefully choosing the acid that is used in the dehydration. Thus, sulfuric is to be preferred to hydrochloric acid if antimony is present, for hydrochloric acid gives rise to insoluble basic chlorides which undergo indefinite changes in weight. On the other hand, perchloric acid is more desirable than either hydrochloric or sulfuric acid if lead is present.

hydrofluoric and a few drops of sulfuric acid, and the residual oxides weighed in order to obtain the weight of the silica. The residue must then be fused with alkali pyrosulfate or carbonate (which to use will depend on the composition of the residue) and the melt given appropriate treatment for separating and determining its components.

The not too acid filtrate from the silica is treated cold with hydrogen sulfide. Lead and tin are metals most commonly found in the resulting precipitate, which should be treated by appropriate methods for whatever it may contain, in conjunction with any lead, antimony, or tin that may have been extracted from the silica or left as a residue after volatilizing it with hydrofluoric acid.

In the filtrate, freed from hydrogen sulfide, reoxidized by nitric acid, and evaporated if need be, an ammonia precipitation is made (p. 504) and the precipitate dissolved in hydrochloric acid and reprecipitated by ammonium hydroxide as often as may be necessary to eliminate alkaline earths, magnesium, and the alkalies.[12]

The treatment of the ammonia precipitate will vary according to its composition. If the rare earth metals are far exceeded by aluminum and iron, it is convenient to treat the precipitate with hydrofluoric acid, and to proceed as follows: Evaporate the solution to incipient dryness on the steam bath, moisten the residue with 0.5 ml of hydrofluoric acid, add 25 ml of water and then 0.5 ml of hydrochloric acid, digest awhile, filter, and wash with water containing 2 ml of hydrofluoric acid and 2 ml of hydrochloric acid per 100 ml.[13] The fluorides are sluiced into a platinum dish, the filter ignited, the ash added to the dish, the solution evaporated with sulfuric acid, the excess of this expelled by heat over the radiator (Fig. 24), and the sulfates dissolved in cold water. From the solution, they are to be precipitated by oxalic acid, washed with a 1 per cent solution of the same acid, ignited at 1200° C, and weighed. The color of the oxides may afford some indication of the general character of the mixture. They are to be brought into solution in hydrochloric acid if possible (if not, then in sulfuric acid) and treated for the separation and determination of thorium or cerium or both. The filtrate from which the fluorides were separated is to be evaporated from sulfuric acid and heated until the fluorine is expelled (the expulsion must be complete), the residue taken up with dilute hydrochloric acid, and the iron, aluminum, etc., precipitated by ammo-

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[12] For minerals of the kind under consideration, magnesium and the alkali metals are seldom present in amounts requiring more than one or at most two ammonia precipitations. The same may be said of manganese and nickel if the precipitation is made with due care (p. 504).

[13] Alternatively, the hydroxides can be dissolved in hydrochloric acid, evaporated to dryness, dissolved in the smallest possible amount of hydrochloric acid, diluted to 50 ml, treated with oxalic acid, and allowed to stand overnight before filtering.

nium hydroxide (p. 504). The precipitate is ignited, finally at 1200° C, and weighed. In it, total iron (p. 96), zirconium (p. 96), and beryllium (p. 95) can be determined, if present; titanium also, if not determined in a separate portion. Phosphorus is to be determined in a separate portion. After the several oxides thus found are deducted from the weight of the mixed oxides, the residue is to be counted as alumina.

The treatment outlined does not apply to minerals that are essentially phosphates.[14] Except when these are to be assayed for a single constituent (thorium usually), one or more sodium carbonate fusions are called for. The aqueous extract of the melt will contain then the phosphorus;[15] any arsenic, antimony, tin, and tungsten that may be present; also much of the silicon, aluminum, and uranium. The residue having been well washed with dilute sodium carbonate solution, the dissolved constituents in the extract are to be determined after evaporating with nitric acid to render insoluble the silica (tungsten and antimony also in part, if present). After evaporating and treating the silica, the filtrate is treated with hydrogen sulfide to eliminate lead, arsenic, and the rest of any antimony that may be present. After expelling the hydrogen sulfide and evaporating, the phosphorus is precipitated by molybdate solution (p. 699) (which has been proved free from aluminum or any element that ammonium hydroxide precipitates), and determined as described under Phosphorus (p. 702). From the filtrate evaporated to remove excess of nitric acid, the aluminum is precipitated twice by ammonium hydroxide (p. 504), washed with 2 per cent ammonium nitrate solution, ignited, and weighed.

The residue from the sodium carbonate fusion is to be dissolved in hydrochloric acid and treated as in a silicate analysis or according to what has been said for the recovery of silica, aluminum, beryllium, titanium, zirconium, rare earths, alkaline earths, and magnesium, so far as one or another of them has not been determined in a separate portion of the sample.

Cerium can be separated from neodymium, yttrium, holmium, erbium, and dysprosium by oxidizing it to the quadrivalent state and precipitating with potassium iodate.[16] Thorium, zirconium, and possibly some scandium accompany cerium. The procedure is as follows: Prepare a solution of rare earth nitrates containing 25 ml of nitric acid and not more than 0.15 g of CeO_2. Dilute to 75 ml, add 0.5 g of potassium bromate, and stir until dissolved. Add, slowly and with constant stirring, 10 to 15 times as much

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[14] If a sulfuric acid solution of the mineral, such as monazite (p. 534), is poured into ten times its volume of 95 per cent alcohol, the rare earths are precipitated as sulfates. The separation is not quantitative, as precipitation of the rare earths is incomplete, and the precipitate retains some phosphate.

[15] The rare earths are also completely precipitated by sodium hydroxide and can thus be separated from phosphorus and the like.

[16] P. H. M.-P. Brinton and C. James, *J. Am. Chem. Soc.*, **41**, 1080 (1919).

of a solution of potassium iodate (10 g of iodate and 33.3 ml of nitric acid per 100 ml) as is theoretically required for the estimated amount of ceria present. Let settle, filter through a paper of close texture, and rinse the beaker once with a small amount of washing solution (8 g of iodate and 50 ml of nitric acid per liter). Let drain, and then immediately rinse any precipitate on the paper back into the beaker. Break up clots, churn the mixture, again filter, and allow to drain. Rinse back into the beaker, this time with about 50 ml of hot water, heat to boiling, stir constantly, and add nitric acid, dropwise until the precipitate dissolves. From 20 to 25 ml of acid will be required by 0.1 g of CeO_2, and an excess should be avoided. The solution should not exceed 75 ml in volume and should contain about one third of its volume in nitric acid. Add 0.25 g of potassium bromate and about the same amount of iodate as was used in the first precipitation. Let settle, filter through the original paper when cold, and rinse the beaker once. Rinse the precipitate back into the beaker, churn, filter, and wash with three small portions of the washing solution. Transfer the paper and precipitate to the beaker, and add 5 to 8 g of oxalic acid and 50 ml of water. Cover the beaker, heat gently, and then boil until iodine vapors are no longer given off and all sublimate is vaporized from the cover glass and edges of the beaker. Rinse the cover glass and inside of the beaker with water, and let stand for several hours. Filter, wash with cold water, and ignite to CeO_2 over the blast lamp.

A fairly good separation of cerium can be obtained by Mosander's method.[17]

For the separation of thorium and scandium, consult the chapters dealing with these elements. The following method shows promise for the separation of cerium from the rare earths: Oxidize a nitric acid solution of the rare earths as directed in footnote 17. Cool to about 50° C, and add 1 g of ammonium persulfate, and then a suspension of zinc oxide (p. 83) until no further solution of zinc oxide takes place. Boil, filter, and wash with a 2 per cent solution of ammonium nitrate. Test the filtrate with

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[17] C. G. Mosander, *Phil. Mag.*, 23, 241 (1843); P. E. Browning and E. J. Roberts, *Am. J. Sci.*, [4] 29, 45 (1910), who recommended substitution of bromine for chlorine; and S. J. Johnstone, *J. Soc. Chem. Ind.*, 33, 55 (1914). The method is as follows:

Dissolve the rare earth oxides in hydrochloric acid by the aid of a little hydrogen peroxide, boil to remove the latter, and treat the solution with sodium hydroxide in slight excess. Boil for a few minutes, let settle, decant the supernatant liquid, and wash the precipitate by decantation. Dissolve the precipitate in as little dilute hydrochloric acid as possible, dilute to about 200 ml, neutralize with potassium hydroxide, and add about 2 g in excess. Pass in chlorine until the solution no longer reacts alkaline. Boil for 5 minutes, dilute to 400 ml, and let stand for 12 hours. Filter, wash the ceric hydroxide with hot water, dissolve in hydrochloric acid, and repeat the whole operation 5 to 10 times. Entire freedom from the other earths can never be obtained.

hydrogen peroxide for complete precipitation of cerium. If a precipitate forms, filter, wash with the ammonium nitrate solution, and combine with the first precipitate. Reserve the filtrate for determinations of rare earths other than cerium. Transfer the precipitate to a 400-ml beaker, dissolve any residue on the paper in hot 2 *N* sulfuric acid, and wash the paper thoroughly with hot sulfuric acid (1 + 100). Dilute to 200 ml, and add enough dilute sulfuric acid (1 + 1) to dissolve the precipitate completely. Repeat the oxidation with persulfate and treatments as described, testing the filtrate with peroxide and finally adding it to the reserved filtrate. If cerium preponderates considerably, a third treatment may be needed. For the recovery of rare earths other than cerium, combine the reserved filtrates, and treat with ammonium hydroxide until the zinc hydroxide, which is at first formed, redissolves. Filter, and wash with dilute ammonium hydroxide (1 + 20) containing 2 per cent of ammonium nitrate. Dissolve the precipitate in hot dilute hydrochloric acid (1 + 5), wash the paper with hot water, and proceed with evaporation and precipitation with oxalic acid as described in footnote 13, page 554. To recover cerium, dissolve the final zinc oxide precipitate in hot dilute hydrochloric acid (1 + 5), and proceed with precipitations with ammonium hydroxide and oxalic acid as just described.[18]

Europium, and probably ytterbium, can be qualitatively separated from accompanying rare earth elements such as thulium and lutecium, by means of the amalgams which they form when solutions of their acetates in aqueous solutions of tertiary potassium citrate are shaken with potassium amalgam or electrolyzed with a mercury cathode. Special precautions must be taken in the presence of samarium, which also tends to form an amalgam.[19]

During World War II ion-exchange methods for the separation of rare earth elements were developed to aid in the determination of the rare earths which are formed as fission products during fission of the heavy elements. These methods have in many cases made possible much more rapid separations than the conventional crystallization procedures. In general, a solution of a mixture of rare earths is passed through a column of Amberlite-type resin. The rare earths are adsorbed on the resin and are then washed out or eluted by means of citric acid-ammonium citrate solutions at controlled *p*H. The citrate complexes of the individual rare earths are washed down the column at different rates so that, by taking judicious portions of the eluate, rather sharp separations can be made. Such separations

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[18] For a study of the use of aromatic bases as precipitants of the rare earths, consult A. M. Jefferson, *J. Am. Chem. Soc.*, 24, 540 (1902).

[19] H. N. McCoy, *ibid.*, 63, 3432 (1941). See also J. K. Marsh, *J. Chem. Soc.*, 8–10 (1943), and T. Moeller and H. E. Kremers, *Ind. Eng. Chem. Anal. Ed.*, 17, 798 (1945).

require means of detecting the point where all of one element is eluted. Radioactive isotopes and other means have been used for this purpose. Usually there is some overlapping in the eluate, that is, some of the second element appears before all of the first one is eluted. In this respect ion-exchange methods resemble separations by distillation, but, because of the ease with which a cycle can be repeated, these procedures offer a tremendous advantage over the older methods of separation by crystallization.

The scope of this book is too limited to include detailed descriptions and specific applications of ion-exchange methods in applied analysis. These methods should provide a powerful tool for certain difficult separations.[20]

IV. METHODS OF DETERMINATION

Methods for the quantitative separation and determination of all the rare earths are quite incomplete, as only a limited number of the elements of this group can be quantitatively separated by conventional methods in oxide mixtures of the group elements. Several methods have been suggested for the analysis of mixtures of the rare earths by means of spectrographic analysis. One that has received considerable attention is X-ray spectrographic analysis.[21] Certain of the rare earth elements show characteristic absorption lines and bands in the visible spectrum, which are generally used to detect one or another of the elements in a mixture.[22] Their use in determinations of the elements in mixtures of the rare earths has been suggested by various workers.[23] The use of emission spectra for approximate estimations of the rare earths has been suggested by several workers.[24]

Cerium, when mixed with other elements such as thorium, lanthanum, neodymium, praseodymium, yttrium, erbium, samarium, gadolinium, titanium, or zirconium, can also be determined volumetrically after oxidation

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[20] For references on this work, see a series of papers in *J. Am. Chem. Soc.*, **69**, 2769–2881 (1947).

[21] For a survey of the literature and the determination of La, Nd, and Gd in the presence of other rare earth elements, consult Kenjiro Kimura, *Bull. Chem. Soc. Japan*, **13**, 10 (1938).

[22] Consult J. Bahr and R. Bunsen, *Ann. Chem.*, **137**, 30 (1866); W. Muthmann and L. Stützel, *Ber.*, **32**, 2653 (1899); G. and H. Krüss, *Kolorimetrische und Quantitative Spectralanalyze,* Leopold Voss, Hamburg and Leipzig; and W. Prandtl and K. Scheiner, *Z. anorg. u. allgem. Chem.*, **220**, 107 (1934).

[23] For example, Haas [*Beitr. Kenntnis Pr. u. Nd. Dissert.*, **47**, 51, 54, Berlin (1920)] described a dilution method, whereby the solution is diluted until a certain characteristic absorption band vanishes. With the double ammonium nitrates, he found the concentrations at the vanishing point to be 0.0059 per cent with Nd_2O_3 and 0.0091 per cent with Pr_2O_3. See also L. F. Yntema, *J. Am. Chem. Soc.*, **45**, 907 (1923); E. Delauney, *Compt. rend.*, **185**, 354 (1927); and J. N. Friend and D. A. Hall, *Analyst*, **65**, 152 (1940).

[24] See, for example, C. N. McCarthy, L. R. Scribner, M. Lawrenz, and B. S. Hopkins, *Ind. Eng. Chem. Anal. Ed.*, **10**, 184 (1938).

to the quadrivalent stage by bismuth tetroxide,[25] sodium bismuthate,[26] or alkali persulfate.[27] A sensitive test for cerium is that based on the yellow to red-yellow color which cerous nitrate gives when a neutral solution is treated with 30 per cent hydrogen peroxide, followed by the addition of solid quinine hydrochloride.[28]

Europium, which readily forms a bivalent salt, can be determined in mixtures of the rare earths by passing a hydrochloric acid solution of the rare earth chlorides through a Jones reductor (p. 108), catching the solution of europous chloride under ferric sulfate, adding titration mixture (p. 396), and oxidizing the ferrous equivalent of the europous salt by a standard solution of permanganate.[29] No other rare earth element behaves in a similar fashion.[30]

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[25] A. Waegner and A. Müller, *Ber.*, **36**, 282 (1903). In this method, the cerium is oxidized by shaking with a goodly excess of bismuth tetroxide in a cold dilute nitric acid (1 + 1) solution, allowed to stand 30 minutes, and then diluted to a definite volume. After settling 1 to 2 hours, the solution is decanted through a dry filter, and an aliquot portion is treated with an equal volume of water and then with a standard solution of hydrogen peroxide in slight excess, which is finally determined by titration with permanganate.

[26] F. J. Metzger, *J. Am. Chem. Soc.*, **31**, 523 (1909); K. Someya, *Z. anorg. u. allgem. Chem.*, **168**, 56 (1927); N. H. Furman, *J. Am. Chem. Soc.*, **50**, 755 (1928). In this method, the elements are obtained as sulfates in a solution containing 20 per cent by volume of sulfuric acid and 2 per cent of ammonium sulfate, boiled with an excess of sodium bismuthate, and cooled. The solution is then diluted with 50 ml of dilute sulfuric acid (2 + 98) and filtered through asbestos and the residue washed with the dilute acid. The filtrate is treated with an excess of standard ferrous sulfate and titrated with permanganate.

[27] G. von Knorre, *Z. angew. Chem.*, **10**, 717 (1897); *Ber.*, **33**, 1924 (1900). Oxidation with persulfate is best done with the aid of silver nitrate [H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **50**, 1379 (1928)] as follows: Prepare a solution containing 0.1 to 0.3 g of Ce and 2.5 to 10 ml of sulfuric acid or 5 ml of nitric acid per 200 ml, and treat with 1 to 5 g (according to the acidity) of $(NH_4)_2S_2O_8$ and 2 to 5 ml of a solution of silver nitrate containing 2.5 g per liter. Boil for 10 minutes, cool to room temperature, and titrate, preferably potentiometrically with a standard solution of ferrous sulfate.

[28] J. Lucas and A. Jílek, *Z. anal. Chem.*, **76**, 350 (1929).

[29] H. N. McCoy, *J. Am. Chem. Soc.*, **58**, 1577 (1936); **61**, 2455 (1939).

[30] Trivalent europium is easily reduced to the bivalent state by magnesium, aluminum, and sodium amalgam as well as by zinc; trivalent ytterbium is not reduced appreciably by zinc but is reduced by sodium amalgam; and trivalent samarium resists reduction by wet methods [*ibid.*, **58**, 1577 (1936); **61**, 2455 (1939); and **63**, 3432 (1941)]. It has been asserted that samarium can be reduced to the bivalent state by calcium amalgam in a nonaqueous solvent [A. Brukl, *Z. angew. Chem.*, **52**, 151 (1939)], and that ytterbium can be determined by quantitative reduction at a mercury cathode in an acid electrolyte, followed by treatment with ferric ammonium sulfate [*ibid.*, **50**, 25 (1937)].

Crystalline europous sulfate is not appreciably changed by months of exposure to the air; ytterbous sulfate is oxidized in air and also in water in a few hours; whereas samarous sulfate is completely oxidized by water, with liberation of hydrogen in a few minutes [McCoy, *loc. cit.*].

Methods for spectrophotometric determinations of praseodymium, neodymium, and samarium of the cerium group, and of dysprosium, holmium, erbium, thulium, and ytterbium of the yttrium group, based on measurements of transmittancies of solutions of their nitrates, have been developed by C. J. Rodden.[31] In these methods, the rare earth elements are first separated from other elements, and the cerium and yttrium groups then separated by means of sodium sulfate. The cerium group elements are determined in the insoluble portion, and the yttrium group elements in the soluble portion after conversion of the mixed oxides to nitrates. Transmittancies are measured at 446 mμ for praseodymium, 521 and 798 for neodymium, 402 for samarium, 910 for dysprosium, 643 for holmium, 521 and 653 for erbium, 684 for thulium, and 950 and 973 for ytterbium. Of the elements that show negligible absorption bands, cerium and europium can be determined by other methods, whereas lanthanum, gadolinium, terbium and yttrium are determined by difference.

The separative extraction, into chloroform, of neodymium and erbium as 5,7-dichloro-8-quinolinol chelates and their subsequent spectrophotometric estimation in the chloroform solutions are described by T. Moeller and D. E. Jackson.[32]

More or less complete separations of all the elements of the group have of course been made, but only by working with large amounts of material and usually through hundreds and even thousands of fractionations. Nevertheless the analyst can take one other step and separate the mixed elements approximately into two major groups by saturating their solutions with potassium or sodium sulfate, whereby the elements of the so-called cerite subgroup[33] and scandium and thorium (also zirconium, if present) are precipitated as double sulfates. Thorium is more completely precipitated by potassium sulfate than by sodium sulfate, and scandium is not precipitated by the sodium salt; hence, if thorium is present, the potassium salt is commonly chosen as the precipitant in order to obtain all the thorium in the insoluble precipitate. If both thorium and scandium have been precipitated by potassium sulfate, they can then be separated from each other by

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[31] *J. Research NBS*, **26**, 557 (1941); **28**, 265 (1942).

[32] *Anal. Chem.*, **22**, 1393 (1950). For the spectrophotometric determination of praseodymium, neodymium, and samarium, see also A. W. Wylie, *J. Soc. Chem. Ind.*, **69**, 143 (1950).

[33] The rare earths are usually divided into three subgroups, namely: (1) the cerium group composed of lanthanum, cerium, praseodymium, neodymium, promethium and samarium; (2) the terbium group composed of europium, gadolinium, and terbium; and (3) the yttrium group composed of yttrium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium. Dysprosium, holmium, erbium, and thulium are sometimes called the erbium group.

sodium sulfate, in which scandium is soluble. The precipitation is carried out as follows:

If the rare earths are present as nitrates or chlorides, dissolve the salts in as little water as possible, add 200 to 300 ml of a saturated solution of potassium sulfate, and then 5 g of the powdered salt. Stir thoroughly, set aside for 12 hours, filter, and wash the double sulfates with a saturated solution of potassium sulfate. Digest the sulfates in a hot 5 per cent solution of sodium hydroxide, filter, and wash the hydroxides with hot water. Dissolve in dilute hydrochloric acid, evaporate the solution to dryness, and repeat the operation. If the rare earths are present as sulfates, heat at about 450° C until fumes of sulfuric acid are no longer given off, break up the mass, and dissolve in as little ice-cold water as possible. Dilute with an equal volume of water, stir in powdered sodium sulfate until the solution is saturated, and set aside for 12 hours. Filter, and wash the double sulfates with a saturated solution of sodium sulfate. Digest the sulfates with sodium hydroxide, dissolve the hydroxides in hydrochloric acid, evaporate to dryness, and reprecipitate with either potassium or sodium sulfate. The sulfates must then again be converted to chlorides if the rare earths are to be precipitated as oxalates and weighed as oxides, for oxalates precipitated in the presence of high concentrations of sodium salts are always contaminated by sodium.

Although it is possible in this way to obtain a number of the elements at each end of the series free from those at the other end—that is to say the so-called cerite subgroup free from the yttrium subgroup proper—the solubilities of the potassium double sulfates of the whole rare earth series increase so uniformly from the most insoluble lanthanum that a sharp division is impossible. The intermediate members will be found in both mixtures of the double sulfates. By varying the conditions of fractionation other subgroups can be obtained, but the results are by no means quantitative. Variations in temperature during fractionation produce different results; therefore room temperatures are employed when the analyst endeavors to obtain the two major subgroups. Fractionation of the ethyl sulfates is said to effect a better separation of the two major subgroups,[34] but the method has not been much used in analysis.

The object in quantitative analysis of these partial separations into two or more subgroups is to obtain light upon the general nature of the components of each group and upon the relative abundance of the two in a

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[34] G. Urbain, *Ann. chim. phys.* [7], **19**, 184 (1900). J. Kleinberg, W. A. Taebel, and L. F. Audrieth [*Ind. Eng. Chem. Anal. Ed.*, **11**, 368 (1939)] state that sulfamic acid can be used to separate cerium-free rare earth oxide mixtures into insoluble lanthanum (La, Pr, Nd, and Sm) and soluble yttrium (Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu) subgroups.

mineral. In cerite and monazite, for instance, the cerite group predominates; in gadolinite, the yttrium group.[35] The color of the oxalates and of the ignited oxides may be indicative, as is also a determination of the approximate average atomic weight made upon the mixed oxides. This last is a simple operation compared with a true atomic weight determination and involves, by one of the methods, only a comparison of the weight of mixed oxides with that of their anhydrous sulfates.[36]

In determinations of the average atomic weight of the rare earths in a mixture by the oxalate to oxide, oxalate to permanganate method, the permanganate solution should be standardized against a pure sample of the oxalate of that rare earth which is the principal component of the mixture.[37] Although atomic weight determinations are of most use in controlling large-scale separations, they may yield, in a general analysis, information of value regarding the probable relative proportions of certain elements or of subgroups, particularly among the members of the yttrium series which offer few distinctive physical differences or chemical reactions.

As to the color of the mixed oxides,[38] that of the cerite subgroup is characteristically different from that of the yttrium earths. Very small amounts

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[35] An illustration of the usefulness of such tests and at the same time of their probable reproducibility is afforded in a footnote on page 150 of an article by the senior author [*Am. J. Sci.*, [4] 13 (1902)], which is here reproduced. The three minerals gadolinite, yttrialite, and rowlandite occur in Llano County (Texas) in most intimate association, suggestive of close community of origin, a suggestion which is emphasized by the marvelous agreement for gadolinite and yttrialite, not only in the relative proportions of the trivalent earth metals but in their absolute amounts as well.

	Ce_2O_3	La_2O_3, Etc.	Y_2O_3, Etc.
Gadolinite (Genth)	2.65	5.22	44.35
Gadolinite (Genth)	2.66	5.01	44.45
Gadolinite (Eakin)	2.62	5.22	41.55
Yttrialite (Hillebrand)	3.07	5.18	43.45
Rowlandite (Hillebrand)	5.06	9.34	47.70

This concordant testimony of three analysts may be regarded as strong evidence of the correctness of the earth separations made by them in these cases. Nearly the same relation (as for gadolinite and yttrialite) is shown by the trivalent earth metals of rowlandite as seen in the table.

[36] Consult R. J. Meyer and O. Hauser, *Die Analyse der Seltenen Erden und Erdsäuren*, pp. 216–19 (1912).

[37] G. L. Barthauer, R. G. Russel, and D. W. Pearce, *Ind. Eng. Chem. Anal. Ed.*, **15**, 548 (1943).

[38] The trivalent oxides of lanthanum, cerium, gadolinium, terbium, yttrium, dysprosium, ytterbium, and lutecium are white. Of the others, thulium is white with a greenish tinge, samarium is yellowish white, holmium pale yellow, praseodymium greenish yellow, europium pale pink, erbium rose, and neodymium lilac. Tb_4O_7 (obtained by igniting the oxalate) is dark brown, Pr_6O_{11} (obtained by heating in air) is brownish black, and CeO_2 (obtained by ignition in air) is yellow when hot and white when cold.

of praseodymium oxide in solid solution with CeO_2 suffice to color a cerite-earth mixture cinnamon brown. The lighter the color of a mixture of the earths of both subgroups, the greater is the proportion of yttrium earths. Mixtures of the yttrium earths free from cerite earths and poor in the erbium subgroup are colorless to pale yellow, but, with increasing concentration of the erbia earths, the color becomes deeper yellow, even reddish.[39]

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[39] Consult Meyer and Hauser, *Die Analyse der Seltenen Erden und Erdsäuren*, pp. 27 and 191 (1912).

Chapter 37

ZIRCONIUM (HAFNIUM)

Zirconium is shown by the microscope to be one of the most constant rock constituents, usually in the form of zircon, in which occurrence its amount can be approximately judged under the microscope and a chemical test rendered almost unnecessary, but it occurs also in other mineral components of some rocks and is then unrecognizable under the microscope. It may be present up to a few per cent, rarely reaches 0.2 per cent, and is usually much less than 0.1 per cent. The use of zirconium for refractories, enamels, metallurgical products, and other purposes makes methods for its determination in ores of special interest. The ore minerals are zircon ($ZrSiO_4$) and baddeleyite (ZrO_2), but the element is a more or less important constituent of many minerals. D. Coster and G. Hevesy[1] found hafnium in all of the zirconium minerals that they tested; in some, the amount was estimated to be as high as 1 per cent. It is estimated that its percentage in the earth's crust is 4×10^{-4}.

No entirely satisfactory methods of quantitatively separating hafnium from zirconium are known, but ion-exchange methods have been proposed for this separation. Proper choice of cation-exchange resins and eluant should prove advantageous in analytical work, but such separations have not been worked out in sufficient detail to be included here. Oxalate and fluoride complexes of zirconium and hafnium were chromatographically separated on an anion exchanger of the strong base type by K. A. Kraus and G. E. Moore.[2] For other separations, see Purification of Zirconium by Ion Exchange Columns by John A. Ayres,[3] and Ion Exchange Separation of Zirconium and Hafnium by G. T. Seaborg.[4] Differences in the vapor pressures of zirconium tetrachloride and hafnium tetrachloride as well as of the phosphoryl chlorides have been suggested as means of separation.

In the discussion that follows the statements that are made concerning zirconium apply to hafnium as well.

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[1] *Nature,* **111,** 182 (1923); *Naturwissenschaften,* **11,** 133 (1923); *Chemistry & Industry,* **42,** 258 (1923).

[2] *J. Am. Chem. Soc.,* **71,** 3263 (1949).

[3] *Ibid.,* **69,** 2879 (1947).

[4] *Ibid.,* **70,** 4268 (1948).

I. GENERAL CONSIDERATIONS

In silicate analyses, zirconium, like titanium, will come down with silicon in part, owing to hydrolysis of its salts, and in larger part when the phosphate radicle is present, because of the insolubility of zirconium phosphate. Upon volatilizing the silica, its zirconium content can be recovered and combined with that which is still in solution. If no provision is made for zirconium, it will fall with the ammonia precipitate and be reported as aluminum. If the precipitate consists only of zirconium hydroxide, it can be ignited and weighed as ZrO_2 after correction for a possible slight content of SiO_2 (p. 573); if it is composite, the zirconium in it can be separated, or, perhaps preferably determined in a separate portion of the sample in which barium and the rare earth metals can also be determined (p. 888).[5]

II. DECOMPOSITION OF ZIRCONIUM MINERALS

The small amounts of zirconium usually found in rocks are easily gotten into solution by the procedure employed for silicate rocks. It is not so easy to break up ores of zirconium like zircon or baddeleyite; nevertheless that procedure must be used for the complete analysis of phosphatic or fluoriferous minerals. Fusion with sodium carbonate in these cases is usually tedious and often incomplete, even though the material has been ground to a very fine powder, and usually must be repeated on the residue left after leaching the melt with water. Potassium pyrosulfate gives good fusions of baddeleyite but works slowly with zircon.[6]

The corresponding sodium salt was recommended by J. Lawrence Smith[7] as being far preferable for the decomposition of emery and might prove more satisfactory for fusions of zirconium ore. Sodium peroxide has been recommended by M. Travers[8] and also by Holladay[9] who protects the

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[5] A nearly specific spot test for minute amounts of zirconium, in which it is said that only tantalum gives an analogous test, is its reaction with paradimethylaminoazophenylarsenic acid in hydrochloric acid solution (slightly modified in the presence of certain compounds) to yield a brown-colored compound [F. Feigl, P. Krumholz, and E. Rajmann, *Microchem.,* **9,** 395 (1931); *Analyst,* **56,** 615 (1931)].

[6] With some materials it is desirable to fuse with sodium carbonate, thoroughly extract the melt with water, filter, and wash the residue, and then to fuse the residue with pyrosulfate and dissolve the melt in dilute sulfuric acid. The first fusion and extraction leaves an insoluble zirconium compound which is decomposed and easily dissolved after the second fusion. This compound is often called sodium zirconate. It is apparently zirconium oxide, for in tests by H. B. Knowles 0.1143 g of ZrO_2 gave 0.1148 g of residue after thorough fusion with sodium carbonate, extraction with water, and ignition of the well-washed residue.

[7] *Compt. rend.,* 31, 48–50, 191–93 (1850); *Sill. Am. J. Sci.,* **10,** 354–69 (1850).

[8] *Chimie & industrie,* **2,** 385–392 (1919).

[9] J. A. Holladay, Electro Metallurgical Co. (private communication).

platinum crucible by first fusing a layer of carbonate on the bottom and sides and then coating with a layer of fused peroxide before introducing the ore mixed with peroxide. M. Axt[10] states that zircon sand can be disintegrated by fusion with sodium hydroxide at 600° C.

Potassium-hydrogen fluoride or a mixture of 1 part of it with 10 parts of pyrosulfate followed by treatment with 1 to 2 ml of sulfuric acid and careful heating to 900 to 1000° C have been mentioned favorably. Both require subsequent removal of all fluorine; no zirconium is lost as fluoride if the fusion is made at as low a temperature as will keep the contents molten,[11] which is at first thought surprising in view of its volatility when evaporated with hydrofluoric acid alone. The difference is perhaps due to formation of a less volatile double fluoride when the alkali-fluoride flux is used. Of course neither of these fluxes is permissible for silica or alkali determinations. For the last, fusion with ammonium fluoride at the lowest possible temperature will serve if it decomposes the mineral completely. Borax was used with success for zircon and baddeleyite at the National Bureau of Standards.[12] It will of course not serve for an alkali determination, but boric oxide (Fluxes, p. 848) will, if it decomposes the mineral at a temperature low enough to avoid loss of alkali by volatilization.

The procedure with borax is as follows:

Fuse 4 g of borax in a platinum crucible, cool, and place on top of the fused mass a 0.3-g sample of ore which has been ground to pass a sieve of approximately 100 meshes to the linear inch or 40 to the centimeter. Cover the crucible, and fuse thoroughly over a Meker burner, stirring the melt occasionally with a short, stiff platinum rod or wire kept in the crucible. When the decomposition of the ore is complete and the melt is clear, which does not usually require more than half an hour, remove the cover and rod, and put them in the beaker that is to be used for the solution of the melt. As the melt cools, run it up on the sides of the crucible. Dissolve the cooled melt in 150 ml of dilute hydrochloric acid (1 + 5) by filling the crucible with acid and inverting it in such a manner that one edge of the crucible rests on the crucible cover, thus allowing free circulation of the solvent. Allow to digest on the steam bath until solution is complete. This operation proceeds slowly and is best done by letting the solution stand overnight. Boric acid in no way interferes with the subsequent determination of zirconium by the phosphate or cupferron methods. If, however, precipitation is to be made with ammonium hydroxide, boric acid must be removed by the customary evaporation with methyl alcohol and hydrochloric acid

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[10] *Ing. chim.*, 23, 142 (1939).

[11] For example, H. B. Knowles obtained 0.2309 and 0.2313 g of ZrO_2 after thorough fusion with KHF_2, as against 0.2312 and 0.2311 g originally present.

[12] G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, 42, 1439 (1920).

(p. 672), for it is partially precipitated in spite of as many as three precipitations.

Because of the insolubility of zirconium phosphate, it should always be borne in mind that zirconium and phosphorus are apt to cause trouble in analyses where they occur together. In general, compounds containing zirconium and phosphorus had better be fused with sodium carbonate, extracted with water, and the water extract and insoluble matter handled separately. It should also be remembered that zirconium hydrolyzes quite readily and may separate from solution if too little acid is present.

III. METHODS OF SEPARATION

The most effective method for the separation of zirconium from other elements lies in its precipitation as the secondary phosphate in a solution containing about 10 per cent by volume of sulfuric or hydrochloric acid and also hydrogen peroxide if titanium, columbium, or tantalum is present. It is probable that very few elements, save hafnium, protactinium, columbium, and tantalum, interfere if they can be gotten into sulfuric acid solution. The two latter do not precipitate except on long standing when alone in sulfuric acid-hydrogen peroxide-phosphoric acid solution at room temperatures but are partially precipitated in the presence of zirconium. The method of precipitation and subsequent treatment for zirconium is given in IV, A, below. Other elements such as iron, titanium, thorium,[13] and the rare earths can then be separated from the excess of phosphoric acid by precipitation with sodium hydroxide and determined by usual procedures.

Precipitation with phenylarsonic acid, $C_6H_5AsO(OH)_2$, in boiling dilute sulfuric acid (1 + 9) solution serves for the separation of zirconium (and hafnium) from most other elements. As in the phosphate method, hydrogen peroxide is added if titanium or columbium is present, and double precipitations are needed if thorium or phosphorus is present.[14] Tantalum interferes in any case.

Precipitation with *n*-propylarsonic acid in hot dilute hydrochloric acid (3 + 100), followed by digestion for 30 to 60 minutes, filtration, and washing with hot water serves for the separation of zirconium from titanium,

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[13] For complete separation from thorium, the zirconium must be reprecipitated from dilute H_2SO_4 (1 + 10). To do this, the paper containing the first precipitate can be destroyed and the precipitate dissolved by treatment with HNO_3 and H_2SO_4 (p. 388), the solution evaporated to fumes, and the zirconium again precipitated by adding the necessary $(NH_4)_2HPO_4$, diluting with water, and digesting at 40 to 50° C. By such treatment, H. B. Knowles obtained 0.1021 and 0.1022 g of ZrP_2O_7 as against the true value 0.1024 in solutions to which 0.0232 g of ThO_2 as $Th(SO_4)_2$ had been added. Single precipitations in the presence of the same amounts of zirconium and thorium gave 0.1057 and 0.1058.

[14] A. C. Rice, H. C. Fogg, and C. James, *J. Am. Chem. Soc.*, 48, 895 (1926).

aluminum, chromium, cobalt, nickel, copper, uranium, vanadium, thorium, molybdenum, and such small amounts of silicon and tungsten as may survive a preliminary dehydration in acid solution.[15] If large amounts of iron are present, as in steel, the paper and precipitate must be disintegrated by warming gently with 10 ml of concentrated hydrochloric acid, the solution diluted with 100 ml of water and the zirconium reprecipitated as before. The precipitate can be ignited, in porcelain, to the oxide ZrO_2. Tin is partially precipitated, but can be removed by treatment of the ignited oxide with ammonium iodide as described on page 294. If sufficient phosphorus is present to cause precipitation of zirconium phosphate in the original solution, the solution must be filtered, and the zirconium separated from the phosphate ion by fusing with sodium carbonate, extracting the melt with water, filtering, igniting the residue, fusing with pyrosulfate, and dissolving the melt in water containing a few drops of sulfuric acid.

According to Schoeller,[16] the most satisfactory separation of zirconium from titanium, columbium, and tantalum is obtained by fusing the mixed oxides with potassium bisulfate, dissolving the melt in a saturated solution of ammonium oxalate, rendering feebly acid, half saturating with ammonium chloride, heating to boiling, precipitating with tannin, filtering, washing with a solution containing 5 per cent of ammonium chloride and 1 per cent of ammonium oxalate, drying, and igniting in a silica crucible. In these operations, tantalum, columbium, and titanium are precipitated, while beryllium, aluminum, iron, thorium, and uranium accompany zirconium in the filtrate. If but little zirconium is present, it is desirable to first remove most of the earth acids by fusing with potassium carbonate, dissolving the melt in water containing a little potassium hydroxide, filtering, washing with a 2 per cent solution of potassium carbonate, digesting the paper and precipitate with dilute hydrochloric acid, precipitating with ammonium hydroxide, and refiltering. Success in the separation depends on careful attention to details for which the reference must be consulted. Protactinium does not dissolve in water after fusion with potassium carbonate when by itself.[17] Its behavior when associated with the other elements is not known.

Zirconium can be quantitatively separated from aluminum, iron, chromium, neodymium, yttrium, uranium, beryllium, manganese, and nickel by precipitating with tannin in a hydrochloric acid solution of the chlorides. The most of the zirconium is precipitated in 0.25 *N* (0.5 *N* if thorium or vanadium is present) hydrochloric acid solution containing ammonium chloride. The small unprecipitated portion remaining in solution is recovered by reducing the acidity of the filtrate to 0.1 *N* and again filtering. Titanium and tin are precipitated with the zirconium.[18]

The separation of zirconium from phosphorus is done by fusion of the original material with sodium carbonate or sodium peroxide and extraction with water as described in IV, A (p. 571), or by like treatment of the ignited precipitate obtained with ammonium hydroxide.

In the main, zirconium behaves like titanium (p. 578), aluminum (p. 496), and the like when treated with reagents such as hydrogen sulfide, ammonium hydroxide, ammonium sulfide-tartrate, or phenylhydrazine, or when separations based on extraction with ether (p. 134) or electrolysis with a mercury cathode (p. 138) are applied.

Interesting separations are those based (1) on the use of cupferron as in IV, B (p. 572), whereby zirconium can be quickly and quantitatively separated in strong acid solution from elements such as aluminum, chromium, or sexivalent uranium, and (2) on the use of hydrofluoric or oxalic acid (p. 551), whereby the rare earths are separated from zirconium.

The fractional precipitation of hafnium and zirconium by means of triethylphosphate is described by H. H. Willard and H. Freund,[19] but in our hands it has been difficult to obtain an entirely clean-cut separation.

IV. METHODS OF DETERMINATION

A. PRECIPITATION AS PHOSPHATE

The precipitation of zirconium as the secondary phosphate is quantitative in solutions containing as much as 10 per cent by volume of sulfuric acid, provided an excess of phosphate precipitant is used and the solution is allowed to stand at 40 to 50° C for a few hours. This reaction affords a nearly ideal method of analysis, but unfortunately the precipitate tends to hydrolyze and lose P_2O_5 during washing. If the washing is prolonged, the ignited precipitate contains less P_2O_5 than is required by the pyrophosphate, ZrP_2O_7. With small amounts of zirconium, such as 2 or 3 mg, the error is of no consequence, but, with larger amounts, it may reach 1 to 2 per cent of the total ZrO_2 content.[20] In such cases the ignited residue has to

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[15] H. H. Geist and G. C. Chandlee, *Ind. Eng. Chem. Anal. Ed.*, **9**, 169 (1937).

[16] W. R. Schoeller and A. R. Powell, *Analyst*, **55**, 605 (1930); **57**, 550 (1932); and W. R. Schoeller and H. W. Webb, *ibid.*, **58**, 143 (1933).

[17] A. V. Grosse, *J. Am. Chem. Soc.*, **52**, 1742 (1930).

[18] W. R. Schoeller, *Analyst*, **69**, 259 (1944).

[19] *Ind. Eng. Chem. Anal. Ed.*, **18**, 195 (1946).

[20] The following results are typical:

ZrO_2 as Calculated from ZrP_2O_7 Obtained, g	ZrO_2 Taken for Analysis, g
0.00065	0.00064
0.00106	0.00107
0.00185	0.00193
0.0212	0.0216
0.0426	0.0431

be decomposed by fusion with sodium carbonate, phosphorus removed by extraction with water, and zirconium precipitated twice by ammonium hydroxide after fusion of the insoluble residue with potassium pyrosulfate and solution of the melt in dilute sulfuric acid (5 + 95). Pape[21] recommends that the washed phosphate be boiled twice with a 5 per cent solution of sodium hydroxide to separate zirconium from phosphorus. This procedure is attractive, but we do not recommend it for accurate analyses because it does not work well with a zirconium phosphate that has been allowed to stand for sometime; in addition, there is a slight solubility of zirconium in the alkaline liquid, and the final solution of the zirconium residue is sometimes difficult.[22]

If titanium is present, an excess of hydrogen peroxide must be added before the addition of the phosphate precipitant and be maintained during the precipitation.[23] The complete separation from thorium requires two precipitations. Columbium and tantalum are precipitated in part and had therefore better be separated first (p. 568). A better separation of zirconium from cerium results if the latter is kept in the trivalent condition. Hafnium is precipitated completely, as is also protactinium.[17, 24]

PROCEDURE.[25] Prepare a sulfuric acid solution of zirconium sulfate, and dilute in accordance with its amount, for example 25 ml for 0.5 mg and 200 ml for 0.1 g. Add a drop or two of hydrogen peroxide. If titanium is indicated, add an excess of pure hydrogen peroxide and make sure that an excess is maintained throughout the precipitation. Adjust the acidity so that the solution contains a little more than 10 per cent by volume of sulfuric acid, and then add a freshly prepared 10 per cent solution of $(NH_4)_2HPO_4$ in 10- to 100-fold excess of that required by the ratio Zr:2P, the larger excess being desirable when but little zirconium is present. Adjust the acidity to 10 per cent by volume of sulfuric acid, and digest at 40 to 50° C.[26] If appreciable zirconium is indicated at the end of 2 hours,

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[21] H. Pape, Inaugural Dissertation, p. 37, Friedrich-Wilhelms-Universität, Berlin (1917).

[22] We have never been able to verify Pape's statement that it is impossible to free zirconium from sodium salts by precipitation with ammonium hydroxide, after it has once been precipitated by sodium hydroxide.

[23] If hydrogen peroxide is not used, the precipitation of titanium may be nearly complete. For example only 0.0066 g of TiO_2 was found in the filtrate after 0.1248 g of TiO_2, as $Ti(SO_4)_2$, in 200 ml of dilute H_2SO_4 (5 + 95), had been treated with 100 times enough H_3PO_4 to form the phosphate, allowed to stand at 30 to 40° C overnight, and filtered.

[24] A. V. Grosse, *Ind. Eng. Chem.*, 27, 422 (1935); *Ber.*, 61, 233 (1928).

[25] G. E. F. Lundell and H. B. Knowles, *op. cit.*, 41, 1801 (1919).

[26] According to G. Hevesy and K. Kimura [*J. Am. Chem. Soc.*, 47, 2540 (1925)], the solubility of zirconium phosphate in 6 *N* HCl at 20° C amounts to 0.00012 molecular equivalent, and that of hafnium phosphate to 0.00009. In 10 *N* HCl the values are 0.00023 and 0.00012. The above values are for the phosphates alone and are no doubt

add macerated paper, let settle, and filter. If very little is shown, let cool, and stand overnight. For very minute amounts, the solution should be covered and allowed to stand for 2 or 3 days. Filter through paper if the precipitate is subsequently to be examined; otherwise a Gooch crucible can be used, provided it has been given before weighing the same treatment that is called for in the method. Wash the precipitate with a cold 5 per cent solution of ammonium nitrate until the excess of phosphate is removed. Approximately 300 ml of ammonium nitrate solution is required for moderate-sized precipitates, and the necessary amount is a matter of judgment, for, owing to hydrolysis of the precipitate, the washings are never free from phosphorus. To avoid decrepitation during ignition of the precipitate, dry the wet paper and precipitate in the crucible, gently heat until the paper is charred, partly cover, and ignite *very carefully* until carbon is gone. Finally heat over the blast lamp or its equivalent, and weigh as ZrP_2O_7.[27]

When much zirconium is present or the highest accuracy is desired, proceed as follows instead of weighing the precipitate: Thoroughly fuse the ignited residue with sodium carbonate, extract the melt with water, filter, wash with a 1 per cent solution of sodium carbonate and then with water, and ignite the residue. Fuse with pyrosulfate, dissolve the melt in dilute sulfuric acid, boil, and precipitate with ammonium hydroxide. Filter, wash the precipitate with a hot 2 per cent solution of ammonium nitrate, ignite, and weigh as ZrO_2. It is difficult to remove all phosphate by one carbonate fusion and extraction and to eliminate all alkali salt by one precipitation with ammonium hydroxide; hence each of the above operations is better repeated.[28]

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less in the presence of phosphoric acid. The authors believe that the phosphates have the composition $ZrO(H_2PO_4)_2$ and $HfO(H_2PO_4)_2$ and that the ignited phosphates have the formula $ZrO(PO_3)_2$ and $HfO(PO_3)_2$.

[27] In tests of the method, A. Claassen and J. Visser [*Rec. trav. chim.*, 61, 103 (1942); *Chem. Zentr.*, 1942, I, 2304] found (1) that tartaric acid is without effect; (2) that perfect separations are obtained from Al, Cu, Cd, Bi, Ni, Co, Mn, Mg, alkalies, alkaline earths, W, V, Mo and U; (3) that large amounts of Fe are a disturbing factor and Sn always causes trouble; and (4) that, when Ti is present in solutions containing H_2O_2, satisfactory values are obtained only when the amount of zirconium is small.

[28] W. C. Schumb and E. J. Nolan [*Ind. Eng. Chem. Anal. Ed.*, 9, 371 (1937)] point out that zirconium (also hafnium) can be precipitated by ammonium arsenate in boiling 2.5 *N* hydrochloric or 3.75 *N* nitric acid solution, but not in the presence of sulfuric acid, or of hydrogen peroxide in nitric acid solution. The precipitate can be ignited to the oxide, provided sufficient carbon (preferably added as sugar charcoal) is present at the start. Elements that interfere in hydrochloric acid solutions containing hydrogen peroxide, and that require special treatments, are quadrivalent cerium, thorium, tungsten, tantalum, and columbium. See also L. Moser and R. Lessing, *Monatsh.*, 45, 323 (1924); V. Coppieters, *Ing. chim.*, 22, 179, 233 (1938), and M. Axt, *ibid.*, 23, 142 (1939).

B. CUPFERRON METHOD

The precipitation of zirconium by cupferron (the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5 \cdot N \cdot NO \cdot ONH_4$),[29] followed by ignition to the oxide, is an accurate process and possesses the advantage of yielding a weighable compound of definite composition and a complete separation of zirconium from aluminum, chromium, sexivalent uranium, boric acid, and, when present in small amount, phosphorus. On the other hand, many elements interfere, as for example titanium, thorium, cerium (and probably other rare earths), most of the hydrogen sulfide group, iron, vanadium, columbium, tantalum, tungsten, silica, and quadrivalent uranium.

Precipitation by cupferron is carried out in a sulfuric acid solution after separations of silicon, tungsten, and the hydrogen sulfide group. Other preliminary separations are a matter of convenience. For example, if iron is not separated by ammonium sulfide in ammoniacal tartrate solution, it is precipitated with the zirconium and must afterwards be determined and deducted.[30] Similarly, correction must be made for vanadium if it is not separated by treatment with fixed alkali and filtration as in a sodium hydroxide precipitation or water extractions of sodium peroxide or carbonate fusions. The rare earths can be separated by hydrofluoric or oxalic acid treatment, but usually these, like titanium, are precipitated together with zirconium and afterwards determined and deducted. The cupferron precipitate, $Zr(C_6H_5 \cdot N \cdot NO \cdot O)_4$, cannot be dried and weighed as such but must be ignited to the oxide. This ignition must be done *very carefully* in the early stages, owing to excessive liquefaction when wet precipitates are heated, and to the copious liberation of gaseous products when the dried precipitates are ignited. The oxide is not hygroscopic.

PROCEDURE. Prepare a sulfuric acid solution of zirconium sulfate, dilute to 400 ml, and add sufficient sulfuric acid to bring the acidity to 10 per cent by volume.[31] Cool the solution to 5 to 10° C, and precipitate with an excess of a cold aqueous 6 per cent solution of cupferron. An excess of the precipitant is indicated by the formation of a fine white precipitate which redissolves, instead of a curdy one which persists. The color of the precipitate furnishes an excellent indication of the amount of titanium present; a zirconium precipitate is pure white; the titanium precipitate is yellow. A brownish tint indicates iron or vanadium.

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[29] O. Baudisch, *Chem. Ztg.*, 33, 1298 (1909). W. M. Thornton and E. M. Hayden, *Am. J. Sci.*, [4] 38, 137 (1914). G. E. F. Lundell and H. B. Knowles, *J. Ind. Eng. Chem.*, 12, 344 (1920).

[30] According to S. L. Tzinberg [*Zavodskaya Lab.*, 4, 735 (1935)], zirconium can be separated from trivalent iron by precipitating the latter with 8-hydroxyquinoline in an unbuffered acetic acid-tartaric acid solution. Zirconium can then be completely precipitated in the presence of the excess of 8-hydroxyquinoline by strongly acidifying the filtrate and adding cupferron.

[31] Precipitation of zirconium is quantitative in solutions containing 1 per cent of tartaric acid and as much as 40 per cent (by volume) of H_2SO_4.

After 5 minutes, add macerated paper, and filter, using a paper filter and a platinum cone and applying gentle suction. Thoroughly wash the precipitate with cold dilute hydrochloric acid (1 + 10). Cloudy or opalescent filtrates or washings, which indicate incomplete precipitation, occasionally develop, and no explanation for their occurrence has been found, other than that they usually occur when the reagent is old or of uncertain manufacture. If refiltration through a paper of close texture does not yield a clear filtrate, evaporate the solution to a small volume, destroy organic matter by means of nitric acid, evaporate off all nitric acid, cool, dilute, filter if necessary, and again precipitate with cupferron.

Carefully dry and ignite the paper and precipitate in a weighed platinum crucible, and finally ignite at approximately 1200° C. Cool in a desiccator, and weigh as ZrO_2.

A correction for silica is not ordinarily necessary. In exact analyses and in cases where a recovery has been obtained from the first cupferron filtrate, this correction should be made, making sure that sufficient sulfuric acid is added to prevent volatilization of zirconium and titanium fluorides and that no mechanical loss takes place during the expulsion of the sulfuric acid.[32]

C. PRECIPITATION AS BASIC SELENITE

The precipitation of zirconium as a basic selenite, followed by ignition to ZrO_2, was proposed by M. M. Smith and C. James[33] as a substitute for the cupferron method. The method has not been so well tested as the cupferron method but is attractive in that iron and titanium need not be removed. Briefly stated, the method consists in precipitating with selenious acid in hot dilute hydrochloric acid solution, filtering, washing the precipitate with hot dilute hydrochloric acid, and igniting to ZrO_2. No other acids should be present, and the concentration of hydrochloric acid should preferably be 5 per cent and not over 7 per cent by volume.[34] By this

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[32] See under Earth Acids (p. 602).

[33] *J. Am. Chem. Soc.*, 42, 1764 (1920).

[34] The performance of the method, compared with precipitation by ammonium hydroxide or by cupferron, is shown by the following results obtained for aliquot portions of a solution of zirconyl chloride:

By NH_4OH, g	By Cupferron, g	By Selenious Acid, g
0.2107	0.2102	0.2106
0.2111	0.2106	0.2108
		0.2109
		0.2109

method zirconium can be separated from aluminum, certain of the rare earths, moderate amounts of iron, and also titanium, if hydrogen peroxide is used. Thorium and phosphorus are known contaminants, and undoubtedly others, such as columbium and tantalum, will be noted when the method is given more extended trial.

PROCEDURE. As applied to zircon the method is as follows: Mix 1 g of zirconium ore with 12 to 15 g of potassium hydrogen fluoride [35] in a platinum dish, and carefully heat over a very small flame. When the mixture has fused, stir with a platinum rod, gradually increase the flame until the whole is solid and white, and then heat over a powerful burner at as low a temperature as will give a clear liquid. Cool, add 50 ml of dilute sulfuric acid (1 + 1), and gently heat until water is removed, and then until copious fumes of sulfuric acid are evolved. Cool, add water, heat until the melt has dissolved,[36] cool, dilute to exactly 250 ml, and mix. Dilute exactly 100 ml of the solution to 250 ml, heat to boiling, precipitate with ammonium hydroxide, filter, and wash. Transfer the precipitate and paper to the original beaker, and treat with 36 ml of hydrochloric acid and then with 40 ml of water. Boil until the precipitate has dissolved, dilute to 700 ml, heat to boiling, add 30 to 50 ml of a 12.5 per cent solution of selenious acid,[37] and boil for a few minutes. Let settle, filter, and wash the precipitate with hot dilute hydrochloric acid (3 + 97) containing a little selenious acid. Dry the paper and precipitate in a platinum or porcelain crucible, and ignite to constant weight. The weighed ZrO_2 will probably always contain TiO_2 (if no peroxide was used) and, in addition ThO_2, Cb_2O_5, Ta_2O_5 and possibly other oxides such as SnO_2, if these were present in the ore.[38]

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[35] Prepared by treating KF with a slight excess of HF, evaporating over a very small flame until a clear fused mass is obtained, cooling and crushing the melt.

[36] If phosphates are present, filter, wash, and ignite the insoluble residue and fuse with Na_2CO_3. Extract the melt with water, filter, wash, dissolve the residue in HCl, and add to the main solution.

[37] Prepared by treating selenium with concentrated nitric acid until oxides of nitrogen cease to be evolved, evaporating to dryness, purifying the selenium dioxide by sublimation, and then dissolving the oxide in water and diluting to proper volume.

[38] S. G. Simpson and W. C. Schumb [*Ind. Eng. Chem. Anal. Ed.*, **7**, 36 (1935)] recommend a preliminary precipitation of zirconium as basic selenite, followed by solution of the precipitate in hydrochloric acid and reprecipitation as zirconium phosphate. Advantages claimed are that the procedure requires no intermediate fusions, that coprecipitated thorium can easily be removed from the acid solution of the selenite before precipitating as the phosphate, and that the two independent precipitations yield a purer final product in any case. A. Claassen [*Z. anal. Chem.*, **117**, 252 (1939)] describes a modification of the method in which zirconium is precipitated and weighed as the normal selenite, $Zr(SeO_3)_2$. An application of Claassen's method to the determination of zirconia and hafnia in mixtures of the two oxides is described by W. C. Schumb and F. K. Pittman [*Ind. Eng. Chem. Anal. Ed.*, **14**, 512 (1942)], and E. M. Larsen, W. C. Fernelius, and L. L. Quill [*Inorganic Syntheses*, III, 69 McGraw-Hill

D. OTHER METHODS

Precipitation with ammonium hydroxide is excellent but hardly worth while except with pure salts; the same can be said in lesser degree of the use of phenylhydrazine or of precipitation in neutralized chloride solution by sulfurous acid as recommended by C. Baskerville [39] or by iodate according to I. T. Davis.[40] Microgram quantities of zirconium can be determined with Alizarin Red S which forms a pink lake in 0.2 *N* acid solution.[41]

Book Co. (1950)]. The basic selenites are precipitated with a 20 per cent solution of selenious acid and are converted to the normal selenites by digestion on a steam bath. A weighed portion of the dried selenites is ignited to the mixed oxides.

$$\% \text{ HfO}_2 = \frac{374.86[(\text{wt. of oxides}) - 0.35702(\text{wt. of selenites})]}{\text{wt. of oxides}}$$

[39] *J. Am. Chem. Soc.*, **16**, 475 (1894); *Chem. News*, **70**, 57 (1894).

[40] *Am. Chem. J.*, **11**, 27 (1889).

[41] Brita Hok, *Photometric Determination of Zirconium*, M.S. thesis, University of Minnesota, 1949; D. E. Green, *Anal. Chem.*, **20**, 370 (1948).

Chapter 38

TITANIUM

Once held to be rare, for lack of a distinctive qualitative test, titanium is now recognized to be one of the most universally distributed elements and about tenth in actual abundance in the explored crust of the earth. It is probably present in all igneous, metamorphic, or sedimentary rocks of a more or less siliceous character. Though seemingly present even in the most siliceous rocks, it is more abundant in the so-called basic silicate rocks. Chief among its numerous minerals are rutile, octahedrite or anatase, ilmenite, titanite, and perofskite, but it is also a component, in smaller amounts, of many pyroxenes, hornblendes, biotites, garnets, and other ferromagnesian minerals, and is found in some magnetite and hematite. Owing to the refractory nature of some of its compounds, it tends to concentrate in the residual products of decomposition of many rocks; hence its high percentage in clays as a class. In these materials it is very unusual to find titanium present in amounts that can properly be designated only as traces; in the great majority of cases its amount will not exceed 1 per cent, but it may rise to over 5 per cent. Titanium must also be looked for and often determined in many other materials such as ores, refractories, and metallurgical products. Methods for its separation and determination are, therefore, of considerable importance.

I. GENERAL CONSIDERATIONS

In the analysis of rocks and silicate minerals, some, but by no means all, of the titanium is carried down with the silica. This is recovered, and all of the titanium is later weighed with the ammonia precipitate. Before convenient tests for it were known, it was common practice to omit even a qualitative test; so it counted often as alumina and at least two errors resulted—failure to report it and high results for iron or alumina or both, depending on the method of determining iron and the amount of titanium present, as the following illustrations show. If iron is determined by oxidation with permanganate after reduction with reagents such as hydrogen sulfide or sulfur dioxide which do not reduce titanium, then high results for alumina ensue. If the reduction is by zinc, which reduces $2TiO_2$ to Ti_2O_3, high results for Fe_2O_3 and nearly correct results for Al_2O_3 will be

obtained when the amount of TiO_2 is small, for the TiO_2 titer of a standard permanganate solution happens to be almost the same as the Fe_2O_3 titer. When the amount of titanium is large, the reoxidation of Ti_2O_3 by air before the titration with permanganate becomes appreciable, and in this event high results for both Al_2O_3 and Fe_2O_3 are the rule.

II. DECOMPOSITION OF TITANIUM MINERALS

The minerals of titanium are all essentially oxygenated compounds. They are, as a rule, imperfectly attacked by acids except hydrofluoric, the use of which of course precludes determination of silicon. When this acid is used, it is ordinarily in conjunction with sulfuric and nitric, and the excess of it must be removed *completely* by evaporating the solution to fumes of sulfuric acid. To insure complete expulsion of the fluorine, the cooled solution should be diluted; all solid material, especially on the sides of the vessel, brought into clear solution (with more sulfuric acid if necessary); and the evaporation and fuming repeated.[1] This last operation should not be continued to complete or even nearly complete expulsion of the sulfuric acid, for the deposited salts may be hard to redissolve. In all operations the ease with which titanium hydrolyzes should be borne in mind, and solutions must be kept moderately acid if titanium is to be kept in solution.

Artificially prepared titania can be dissolved by heating with concentrated sulfuric acid and ammonium sulfate, or by carefully controlled fusion with ammonium bisulfate (private communication from W. S. Clabaugh).

Attack by fusion fluxes must generally be resorted to, and any one of those enumerated in the chapter on fluxes (p. 836) can be used with due regard to the composition of the sample and the objects in view. Of the alkaline fluxes, sodium hydroxide alone or its mixture with sodium carbonate or peroxide is usually very effective, but the use of these is commonly restricted to commercial assays because of the need for using crucibles of iron or nickel. For the determination of certain constituents, this is no objection, but, for a general analysis, the use of sodium carbonate is to be preferred.

Pyrosulfate fusion is also as a rule effective, but usually less so for siliceous materials than for others.[2] When such a melt is leached with cold water or dilute acid, the titanium goes into solution along with the bases, and

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[1] Nitrates or sulfates of titanium do not, as has been asserted, attack platinum vessels when evaporated in them with nitric or sulfuric acids.

[2] Sodium pyrosulfate fusions of titanium ores are more satisfactory than those carried out with the potassium salt according to G. W. Sears and L. Quill [*J. Am. Chem. Soc.*, 47, 922 (1925)], who also pointed out that the ratio of the salt to the titanium material must be at least 12.5 to 1 with rutile and 35 to 1 with titanite, and that the temperature of the fusion must not exceed 700° C.

most of the silica remains undissolved along with alkaline earth and lead sulfates, according to their nature and amounts. Tantalum and columbium will also be in the residue wholly or in part and, if so, may hold some titanium and zirconium. The remainder of the silica is in solution by virtue of the action of the fused pyrosulfate in forming soluble alkali silicate,[3] a fact that is overlooked in some textbook directions for treating siliceous materials and for purifying silica by a pyrosulfate fusion.

Fusion with acid fluorides may give perfect decomposition but precludes determinations of silicon and alkalies.[4] According to P. Ronchesse,[5] fusion with four parts of dehydrated borax, followed by solution of the melt in 5 *N* sulfuric acid is very satisfactory.

III. METHODS OF SEPARATION

Ordinarily it is not necessary to separate titanium from all other elements. Oftentimes no separation at all is required; again only a few elements need be eliminated. This follows because the two chief methods for the determination of titanium are the the colorimetric method based on the color of titanium peroxide in solution and the volumetric method based on its reduction by zinc. For example, it is evident that a colorimetric determination of titanium can be made directly in the complete solution of a limestone that is free from vanadium, and that its volumetric determination in rutile can be carried out after it is separated from the other elements that are reduced by zinc.

The separation of titanium from the hydrogen sulfide group is carried out by precipitation of the latter by means of hydrogen sulfide in acid solution (p. 60), preferably after the addition of tartaric acid. If this is added, a further separation from iron, cobalt, nickel, zinc, and more or less manganese can be obtained by adding ammonium hydroxide to the filtrate from the sulfide precipitate, continuing the addition of hydrogen sulfide, adding ammonium bisulfite (p. 66), and filtering. This separation is best made after the reduction of iron in acid solution and requires sufficient tartrate to hold the titanium in solution. Iron can also be almost completely separated from titanium by extraction with ether in dilute hydrochloric acid solution (p. 134).

Cupferron (p. 116) affords ordinarily but a group separation, for zirconium, rare earths (at least in part), certain members of the hydrogen sulfide group, iron, vanadium, tungsten, and quadrivalent uranium are precipitated with titanium if present in solution. Cupferron provides, however, a good separation of titanium from elements such as aluminum, chromium, manganese, nickel, and moderate amounts of phosphorus.

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[3] W. F. Hillebrand, *ibid.*, 24, 368 (1902). For its recovery see Silicon (p. 876).

[4] No volatilization occurs in such fusions. For example, after thorough fusion with KHF, 0.1820 and 0.1822 g of TiO_2 were obtained as against 0.1821 and 0.1821 g originally taken.

[5] *Ann. soc. sci. Bruxelles,* **B 54,** 53 (1934).

Precipitation of titanium by boiling in strong acetic acid solution after preliminary separation of iron fails in the presence of zirconium. Phosphorus is also carried down, and in addition it is quite likely that some of the rare earths and possibly other elements are also precipitated. The above can also be said of precipitation by boiling a dilute hydrochloric acid solution containing sulfurous acid.

Zirconium and thorium, but not titanium, can be precipitated by boiling with salicylic acid and ammonium salicylate.[6] A fair separation can therefore be made as follows: Prepare a nitric acid solution of the elements, carefully neutralize as much of the acid as possible with sodium carbonate, boil, and add dropwise a solution of 10 g of ammonium salicylate in 50 ml of water. Boil the solution for 30 to 60 minutes, dilute with boiling water to 200 ml, immediately filter, and wash the precipitate with a boiling hot concentrated solution of ammonium salicylate until the precipitate is white or is no more than faintly yellow.

The separation of titanium from molybdenum, vanadium, and phosphorus, which interfere in the colorimetric determination, and from other elements such as aluminum and beryllium is conveniently done by precipitating it with sodium hydroxide. When titanium alone is present, the precipitation is not quite complete, but, when iron accompanies it, as is usually the case, all of the titanium is precipitated. In this precipitation the acid solution is nearly neutralized with sodium hydroxide, poured with stirring into 200 ml of a boiling 5 per cent solution of sodium hydroxide, boiled for 1 to 3 minutes, filtered, and washed with a hot dilute solution of sodium hydroxide containing sodium sulfate. If much molybdenum or vanadium is present, the separation is to be repeated. As complete solution of the precipitate by dilute acid is difficult, it is better to decompose paper and all by treatment with nitric and sulfuric acids (p. 388), or else to ignite, fuse with pyrosulfate, and dissolve the melt in dilute sulfuric acid (1 + 9). Chromium can be eliminated at the same time, if it is oxidized by alkali persulfate in dilute sulfuric acid solution before the precipitation by sodium hydroxide, or if sodium peroxide or hydrogen peroxide is added to the sodium hydroxide solution. When peroxide is used, the solution must be thoroughly boiled for 10 minutes or longer to precipitate the titanium, which is at first held in solution as a soluble pertitanate. Fusion with sodium carbonate and extraction with water can be substituted for the precipitation with alkali. If the fusion and extraction are to be repeated, it is best to treat the water-insoluble residue with dilute hydrochloric acid and to

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[6] M. Dittrich and S. Freund, Z. *anorg. Chem.*, **56**, 344 (1908).

boil, treat with a slight excess of ammonium hydroxide, and filter before the ignition and second fusion. Fusion with sodium hydroxide and extraction with water are not permissible in the absence of iron, for large losses of titanium may result.[7, 8, 9]

Small amounts of earth acids in titania residues can be recovered by fusing the mixed oxides with potassium pyrosulfate, dissolving the melt in a hot solution of tannin in dilute sulfuric acid, boiling, and filtering to recover the earth acids. For centigram amounts the melt is dissolved in a solution of tartaric acid, boiled with dilute nitric acid, and filtered to recover the acids. For best separations, the melt is dissolved in a hot strong solution of ammonium oxalate and the solution treated in turn with salicylic acid and calcium chloride and then filtered. For details, the original references must be consulted.[10]

IV. METHODS OF DETERMINATION

The most important methods for the determination of titanium are the colorimetric method based on the use of hydrogen peroxide and the volumetric method based on reduction by zinc and titration with permanganate. The former is limited to use in solutions containing no more than 0.1 mg of TiO_2 per ml and is therefore best suited for the small amounts of titanium found in rocks and clays. The volumetric method is usually applied when the material contains more than 5 per cent of titania. Gravimetric methods such as precipitations by the use of the alkaline hydroxides or sulfides, by cupferron, or by boiling dilute acetic [11–14] or hydrochloric acid solutions [15] are capable of giving complete precipitation of titanium, but are not sufficiently selective when applied to mixtures.

In the preparation of solutions for the determination of titanium, it should be borne in mind that titanium will hydrolyze if the acidity of the solution is low, especially if it is also hot, and that, as titanium phosphate is very insoluble in acid, it is apt to separate from solution when titanium and phosphorus occur together. Still another precaution is needed when titanium hydroxide is dissolved on paper, for appreciable amounts of invisible precipitate can easily be left in spite of most careful washing.

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[7] F. A. Gooch, *Proc. Am. Acad. Arts. Sci.* [New Ser.], **12**, 436 (1884–85).

[8] W. F. Hillebrand, *U. S. Geol. Survey Bull.* **700**, 132.

[9] Consult also V. Auger, *Compt. rend.*, **177**, 1302 (1923).

[10] W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium*, pp. 109–16 (1937); W. R. Schoeller and C. Jahn, *Analyst*, **57**, 72 (1932); **54**, 320 (1929).

[11] F. A. Gooch, *op. cit.*, 435.

[12] T. M. Chatard, *Am. Chem. J.*, **13**, 106 (1891).

[13] *Chem. News*, **52**, 55, 68 (1885); **63**, 267 (1891).

[14] W. F. Hillebrand, *op. cit.*, 162.

[15] Charles Baskerville, *J. Am. Chem. Soc.*, **16**, 427, 475 (1894).

A. COLORIMETRIC METHOD

a. *General Considerations.* The colorimetric method for titanium is based on a comparison of the color produced by hydrogen peroxide in a dilute sulfuric acid solution of the material with that obtained in a standard solution of titanic sulfate. In rock analyses, the test is usually made after the volumetric determination of iron in the sulfuric acid solution of the pyrosulfate fusion of the weighed ammonia precipitate (Silicon, p. 874). The test can of course be made before this stage, provided the conditions to be numerated are met.

The strength of the peroxide, which need not be over 3 per cent, should be approximately measured by titration with permanganate on opening a fresh bottle and at intervals thereafter; otherwise serious error may arise through deterioration of the reagent. Occasionally peroxide has been found to contain fluorine, and the absence of this element must be assured by careful test (p. 38).

The oxidation should be done in the presence of at least 5 per cent by volume of sulfuric acid to insure complete oxidation of the titanium. The color intensity is increased by increase of temperature, and therefore the solutions to be compared should have the same temperature, preferably 20 to 25° C.

Elements that interfere are: (1) iron, nickel, chromium, and the like which interfere because of the color of their solutions; (2) vanadium, molybdenum, columbium,[16] and, under some conditions, chromium which interfere because they form colored compounds with hydrogen peroxide; and (3) fluorine (even in minute amount) and large amounts of alkali salts or phosphate, all of which bleach the color.[17] The interference of elements in the first class can be overcome, if they are present in small amount, by matching the color by addition of like quantities of the colored elements to the standard before hydrogen peroxide is added. When large amounts of iron are present, phosphoric acid can be added in like amount to both standard and unknown, after the addition of the peroxide. Large amounts of the other coloring elements must be removed. Of the interfering elements in the second class, vanadium and molybdenum can easily be removed by precipitation of the titanium with sodium hydroxide in the

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[16] Columbium yields a pale-yellow color with hydrogen peroxide in solutions containing less than 25 per cent (by weight) of sulfuric acid. The color increases as the strength of the acid is raised, and reaches a maximum intensity at 100 per cent (sp. gr. 1.845/15° C) of the acid. The color of the titanium compound, on the other hand, decreases gradually as the acidity is raised to 25 per cent, and fades considerably but not completely at 100 per cent.

[17] According to R. D. Hall [*J. Am. Chem. Soc.*, **26**, 1241 (1904)], the color is bleached by citric acid, but not appreciably so by tartaric or oxalic acids. Succinic acid is also without marked effect.

presence of a little iron. Of the elements that bleach the color, fluorine is by far the worst, but fortunately its separation can be easily accomplished by repeated heating with sulfuric acid. The bleaching action of alkali salts is less in a 10 per cent (by volume) solution of sulfuric acid than in one containing 5 per cent; when moderate amounts are present, the stronger acid should be used with both unknown and standard and like amounts of the salts added to the standard. When large amounts are present, titanium should be separated by precipitation with ammonium hydroxide and redissolved in sulfuric acid. The bleaching effect of a small amount of phosphoric acid in the sample can be overcome by adding a like amount to the standard. Whenever much of it is present together with appreciable amounts of titanium, difficulty may be experienced in obtaining a clear sulfuric acid solution because of the formation of insoluble titanium phosphate. In this event, the sodium hydroxide separation should be employed as a preliminary step.

b. *Preparation of the Standard Solution.* Standard solutions prepared from the National Bureau of Standard's standard sample of titania no. 154 (which contains 98.7 per cent of TiO_2) are entirely satisfactory. These are conveniently prepared by dissolving weighed portions of the dried sample in concentrated sulfuric acid and ammonium sulfate, diluting, filtering, washing, and making up to definite volume.

Standard solutions can also be prepared from potassium titanium fluoride, $K_2TiF_6 \cdot 2H_2O$, as follows: Recrystallize a quantity from boiling water in platinum one or more times, dry, and preserve in a glass-stoppered bottle. Roughly weigh enough of the salt to provide a little more than 1 g of TiO_2, transfer to a platinum dish, treat with 100 ml of dilute sulfuric acid (1 + 1), and evaporate until fumes of sulfuric acid escape freely. Cool, wash down the inside of the dish, evaporate as before, and then repeat the operation again to make sure that all hydrofluoric acid is expelled. Cool, and dilute with water to 1 liter. Withdraw two or more 50-ml portions, dilute to 200 ml, heat to boiling, and render faintly ammoniacal. Continue the boiling for 1 to 3 minutes, filter, and wash the precipitate with hot water until free from alkali salts. Ignite the moist filter, and finally heat to constant weight at 1100 to 1200° C. Calculate the TiO_2 content per milliliter of solution, and affix the result to the bottle containing it.[18] The stopper of

the bottle should be coated with Vaseline and the needed quantities of solution withdrawn by a dry pipette, never poured. In a solution so prepared, there is not enough alkali sulfate to weaken the color when peroxidized.[19]

c. *Preparation of the Test Solution.* The test solution should preferably contain titanium as sulfate in a sulfuric acid solution containing none of the undesirable constituents mentioned in a. The solution can be that obtained by concentration of the solution which has served for the titration of iron in the ammonia precipitate (p. 877), if no other acid than sulfuric has been introduced. The presence of manganese derived from the permanganate used in titrating the iron is not objectionable. The direct use of this solution is not desirable when vanadium or much phosphorus is present, and, for this reason as well as to eliminate the alkali salts introduced in the fusion of the ammonia precipitate (Silicon, p. 874), it is desirable first to separate the titanium by precipitation with sodium hydroxide (p. 84). If only alkali salts are present, good results are obtained by adding like amounts of alkali to the standard and by making the comparisons in 10 per cent sulfuric acid solutions, but it is better in this case first to separate the titanium with ammonium hydroxide, to filter, and to dissolve in dilute sulfuric acid.

Other solutions obtained by direct attack of the material or by solution of certain weighed precipitates can be used with due regard to the interfering elements cited in a. Thus, the use of a solution obtained by direct attack of a rock by hydrofluoric and sulfuric acids requires great care that all hydrofluoric acid is expelled, whereas the use of a cupferron precipitate requires attention to vanadium which may be present.

d. *The Color Comparison.* Evaporate the sulfuric acid solution containing the titanium sulfate to less than 100 ml, and oxidize fully with hydrogen peroxide. If the color is less intense than that produced by 0.01 g of TiO_2, add enough sulfuric acid to make a total of 5 ml, and dilute to 100 ml in a measuring flask. If the color is more intense than that produced by 0.01 g of TiO_2, the solution must be diluted to a larger definite volume containing 5 per cent sulfuric acid. The color comparison is then easily made in the various forms of photometers, spectrophotometers, or simple

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[18] The titer so obtained is apt to be a little high, for titanium hydroxide carries down a little potassium. The error is of no consequence in ordinary work. In work of the highest accuracy, the precipitation had better be repeated two or three times or else made with cupferron. Such treatments give closely agreeing results. For example, after three precipitations with NH_4OH in which the first two precipitates were dissolved in dilute HCl and the well-washed papers burned with the final paper and precipitate, two 25-g portions of solution gave 0.002008 and 0.002004 g of TiO_2 per g of solution, whereas single precipitations with cupferron in two 25-g portions of the same solution gave 0.002008 and 0.002002.

[19] W. W. Plechner and J. M. Jarmus [*Ind. Eng. Chem. Anal. Ed.*, 6, 447 (1934)] describe a method in which pure TiO_2 is obtained from $TiCl_4$ and then dissolved by boiling with concentrated sulfuric acid and ammonium sulfate. W. M. Thornton, Jr., and R. Roseman [*Am. J. Sci.*, **XX**, 14 (1930)] recommend $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ as the starting material, as follows: Recrystallize the CP salt once from water, and dry for several days at room temperature. Mix 4.5 g (representing about 1 g of TiO_2) with 8 g of ammonium sulfate, transfer to a Kjeldahl flask, and add 100 ml of concentrated sulfuric acid. Heat gradually until the solution boils, and then boil for 10 to 15 minutes. Cool, dilute to approximately 1 liter, and filter if not clear. Test a portion of the solution with permanganate to make sure that oxalic acid which bleaches peroxidized titanium is absent, and determine the TiO_2 content as usual.

colorimeters (p. 27).[20] If the presence of vanadium is suspected, hydrofluoric acid can be added at the completion of the test. The color caused by titanium is bleached while the brownish red color caused by vanadium is not.[21]

According to Klinger and Koch,[22] a very satisfactory colorimetric determination of small amounts of titanium (<1 mg of Ti per 100 ml) is that based on the intense red color which quadrivalent titanium gives with chromotropic acid. The determination of titanium in the mixed oxides of tantalum and columbium is made as follows: Fuse with potassium pyrosulfate, dissolve the melt in 20 ml of a 2 per cent solution of oxalic acid, and dilute to 80 ml. Add 10 ml of an aqueous 6 per cent solution of chromotropic acid, dilute to 100 ml, and determine the transmission of the solution in a photometer, with a suitable filter (470 mμ), using a solution containing the reagents alone as a blank. Determine the titanium content from a curve obtained by using known amounts of titanium. Stannous, ferric, uranyl, and nitrate ions interfere; zirconium, molybdenum, columbium, and tantalum do not. Under suitable conditions, a determination of titanium can be made in the whole solution of steels and alloy steels.[22]

B. VOLUMETRIC METHOD

If titanium is reduced by zinc in sulfuric or hydrochloric acid solution, as in the Jones reductor, complete reduction to the trivalent state proceeds quickly. The reduced compound is, however, very easily oxidized and must therefore be collected under a solution of ferric sulfate, whereby the titanium is immediately oxidized to the quadrivalent state with the formation of an equivalent reducing amount of the more stable ferrous sulfate.[23] All elements or compounds that form soluble reduction products that subsequently consume permanganate must be excluded, unless their effect can be calculated. The ordinary reducible compounds and elements are: certain organic compounds, nitric acid, tin, arsenic, antimony, molybdenum, iron, chromium, vanadium, tungsten, uranium, and columbium. The first two can usually be removed by evaporation with sulfuric acid; two evaporations with intervening cooling and washing down of the inside of the vessel are always desirable, and occasionally stubborn organic compounds require for their destruction the cautious dropwise addition of a saturated solution of permanganate through the lip of a covered beaker containing the boiling concentrated sulfuric acid solution. Tin, arsenic, antimony, and molybdenum are easily removed by hydrogen sulfide in a cool solution sufficiently acid to prevent hydrolysis of titanium. When hydrogen sulfide is used, polythionic compounds are formed,[24] and these must be destroyed after boiling to expel hydrogen sulfide, by adding permanganate to a permanent pink tint. Iron can be removed by precipitation with ammonium sulfide in ammoniacal tartrate solution, followed by the destruction of the tartrate (p. 66). Chromium, vanadium, uranium, and tungsten can be removed, after oxidation to their higher valencies, by precipitation of the titanium, repeated if need be, with sodium hydroxide. In this operation titanium is not perfectly precipitated in the absence of iron, and so this separation should precede that of the iron. No entirely satisfactory method for the separation of columbium is known (p. 603). The method is therefore not serviceable when that element is present.

PROCEDURE. Prepare a sulfuric or hydrochloric (preferably the former) acid solution of titanium with regard to what has been said, and reduce as described on page 108. Titrate the solution with a standard 0.1 or 0.05 *N* solution of permanganate, and subtract the volume required in a like run on the reagents alone.[25]

C. PRECIPITATION BY CUPFERRON

Titanium is quantitatively precipitated by cupferron in dilute sulfuric acid solution[26] and separated from elements such as aluminum, chromium, sexivalent uranium, phosphorus, nickel, and the alkaline earths. The only drawback to this method is that many other elements are also precipitable; iron, zirconium, the earth acids, and vanadium quantitatively, and certain rare earths, tungsten, and several members of the hydrogen sulfide group partially. The chief differences between this method and the volumetric

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[20] G. H. Ayres and E. M. Vienneau [*Ind. Eng. Chem. Anal. Ed.*, 12, 96 (1940)] state that the yellow color developed by titanium and hydrogen peroxide in dilute sulfuric acid solution remains unchanged for at least 2 years.

[21] M. Schenk [*Analyst*, 61, 872 (1936)] states that the intense red color which titanium yields in a solution containing 0.7 to 1.4 g of salicylic acid per 100 ml of 86 per cent (by weight) sulfuric acid is 5 times as sensitive as the peroxide test. Nitric, nitrous and permanganic acids interfere.

[22] P. Klinger and W. Koch, *Tech. Mitt. Krupp Forschungsber.*, 14, 179 (1939) and *Arch. Eisenhüttenw.*, 13, 127 (1939).

[23] A. S. Russell [*J. Chem. Soc.*, 129, 497 (1926)] recommended that the reduced titanium be obtained in 4 *N* sulfuric acid solution, in which it is but very slowly oxidized by air. For a method for the detection of quadrivalent titanium in the presence of trivalent titanium based on the colored compounds produced by the former with chromotropic acid, pyrocatechol, and other polyphenols in slightly acid solutions, consult V. I. Kuznetsov, *J. Gen. Chem. USSR*, 14, 902 (1944).

[24] G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, 43, 1563 (1921).

[25] If the dimensions of the column of amalgamated zinc are smaller than those specified in the reference, the analyst must determine whether operating conditions must be changed. For example, shorter columns may require a slower rate of flow, or preheating of the solution to, say, 40 to 60° C. The National Bureau of Standards sample no. 154 of titanium oxide is desirable for use in checking the reduction-oxidation technique. For the use of zinc amalgam to reduce titanium, see p. 114.

[26] Precipitation is complete in solutions containing as much as 40 per cent by volume of H_2SO_4 and 1 per cent of tartaric acid.

method are that the latter is not subject to interference by zirconium, the rare earths, or tantalum whereas the cupferron method is not subject to interference by uranium in the sexivalent state.

PROCEDURE. Prepare a hydrochloric or sulfuric acid solution which is free from members of the hydrogen sulfide group and which contains the elements in their ordinary valencies. Proceed as described on page 116 (cupferron) until the precipitate has been ignited and weighed. If the constituents of the original material are not known, the precipitate must be examined for such possible contaminants as have not previously been removed.

D. PRECIPITATION IN SOLUTIONS OF ACETIC ACID OR OF DILUTE HYDROCHLORIC ACID

The separation of titanium from aluminum and final precipitation from a boiling acetate-acetic acid solution after removal of iron and phosphorus, as proposed by Gooch [11] and subsequently slightly modified by Chatard,[12, 14] was for quite a time unequaled in rock analysis. It is not much used today, in part because of the more reliable colorimetric and volumetric methods and in part because of the interference of zirconium which prevents complete precipitation.[27]

Precipitation of titanium by boiling in dilute hydrochloric acid solution as proposed by Baskerville [15] is subject to interference by zirconium which is precipitated wholly or in part according to the acidity, by phosphorus, and no doubt by other elements whose action has not been investigated.

E. OTHER METHODS

Chief among other methods are the volumetric ones based on the reduction of titanium by zinc and titration with ferric alum in the presence of potassium thiocyanate as indicator [28] or with methylene blue.[29] Of these two, the latter is to be preferred because of the better end point. Both are subject to error unless great care is taken to prevent reoxidation of the reduced compound before and during titration and are less dependable than the method described under B. They possess one advantage in that they can be applied in the presence of iron. In the methylene blue method, a hydrochloric acid solution of titanic chloride is reduced by zinc, preferably in a Jones reductor (p. 108), and the reduced solution is kept in an atmosphere of carbon dioxide and titrated with a standardized solution of methylene blue until a permanent blue color is obtained. The reduction and titration are done best in hot solution. Nitric and sulfuric acids interfere with the end point and are undesirable, as are also molybdenum, vanadium, tungsten, chromium, and tin, which react with methylene blue. The method is applicable in the presence of silicon, iron, aluminum, antimony, arsenic, and phosphorus. The methylene blue solution is made by dissolving 3.9 or 7.8 g of the reagent, corresponding to 1 to 2 mg of Ti per ml, in 1 liter of water and standardizing against portions of a standard solution of titanic chloride which have been reduced as in the method.[30]

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[27] W. F. Hillebrand, *U. S. Geol. Survey Bull.* 700, 163–164.

[28] Knecht and Hibbert, *Ber.*, 36, 1550 (1903); G. Gallo, *Atti accad. nazl. Lincei*, 16, Part 1, 325 (1907); E. Knecht, *Z. angew. Chem.*, 26, Part 1, 734 (1913).

[29] Eva Hibbert, *J. Soc. Chem. Ind.*, 28, 189 (1909); B. Neumann and R. K. Murphy, *Z. angew. Chem.*, 26, Part 1, 613 (1913).

[30] For methods of analysis, see also W. M. Thornton, Jr., *Titanium*, American Chemical Society Monograph Series, Chemical Catalog Co., New York (1927).

Chapter 39

THE EARTH ACIDS

COLUMBIUM (NIOBIUM) AND TANTALUM

Columbium and tantalum are rare acid-forming elements which are usually found together. Both form salts with iron, manganese, calcium, uranium, and the rare earth metals, of which the minerals columbite, tantalite, and samarskite are typical examples. All of these minerals are most abundant in pegmatite veins[1] and are found in certain granites. Tantalite sometimes occurs with wolframite and cassiterite.

I. GENERAL CONSIDERATIONS

The term earth acids is applied by some writers to the pentoxides of columbium and tantalum, but, just as thorium is commonly treated with the rare earth metal group, so titanium is by other writers treated as an earth-acid metal, for the reasons that the three metals have certain chemical characteristics in common that are important in analysis besides being closely associated in nature. Chemically they are characterized by such a strong tendency to hydrolize that this property has been taken advantage of to effect their separation from some of the other elements. Titanates free from columbium and tantalum are common, and columbates and tantalates occur without titanium, but there is perhaps no natural columbate known that is entirely free from tantalum nor a tantalate mineral that is free from columbium. Quinquevalent phosphorus, arsenic, and antimony replace part of the columbium and tantalum in a few rare minerals. Tungsten and tin are of frequent occurrence, but almost always in very subordinate amounts.

Among other acidic constituents, silicon is important and zirconium is common, the latter apparently functioning now as acid, now as base, by virtue of its amphoteric character. Hafnium probably accompanies zirconium. Boron, fluorine, chlorine, and carbon dioxide also are met with. Several of the acidic elements may occur in one and the same mineral. Among the basic components of the minerals of this group, iron and manganese are characteristic of some, as in the relatively simple columbite and tantalite, calcium of others (perofskite, titanite). The rare earth metals and thorium are chief or subordinate constituents of a great number, and of frequent occurrence are uranium and beryllium. Possibly nitrogen and helium occur very sparingly in those that carry uranium or thorium. Germanium has been found. Most of the common elements appear in them scatteringly.

In general it appears that arsenic and antimony are not found in titanium minerals which carry no columbium or tantalum, and that boron is associated rather with silicon (cappelenite, homilite, tritomite) or titanium (warwickite) than with columbium or tantalum. Fluorine (possibly chlorine) in other than a simple fluoride or fluorcarbonate is ordinarily regarded as entering into a silico or titano complex. By some mineralogists both fluorine and chlorine are assigned to basic oxy complexes. Boron occurs predominately in the form of borates, but, with fluorine also present, it is not impossible that there may be a fluoborate complex.

From the foregoing presentation, it is apparent that many of the minerals of the group are extraordinarily complex and that the assignment of valid formulas is most difficult. Many of the formulas that have been assigned are purely hypothetical, being based on unproved and in part probably unprovable assumptions.

Before starting upon a quantitative analysis, it is here even more important than usual to make a thorough qualitative examination, if possible spectrographically. The information gained from it may be decisive in indicating the best methods of attack or of separation. Unfortunately, it happens very often that material is lacking for exhaustive preliminary tests, and the analyst is then seriously handicapped. There is no other class of minerals of which the analysis is so beset with difficulties. No methods are known for a simple quantitative separation of columbium and tantalum from each other and still less from titanium. If not in too large amount, this last can be determined colorimetrically in presence of the others.

The literature is full of statements that were perhaps more or less true for the particular conditions that led to their formulation but untrue as generalizations. Unfortunately, some of them came to be accepted as true for all cases and conditions, and hence arose, no doubt, much of the confusion that has prevailed and still prevails. Doubtless many analyses and formulas reported are worthless quantitatively and defective qualitatively because of this confusion, which was intensified if not brought about by the marked influence that one element exercises on the normal reactions of another when in the same solution. These effects in masking each other's normal behavior are similar to those that have long been known with respect to zirconium and titanium.

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[1] F. W. Clarke, The Data of Geochemistry, 5th ed., *U. S. Geol. Survey Bull.* 770.

As perhaps the most striking illustration of this effect may be cited the action of water upon the melt that results from a pyrosulfate fusion of a mixture of the three oxides or of a mineral that contains the three elements (Ti, Cb, Ta). It was formerly supposed that, from such a melt, cold water extracted all the titanium and left the columbium and tantalum unaffected, as is in fact practically the case in the absence of titanium. The method was in general use, but it is now agreed that this was a great mistake, and that not only do tantalum and particularly columbium pass into solution according to the relative amount of titanium present but also that tantalum particularly, when in excess, prevents some of the titanium from dissolving.

Again, it was supposed that, from a mixture of the oxides obtained from a pyrosulfate fusion, yellow ammonium sulfide extracted fully the tungstic and stannic oxides which it often contains and left the earth-acid oxides unaffected. Also that fusion of the ignited mixture with sodium carbonate and sulfur, followed by extraction with water, released similarly the tungstic and stannic oxides without dissolving columbium or tantalum. Neither of the suppositions is correct. The fusion method, if repeated one or more times, especially when done at a high temperature, will no doubt yield the tungsten and tin, but at the cost of dissolving some columbium and tantalum. The latter effect is lessened by fusing at a lower temperature, but then some of the tungsten and tin is not released.[2]

In view of the difficulties and uncertainties involved, our descriptions of methods will be less didactic than we have felt was justified for well-established methods. Also, we shall mention, in greater detail than usual, some methods that have been put forth without sufficient support to justify their unqualified acceptance. This course seems desirable in order to bring to the analyst's attention a number of possibilities which may be worth further investigation.

In an ordinary analysis, most of the columbium and tantalum separate with the silica and will be contained in the nonvolatile residue left after the volatilization of the silica with sulfuric and hydrofluoric acids. If the nonvolatile residue is fused with sodium carbonate or pyrosulfate, difficulty will usually be experienced in getting a clear solution of the melt because of hydrolysis of the earth acids. Both of the elements will finally be weighed with the ammonia precipitate in any case, and most if not all will be counted as aluminum. If the ammonia precipitate is treated for its silica content, the earth acids will again separate. If an attempt to determine iron by reduction with zinc is made, the presence of columbium will be betrayed by the deep-brown color of the reduced compound, and high results for iron will ensue if its presence is ignored.

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[2] W. B. Giles, *Chem. News*, **95**, 1, 37 (1907); **99**, 1, 25 (1909).

Serious difficulties in the analysis of materials containing the earth acids are caused by the ease with which these elements hydrolyze. Desirable aids in keeping the earth acids in solution are tartaric acid,[3,4] oxalic acid,[5] hydrogen peroxide,[6] hydrofluoric acid,[7] and mannitol.[8]

II. ATTACK OF EARTH-ACID MINERALS

A. ATTACK BY HYDROFLUORIC ACID AND OUTLINE OF SUBSEQUENT TREATMENT

The method of attack by hydrofluoric acid originated with J. Lawrence Smith [9] and its use is restricted almost exclusively to the columbates and tantalates of the rare earths that are free from silica unless this is to be determined in a separate portion of the sample. When applicable, it should always be used, for it affords very quickly and easily an almost perfect separation of the insoluble rare earth and alkaline earth fluorides from the soluble fluorides of the earth-acid and other metals. The method introduces no alkali salts and has the further advantage, shared by no other, not only of showing whether quadrivalent uranium is present but also of separating it quantitatively from sexivalent uranium if both are present. Uranous fluoride, UF_4, is insoluble in dilute hydrofluoric acid and at once reveals its presence in more than traces by its green color, even when mixed with a large amount of rare earth fluorides. If uranous fluoride is not in question, the sample can be attacked with hydrofluoric and nitric acids, with final evaporation with hydrofluoric acid alone.

Some natural columbates and tantalates dissolve with great ease in concentrated hydrofluoric acid (samarskite for example), but others do not (columbite and tantalite). Smith said that the less soluble minerals could be completely decomposed when ground to an impalpable powder and treated with successive portions of the acid, but our experience and that of others does not fully bear him out in this contention.

a. *Solution and Preliminary Treatment.* The mineral attack is best carried out by transferring the mineral, finely powdered and dried at 150° C, to a dish or capacious crucible of platinum, moistening with water, and treating with 5 to 10 ml of hydrofluoric acid. If the mineral is not at once soluble, evaporate the liquid not quite to dryness at a gentle heat with

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[3] A. R. Powell, *J. Soc. Chem. Ind.*, **37**, 285 T (1918).

[4] W. R. Schoeller and A. R. Powell, *J. Chem. Soc.*, **119** ^{2}, 1928 (1921).

[5] H. Pied, *Compt. rend.*, **179**, 897 (1924).

[6] L. Weiss and M. Laudecker, *Z. anorg. Chem.*, **64**, 65 (1909).

[7] F. Pisani, *J. prakt. Chem.*, **102**, 448 (1866).

[8] O. Hauser, *Z. anorg. Chem.*, **60**, 231 (1908).

[9] *Am. Chem. J.*, **5**, 44, 73 (1883); W. F. Hillebrand, *Colo. Sci. Soc. Proc.*, **3**, 38 (1888); R. C. Wells, *J. Am. Chem. Soc.*, **50**, 1017 (1928).

occasional stirring, and add fresh acid and evaporate as often as need be. When no more undecomposed mineral is left, dilute so that the solution contains 5 to 10 ml of hydrofluoric acid per 100 ml; collect the fluorides on a paper filter held in a funnel of platinum, hard rubber, or Bakelite; and wash with dilute hydrofluoric acid (1 + 20). Rinse the precipitate back into the vessel, burn the filter, and add its ash to the contents of the dish. The precipitate may contain as fluorides the rare earths, quadrivalent uranium, lead and zirconium in part, the alkaline earth metals, and perhaps a very little iron. If alkali metals were present, which is rarely the case, the precipitate might contain double fluorides of these with one or another of the other metals.

b. *Subsequent Treatment.* α. *The fluoride precipitate.* Convert the fluorides to sulfates by evaporating with sulfuric acid, and heat till all fluorine is expelled. If UF_4 is present, add nitric acid also in order to oxidize the uranium.[10] Dissolve the sulfates in cold water, and swirl the liquid so as to collect a possible precipitate at the center of the dish. If there is one, it is probably lead sulfate or less probably alkaline earth sulfate, although, if the washing of the fluorides was not thorough, it may consist wholly or in part of the oxides of columbium and tantalum. Collect it on a paper filter, and reserve the filtrate, extract the residue with hot ammonium acetate, and add ammonium sulfide to the extract. If lead sulfide appears, filter, dissolve in hot dilute nitric acid, evaporate with sulfuric acid, and eventually weigh the precipitate as lead sulfate (p. 227). Test the filtrates from the lead sulfate and lead sulfide for alkaline earth metals. If the ammonium acetate left a residue, ignite and weigh it, and test for earth acids and alkaline earth metals.

Precipitate the rare earth metals and uranium by adding ammonium hydroxide to the reserved filtrate, filter, and wash the precipitate with a 2 per cent solution of ammonium chloride. Evaporate the filtrate and determine any calcium it may contain (p. 623), with due care to see that it is free from any contamination.

Dissolve the ammonia precipitate in a slight excess of hydrochloric acid, and throw out the rare earth metals by oxalic acid (see Rare Earths, p. 550) and with addition of a little ammonium oxalate (the latter merely to reduce the acidity and leave no excess of the ammonium oxalate to dissolve certain of the rare earth oxalates). Wash with 1 per cent oxalic acid solution, and,

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[10] The washed fluorides are in our experience entirely free from earth-acid metals. J. Lawrence Smith, in analyzing samarskite, found, on dissolving the sulfates in water, a small white residue which he held to be columbic and tantalic oxides. One of us, in analyzing a mineral similar to samarskite, observed also a white substance, but it was lead sulfate without a trace of columbium or tantalum. This is conclusive evidence that lead fluoride, in spite of its rather free solubility in hydrofluoric acid, may be carried down with other fluorides.

if uranium was present, convert the oxalates to chlorides, and reprecipitate. Reserve the precipitate. Whether uranium is present or not, evaporate the filtrate or filtrates to dryness, and destroy the oxalic acid by heating. Then, in absence of uranium, recover the remainder of the earths by resolution and precipitation with oxalic acid in a very small volume of solution. Examine the filtrate for iron and zirconium. With uranium present, take up the residue with hydrofluoric acid, evaporate nearly to dryness, filter, wash with weak hydrofluoric acid, and reserve the filtrate. Treat with sulfuric acid, convert to oxalates, and add to the rare earth oxalates already obtained. See Rare Earths (p. 558) for further treatment of the oxalate mixture.

Evaporate the reserved filtrate containing the uranium, expel the hydrofluoric acid by sulfuric acid, take up with dilute nitric acid, and precipitate the uranium by ammonium hydroxide. Ignite the precipitate to U_3O_8 in air. Examine it for a possible content of iron and zirconium. Calculate the final weight as percentage of UO_2, for it is only the UO_2 content of the mineral that has thus been obtained.

β. *The filtrate from the fluorides.* Evaporate the hydrofluoric acid filtrate containing the earth acids, etc., nearly to dryness; add sulfuric acid; continue the evaporation to fumes of the acid; cool; dilute with a strong solution of tartaric acid; and pass in hydrogen sulfide. If sulfides are found, filter, wash with hydrogen sulfide water, and treat appropriately. Lead, copper, tin, and possibly other metals may be present. Treat the hydrogen sulfide filtrate as described on page 595.

B. ATTACK BY FUSION WITH POTASSIUM HYDROXIDE, POTASSIUM CARBONATE, OR SODIUM PEROXIDE

Fusion with potassium hydroxide in a silver, gold, or nickel crucible or potassium carbonate in a gold or platinum crucible serves very well for the decomposition of columbates or tantalates. To make the fusion with the hydroxide, heat (preferably with the crucible placed in a hole in an asbestos shield) 3 g of the hydroxide until the melt is quiet, remove the lid, and carefully drop in 0.5 g of the finely powdered and dried mineral. Quickly rotate to mix the contents, heat for 5 to 10 minutes at a dull red heat, and again rotate the crucible. Heat for 20 to 30 minutes at a bright red heat. Remove and cool the crucible cover without losing any of the melt on it. Tilt the crucible so that the melt is on one side, cool, and treat the melt with the appropriate solvent. If the melt is extracted with water and the fusion is to be repeated, it is desirable first to decompose any alkali salt in the washed water-insoluble residue. This can be done by transferring the residue to a beaker, digesting at 100° C with a moderate excess of dilute hydrochloric acid, rendering the solution ammoniacal, filtering, and washing to remove the chlorides. The filtrate may contain other constituents besides the extracted alkali and should be evaporated and combined with the water extract, after such treatments as may be necessary to conform with the scheme of analysis.

To fuse with potassium carbonate, mix 0.1 to 0.5 g of the finely powdered and dried mineral with 3 g of potassium carbonate in a platinum crucible. Heat at 1000 to 1100° C until a clear melt is obtained, and then swirl to run it up on the sides of the crucible as the melt cools. Melts containing considerable tantalum may show a faint cloudiness. For such minerals as can be decomposed at lower temperatures, a gold crucible can be used. Add approximately 0.5 g of solid potassium hydroxide, and then enough warm water to cover the melt. Warm gently until solution is complete, and then transfer to a 250-ml beaker, using as little warm water as possible.

For the determination of constituents such as sulfur or silicon, fusion with sodium peroxide offers a desirable attack. After the fusion, sulfur is separated by boiling the melt with water, filtering, acidifying, rendering the solution ammoniacal, and again filtering. Silicon, together with more or less of the earth acids, can be separated by dehydrating with sulfuric acid after attack with peroxide in a crucible of Armco iron, or with potassium hydroxide or carbonate. The separation of silica from the earth acids is described in Section III.

C. ATTACK BY PYROSULFATE AND OUTLINE OF SUBSEQUENT TREATMENT

Most columbates and tantalates are said to yield, when finely powdered, to the effect of hot concentrated sulfuric acid.[11] Titanates are more refractory, but all succumb more or less readily to fusion with an alkali pyrosulfate,[12] the sodium salt being preferred to the potassium salt because some of the resulting products are more soluble.[13] This has particular reference to minerals that contain rare earth metals and zirconium. However, the use of either the free acid or the alkali salt is counterindicated for determining the following: silicon when fluorine is present in appreciable amount;

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[11] G. C. Hoffmann, *Am. J. Sci.*, [3] **24**, 475 (1882).

[12] L. F. Nilson, *Ber.*, **13**, 1430 (1880).

[13] It was asserted by G. W. Sears [*J. Am. Chem. Soc.*, **48**, 343 (1926)] that a separation of columbium and tantalum from elements such as iron and manganese, and of tantalum from columbium can be accomplished as follows: Fuse one part of tantalate with nine parts of sodium pyrosulfate at 835 to 875° C, digest the melt with warm water, filter, and wash the residue of columbium and tantalum with hot 3 *N* hydrochloric acid to remove iron and manganese. Treat the residue with dilute sulfuric acid (1 + 1), boil until the volume has been reduced one third, cool, filter through asbestos, and wash the tantalum residue with cold 6 *N* sulfuric acid until the washings give no precipitate with ammonium hydroxide.

Our experience with such treatments would lead us to expect imperfect separations, especially if elements such as titanium or zirconium are present.

fluorine except by evolution; boron; carbon dioxide; sulfur; and phosphorus. The reason for most of these restrictions are obvious; those for phosphorus are due to the possibility of volatilizing[14] some P_2O_5.

Regarding the choice of a mode of attack, it may be said that, although pyrosulfate fusion will decompose probably all the earth acid minerals, hydrofluoric acid should be chosen for all rare earth columbates or tantalates that are fully broken up by it, with due reservation that for silica some other procedure must be adopted. Disadvantages of the pyrosulfate attack are that one fusion may not suffice and that the residue of earth acids always contains certain other elements if originally present, some of which are extractable or otherwise removable only with difficulty if at all, and that, dependent upon the relative proportions of the earth acids, some portions of these are likely to pass into solution and their subsequent recovery may be difficult.

As the general treatment after attack by sulfuric acid is like that after fusing with pyrosulfate and only the latter is extensively used, it only of the two procedures will be described.

a. *Fusion.* Fuse the finely ground powder[15] with 5 to 10 parts of sodium pyrosulfate in a covered silica crucible at a dull red heat, stirring from time to time with a stiff platinum wire. If need be, cool occasionally, add a few drops of concentrated sulfuric acid and renew the heating.[16] Decomposition is complete ordinarily within an hour if the mineral is unmixed with refractory foreign matter.

b. *Treatment of the Pyrosulfate Melt.* α. Probably the most satisfactory treatment of the pyrosulfate melt of the mineral itself, or of the crude earth acids obtained by other procedures, is that recommended by W. R. Schoeller and A. R. Powell.[4] This is essentially as follows: Leach the cooled melt with a solution of 10 g of tartaric acid in 50 ml of water. Filter, reserve the filtrate, and repeat the fusion and extraction if a residue remains. The final residue may consist of silica, lead sulfate, cassiterite, and the like, and is fused and analyzed by ordinary procedures. Treat the filtrate so that it contains 1 per cent (by volume) of sulfuric acid and 5 per cent of tartaric acid, pass in hydrogen sulfide, filter, wash with a solution that is saturated with hydrogen sulfide and contains 1 per cent of sulfuric and 5 per cent of tartaric acids, and analyze the precipitate for the hydrogen

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[14] W. F. Hillebrand and G. E. F. Lundell, *ibid.*, **42**, 2609 (1920).

[15] One to two grams but much more if columbium and tantalum are to be separated by the fluoride method of Marignac (see p. 605).

[16] A silica instead of a platinum crucible should be used so as to avoid introducing platinum, which would greatly complicate the procedures for determining antimony, tin, and tungsten. This may necessitate the use of a separate portion of sample treated in platinum for the silica determination, but, if the fusion is made at as low a temperature as possible, a silica crucible does not undergo sensible attack.

sulfide group.[17] Render the hydrogen sulfide filtrate ammoniacal, again treat with hydrogen sulfide, and filter to remove the sulfides of iron, nickel, cobalt, and part of the manganese. It seems probable that the earth acids, titanium, zirconium, vanadium, and part of the rare earths could be precipitated by cupferron (p. 120), after the ammonium sulfide filtrate is acidified, and that determinations of aluminum, the remainder of the rare earths, uranium, beryllium, and the like could be made by usual procedures after tartaric acid and cupferron are destroyed with nitric and sulfuric acids (p. 118).

β. According to H. Pied,[5] a solution of oxalic acid is a desirable solvent for the pyrosulfate melt of the minerals containing rare earths and the earth acids, for the former are precipitated and the latter are not. Moreover, oxalic acid does not retard subsequent precipitation by sodium hydroxide. Following this suggestion, the pyrosulfate melt might be dissolved in oxalic acid, and the rare earths separated by filtering after a suitable digestion period (p. 551). Titanium could then be determined colorimetrically after the addition of hydrogen peroxide to the filtrate.[18] Proceeding from this point, there is no apparent reason why the solution cannot be treated with sulfuric acid, evaporated to destroy the oxalic acid, diluted with a solution of tartaric acid, and treated as in α.

γ. *By hydrofluoric acid.* Still another way of treating the pyrosulfate melt is to dissolve it in water, add a slight excess of ammonium hydroxide, filter, wash the precipitate thoroughly, and finally dissolve the precipitate in hydrofluoric acid. This treatment, however, will be useful only in special cases and particularly for rare earth columbates and tantalates that are not directly and readily decomposed by that acid. In case the method is used, the procedure follows in general that in which hydrofluoric acid is used for attacking the mineral itself as in A. It should not be used if silica is present, unless this is to be determined in a separate portion of the sample. Furthermore, the ammonia precipitate must be washed completely free from alkali salt, otherwise silico-, titano- or zircono-fluorides of the alkali metal will be precipitated with the insoluble fluorides which the method aims to produce, particularly if fusion should have been made with potassium instead of sodium pyrosulfate. Further, if the mineral contains quadrivalent uranium, none of it will appear with the rare earth fluorides, because the effect of the fusion is to oxidize it to the sexivalent state, for which there is no insoluble fluoride.

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[17] By such treatment, H. B. Knowles obtained perfect separations of antimony, tin, lead, and copper from solutions containing as much as 0.1 g each of Cb_2O_5 and Ta_2O_5.

[18] R. D. Hall [*J. Am. Chem. Soc.*, **26**, 1241 (1904)] stated that oxalic or tartaric acid does not affect the $TiO_2-H_2O_2$ color, but citric acid does.

D. ATTACK BY SULFUR CHLORIDE AND OUTLINE OF SUBSEQUENT TREATMENT

A method of attack of columbates, tantalates, and tungstates which has much in its favor is that by sulfur monochloride or by a mixture of so-called sulfur dichloride and chlorine.[19] It has been shown that rutile and probably most if not all tungstates, columbates, and tantalates are completely decomposed when heated in a current of the vapors, and that titanium, columbium, tantalum, tungsten, tin, molybdenum, antimony, arsenic, and part or all of the iron volatilize as chlorides or oxychlorides, leaving behind as chlorides or unchanged the other metals and silicon and possibly boron, besides gangue. When the dichloride alone is used, much sulfur is separated in the receivers. With the dichloride and chlorine none separates, which is an analytical advantage. If the statement concerning boron holds true, this method above all others may be most suitable for boron-carrying minerals of the classes named above. The method of attack and subsequent treatment merit more careful study than they have received.

When sulfur dichloride and chlorine are used, the dried sample is placed in a porcelain boat contained in a suitable tube. This is gradually heated, first in the range 150 to 240° C in the course of 45 to 60 minutes, and then at 240 to 280° C for a like period as a stream of dry chlorine and sulfur dichloride is passed through. The latter is generated in an outside flask by gently heating the reagent at 40 to 50° C, and the escaping gases are condensed in water. Finally, the boat and near parts of the tube are heated for 5 minutes at 280 to 550° C[20] as a stream of chlorine alone is passed through to remove the volatile products that have condensed near the boat.

For columbates and tantalates, Meyer and Hauser[21] direct to evaporate the distillate and washings with sulfuric acid and to heat and treat the residue by one or another of the schemes outlined in II, A or C. W. B. Hicks,[22] operating with sulfur monochloride without chlorine and with dilute nitric acid in the receivers, and a current of dry hydrochloric acid at the end of the operation, broke up the sulfur clots as much as possible with a flattened glass rod, added ammonium hydroxide, and introduced hydrogen sulfide, whereby the sulfur, tungsten, tin, etc. were dissolved and iron was precipitated as sulfide, together with the earth acids. The further treatment of the precipitate will follow one or more of the schemes outlined in B and C, perhaps with suitable modifications.

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[19] F. Bourion, *Ann. chim. phys.*, [8] **21**, 89 (1910); E. F. Smith, *J. Am. Chem. Soc.*, **20**, 289 (1898).

[20] At high temperatures there is risk of volatilizing certain chlorides, such as those of zirconium and thorium, from the boat.

[21] *Die Analyse der seltenen Erden und Erdsaueren*, p. 276 (1912).

[22] *J. Am. Chem. Soc.*, **33**, 1492 (1911).

The analytical treatment of the residue of chlorides, silica, etc., in the boat calls for no special comment. It may contain lead and other metals precipitable by hydrogen sulfide, besides silica, rare earths, all of the manganese, part of the iron if the temperature was not high enough to volatilize it all, aluminum, calcium, magnesium, and the alkalies.

III. METHODS OF SEPARATION

Several methods of treating the crude earth acid mixture have been proposed, one or another perhaps good up to a certain point or for special determinations, but no one meeting all needs. Some of these are described in the following sections.

Probably the simplest method for separating zirconium from the earth acids consists in fusing the mixed oxides with potassium carbonate and extracting with water as follows:[4] Intimately mix 0.25 to 0.5 g of the mixed oxides with 5 to 20 parts of potassium carbonate, heat gently, and finally fuse at approximately 1200° C until the fusion is tranquil. Leach the cooled melt with hot water, add macerated paper, filter, and wash with a hot 2 per cent solution of potassium carbonate, and finally with a little hot water. Reserve the filtrate. Treat the residue as in II, B, ignite the paper and residue, and repeat the fusion and extraction once if columbium predominates, twice if tantalum does. Combine the filtrates for the determination of the earth acids. Titanium dissolves in part and will be found in both filtrate and residue. The separation of zirconium from columbium is excellent, that from tantalum is not quite quantitative.

Tannin quantitatively precipitates tantalum, columbium, and titanium from a barely acid oxalate solution which is half-saturated with ammonium chloride. Zirconium, hafnium, thorium, uranium, beryllium, and aluminum are not precipitated under these conditions. A quantitative separation of any or all of the precipitable, from any or all of the nonprecipitable, elements can thus be obtained.[23]

For the complete separation of earth acids from zirconium, W. R. Schoeller and E. F. Waterhouse[24] proceeded as described in the following paragraphs.

A. SMALL QUANTITIES OF EARTH ACIDS AND MUCH ZIRCONIA

Fuse the mixed oxides with potassium pyrosulfate in a silica crucible, and dissolve the melt in a saturated solution of as much ammonium oxalate as pyrosulfate taken. Boil, add 0.2 g of tannin dissolved in hot water, and then dilute ammonium hydroxide (1 + 1), drop by drop with constant stirring. At or near the neutral point a precipitate will form, which will be whitish if earth acids are present in very small amount, and yellow, orange, or red if they are present in appreciable amount. Continue the addition of ammonium hydroxide until the color of the precipitate lightens as the white zirconium compound starts to precipitate. Let stand at 50 to 70° C until the liquid becomes clear, filter, wash the residue with a 2 per cent solution of ammonium chloride, and ignite in the original crucible. Fuse and dissolve as before, but with less pyrosulfate and oxalate. Boil the clear solution, 50 ml or less, stir, and add dilute ammonium hydroxide until a cloudiness is perceptible. Remove with a minimum of hydrochloric acid (1 + 1). Boil, treat the clear solution with 1 g of ammonium chloride, and then with a freshly prepared 1 per cent solution of tannin (usually less than 10 ml) until the precipitate flocculates and the solution is decolorized. Digest at 50 to 70° C, filter, wash, ignite, and weigh as $Cb_2O_5 + Ta_2O_5$. Retreatment of the boiling filtrate with a little more tannin and a drop of ammonium hydroxide if necessary should produce no change or only a whitish precipitate if the precipitation of earth acids was complete. The weighed precipitate can be fused and the operation repeated to make sure of the absence of zirconium. The behavior of elements such as titanium or thorium is not stated.

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[23] For details of the method, consult W. R. Schoeller and A. R. Powell, *Analyst*, 57, 550 (1932), and W. R. Schoeller and H. W. Webb, *ibid.*, 58, 143 (1933).

[24] *Analyst*, 53, 517 (1928).

B. LARGE QUANTITIES OF EARTH ACIDS AND ANY QUANTITY OF ZIRCONIUM

Fuse the mixed oxides with 6 g of potassium carbonate in a platinum crucible, at 1100 to 1200° C. Let the melt solidify against the inside of the crucible, and disintegrate completely by digesting for 1 to 2 hours with about 1 g of pure potassium hydroxide and enough water to cover the melt in the crucible covered and heated on a hot plate. Transfer the contents of the crucible to a small beaker, stir in paper pulp, and filter. If the filtrate is turbid, refilter. Wash the residue with a 2 per cent solution of potassium carbonate. Ignite in the same crucible, and repeat the operation. Again ignite the residue, moisten with dilute sulfuric acid, dry and remove any remaining earth acids as in A. To obtain the earth acids in the potassium carbonate filtrate or filtrates, acidify with hydrochloric acid, boil, and add a slight excess of ammonium hydroxide. Add a little paper pulp, again boil, filter, and wash the residue with a 2 per cent solution of ammonium nitrate. Ignite gently, digest with 10 ml of hydrochloric acid, dilute with 100 ml of water, boil, treat with ammonium hydroxide, etc., as before, ignite, and weigh as $Cb_2O_5 + Ta_2O_5$.

A fair separation of earth acids from titanium, but not from zirconium or thorium can be obtained by repeated precipitation with salicylic acid.[25]

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[25] J. H. Müller, *J. Am. Chem. Soc.*, 33, 1506 (1911).

The precipitation of the earth acids is never quite complete, and a little titanium remains in the precipitate.[26] The separation is usually made by fusing the mixed oxides with 5 g of potassium carbonate, dissolving the melt in 200 to 300 ml of water at 60° C, pouring slowly and with stirring into a boiling solution containing 15 g of salicylic acid, heating at 100° C for 3 to 4 hours, filtering, and washing the residue with dilute salicylic acid solution. The whole treatment must be repeated as long as the salicylic solution becomes yellow on boiling. Titanium can be precipitated in the filtrate by boiling with an excess of ammonium hydroxide, but the precipitate is contaminated by alkali salts, as is also the earth acid precipitate.

A reasonably complete separation of the earth acids from titanium can be made by boiling their tartaric acid complexes with nitric acid as follows:[26] Fuse 0.1 to 0.2 g of the mixed oxides with 2 g of potassium pyrosulfate in a silica crucible. Cool, dissolve the melt in a strong solution containing 3 g of tartaric acid, and then dilute to 300 ml. Add 30 ml of nitric acid, boil for 15 to 20 minutes, add paper pulp, filter, and wash the crude earth acids with a 1 per cent solution of nitric acid. Ignite, repeat the process, and unite the filtrates which contain most of the titanium, together with a small amount of the earth acids. The small amount of titanium in the crude acids can be determined colorimetrically or separated by the salicylic acid method. The earth acids can be recovered in the combined filtrates by destroying the tartaric acid (p. 66), boiling with more than enough ammonium salicylate to react with the sulfuric acid, and filtering—while the titanium can be obtained by adding ammonium hydroxide to the salicylic acid-ammonium salicylate filtrate.[27]

Aluminum can be quantitatively precipitated and separated from the earth acids by obtaining the three in a dilute sulfuric acid solution containing hydrogen peroxide, adding an excess of 8-hydroxyquinoline, then ammonium hydroxide until the solution contains 10 ml in excess per 100 ml of solution, and precipitating as described under Precipitation by 8-Hydroxyquinoline (p. 122).

The separation of tungsten from the earth acids is very difficult. Extraction of the mixed acids, obtained by hydrolysis, with ammonium hydroxide or ammonium sulfide, or extraction with water after a fusion with sodium carbonate and sulfur as well as the boiling of an alkaline solution of the

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[26] W. R. Schoeller and E. C. Deering, *Analyst,* **52,** 625 (1927). This article presents an excellent review of the methods that have been recommended for the separation of titanium from the earth acids.

[27] By this method, one of us (L.) obtained 0.0321 g of TiO_2 and 0.0599 g of $Cb_2O_5 + Ta_2O_5$ in the analysis of a mixture of 0.0307 g of the former and 0.0620 g of the latter, and 0.0344 g of TiO_2 and 0.0584 g of $Cb_2O_5 + Ta_2O_5$ instead of 0.0325 and 0.0602. The mixtures of earth acids were made up of equal parts of the oxides.

tungstate, columbate, and tantalate are all unsatisfactory.[28] Moreover, tungsten may be incompletely precipitated by cinchonine (p. 689) in the presence of the earth acids. For such separations three procedures,[29] dependent on the elements associated with tungsten, are available, among [illegible] the magnesia method is recommended as generally applicable for [illegible]paration of tungsten in the presence of titanium, columbium, tantalum, [illegible] zirconium. The procedure is as follows: The mixed oxides (0.2 to [illegible] g), are fused with 4 g of potassium carbonate in a platinum crucible over a strong burner for 10 to 15 minutes. The fused mass is taken up in 200 ml of hot water, care being taken to disintegrate any lumps by gentle boiling and manipulation with a glass rod. The crucible is rinsed, and the hot solution is treated with freshly prepared reagent (1 g of crystallized magnesium sulfate, 2 g of ammonium chloride, 25 ml of water, 4 drops of ammonia). The covered beaker is kept on a covered water bath for an hour. The flocculent precipitate is collected on an 11-cm no. 40 Whatman filter, and washed with quarter-saturated ammonium chloride solution.

a. *Determination of the Mixed Earths.* The precipitate is washed back with the same wash liquor; the filter is placed in the platinum crucible intended for the ignition of the tannin precipitate, TP^1. The suspension of the magnesia precipitate (150 ml) is acidified with hydrochloric acid and digested on the water bath for an hour. An equal volume of a saturated solution of ammonium chloride is then added, and the reaction is adjusted with ammonia to slight acidity to litmus paper. The liquid is now treated with 2 g of ammonium acetate and heated to boiling, and fresh 5 per cent tannin solution is added until flocculation is complete. The precipitate, TP^1, is allowed to settle on the water bath, collected with the aid of gentle suction, washed with the ammonium chloride solution, and ignited with the filter from the magnesia precipitate. If TP^1 requires retreatment, it is again fused with potassium carbonate, and the operations above described are repeated, yielding a second magnesia precipitate and a filtrate therefrom which is added to the first. The magnesia precipitate is again treated with tannin as for TP^1, giving TP^2, which is ignited, leached as usual,[30] and weighed as mixed earths.

b. *Determination of the Tungsten.* The filtrate (or combined filtrates) from the magnesia precipitate or precipitates is treated by the tannin and cinchonine method. This procedure,[28] as originally described, is carried out in a solution of high sodium chloride concentration; in the magnesia

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[28] For a discussion of such methods, see W. R. Schoeller and C. Jahn, *Analyst,* **52,** 504 (1927).

[29] A. R. Powell, W. R. Schoeller, and C. Jahn, *ibid.,* **60,** 512 (1935).

[30] Purified by digesting with hot 5 per cent hydrochloric acid, rendering ammoniacal, filtering, washing with 2 per cent ammonium nitrate, and again igniting [W. R. Schoeller, *ibid.,* **56,** 304 (1931)].

method, a filtered, hot-saturated solution of 20 to 30 g of ammonium chloride is added before precipitating the tungsten complex.

Large amounts of silica in the presence of small amounts of the earth acids can be determined by evaporating as usual with hydrofluoric and sulfuric acids. Direct volatilization is not satisfactory with large ar100° C of the earth acids and must be carried out as follows: Transfer the ic acid and weighed oxides to a good-sized platinum dish, dissolve by heating icylic sulfuric and hydrofluoric acids, and completely expel the fluorine th evaporating to fumes of sulfuric acid. Cool, and bring the moist and strongly acid mass into complete solution by adding hydrogen peroxide and, if need be, dilute sulfuric acid. If a small white precipitate shows on standing, it is probably lead sulfate. Collect on a Munroe filter, wash with dilute sulfuric acid containing hydrogen peroxide, ignite gently, weigh, and test to make sure that it contains no other substances. To the filtrate add sulfur dioxide, boil to expel all hydrogen peroxide, and add ammonium hydroxide in excess. Filter, wash with a 2 per cent solution of ammonium nitrate, ignite, and weigh. The difference between this and the earlier weight should represent the silica with a fair degree of accuracy if no lead was found. If lead was found, the difference noted is to be decreased by a proper amount for the lead. What this shall be cannot be said with certainty. If the ignited earth acids contained the lead as sulfate, then the correct deduction is that of the lead sulfate found. If, however, the ignition of the earth acids had resulted in expulsion of SO_3 and formation of lead columbate, for example, then the equivalent of PbO should be deducted in order to arrive at the proper value for silica.

According to Schoeller and Powell,[31] the separation of silica from the earth acids can also be carried out as follows: Fuse the mixed oxides with 3 g or more of potassium pyrosulfate, cool, digest on the water bath with 50 ml of water containing 3 g of oxalic or tartaric acids, filter, and wash the residue with hot water. Ignite, weigh, treat with hydrofluoric and sulfuric acids, evaporate, ignite, and again weigh.

Tantalum, together with columbium, titanium, zirconium, hafnium, and tin, can be quantitatively gathered in solutions of rocks by precipitating with 5 to 10 g of phenylarsonic acid in 300 ml of boiling 2 to 3 *N* hydrochloric acid containing moderate amounts of sulfuric acid, 5 g of tartaric acid, and a little paper pulp; digesting on the water bath for 2 hours and then at room temperature for 48 hours; filtering; and washing the precipitate with cold dilute (1 + 10) hydrochloric acid or with a cold 2 per cent solution of ammonium nitrate. Complete solution of the rock may require (1) digestion with hydrofluoric and sulfuric acids, followed by complete expulsion of the hydrofluoric acid, addition of tartaric acid solution, and filtration, (2) fusion of any residue with sodium carbonate, followed by solution in hydrochloric acid and filtration, and (3) fusion of any residue with potassium pyrosulfate, followed by solution of the melt in tartaric acid solution.[32]

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[31] W. R. Schoeller and A. R. Powell, *ibid.*, **53**, 262 (1928).

IV. METHODS OF DETERMINATION

As a general rule, the last stages of the analysis leave columbium and tantalum still associated with more or less of the titanium that was originally present. In the long run it is probably more satisfactory to concentrate on the separation of columbium and tantalum and then to determine the amount of titanium that is contained in each weighed oxide.

Tantalum is finally weighed as the pentoxide, Ta_2O_5, in all of the common procedures. Columbium can be weighed as the pentoxide, Cb_2O_5,[33] or determined volumetrically by reducing with zinc in sulfuric acid solution and titrating with permanganate.[34]

A. SEPARATION OF TANTALUM FROM COLUMBIUM BY PRECIPITATING WITH TANNIN IN OXALIC ACID SOLUTION

Possibly the best method for the separation of tantalum from columbium is that developed by W. R. Schoeller.[35] This method is based on differences in the behavior of oxalotantalic and oxalocolumbic acids in dilute acid solutions of tannin. The former is stable only in the presence of a certain amount of free oxalic acid; the latter is much more stable. The color of the precipitate with tantalum is sulfur yellow; that with columbium is bright vermilion and sufficiently intense to betray its presence in the tantalum precipitate. Titanium,[36] tungsten,[37] and antimony,[38] but not zirconium,[38] are partially precipitated and interfere in the separation. Titania, if present in amounts of 2 per cent of the tantalic oxide being determined, is not harmful.[39]

No doubt there are other elements that interfere, and so in a mineral analysis the oxides of columbium and tantalum had better be separated from other elements before the application of the method.

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[32] K. Rankama, *Bull. comm. géol. Finland* **133** (1944).

[33] The pentoxides of columbium and tantalum can be ignited at 1100 to 1200° C without loss and are not hygroscopic. Both volatilize to a marked extent when ignited after evaporation with hydrofluoric acid alone.

[34] For a comprehensive discussion of methods of determination, consult W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium*, Chapman & Hall, London (1937); see also W. R. Schoeller, *Analyst*, **61**, 806 (1936).

[35] *ibid.*, **57**, 750 (1932).

[36] W. R. Schoeller and A. R. Powell, *ibid.*, **53**, 265 (1928).

[37] W. R. Schoeller and C. Jahn, *ibid.*, **59**, 465 (1934).

[38] A. R. Powell and W. R. Schoeller, *ibid.*, **50**, 494 (1925).

[39] W. R. Schoeller, *ibid.*, **57**, 755 (1932).

Briefly, the method[40] involves fusion of the mixed oxides with acid potassium sulfate in a silica crucible, solution of the melt in a hot solution of saturated ammonium oxalate, filtration, and retreatment of the insoluble, if necessary. The boiling solution, when cautiously and properly treated with a fresh 2 per cent water solution of tannin, preferably added from a burette, followed by the addition of a saturated solution of ammonium chloride, produces either a yellow (Ta) or an orange- to red-colored precipitate (Ta + Cb). Following filtration and washing of the precipitate, further treatment of the filtrate with dilute ammonium hydroxide and tannin results in precipitation of a deeper-colored orange or red precipitate. The pure yellow fraction is ignited in porcelain and weighed as Ta_2O_5, while the orange or red precipitates are combined, ignited, fused with bisulfate, leached as before, and again precipitated with tannin. By repetition of the process, a tantalum fraction is obtained, contaminated with adsorbed salts, silica, titania (if present), and a very small amount of columbium, while the columbium fraction is recovered from the combined filtrates by precipitation with tannin and ammonium hydroxide. Each fraction requires purification and correction for titania.

B. SEPARATION OF COLUMBIUM FROM TANTALUM BY DIGESTING THE OXIDES WITH SELENIUM OXYCHLORIDE

According to H. B. Merrill,[41] columbium can be separated from tantalum by extracting the mixed oxides with selenium oxychloride as follows: Transfer the strongly ignited and weighed mixture of the earth acids (0.2 to 0.3 g and preferably free from titanium) to a flask, treat with 50 ml of a mixture in equal parts of selenium oxychloride[42] and sulfuric acid, and boil on a sand bath for half an hour, but not so strongly that clouds of vapor are given off. After cooling and settling, decant the liquid with suction through a weighed Gooch crucible with asbestos mat. Boil the residue in the flask with 20 ml of the reagent for 15 minutes, and decant through the crucible. Repeat until the filtrate, when poured into 1000 ml of water and boiled, gives only a faint precipitate caused by traces of dissolved tantalic oxide. Take care that as little as possible of the solid passes onto the filter. Three or four treatments usually suffice. Then transfer the residue to the filter by means of a jet of water, and wash with water. The washing need not be thorough, as the decomposition products of the reagent are volatile. Ignite, and weigh as Ta_2O_5. If titanium was present, it is with the columbium, and should be determined colorimetrically in a

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[40] For details concerning the procedure and illustrative examples, reference should be made to the original article or to W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium, loc. cit.*

[41] *J. Am. Chem. Soc.*, 43, 2378 (1921).

[42] V. Lenher, *ibid.*, 29.

separate sample and its weight deducted from the sum of the columbic and titanic oxides found by difference.

In Merrill's tests, the maximum divergence on prepared mixtures of Cb_2O_5 and Ta_2O_5 was 3 per cent of the total, and in most cases less. Greater divergencies would no doubt be found if the method is applied to mixtures containing impurities.

C. SEPARATION OF COLUMBIUM AND TANTALUM FROM EACH OTHER BY MARIGNAC'S METHOD

For the actual separation of columbium and tantalum from each other, the oldest method is the classical one of C. Marignac[43] which leaves much to be desired, being tedious and only approximate. According to Meyer and Hauser, an accuracy of 0.5 per cent can be attained by careful work and by using large samples—15 to 30 g. The method depends upon a difference in the solubilities in hydrofluoric acid of potassium-tantalum fluoride, K_2TaF_7, and potassium-columbium oxyfluoride, K_2CbOF_5. It has been modified, primarily for factory control, by several analysts. Mellor[44] employed the method in the following form: Dissolve the freshly precipitated and washed mixed oxides, preferably free from titanium and zirconium, in just enough hydrofluoric acid. Avoid an excess. Boil and add, slowly and with constant stirring, a boiling solution of potassium fluoride twice the weight of the oxides. Evaporate to a volume of 10 ml, washing down the inside of the dish with a few drops of water toward the end, and cool slowly to 15° C or lower. Decant the clear solution through a small paper in a rubber or Bakelite funnel, and wash the felted mass of crystals of potassium fluotantalate with a little cold water four times. Evaporate the decanted liquid and washings to 5 ml, let cool slowly, decant through a second smaller paper and wash as before. If flakes of columbium salt are visible, wash until dissolved. Evaporate the filtrate and washings to dryness on the water bath, cool, add one drop of hydrofluoric acid, take up the residue in 1 to 5 ml of water added from a burette, and warm until all is dissolved. Add 0.1 g of potassium fluoride dissolved in 1 ml of water. Record the volume of the solution (A). Cool for 30 to 60 minutes at 15° C, filter into a small platinum dish, and wash three or four times with a few drops of cold water. Record the volume of washings (B).

To determine the columbium, evaporate the filtrate with sulfuric acid, making sure that all fluorine is expelled, cool, dilute, and precipitate with ammonium hydroxide in slight excess, at boiling heat. Filter, wash with

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[43] *Ann. chim. et phys.*, [4] **8**, 60 (1866).

[44] *A Treatise on Quantitative Inorganic Analysis*, p. 421, Charles Griffin and Co., London (1913).

a hot 2 per cent solution of ammonium nitrate, and ignite. Add solid ammonium carbonate, cover the crucible, heat cautiously, ignite at 1100 to 1200° C, and weigh. Allow for a tantalum content of the columbic oxide as follows: For each milliliter of acid liquid (A), deduct 0.002 g, and, for each milliliter of washings (B), deduct 0.00091 g. The tantalum is found by difference if the weight of the oxide mixture was known, or it can be determined directly like the columbium, with due plus correction for the Ta_2O_5 that was deducted from the Cb_2O_5. Should titanium be present, determine this colorimetrically in each oxide.

E. Meimberg and P. Winzer [45] dissolved the mixed oxides in just enough hydrofluoric acid to form the double fluorides, and proceeded as follows: Add an excess of a saturated solution of potassium chloride, let cool, and adjust the solution so that potassium-columbium oxyfluoride remains in solution (solubility of potassium-columbium oxyfluoride in water, 1 in 12). Filter, wash with a cool saturated solution of potassium chloride, dissolve in water containing a little hydrofluoric acid, add more potassium chloride solution, cool, filter, and wash as before. Heat the precipitate with sulfuric acid, expel the fluorine, and precipitate the tantalum by ammonium hydroxide after taking up with water acidulated with hydrochloric acid. Evaporate the filtrates with sulfuric acid, heat to expel fluorine, and determine the columbium as in the preceding method. If titanium was present in the mixed oxides, it should be determined colorimetrically in both the columbic and tantalic oxides.

The studies of O. Ruff and E. Schiller enabled them to devise the following modification: [46] Dissolve 0.5 to 1 g of the oxides, preferably free from titanium, in just enough hydrofluoric acid. If more than enough was used, evaporate the excess, and take up the residue with water. Add hydrofluoric acid so as to have 4.3 per cent in excess, and then potassium fluoride in a calculated amount (to form K_2CbOF_5) based on regarding the whole of the weighed oxides as columbium. Evaporate to dryness, boil the residue with hydrofluoric acid in 0.75 per cent strength, filter hot, wash at once with two portions of hot water each of 10 ml. Reserve the residue, evaporate the filtrate to dryness, and heat at 120°. Take up with an excess of hot water, and treat with 0.1 *N* potassium hydroxide solution as long as the precipitate that forms redissolves. Evaporate, take up the residue with 10 ml of water, and again evaporate. Repeat twice more the taking up with water and evaporating. In this way the salt, $K_4Ta_4O_5F_{14}$ is stabilized and can be filtered. All the columbium is said to be in the filtrate, from which it can be recovered as set forth above. The combined precipitates can be treated similarly for their tantalum content.

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[45] *Z. angew. Chem.*, 26, 158 (1913).
[46] *Z. anorg. Chem.*, 72, 348 (1911).

According to Fucke and Daubländer,[47] tantalum can be precipitated and separated from columbium in 0.1-g mixtures of their oxides containing from 0.01 to 0.09 g of Cb_2O_5, by precipitating with phenylarsonic acid, $C_6H_5 \cdot AsO \cdot (OH)_2$, in sulfuric acid solution containing hydrogen peroxide. Separations are not strictly quantitative, but are said to suffice for routine work in which plus or minus errors, of say 5 per cent of the amount of oxide present, are not serious. See also Zirconium (p. 567).

A chromatographic separation (99%+) of columbium from tantalum in HCl—HF mixtures, using an anion exchange resin of the strong base type, is described by K. A. Kraus and G. E. Moore.[48]

D. VOLUMETRIC DETERMINATION OF COLUMBIUM [49]

The quantitative determination of columbium, based on reduction by amalgamated zinc and reoxidation with potassium permanganate has, in general, produced results that lack both accuracy and precision. A study of the various factors involved indicates that essential conditions require adequate duration of reduction in the presence of an excess of zinc and a proper concentration of both acid and columbium. In the procedure to be described, columbium, in a sulfuric acid solution, is quantitatively reduced by amalgamated zinc to the trivalent state and subsequently oxidized to the quinquevalent state. For satisfactory results, careful attention must be given to the amalgamation of the zinc, the length of the reductor, and to the acidity, temperature, and concentration of columbium in the solution to be reduced.

A study of the reducing action of amalgamated zinc [50] indicates that, for a number of elements, it is requisite that the zinc be but lightly coated with mercury. Satisfactory amalgamation is accomplished as follows: Transfer 1000 g of 20-mesh zinc metal (low in iron) to a stout, wide-mouthed glass bottle, add 500 ml of a 2 per cent aqueous solution of mercuric chloride, mix continuously for 45 to 60 seconds, discard the solution, and wash five times with distilled water. Treat the washed amalgamated zinc with 500 ml of warm, dilute sulfuric acid (1 + 99), mix, discard the acid, and wash thoroughly with distilled water. The prepared amalgam is preferably preserved in water to which a few drops of hydrochloric acid have been added. The period of use of an amalgam thus prepared is limited. With continued use, it eventually loses its efficiency and can no longer be used for this purpose.

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[47] H. Fucke and J. Daubländer, *Tech. Mitt. Krupp*, **14**, 174 (1939).
[48] *J. Am. Chem. Soc.*, **71**, 3855 (1949).
[49] H. B. Knowles and G. E. F. Lundell, *J. Research NBS*, 42, 405 (1949).
[50] H. W. Stone and D. N. Hume, *Ind. Eng. Chem. Anal. Ed.*, 11, 598 (1939); H. A. Liebhafsky, *J. Am. Chem. Soc.*, **59**, 452 (1937).

A study of the acid concentration necessary for the quantitative reduction of columbium indicates that the solution should contain preferably 20 per cent by volume but never less than 15 per cent by volume of sulfuric acid. With the latter concentration, there is a general tendency to slightly low but still satisfactory values. Under these conditions the reduced solution is clear and possesses an "amethyst-like" color. At lower concentrations of acid, the reduced solution exhibits a dark (blackish) color and yields low values on titration.

The presence of small amounts of succinic acid, introduced as an aid to prevent hydrolysis, if not beneficial at least exerts no harmful influence.

Experiments indicate that essential factors for satisfactory reduction involve the time of contact of the solution with the amalgam and the amount of available zinc. The latter, in turn, is a function of both the active area of the amalgam and the degree of amalgamation. The time for the passage of all solutions through the reductor should be not less than 25 minutes.

Definite limitations regarding the maximum concentrations of columbium for use with various reductors are difficult to define, because the solution, when introduced into the reductor, undergoes dilution and, owing to nonuniform mixing, lacks homogeneity. Although concentrations of as high as 1.7 mg of Cb_2O_5 per ml have been reduced quantitatively at times with a long (33-in.) reductor, a critical study indicates a concentration not greatly exceeding 1.0 mg per ml to be desirable. Similarly, the concentration for use with a short (18-in.) reductor should not exceed 0.7 to 0.8 mg per ml.

Although heat is not essential to quantitative reduction, all reductions are preferably conducted at a temperature of 65 ± 5° C. This temperature facilitates the diffusion of zinc through the amalgam and effects more vigorous action during passage of the solution through the reductor.

The following procedure describes conditions suitable for solutions that may contain as much as 300 mg of Cb_2O_5 and requires the use of a reductor having a long column (33-in.) of amalgamated zinc. With solutions containing not more than 175 mg of the oxide, satisfactory reductions can be effected in a shorter reductor, such as one with an 18-in. column.

RECOMMENDED PROCEDURE. Fuse a dry weighed sample of not more than 300 mg of the oxide in a 25-ml covered silica (or equivalent) crucible with 3 to 5 g of potassium pyrosulfate. Cool, transfer the covered crucible with contents to a covered 250-ml beaker, add 20 ml of sulfuric acid, and heat moderately to dissolve the melt. Cool, add 1 to 2 ml of hydrogen peroxide (30%), cautiously dilute with 100 ml of water, and rinse and remove the crucible and cover. Cool, add 20 ml of sulfuric acid, dilute to 200 ml with water, add 2 g of succinic acid, and heat moderately, while stirring, until the succinic acid dissolves.

Reduce the columbium in a reductor having a 33-in. column in the following manner: First clean and preheat the reductor by pouring through it hot dilute sulfuric acid (1 + 19) and then hot water (90° C). Discard the washings. Place a three-fold excess of ferric iron in the receiver, and attach to the reductor. Pour into the reductor 100 ml of sulfuric acid (1 + 4) heated to 65 ± 5° C. With the aid of suction, draw through the reductor the foregoing solution, then the solution of the columbium, then 150 ml of sulfuric acid (1 + 4) containing 1 per cent of succinic acid, each at 65 ± 5° C, and finally 200 to 250 ml of cold water, slowly and without interruption at such a rate (unchanged) that the total time for the passage of all solutions is not less than 25 minutes. Cool the solution of reduced columbium by immersion of the receiver in ice water during the operation. Remove the receiver from the reductor, rinse, and drain the outlet tube in the customary manner. Add 10 ml of phosphoric acid (85%) and titrate with a 0.1 *N* solution of potassium permanganate (0.0066455 g of Cb_2O_5 per ml), using orthophenanthroline as an indicator. Correct the titration by deducting the amount of potassium permanganate consumed by a blank determination, involving all reagents, obtained under identical conditions. To insure absence of oxidizable impurities, each of the acid-wash solutions is permanently tinted, while hot, by the addition of a few drops of a solution of potassium permanganate.

E. DIRECT COLORIMETRIC DETERMINATION OF COLUMBIUM

At low concentrations of sulfuric acid, columbium yields a light-yellow color with hydrogen peroxide. The intensity of the color increases as the strength of the acid is increased, and reaches its maximum in 100 per cent of acid (sp. gr. 1.845 at 15° C).[51] Tantalum yields no color. The color of the titanium compound fades with increasing acidity, and reaches such a low intensity at 100 per cent acid that colorimetric determinations of columbium, with correction for any titanium present, can be made as follows:

PROCEDURE. Obtain the mixed oxides of tantalum and columbium, preferably weighing about 0.1 g and obtained by a method that removes most of the titanium. Ignite and weigh. Fuse with 5 g of potassium pyrosulfate, and dissolve the melt in 10 milliliters of sulfuric acid, and an equal volume of hydrogen peroxide (3%). Add 20 ml of the peroxide, and dilute to definite volume, keeping the acidity at approximately 10 to 20 per cent by volume. Determine the transmittancy of the whole solution, or a definite part of it, in a photometer with an appropriate filter (Hg 436), and calculate the percentage of titanium oxide by comparison with known standards or by interpolation from a prepared curve. Evaporate the solution to fumes

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[51] P. Klinger and W. Koch, *Tech. Mitt. Krupp Forschungsber.*, **14**, 179 (1939).

of sulfuric acid, dilute to definite volume with 100 per cent acid, add 1 milliliter of hydrogen peroxide (30%), and determine the transmittancy of the whole, or a definite part of it, through an appropriate filter (Hg 436). Calculate the apparent columbium content from a curve prepared by using known amounts of columbium. To obtain the true amount, subtract 0.70 mg of columbium for each 0.422 mg of titanium found. Tantalum is obtained by difference.[52]

F. PHOTOMETRIC DETERMINATION OF TANTALUM

A photometric procedure for the determination of tantalum based on the formation of a yellow complex with pyrogallol in faintly acid ammonium oxalate solution is described by G. Thaneiser.[53] Titanium and molybdenum also form colored complexes with pyrogallol, and provision must be made for the color of ferric oxalate.

G. PROTACTINIUM (EKATANTALUM)

Protactinium is apparently a very rare element, its percentage in the earth's 10-mile crust, 7×10^{-11} according to present estimates, being lower than that of any of the known elements save radon. What little has been isolated was separated from zirconium phosphate residues obtained in the process of refining radium from pitchblende.

In its behavior toward reagents, protactinium is quite unlike columbium or tantalum.[54] Analytically it shows marked resemblance to zirconium in (1) yielding a solution when the oxide is fused with pyrosulfate and the melt is dissolved in dilute sulfuric acid, (2) remaining insoluble when the oxide is fused with potassium carbonate and the melt is dissolved in water, (3) being completely precipitated by (*a*) hydrogen peroxide added in excess to warm (40 to 60° C) 2 per cent sulfuric acid, (*b*) ammonium hydroxide, and (*c*) phosphoric acid in dilute sulfuric acid containing hydrogen peroxide, and (4) yielding no precipitate with hydrofluoric acid.[55]

Protactinium pentoxide is a heavy white powder which has a high melting point and is insoluble in concentrated sulfuric, nitric, or hydrochloric acid. It is a distinctly, though feebly, basic oxide without acidic properties.

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[52] For the ultraviolet spectrophotometric determination of columbium, see G. Telep and D. F. Boltz, *Anal. Chem.*, **24**, 163 (1952).

[53] *Mitt. Kaiser Wilhelm Inst. Eisenforsch. Düsseldorf*, 22, 255 (1940).

[54] A. V. Grosse, *J. Am. Chem. Soc.*, **52**, 1742 (1930); M. Bachelet and G. Bouissières, *Bull. soc. chim.*, **11**, 169 (1944).

[55] For a method for the radioactive determination of protactinium in siliceous terrestrial and meteoric material, following coprecipitation with zirconium phosphate and purification of the ignited pyrophosphate, consult W. C. Schumb, R. D. Evans, and J. L. Hastings, *J. Am. Chem. Soc.*, **61**, 3451 (1939).

THE ALKALINE EARTHS AND MAGNESIUM

Calcium, Strontium, Barium, Magnesium, (Radium)

Chapter 40

THE ALKALINE EARTHS—CALCIUM, STRONTIUM, BARIUM

Calcium is one of the most abundant metals, but, like strontium and barium, it is never found in nature uncombined. It is an essential constituent of many rock-forming minerals, and occurs as the carbonate, limestone; the sulfate, gypsum; the fluoride, fluorspar; the fluo- or chlorophosphate, apatite; and in many other mineral species. Feldspathic rocks are those most likely to carry barium and strontium, the former almost always in excess of the latter.[1] Barium has been found in a few peculiar rocks in excess of 1 per cent, in terms of the oxide, but, in the greater part of the silicate rocks of the United States, its percentage is well below 0.2. It is found also as the sulfate, barite, and the carbonate, witherite. Strontium has been found as high as 0.3 to 0.4 per cent, but generally there is little more than a trace of it. The most important strontium minerals are the sulfate, celestite, and the carbonate, strontianite.

I. GENERAL CONSIDERATIONS

The alkaline earth metals cause no trouble in an ordinary analysis if the solution contains only chlorides or hydrochloric acid. Other acids or their salts may cause difficulties. For example barium (and sometimes strontium and calcium) will be found with silica if sulfuric acid or sulfates are present; calcium will be precipitated by ammonium hydroxide if the solution contains fluorides; and all three earths may be found in the ammonia precipitate if carbonates are present or phosphoric acid preponderates over iron or aluminum.

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[1] There is some evidence that barium is apt to be most abundant in rocks that are high in potash. Barium occurs in the feldspars, especially orthoclase, as the celsian molecule, in the rare hyalophane, in some zeolites, as well as in a few biotites and muscovites. We can at present form no definite conclusion concerning the character of the rocks most likely to carry strontium, and more analytical data on this point would be of interest.

II. DECOMPOSITION OF ALKALINE-EARTH MINERALS

The decomposition of alkaline earth minerals presents no difficulties and is carried out by direct solution in acids, usually hydrochloric; by fusion with carbonate, followed by solution in acid; or by preliminary solution in acid, as with limestone, followed by fusion of the insoluble matter.

III. METHODS OF SEPARATION

In general, the alkaline earths are easily separated from interfering elements by the use of ordinary procedures, such as precipitation with hydrogen sulfide in acid solution, with ammonium hydroxide (avoiding any large excess), or with ammonium sulfide. Sulfates must of course be avoided if barium or an appreciable amount of strontium is present, and substances such as phosphates and arsenates cause trouble in ammoniacal solutions that do not contain enough iron, aluminum or the like to take care of them.

Electrolysis with a mercury cathode in dilute acid solution (p. 138) yields excellent separations of the alkaline earths and magnesium from elements, such as zinc, iron, or chromium, that can be deposited in the mercury.

A. SEPARATION OF CALCIUM FROM MAGNESIUM

When calcium is preponderant, it is usually separated from magnesium by double precipitation with ammonium oxalate as described on page 622. Satisfactory separations can also be had by this method if the amount of magnesium equals or is in moderate excess over that of calcium, but triple precipitations may be required.[2] In such cases the same end is attained in fewer precipitations, but with more labor by Richard's method as outlined on page 624.[3]

Calcium can be quantitatively separated from magnesium by precipitation with ammonium molybdate in a boiling feebly acid or feebly alkaline solution.[4] The precipitated calcium molybdate can be caught in a filtering crucible, washed with hot water, dried at 130° C, and weighed as such.

When an extremely accurate determination of very little calcium is desired, especially in the presence of much magnesium, as in magnesite, direct precipitation as oxalate is not satisfactory. The hitherto available methods are all based on the precipitation of the calcium, first as sulfate by the aid of alcohol, then as oxalate. Precipitation as sulfate, however, presupposes absence of alkali metals, the sulfates of which are for the most part difficultly soluble in alcohol. Hence the method is not suitable for those mineral substances that must first be attacked by an alkali fusion, of which most of the natural silicates are the foremost examples. Moreover, of the available methods—that of C. Stolberg[5] as modified by O. Kallauner and I. Preller[6] and the E. Murmann method[7]—one involves the use of lithium sulfate, and the other presupposes knowledge of the amount of calcium present. A much more satisfactory method is based on one that was devised by the senior author for the recovery from the magnesium pyrophosphate precipitate of the small amount of calcium that escapes precipitation as oxalate. As here applied, the usual precipitation with oxalate is omitted, and calcium is precipitated as phosphate along with the magnesium and recovered as follows: Precipitate the magnesium together with the calcium as phosphate by the method given under Magnesium (p. 636).[8] Transfer the weighed precipitate to a small beaker, and dissolve it in a little dilute sulfuric acid, avoiding more than approximately 0.5 ml in excess. In case the precipitate dissolves with difficulty, boil it with nitric acid, and evaporate until copious fumes of sulfuric acid appear. Add 100 ml of 75 per cent alcohol (by volume) for every 0.3 g of pyrophosphate originally present, and allow the solution to stand for several hours, or preferably overnight if the amount of calcium is very small.[9] Filter, wash the residue of calcium sulfate with alcohol of 75 per cent strength, and dry the precipitate. Dissolve it in very little dilute hydrochloric acid, precipitate as oxalate in as small a volume as possible, and finally ignite to oxide.[10] If magnesium is not to be determined, the precipitated phosphate may be dissolved at once without igniting and weighing it.[11]

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[2] For example, in three analyses of a dolomite containing 21.54% of MgO, the percentages of CaO indicated after double precipitations were 30.63, 30.62, and 30.68. When the weighed residues were dissolved and reprecipitated, the percentages dropped to 30.48, 30.45, and 30.49. When these in turn were dissolved and precipitated for the fourth time, the percentages remained exactly the same.

[3] For example, in analyses of the dolomite mentioned in the preceding footnote, single precipitations gave 30.84, 30.79, and 30.78; double precipitations gave 30.42 and 30.40; whereas a triple precipitation gave 30.44.

[4] R. C. Wiley, *Ind. Eng. Chem. Anal. Ed.*, **3**, 127 (1931).

[5] Z. *angew. Chem.*, **17**, 741 (1904).

[6] *Chem. Ztg.*, **36**, 449, 462 (1912).

[7] Z. *anal. Chem.*, **49**, 688 (1910).

[8] Barium also accompanies magnesium, but precipitation of the barium is not quite quantitative, even when magnesium preponderates. Lithium is not retained at all if magnesium is precipitated twice in cool solution.

[9] This mixture dissolves approximately 0.06 g of MgO as $MgSO_4$ and less than 0.1 mg of CaO per 100 ml. A mixture containing 90 parts of ethyl alcohol, 10 parts of methyl alcohol, and 1 part of sulfuric acid is equally satisfactory as regards the precipitation of calcium sulfate and dissolves 0.46 g of MgO as $MgSO_4$ per 100 ml.

[10] Tests made for us by H. B. Knowles showed that the recovery of calcium was complete by this method in mixtures of 0.0005 g CaO and 0.1 g MgO, 0.001 g CaO and 0.05 g MgO, and 0.05 g of both CaO and MgO.

[11] For the separation of calcium as sulfate in alcoholic solution prior to the determination of magnesium in phosphate rock, see J. I. Hoffman, *Bur. Standards J. Research*, **9**, 487 (1932).

According to A. C. Shead and B. J. Heinrich,[12] calcium oxide can be extracted by a 30 per cent solution of cane sugar and quantitatively separated from magnesium oxide in a freshly ignited mixture of the two oxides.

B. SEPARATION OF CALCIUM, STRONTIUM, AND BARIUM FROM OTHER ELEMENTS

It is preferable that, for their separation from one another, the three alkaline earth metals be brought to the condition of chlorides or anhydrous nitrates. Before this can be done, they must as a rule first be separated from other elements by removing some of these and completing the separation of the remainder by a group precipitation of the alkaline earth metals themselves.

a. *Group Separation as Oxalates.* Ordinarily the group separation is imperfectly made as oxalates, and these are converted by ignition to oxides in the manner prescribed for calcium (IV, A, p. 624). See C below for further treatment. The differing behavior of the metals toward ammonium oxalate needs to be well understood. No one of the oxalates is entirely insoluble under the conditions that obtain. Strontium precipitates nearly as completely as calcium, but barium very incompletely.[13] When present in amounts up to 3 or 4 mg, barium will never be found with the calcium and strontium oxides after a second precipitation, and very often not when in even greater amount. It must be recovered from the combined filtrates from the oxalate precipitates, of which there will be two ordinarily. If, however, the amount of barium is such that a third oxalate precipitate will hold none of it, a third precipitation may be advisable, as is the case also when much magnesium is present. In any event, the filtrates must be evaporated, the contained ammoniacal salts expelled by careful heating in a dish of platinum or porcelain, or by the action of concentrated nitric acid in a dish of porcelain (with a large funnel inverted over the liquid to prevent loss by spattering), the residue taken up with barely enough water to effect ready solution, and a little sulfuric acid added, followed by alcohol in volume equal to that of the solution. This will insure throwing out the barium and strontium, but perhaps not all of the little calcium that is sure to have escaped precipitation as oxalate, which remainder will be recovered from the magnesium pyrophosphate. The small sulfate precipitate is to be filtered, ignited, converted to nitrate, and this added to the nitrate solution of the main portion. Direct recovery of barium by precipitation with magnesium phosphate, as is done with calcium and strontium, is not permissible because of the slight solubility of barium phosphate.

b. *Group Separation as Sulfates.* Under special conditions, the separation as sulfates may be made as prescribed for calcium (IV, A, p. 629) and is superior to the oxalate method above described as regards completeness of precipitation, but it has drawbacks in other respects. The sulfates must be ignited and fused with sodium carbonate, and the melt leached with water and then dissolved in hydrochloric or nitric acid, of which the excess is to be expelled by evaporation. See next section for further treatment.

C. SEPARATION OF CALCIUM, STRONTIUM, AND BARIUM FROM EACH OTHER

No really good methods for separating calcium, strontium, and barium from each other are known. They are all imperfect and give correct results only through compensating errors. The separation is done in either of two ways, according to whether nitrates or chlorides are dealt with. (1) From the dry nitrates, calcium nitrate is extracted through its solubility in a mixture of absolute alcohol and ether or in concentrated nitric acid. From the aqueous solution of the residual nitrates, barium is removed and weighed as chromate, and strontium is determined in the filtrate. (2) From the chlorides, barium is precipitated as chromate, and, from the filtrate, calcium and strontium are thrown out as carbonates, these converted to nitrates, and the latter in turn separated by alcohol-ether as in a below.

a. *Separation of Calcium from Barium and Strontium.* 1. *By alcohol-ether.* R. Fresenius[14] stated that the solubility of strontium nitrate (dried at 130°) in a mixture of equal volumes of absolute alcohol and absolute ether at room temperature is 0.0023 g in 250 ml, whereas under the same conditions 0.37 g of calcium nitrate is soluble in 1 ml of the solvent. His tests of the method showed that results for strontium are high while those for calcium are correspondingly low.

First will be given directions for handling precipitates that contain strontium and barium in small amounts relative to the calcium (as will happen in the great majority of cases as in rocks), and then for the conditions that obtained in Fresenius's tests of the method.

α. With small amounts of strontium or barium or both. The first step is to convert to nitrates either the mixed carbonates obtained from the sulfates as described above (b), or the weighed oxides resulting from ignition of the oxalates (p. 614). Ignite the carbonates to oxides. Transfer the oxides in either case to a flask of small capacity (20 to 25 ml is quite large enough as a rule), using a drop or two of nitric acid if necessary;

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[12] *Ind. Eng. Chem. Anal. Ed.*, **2**, 388 (1930); see also A. C. Shead and R. K. Valla, *ibid.*, **4**, 246 (1932).

[13] W. F. Hillebrand, *J. Am. Chem. Soc.*, **16**, 83 (1894); C. A. Peters, *Am. J. Sci.*, [4] 12, 216 (1901). According to the latter, strontium is almost completely precipitated in a solution containing one-fifth its volume of 85 per cent alcohol, and barium in a solution containing one-third its volume.

[14] *Z. anal. Chem.*, **32**, 189 (1893).

add enough of the same acid to dissolve all of the oxides; and evaporate to complete dryness without spattering. Aspiration helps greatly. The final temperature should be 150 to 160° C, though, according to Fresenius, 180° does no harm.[15] When cool, pour upon the dry mass 10 times its weight of absolute alcohol, cork, swirl gently, and let stand for 1 to 2 hours. Add then an equal volume of absolute ether, cork, swirl gently, and let stand overnight. Collect the insoluble nitrates of barium and strontium on a perforated filter with thin asbestos pad, or a platinum felt, and under gentle suction. If a paper filter is used, it should be as small as is consistent with the size of the precipitate and with speed in washing. The wash fluid is a mixture of absolute alcohol and absolute ether in equal volumes. If there is much insoluble matter, dissolve the washed and dried contents of the filter in hot water, evaporate, and dry in the flask as before, and repeat the treatment with alcohol and ether. In the combined filtrates and washings, after evaporating at a low temperature, determine the calcium, if desirable, by one of the methods given under IV, A.

Dry the undissolved nitrates by very gentle warming, and pass enough hot water through the filter to dissolve them. Burn the extracted paper, and weigh the ash, or weigh the Gooch crucible. The residue will seldom if ever weigh half a milligram and is usually free from any alkaline earth compound; hence its weight is to be deducted from the gross weight of the oxides, unless it can be shown that it came from the glass of the flask in which the nitrates were evaporated. For the treatment of the solution see D below.[16]

β. With large amounts of strontium or barium or both. Dry the nitrates in a casserole at 130°, crush them, and extract with five 5-ml portions of the alcohol-ether mixture. Stir the solution after each addition, and decant into a small flask as soon as the residue settles. Stopper the flask and set it aside. Dissolve the residue in water, evaporate to dryness, and again dry at 130°. Crush the residue, transfer it to the flask, and sluice as much of any adhering nitrates as possible from the casserole to the flask by means of three 5-ml portions of the solvent. Reserve the casserole. Stopper the flask, shake occasionally, and let stand for 24 hours, filter through a small filter, and wash by decantation with twelve 5-ml portions of the solvent. If the calcium is to be determined, treat the filtrate as indicated in α above.

Dissolve the nitrate that is in the casserole, the filter, and the small flask in water; add alcohol; precipitate with sulfuric acid; and weigh as sulfates.

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[15] Manganese nitrate is decomposed before these temperatures are reached and gives rise to black oxides. It must therefore be separated before the separation of strontium is attempted.

[16] By a single extraction, H. B. Knowles obtained 0.0094 g of SrO in a mixture containing 0.008 g of SrO and 0.1 g of CaO, and 0.0661 g of SrO in a mixture of 0.0641 g of SrO and 0.05 g of CaO.

2. *By extraction with nitric acid.* S. G. Rawson[17] based a method upon the fact that calcium nitrate is soluble in concentrated nitric acid whereas the nitrates of strontium and barium are not appreciably so. Rawson preferred an acid having a specific gravity of 1.46 but stated that one of 1.42 is satisfactory. Approximately 0.7 g of calcium nitrate is soluble in 100 ml of the former, whereas 7 g is soluble in a like volume of the latter.

Upon the dry nitrates, pour concentrated nitric acid in excess, and stir well for some time. The crystals settle rapidly. Pour the clear supernatant liquid through a platinum-felted Gooch crucible, or, lacking that, through a double filter paper which has been moistened with concentrated nitric acid. Wash with the acid in small portions at a time.[18]

3. *By precipitation with nitric acid.* According to Willard and Goodspeed,[19] strontium nitrate can be completely precipitated in a dense crystalline form from a water solution, and separated from calcium, magnesium, beryllium, and 25 other elements by stirring vigorously and adding 100 per cent nitric acid, drop by drop until the resulting solution contains 79 to 81 per cent of the acid. The separation from calcium is made as follows:

Dissolve the dry nitrates in 10.0 ml of H_2O, add 26.0 ml of 100 per cent HNO_3, drop by drop from a burette as the solution is mechanically stirred, and let stand for 30 minutes. Filter on a tared Gooch crucible, transfer the precipitate by using jets of 80 per cent acid, and wash 10 times with approximately 1-ml portions of the 80 per cent acid. Dry for 2 hours at 130 to 140° C, cool, and weigh as $Sr(NO_3)_2$.

A precipitation temperature of 20 to 70° C is permissible, the solution should be stirred mechanically for 45 minutes if less than 5 mg of strontium are present, the total volume of the solution must be increased if much calcium is present (as for example 30 ml of water and 78 ml of nitric acid with 500 mg of calcium), and the first precipitate must be dissolved in warm water containing a little nitric acid and reprecipitated if more than 50 mg of calcium are present.

Barium and lead interfere, precipitation of the former being complete at 76 per cent, and of the latter at 84 per cent acidity. Moderate amounts of hydrochloric and perchloric acids do not interfere.

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[17] *J. Soc. Chem. Ind.*, 16, 113 (1897).

[18] In tests of the method by H. B. Knowles, the nitrates were dried at 130°, and extracted with 5 to 7.5 ml of nitric acid (sp. gr. 1.42) in a glass-stoppered flask, and the solution agitated and allowed to stand overnight. The residue was then crushed with the end of a glass rod, and the solution filtered through a platinum-felted crucible and washed with 20 to 25 ml of the concentrated acid. It was finally dissolved in hot water, converted to sulfate, and weighed. By this modification of the procedure, Knowles obtained 0.0150 and 0.0149 g of SrO in like mixtures containing 0.0144 g of SrO and 0.1 g of CaO, and 0.0055 and 0.0057 g of BaO in like mixtures containing 0.0055 g of BaO and 0.1 g of CaO.

[19] H. H. Willard and E. W. Goodspeed, *Ind. Eng. Chem. Anal. Ed.*, 8, 414 (1936).

D. SEPARATION OF BARIUM AND STRONTIUM FROM EACH OTHER

a. *Separation of Barium as Chromate.* The nitrates, obtained as in C (p. 615), or the chlorides are treated for the separation and determination of barium by the chromate method as modified by A. Skrabal and L. Neustadtl,[20] who, profiting by the experience of R. Fresenius and others, showed in what manner alone a very nearly accurate separation of barium can be made from both calcium and strontium. The following solutions are requisite:

Ammonium bichromate free from sulfuric acid, 100 g per liter.

Ammonium acetate *a*. 300 g per liter (neutralized by ammonium hydroxide).

Ammonium acetate *b*. 20 ml of *a* diluted to 1 liter.

The reaction of the acetate solutions should be alkaline rather than acid. The method for the amounts used by Skrabal and Neustadtl (0.135 g of each oxide taken as chloride) is as follows:

Add to the neutral or weakly acid solution ammonium acetate (10 ml of solution *a*) in excess. Bring the solution to boiling, and, while swirling, add about 5 ml of the bichromate solution. After allowing to settle and cool, decant the clear liquid through a filter, and wash the precipitate with ammonium acetate (solution *b*) until the filtrate is no longer perceptibly colored (100 ml of wash solution). Transfer the precipitate by a jet of water to the beaker, place the beaker under the funnel, dissolve the precipitate on the paper with warm dilute nitric acid, and wash the paper. Add more acid if need be until all is dissolved, and then dilute ammonium hydroxide slowly and with stirring until the precipitate forming again no longer dissolves. Pour in ammonium acetate (10 ml of solution *a*), bring the liquid to boiling while keeping it in swirling motion, allow to cool slowly, and wash by decantation with ammonium acetate (solution *b*). Dry, ignite the filter and precipitate separately, and weigh the yellow barium chromate. If green spots of chromic oxide, due to reduction of chromate, should appear, continued ignition will cause reoxidation.

It is probable that, for the small amounts contained in rocks and some minerals, a single precipitation of the barium by bichromate will suffice, but this is not so when considerable quantities are to be separated. Skrabal and Neustadtl gave plus and minus errors of 0.2 to 0.5 mg on the barium when operating upon a mixture of 0.135 g of each of the three oxides.[21]

b. *Determination of Strontium in the Filtrate from Barium Chromate.* Add a little nitric acid to the combined filtrates from the barium chromate, evaporate to a small volume, precipitate the strontium in that solution by ammonium hydroxide and ammonium carbonate, filter, wash a little with hot water, dissolve in just enough hydrochloric acid, and precipitate the strontium by sulfuric acid as described on page 629, whereby it is freed from contaminating chromate.

IV. METHODS OF DETERMINATION

The determination of any one of the alkaline earth metals, when free from the others, is relatively simple, but, when two or all three are associated, it is otherwise, for their separation is then influenced by their relative proportions. A method suitable for one proportion may not work with another. Hence foreknowledge of the presence or absence of one or another of the metals and an approximate idea of their relative amounts are much to be desired before deciding on the quantitative procedure.[22]

A. CALCIUM

a. *General Considerations.* Calcium is almost always precipitated as the oxalate, $CaC_2O_4 \cdot H_2O$, after preliminary treatments which aim at the separation of all of the other elements save the alkali metals, magnesium, and the other alkaline earth metals. The precipitation is never quite complete, and the first precipitate is seldom pure. Its ordinary contaminants are the alkali metals, magnesium, barium, and strontium. Among the possible contaminants may be mentioned platinum, silicon, manganese, aluminum, and certain rare earths.[23] These are what are to be expected when the usual preliminary separations have been made. If not made, the list of contaminants might be very materially increased, as ammonium oxalate precipitates many elements.

Of the possible contaminants, platinum is likely to be present only if certain prior operations were carried out in vessels of that metal, while silicon would not be found unless ammoniacal solutions had been heated

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[20] *Z. anal. Chem.*, **44**, 742 (1905).

[21] According to F. W. Mar [*Am. J. Sci.*, [3] 43, 521 (1892)], barium can be precipitated and separated from calcium and magnesium by dissolving not over 0.5 g of the mixed chlorides in as little hot water as possible, adding 25 to 50 ml of HCl, slowly and with stirring, and then cooling, and adding 5 to 10 ml of ether. F. A. Gooch and M. A. Soderman [*ibid.*, [4] **46**, 538 (1918)], stated that the method also serves for the separation of barium from strontium if a 4 + 1 mixture of 33% HCl and ether is used (50 to 75 ml for 0.5 g of chloride containing not over 0.3 g of $SrCl_2$). After filtration, the $BaCl_2$ is washed with the acid-ether mixture used with calcium and magnesium.

[22] In the improbable event that radium is present in weighable amount in the material under test, it will be found in any precipitate formed in the presence of the sulfate ion. For the determination of radium in carnotite and pitchblende by an electroscopic method, see L. D. Roberts, *Ind. Eng. Chem. Anal. Ed.*, **8**, 5 (1936).

[23] Iron is quantitatively precipitated by oxalate in ammoniacal solution, but more or less of the precipitate is dissolved if it is washed with a cold solution of ammonium oxalate. Aluminum when alone is not precipitated by oxalate in weak ammoniacal solution.

for some time in glass or porcelain. Manganese will come down in part with calcium, especially in alkaline solutions. Repeated precipitation of the calcium as oxalate will not eliminate all of the manganese; hence it should be removed beforehand. Aluminum should not be present if prior treatments were properly performed; these may however have been imperfect, as for example when an excess of ammonium hydroxide was used or when organic matter or fluorides were present. Rare earths will not be present if a proper precipitation with ammonium hydroxide has been made (p. 504), but certain of the earths may be present if the basic acetate method was used. The remedy for both of these cases lies in ignition of the impure oxalate, followed by recovery of the aluminum and rare earths as described below and reprecipitation of the calcium as oxalate.

Of the ordinary contaminants, the alkali metals are removed by double precipitation of the oxalate. This treatment also serves to separate such small amounts of barium as are usually encountered in silicate rocks.[24] When much barium is present, it will appear in part in the precipitate and will be separated later with the strontium. Strontium oxalate is nearly as insoluble as calcium oxalate, and its precipitation with calcium is nearly complete under the conditions that give a good precipitation of calcium.[13] Strontium is therefore weighed with calcium and afterwards separated and deducted.

Magnesium is the most common of the contaminants of calcium oxalate. Its oxalate is occluded by calcium oxalate, and the degree of occlusion is directly proportional to the concentration of the undissociated magnesium oxalate in the solution during the precipitation. Magnesium oxalate is also slowly adsorbed by the calcium oxalate; the amount of contamination by it is proportional to the time that elapses before filtration. The concentration of undissociated magnesium oxalate is increased by adding either constituent ion in excess, as for example by the addition of a large excess of ammonium oxalate at the moment of precipitation. The concentration is diminished by the hydrogen ion, by an increase in the concentration of ammonium salts (which form complex compounds with magnesium), or by dilution of the solution. Unfortunately, all of these remedies also tend to hinder precipitation of calcium. Furthermore, although precipitation by oxalate may eliminate the magnesium, it is not quite quantitative as to the calcium. Hence, in ordinary analyses, no attempt at a complete separation is made; the calcium result is raised by the magnesium which was occluded by the oxalate precipitate, while the magnesium result is raised by the calcium which remained in solution and was precipitated as phosphate with the magnesium. As the recovery of small amounts of calcium from magnesium pyrophosphate is much more convenient than the recovery of magnesium

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[24] W. F. Hillebrand, *loc. cit.*

from calcium oxide, accurate analyses should aim at complete separation of the magnesium and should provide for the recovery of the lost calcium which is subsequently to be found in the magnesium pyrophosphate.

The extent of the loss of calcium through the solubility of the oxalate depends of course on the conditions that obtain during the precipitation and washing.[25] If the precipitate is washed with a cool solution of ammonium oxalate, the total loss need not exceed 0.1 mg for each precipitation of the oxalate.[26] The calcium so lost is subsequently caught in the magnesium ammonium phosphate precipitate and recovered as described in III, A.

Calcium may be lost through other causes than the solubility of the oxalate. Whenever precipitations of other elements are made with ammonium hydroxide in solutions containing calcium, losses will occur if the

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[25] The amount of pure or of impure calcium oxalate that is dissolved during washing is shown by the following data. A pure oxalate precipitate was obtained by precipitating 0.2-g portions of CaO, as pure $CaCl_2$, by the recommended procedure, divided between four 9-cm filters and each portion then washed with 1 liter of the cool washing solution in question. A new pure oxalate was next obtained, divided as before, and washed with hot solutions, while two impure oxalate precipitates, obtained by single precipitations of 0.2-g portions of CaO each in the presence of 0.1 g of MgO, 10 g of NaCl and 10 g of NH_4Cl, were similarly treated. The 16 solutions so obtained were evaporated to dryness in platinum, the ammonium salts expelled, the small residues taken up in a very little HCl, and the calcium precipitated according to the recommended procedure and weighed as oxide.

Temperature of Washing Solution, °C	Precipitate	Milligrams of CaO per Liter of			
		H_2O	0.01% $(NH_4)_2C_2O_4$	0.1% $(NH_4)_2C_2O_4$	1% $(NH_4)_2C_2O_4$
25	Pure CaC_2O_4	2.6	0.4	0.1	0.0
	Impure CaC_2O_4	2.7	0.5	0.1	0.1
100	Pure CaC_2O_4	4.9	0.9	0.5	1.1
	Impure CaC_2O_4	4.3	1.7	1.2	1.2

It is evident that a 0.1 per cent solution of $(NH_4)_2C_2O_4$ is satisfactory and that hot solutions should be avoided.

[26] For example, H. B. Knowles obtained but 0.2, 0.3, and 0.2 mg of CaO in the weighed $Mg_2P_2O_7$ precipitates obtained in analyses of three 1-g portions of a dolomite (30.5% CaO and 21.5% MgO), in spite of the fact that, in each analysis, the calcium had been precipitated as oxalate, four times in order to insure freedom from magnesium. Each time the precipitation was made in a volume of approximately 250 ml and the precipitate was washed with 25 to 50 ml of a 1 per cent solution of ammonium oxalate, making a total volume of over 1000 ml of combined filtrates and washings. Practically all of the solubility loss apparently took place in the first precipitation, for the weights of CaO obtained after four precipitations were exactly the same as those obtained after three precipitations. The larger amount of calcium remaining in solution after the first precipitation is no doubt due to the much greater concentration of magnesium and ammonium salts.

ammonia precipitate is large and only a single precipitation is made, if the ammonium hydroxide contains carbonate or the alkaline solution is exposed for a considerable time to air containing carbon dioxide, if the solution contains much phosphate, or if fluorides are present. The first two losses are easily avoided. The precipitation of calcium as phosphate during a precipitation by ammonium hydroxide is dependent on the ratio between phosphoric acid and bases of such elements as ferric iron and aluminum. If iron is in considerable excess, no calcium is thrown out; if calcium and phosphorus are preponderant, as in phosphate rock, practically all of the calcium comes down. Tests made for us by H. B. Knowles showed no calcium in the ammonia precipitate when solutions containing 0.05 g of lime, 0.005 g of phosphorus pentoxide, and a ten-fold excess of either ferric oxide or alumina were precipitated twice with a slight excess of ammonium hydroxide. These tests represent the ordinary conditions that obtain in rock analysis, and show that under such conditions no loss of calcium takes place. When phosphorus is preponderant and calcium alone is desired, several procedures are open to the analyst, no one of which is free from difficulty or objection, however. For example: (1) A sufficient excess of iron or aluminum can be added. (2) The calcium can be precipitated by sulfuric acid and alcohol from a solution slightly acid with hydrochloric or nitric acid as described on page 629, or by direct precipitation as oxalate in an oxalic acid-ammonium oxalate solution as on page 626. (3) The P_2O_5 can be precipitated as phosphomolybdate and the calcium determined in the filtrate. Of course, this procedure calls for a precipitant free from calcium. Neither molybdenum nor phosphorus interferes in the precipitation of calcium oxalate in either ammoniacal or oxalic acid solution.

When the sample contains fluoride, repeated evaporations with hydrochloric or nitric acid do not always remove all the fluorine, and in such cases calcium is partially carried as fluoride into the ammonia precipitate. The remedy in such cases lies in a preliminary evaporation with sulfuric or perchloric acid, or with concentrated nitric acid while pure finely powdered silica is dusted into the solution.[27]

b. *Oxalate Separation.* α. *In alkaline solution.* The following method for separating calcium from magnesium and alkali metals is applicable in all cases save when magnesium preponderates greatly and very little calcium is present. Most rocks and silicate minerals can be treated under this section. As has been noted in the preceding remarks, at least two precipitations of calcium are necessary if the analysis is to be accurate. The salts should be present as chlorides or nitrates, preferably the former. The correct amount of ammonium chloride to have present is a problem; a large excess reduces the precipitation of magnesium and barium but at the same

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[27] A. A. Noyes, *Technol. Quart.*, **16**, 101 (1903).

time retards the precipitation of calcium and more especially of strontium. If the analysis has followed the usual course, no destruction of the ammonium salts is necessary. If special operations have introduced excessive amounts of ammonium salts, these should be removed, as described on page 133, or by evaporating the acidified solution in porcelain or platinum to complete dryness, followed by careful heating in any way that distributes the heat uniformly over the outer surface and does not cause violent escape of fumes.[28] If this has been done, moisten the residue of chlorides or nitrates with 2 or 3 ml of the corresponding acid, dissolve the salts in a little water, and filter if necessary.

1. *First precipitation.* Prepare a solution that is free from silica, sulfur,[29] the hydrogen sulfide group, and elements precipitable by ammonium hydroxide or ammonium sulfide. Dilute to 100 to 400 ml, and render the solution slightly ammoniacal.[30] The solution should not contain more than the equivalent of 1 mg of CaO per ml in any case. Heat to boiling, and slowly add, while stirring, sufficient of a hot 4 per cent solution of ammonium oxalate to precipitate all of the calcium and to provide an excess of 1 g per 100 ml of solution.[31] Boil for 1 to 2 minutes, and heat on a steam

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[28] There is less danger of mechanical loss in volatilizing ammonium chloride than nitrate. The latter melts and gives off bubbles that burst and spatter. Moreover, the decomposing nitrate attacks platinum to some extent; hence ammonium nitrate should not be volatilized from platinum vessels. The prohibition applies of course still more to mixtures of nitrate and chloride.

[29] Calcium oxalate that has been precipitated in a solution containing free sulfur, as for example an ammonium sulfide filtrate that has been acidified, treated with ammonium oxalate, and then gradually neutralized, should not be ignited and weighed, because the sulfur is oxidized and fixed during the ignition. The error is not overcome by solution of the wet precipitate, and reprecipitation, because finely divided sulfur passes into the filtrate and is again carried down. The difficulty can be avoided by igniting the precipitate, dissolving it, and again precipitating, or the sulfur can be destroyed in the original solution by acidifying, boiling sufficiently to expel hydrogen sulfide but not to coagulate sulfur, and then oxidizing with bromine. If sulfur separates, the solution must of course be filtered.

[30] In an ordinary analysis, such a solution is made up of the combined filtrates obtained after a double precipitation of iron, aluminum, and the like by ammonium hydroxide as described under 8 B (p. 868). If elements such as manganese or zinc were present, the solution is the filtrate obtained by precipitation with ammonium sulfide as described under 8 C (p. 879). If the amount of calcium is very small and large amounts of ammonium salts are present, it is advisable to remove the latter.

[31] If appreciable magnesium is present, a better separation and a coarser precipitate can be had if the precipitation is made from an acid solution as follows: Render the solution acid with hydrochloric acid, and add 1 ml in excess for each 100 ml of solution, and then enough oxalic acid or ammonium oxalate to combine with all of the calcium. Avoid any large excess at this time. Heat the solution to boiling, stir continuously, and add dilute ammonium hydroxide (1 + 3) dropwise from a pipette until a precipitate begins to form. At this point add the ammonium hydroxide still more

bath for one-half hour. Allow to cool, and filter at the end of 1 hour. Wash the paper and precipitate with five 10-ml portions of a cold neutral 0.1 per cent solution of ammonium oxalate.[32] Reserve the filtrate and washings if a determination of magnesium or a recovery of unprecipitated calcium is to be made.

2. *Second precipitation.* Dissolve the washed oxalate precipitate in 50 ml of dilute hydrochloric acid (1 + 4). Dilute, and add an excess of oxalate as in 1. Heat to boiling, stir continuously, and slowly add dilute ammonium hydroxide until alkaline. Digest, filter, and wash as in 1.[33] Combine the filtrate and washings with those obtained after the first precipitation.

3. *Ignition of the final oxalate precipitate.* Wrap the moist precipitate in the filter paper, place in a platinum crucible weighed with a snugly fitting cover, and heat with the cover off or at the side so as to char but not inflame the paper. When the paper is fully charred, increase the flame, and, when the carbon has disappeared, set the crucible upright in the triangle, cover it, and heat at about 1200° C for 5 minutes. Throughout the heating it is well to protect the oxide from contamination by oxides of sulfur from burning gases or by volatile matter given off in muffles that are in general use (see p. 28). Remove the lid for a moment to permit escape of entrapped carbon dioxide, place the covered crucible in a desiccator containing sulfuric acid or phosphorus pentoxide (never calcium chloride), and weigh as soon as cool. If left long in the desiccator, the lime may gain appreciably in weight. The first weighing is a preliminary one and should be followed by a short ignition and a second weighing in which the weights are already placed on the pan and only the rider is quickly adjusted. A well-covered crucible containing ignited calcium oxide does not gain in weight during exposure for 1 minute under ordinary atmospheric conditions.[34]

The presence of manganese in the ignited oxide is usually revealed by a yellowish to brown discoloration, occasionally by a green color due to calcium manganate. The weighed calcium oxide is reserved for the determination of any strontium or barium it may contain as described on page 615. For the recovery of the calcium that is not precipitated as oxalate, see III, A.

4. *Remarks on the ignition.* It is a mistaken idea that it takes long to reach constant weight at approximately 1200° C as has been frequently asserted or assumed. If a blast flame is inclined so that the gases do not enter the crucible, 5 minutes is ample ordinarily for any amount of lime that is likely to be dealt with. The heat of a Teclu, Meker, or a Bunsen burner of the Tirrill form, is in reality sufficient, notwithstanding that their flames envelop the crucible. Fifty minutes heating, over a Tirrill burner, of 3 g of precipitated calcium carbonate contained in a platinum crucible, sufficed to convert the mass so nearly to oxide that the blast afterward caused a further loss of only 1 mg.

These remarks are offered to counteract the effect of certain conclusions reached by O. Brunck [35] as a result of comparing the weighing of calcium as oxide, carbonate, sulfate, and fluoride. His results by the oxide method were all appreciably higher than those otherwise obtained and also more variable, and he concluded that the other methods were likely in average hands to lead to better results. No such variable and high results as those reported by Brunck were ever obtained in the U. S. Geological Survey laboratory, where only the oxide method was used. Duplicates by that method agreed as well as Brunck's by the other methods.

Brunck attributed one source of error in the oxide ignition to a loss in weight of the platinum crucible, due to the powerful heat that is called for.

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slowly, and allow as much as possible of the precipitate to form between each addition. Continue until methyl red just turns yellow, and then add 2 to 3 g of ammonium oxalate in excess. Let the solution stand for 1 hour as it slowly cools. Filter, and wash as in 1.

A still better separation can be obtained by proceeding according to T. W. Richards [*Proc. Am. Acad. Arts Sci.*, **36**, 392 (1900–1901)], as follows: Dilute the solution so that the concentration of magnesium is approximately 0.02 *N*, and add 10 ml of hydrochloric acid, a few drops of methyl orange, and then ammonium hydroxide until neutral. Add sufficient oxalic acid to combine with the calcium, together with three times its equivalent of hydrochloric acid. Heat the solution to boiling, and add dilute ammonium hydroxide (1 + 5), slowly and in small portions, to the boiling solution during the course of 30 minutes. At the end of this time, the solution should be just neutral. Add 5 g of ammonium oxalate, and let the solution cool and stand for 1 hour. Filter, and wash as in 1.

[32] It is unnecessary to ignite the precipitate before the second precipitation unless the analyst has reason to believe that elements such as iron and the rare earths might have been present when the precipitation was made. These elements should not be present if a proper precipitation with ammonium hydroxide preceded the precipitation with oxalate. They might be present if precipitation was made by the basic acetate method or if improper conditions, such as the presence of soluble organic matter, obtained in the ammonia precipitation. If the oxalate precipitate has been ignited, place the open crucible upright in a beaker containing a little water, cover the beaker, and let stand a while until the lime is partly slaked. Moisten with water, dissolve the residue in 50 ml of dilute hydrochloric acid (1 + 4), heat to boiling, and add dilute ammonium hydroxide until in slight excess (p. 504). Boil for 1 to 2 minutes, and filter immediately. Wash the paper and precipitate with a hot 2 per cent solution of ammonium chloride, and reserve the filtrate and washings for the second precipitation of calcium. If the analysis is a continuing one, ignite the paper and ammonia precipitate, weigh, and make the proper corrections in the Fe_2O_3, Al_2O_3, etc., already found.

[33] In accurate analyses of material containing appreciable magnesium, the whole procedure must be repeated until the weight of lime remains constant (see III, A).

[34] Alternatively, the oxalate may be caught on a tared Gooch, or other suitable filtering crucible, ignited at 475 to 525° C, and weighed as the carbonate, $CaCO_3$ [H. H. Willard and A. W. Boldyreff, *J. Am. Chem. Soc.*, **52**, 1888 (1930)].

[35] *Z. anal. Chem.*, **45**, 77 (1906).

Either he heated his oxide far longer than was necessary or he mistook the cause of the platinum loss. Like barium oxide, but in lesser degree, calcium oxide attacks platinum when strongly heated in contact with it. That it does so can be demonstrated readily by dissolving in hydrochloric acid lime that has been heated over the blast in a platinum crucible for half an hour and then precipitating and weighing the dissolved platinum. If Brunck assumed the difference between the weights determined before and after igniting the cleaned crucible to represent volatilized platinum, it is easy to see how he may have been led to attribute the loss to a wrong cause. It is true that platinum crucibles lose weight on blasting, especially if iridiferous as most are, but a perceptible loss in the few minutes of blast heat needed could arise only in a very exceptional case.

β. *Precipitation of calcium in feebly acid (pH 3.5 to 4.5) solution.* 1. *General considerations.* Methods have been proposed for precipitating calcium, as oxalate, from solutions containing organic acids such as oxalic, acetic, citric, and salicylic. These methods permit the direct separation of calcium from elements such as iron, aluminum, titanium, manganese (in part), magnesium, molybdenum, and phosphorus, and, although they should be regarded as rapid routine methods, they are capable of giving excellent results.

Precipitation in the presence of acetic acid is described by R. K. Meade,[36] and that for citric by M. Passon.[37] The only method that has been used by us is an oxalic acid-ammonium oxalate method, employed during an analysis of the Bureau of Standards sample of phosphate rock. Careful tests of this method in solutions containing calcium only and in others containing also iron, aluminum, titanium, zirconium, magnesium, and large amounts of phosphorus gave excellent results and showed no greater losses, due to solubility of the calcium oxalate, than are experienced in the usual procedure. Barium, when present in moderate amounts does not appear in the final precipitate. Strontium, however, is divided, part being precipitated and part going into the filtrates.

2. *The method.* Dilute the solution to 150 ml, treat with 10 ml of hydrochloric acid, and add a few drops of methyl red or methyl orange. Heat to about 50° C, neutralize with ammonium hydroxide, and add 1 ml in excess. Just acidify the solution with a 10 per cent solution of oxalic acid, add 12 ml in excess, and boil 1 to 2 minutes as the solution is vigorously stirred. Add approximately 50 ml of a saturated solution of ammonium

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[36] *Chem. Eng.*, **1**, 21 (1895). Calcium can be precipitated as the oxalate in an acetic acid solution containing molybdate, thus permitting a determination of calcium after phosphorus has been precipitated as ammonium phosphomolybdate [R. C. Wiley and A. Yedinak, *Ind. Eng. Chem. Anal. Ed.*, **10**, 322 (1938)]. Separation from chromate is also satisfactory.

[37] *Z. angew. Chem.*, **11**, 776 (1898); **12**, 48 (1899); **14**, 285 (1901); Mellor, *A Treatise on Quantitative Inorganic Analysis*, p. 522 (1913).

oxalate (about a 4 per cent solution), dilute to 250 ml, boil for 1 to 2 minutes, and digest on the steam bath for 1 hour. Let cool to room temperature, filter, and wash with cool ammonium oxalate-oxalic acid solution [2 g $(NH_4)_2C_2O_4 \cdot 2H_2O$ and 1 g $H_2C_2O_4 \cdot 2H_2O$ per liter]. In routine analyses, finally wash the precipitate with 5 to 10 small portions of cold water, and determine calcium by the volumetric method (c, α). In more careful analyses, ignite the crude oxalate to oxide, slake the residue, and dissolve it in 40 ml of dilute hydrochloric acid (1 + 4). Dilute to 200 ml, treat with 0.005 g of iron as $FeCl_3$, and separate any phosphorus and manganese by making the solution slightly ammoniacal, adding 10 ml of bromine water, and digesting at a temperature a little below the boiling point for 15 minutes. Finally add 5 ml more of bromine water, digest for 15 minutes, and filter. Wash the precipitate with hot ammoniacal ammonium chloride solution (10 ml of NH_4OH and 10 g of NH_4Cl per liter), and discard it. Acidify the filtrate with hydrochloric acid, boil to expel bromine, and reprecipitate the calcium as oxalate as in the usual procedure (p. 623).[38]

c. *Other Methods of Determining Calcium After Precipitation as Oxalate.* α. *Permanganate titration.* In the permanganate titration method the oxalate is treated with dilute sulfuric acid and the liberated oxalic acid titrated with standard potassium permanganate. Obviously, if the calcium oxalate contains any strontium, barium, magnesium, or ammonium oxalates, these will be counted as calcium. For material containing calcium alone, the method is capable of giving exact results, and it is extremely valuable and much used as a routine method for the analysis of such products as cement and plaster. For this method, the oxalate is best caught on asbestos, fritted glass, or the like so that washing may be facilitated, and subsequent action of the permanganate on paper may be avoided,[39] If paper is used, the oxalate is finally washed, but not excessively, with cold water until all ammonium oxalate is removed, and the paper is removed from the funnel

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[38] For the volumetric determination of calcium in the presence of silicon, iron, aluminum, magnesium, or phosphorus that is equal to or somewhat greater than the amount of calcium, and also in the presence of small amounts of titanium or manganese, J. J. Lingane [*Ind. Eng. Chem. Anal. Ed.*, **17**, 39 (1945)] recommends precipitation at approximately *p*H 4 as follows: Prepare 100 ml of a solution containing 10 ml of hydrochloric acid and approximately 0.07 g of calcium as oxide. Heat to 90° C, and add 100 ml of a hot (90° C) solution of ammonium oxalate containing 5 g of the monohydrate and a few drops of a 0.1 per cent solution of methyl orange. Precipitate at an initial temperature of about 80° C by the dropwise addition of dilute ammonium hydroxide (1 + 1) over a period of 5 to 10 minutes, with continuous and thorough mixing of the solution by swirling, and stopping at a *p*H of 4.0 ± 0.3 (by comparison of the pinkish yellow color with that of an equal volume of 0.1 *M* potassium hydrogen phthalate solution containing the same quantity of indicator). Set aside to cool during 20 to 30 minutes. Filter, wash sparingly with small portions (totaling <100 ml) of cold water, and titrate as in c, α. Consult also H. D. Chapman, *Soil Sci.*, **26**, 479 (1928).

[39] R. S. McBride and J. A. Scherrer, *J. Am. Chem. Soc.*, **39**, 928 (1917).

and spread out on the inside of the beaker above 100 ml of warm dilute sulfuric acid (1 + 10). The oxalate is then rinsed off with a little warm water, and the solution is gently warmed until decomposition is complete and then titrated at 25° to 30° C with a standard solution of permanganate (p. 187). As soon as a permanent end point is obtained, the paper is dropped into the liquid, the inside of the beaker is rinsed, and the titration is quickly continued. The permanganate is standardized against the standard sodium oxalate of the National Bureau of Standards, or against Iceland spar of known purity which has been dissolved in hydrochloric acid and carried through the method.

β. *Gravimetric methods.* Other methods that are in vogue more or less involve conversion of the oxalate to carbonate, sulfate, or fluoride and weighing of the product. These, like the volumetric method already given, are of value only if the oxalate is free from strontium and barium or the amounts of these are accurately known. The first and second are old methods that seem to have stood the test of time fully and are preferred by some analysts. Brunck[35] gave data concerning all three methods that are most favorable, and, in view of the earlier testimony of eminent analysts, it cannot be gainsaid that in careful hands they will yield excellent results, particularly if the amounts involved are not large. Nevertheless, they require, especially the first and second methods, much more careful attention than the oxide method, and hence will not commend themselves so widely. In general the complete conversion of one solid compound into another, by means of a reagent in which the first is insoluble or nearly so, is not always easy to accomplish, especially if the amount is other than small. This statement is based on experience gained in converting lead chloride and difficultly soluble fluorides to sulfates by sulfuric acid. There is always a tendency, where an insoluble compound is at once formed by the action of one of the acids named, for some of the original compound to be protected from conversion even after two or more evaporations with fresh portions of acid.

1. *Weighing as carbonate.* Ignite the oxalate gently to convert it to carbonate after the paper with adhering matter has been first incinerated. Then digest with a few drops of ammonium carbonate solution, evaporate the liquid cautiously, ignite the residue gently just to visible redness, and weigh. Repeat the treatment with ammonium carbonate, etc., until constant weight is reached.

2. *Weighing as sulfate.* Slake the oxide cautiously, and then add a slight excess of sulfuric acid. Concentrate by evaporation, and remove the excess of acid over the radiator (Fig. 5). Cool, add a little water, again evaporate to dryness, and ignite the dry sulfate to dull redness for a short time, and weigh. Repeat the treatment with acid, etc. Too strong heating causes expulsion of SO_3.

3. *Weighing as fluoride.* With substitution of hydrofluoric acid for sulfuric acid, treat the ignited oxide as in 2 above. Brunck regarded this as simpler than either of the foregoing methods, but he considered the sulfate method best in experienced hands.

d. *Initial Precipitation of Calcium as Sulfate.* Circumstances sometimes permit or require the direct precipitation of calcium as sulfate, either in absence or presence of other elements whose sulfates are insoluble. The solution may be neutral or only slightly acid with hydrochloric or nitric acid.

Add a ten-fold excess of dilute sulfuric acid (1 + 1) and then four volumes of alcohol, stir, let stand 12 hours, wash with alcohol of 75 per cent strength, dry, incinerate precipitate and paper, separately if detachable, in a platinum crucible, heat to dull redness, cool, and weigh as $CaSO_4$. During this final heating, any reduction to sulfide that may have resulted from the charring of the paper is overcome. Should the precipitate contain one or more of the sulfates of other metals—strontium, barium, lead, for example —it may become necessary to effect resolution, and then separation in one of a number of ways. If lead is present, this will usually have to be done without igniting the precipitate, so as to avoid reduction.[40]

B. STRONTIUM

a. *Precipitation and Weighing as Sulfate.* Strontium, when occurring under conditions that permit its determination as sulfate, is best precipitated and weighed in that form. Such conditions will seldom obtain in the usual course of analysis, except after its separation from other elements, like barium and calcium, that had been precipitated with it in some other form, as for instance oxalates. The (preferably hydrochloric) solution should be as nearly neutral as possible.

Add a ten-fold excess of dilute sulfuric acid (1 + 1) and then a volume of alcohol equal to that of the solution. Stir, let stand 12 hours, filter, and wash with 50 per cent alcohol containing a little sulfuric acid, then with 95 per cent alcohol until the acid is displaced. Proceed then as under d, above, and weigh as $SrSO_4$. The remarks under that section apply here also.

b. *Precipitation as Oxalate and Weighing as Oxide.* Usually the strontium is associated with calcium and often with barium, as in mineral analysis.

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[40] E. R. Caley and P. J. Elving [*Ind. Eng. Chem. Anal. Ed.*, 10, 264 (1938)] prefer to precipitate calcium sulfate by adding methanol to a solution of calcium and magnesium in dilute sulfuric acid (20 ml H_2O + 0.25 ml H_2SO_4 + 180 ml of CH_3OH). The method is said to be satisfactory for the determination of calcium in magnesite, but not in limestone or in the presence of elements, such as strontium, that yield insoluble sulfates. At a magnesium-calcium ratio of 200 to 1, precipitation requires 24 hours; at higher ratios of magnesium, it is incomplete.

In that case it is first precipitated with the calcium as oxalate and ignited to oxide (p. 622). It may be here remarked that the behavior of strontium toward ammonium oxalate is much closer to that of calcium than is that of barium to strontium (p. 614). Strontium oxalate is a little more soluble than calcium oxalate, and the oxalate precipitate will not contain quite all of it unless a corrective measure like the addition of alcohol is taken.[41] Such a precaution, although quite desirable when strontium alone is present, introduces complications when other elements like magnesium and barium are involved. If a determination of magnesium is to follow that of strontium, any of the latter that escapes the ordinary oxalate precipitation is caught in the magnesium-phosphate precipitate. The treatment of that precipitate for the recovery of calcium (III, A) serves to recover strontium as well.

C. BARIUM

a. *Precipitation and Weighing as Sulfate.* Whenever circumstances permit, barium, like strontium, is precipitated and weighed as the sulfate. Elements such as lead, strontium, and calcium interfere because of the insolubility of their sulfates, whereas others like chlorine, and aluminum and iron in excessive amounts, contaminate the precipitate. The procedures for such cases are given elsewhere (p. 612).

Barium sulfate is commonly regarded as being extremely insoluble (approximately 1 part in 400,000 parts of cold water). This however is 2.5 mg per liter. In hot water or in dilute hydrochloric or nitric acid, the solubility is greater, whereas, in solutions containing a common ion, it is less. Hence the precipitation must be made in solutions that contain preferably not over 1 per cent of the mineral acids, and the washing of the precipitate even with cold water should not be excessive. Furthermore, although the solubility in the weak hydrochloric acid that is recommended frequently as a wash for barium sulfate that has been precipitated in presence of much ferric iron is slight, saturation seems to be reached almost immediately, in contrast with some wash solutions that are used for other precipitates.

To the boiling solution, weakly acid with hydrochloric acid (not over 200 ml in volume nor containing more than 1 ml of hydrochloric acid per 100 ml), add an excess of hot dilute sulfuric acid (not over 5 ml of sulfuric acid per 100 ml), digest on the steam bath until the precipitate has settled well, filter, and wash with hot water containing two drops of sulfuric acid per liter, and then with a little water until the acid is extracted. Wrap the precipitate in the paper, place it in a weighed platinum crucible, dry, char, and ignite as for calcium (p. 629). A higher temperature is allowable than for calcium sulfate but not that of the blast. Weigh as $BaSO_4$, add a drop

of sulfuric acid, slowly fume this off, and weigh again. If there is a marked change in weight, repeat the treatment with acid, etc.

Some barium chloride is occluded by the precipitate as formed, and the object of the acid treatment is to convert this to sulfate as well as any sulfide that may have been formed in charring the paper. The oxidation of sulfide will probably have been brought about by the ignition alone.

If it is desired to check the purity of the ignited sulfate, dissolve it completely in the crucible in 5 ml of hot concentrated sulfuric acid, cool, pour into 50 ml of water, dilute to 100 ml, and digest for an hour on the bath. Cool, filter, wash with a little hot water, incinerate as before, and weigh. Any difference in weight should be due to other metals, such as calcium, that were in the original solution and were carried down in the precipitated sulfate. If need be, these can be looked for in the filtrate.[42]

b. *Precipitation and Weighing as Chromate.* The use of the chromate method for barium is practically limited to cases that involve separation from calcium or strontium or both (p. 618).

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[41] C. A. Peters, *loc. cit.*

[42] For example, in tests made by H. B. Knowles, an ignited mixture of 0.1641 g of $BaSO_4$ and $CaSO_4$ weighed 0.1525 g after a single, 0.1511 g after a double, and 0.1511 after a triple purification treatment. The mixed sulfates were obtained by treating 50 ml of a solution of pure $BaCl_2$ with 0.00976 g of CaO as $CaCl_2$, boiling, and slowly adding 10 ml of dilute H_2SO_4 (1 + 1). The solution was then allowed to cool, treated with an equal volume of alcohol, filtered, and the precipitate washed with equal parts of alcohol and water. Two 50-ml portions of the $BaCl_2$ solution similarly treated, but with no addition of $CaCl_2$, gave 0.1511 and 0.1509 g of $BaSO_4$.

Chapter 41

MAGNESIUM

Magnesium is one of the most abundant metals. In igneous rocks it is represented by amphiboles, pyroxenes, micas, and olivine. Talc, chlorite, and serpentine are common magnesian silicates, and dolomite, the carbonate of magnesia and lime, is also found in enormous quantities. Magnesium compounds occur in sea water and in many mineral springs. The metal is not found native.[1]

I. GENERAL CONSIDERATIONS

Magnesium causes no difficulties in ordinary analyses except when soluble phosphates or arsenates are present in excess of what can be carried down by iron, alumina, and the like in the precipitation by ammonium hydroxide. In such case magnesium phosphate or arsenate is precipitated, and, if not detected, results for magnesia will be low and those for alumina correspondingly high.

II. DECOMPOSITION OF MAGNESIAN MINERALS

The decomposition of magnesian minerals presents no special difficulties and is done as described under the alkaline earths (p. 612).

III. METHODS OF SEPARATION

Methods for the separation of magnesium preparatory to its determination are, for the most part, simple. Thus, treatments with hydrogen sulfide in acid solution, ammonium hydroxide (avoiding any large excess), ammonium sulfide, and ammonium oxalate serve to remove a host of elements and leave, in the usual case, magnesium associated with ammonium salts and the alkalies, which need not be removed. Barium, if originally present unassociated with the sulfate radical, will also remain. In such an event its removal is easily accomplished by precipitation with sulfuric acid as described under Barium (p. 630).

The separation of magnesium from calcium offers no difficulties when the former is present in appreciable amount and is done as described under

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[1] F. W. Clarke, The Data of Geochemistry, *U. S. Geol. Survey Bull.* 770, 17 (1924).

Calcium (p. 619). If, however, very little magnesium is accompanied by much calcium, special separations must be used. Of these, J. C. Hostetter's[2] application of the method that H. Neubauer[3] devised for separating little magnesium from alkali sulfates is the most satisfactory, although it is not applicable for the determination of calcium in the same solution. As applied to the analysis of a commercial salt of calcium, the separation is as follows: Bring 10 g of the calcium salt into water solution, and dilute to 100 ml. If acid is used to bring the salt into solution, neutralize the excess with sodium hydroxide after expelling CO_2, SO_2, etc., by boiling. Add calcium oxide (made by igniting 0.3 to 0.4 g of the carbonate), heat to boiling, and filter, but do not wash the residue. Dissolve the precipitate in hydrochloric acid, remove the calcium by two precipitations as described under Calcium (p. 622), and determine the magnesium in the combined ammonium oxalate filtrates as to be described in IV, A.

For the separation of small amounts of calcium in the presence of large amounts of magnesium, see the section on Alkaline Earths (p. 612).

It may happen, for lack of sufficient material in the case of silicate minerals decomposed by acid attack, that it is necessary to determine the alkalies as well as other bases and silica and titanium oxide in the same portion of sample, after all of these have been separated by methods that exclude the use of alkali reagents. Then the question of a suitable method for separating magnesium becomes important. In such case, methods such as the mercuric oxide, ammonium carbonate, amyl alcohol, alcohol-ether, or the 8-hydroxyquinoline find use.

In the first, magnesia is precipitated from a solution of the chlorides by moist alkali-free mercuric oxide as follows: Expel ammonium salts, dissolve in a little water, and add a suspension of the oxide (prepared as described under Precipitation by Suspensions of Carbonates or Oxides (p. 82), dropwise and with stirring or swirling between drops, until the yellow oxide no longer dissolves. Evaporate to dryness, add a few drops of water, again evaporate, and repeat a few times. Finally heat gently under a good draft until the poisonous mercuric chloride has volatilized. It is inadvisable to destroy by heat the excess of mercuric oxide at this step if alkalies are to be determined, for fear of volatilizing some. Take up with warm water, filter, and wash with water. With more than 1 per cent of magnesium oxide, dissolve the oxide in the hydrochloric acid, and repeat the operation. Dry the filter and contents in a weighed platinum crucible, incinerate under the hood, and weigh. As the use of hot water causes a little magnesium to dissolve, a desirable modification of the procedure would appear to consist in washing the residue with a saturated solution of calcium

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[2] *J. Ind. Chem.*, **6**, 392 (1914); *Chem. News*, **110**, 155 (1914).

[3] *Z. anal. Chem.*, **43**, 14 (1904).

hydroxide. Any calcium adhering to the residue could then be removed and deducted as described under The Alkaline Earths (p. 612), whereas that which accompanies the alkalies could be removed as described under The Alkalies (p. 651).

The ammonium carbonate method[4] is carried out as follows: Saturate with ammonium carbonate a mixture in the proportion by volume of 18 ml of ammonium hydroxide, 75 ml of water, and 95 ml of 95 per cent alcohol. Evaporate the solution containing not more than 0.4 g of combined chlorides of magnesium and the alkalies to a volume of about 50 ml, and add an equal amount of 95 per cent alcohol and then 50 ml of the prepared reagent. Stir for 5 minutes, and let the mixture stand for 20 minutes. If the amount of alkali salts originally present is small (not exceeding 0.1 g), collect the precipitate on asbestos in a perforated crucible and wash with the precipitant. If the amount of alkali salts is larger, pour the supernatant liquid through the asbestos filter, dissolve the precipitate, and reprecipitate as at first. If it is desired to determine the magnesia as well as the alkalies, carefully ignite the final precipitate, and weigh as magnesium oxide. The fact that lithium would fall in part with the magnesium will seldom invalidate this method for silicate rock analysis, because of the absence of lithium in sensible amount from almost all rocks.

The amyl alcohol and ether-alcohol methods differ from the two just described, in that the alkalies are precipitated instead of magnesium. In the absence of lithium, the amyl alcohol method developed by R. B. Riggs[5] may be satisfactory. It is similar to that of Gooch for separating lithium from sodium and potassium and involves the same solubility corrections. The use of ether-alcohol was recommended by S. Palkin[6] and is a modification of the method for the separation of lithium from the alkali metals described in the section on The Alkali Metals (p. 655). Lithium if present will accompany the magnesium. The only deviation from the lithium method lies in the use for the first treatment of 25 ml of both alcohol and ether instead of 20 ml of alcohol and 60 ml of ether and, if the first precipitate tends to gelatinize, the addition of a few milliliters more of alcohol as the beaker is rotated. The filtrate is to be evaporated and the precipitation repeated.

Magnesium can be separated from the alkalies and from barium, strontium, and calcium by precipitation with 8-hydroxyquinoline.[7] Double precipitations are required when calcium or large amounts of the others are present. The precipitation of magnesium can follow that of calcium as oxalate, thus permitting its removal without the introduction of nonvolatile matter in a continuing analysis. Magnesium (likewise copper, cadmium, and zinc) can also be separated from aluminum if precipitation is made in a solution containing sodium tartrate and moderate amounts of sodium hydroxide. The use of 8-hydroxyquinoline for the separation of magnesium from calcium or aluminum does not appear to offer any advantages over the usual methods, except possibly for the separation of small amounts of magnesium from large amounts of these elements. For a description of the method, see Precipitation by 8-Hydroxyquinoline (p. 122).

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[4] E. A. Wülfing, *Ber.*, 32, 2214 (1899); F. A. Gooch and E. A. Eddy, *Am. J. Sci.*, [4] 25, 444 (1908); *Chem. News*, 97, 280 (1908).

[5] *Am. J. Sci.*, [3] 44, 103 (1892).

[6] *J. Am. Chem. Soc.*, 38, 2326 (1916); 42, 1618 (1920).

[7] F. L. Hahn, *Chem. Ztg.*, 50, 754 (1926); F. L. Hahn and K. Vieweg, *Z. anal. Chem.*, 71, 122 (1927); R. Berg, *ibid.*, 70, 341 (1927); 71, 23, 171, 321, 369 (1927). According to L. Moser and K. Schutt [*Monatsh.*, 51, 23 (1929)] the most satisfactory separation of magnesium from lithium is obtained by precipitating with 8-hydroxyquinoline.

Magnesium can be precipitated and separated from aluminum, iron, zinc, tin, and numerous other elements by direct precipitation with diammonium phosphate in ammoniacal solutions containing citrate as follows: Obtain the magnesium in approximately 100 ml of acid solution in a 300-ml Erlenmeyer flask, add 2 g of citric acid and 15 ml of a 25 per cent solution of diammonium phosphate. Add ammonium hydroxide until the solution is alkaline to litmus, and then add 10 ml in excess. Add 5 to 10 glass beads, tightly stopper the flask, and shake on a shaking machine for at least 1 hour. Allow to stand in a cool place for 4 hours or, preferably, overnight. Filter through a tight paper containing a little paper pulp, and wash thoroughly with dilute ammonium hydroxide (1 + 19) containing 50 g of diammonium phosphate per liter. Pass 25 ml of hot dilute hydrochloric acid (1 + 19) through the paper, catching the solution in the flask in which precipitation took place. Transfer the solution to a 150-ml beaker, and wash the paper and flask thoroughly with more of the dilute acid. To the solution in a volume of 50 to 75 ml and containing no glass beads, add 0.5 ml of a 25 per cent solution of diammonium phosphate. Cool, and then add ammonium hydroxide, while stirring, until the solution is alkaline to litmus. Stir for a few minutes, then add 3 to 4 ml of ammonium hydroxide, and allow to stand for 4 hours or overnight. Transfer the precipitate to a small filter, wash with dilute ammonium hydroxide (1 + 19), and proceed with the ignition to pyrophosphate as usual. Elements such as calcium, strontium, and barium must be removed before the separation is attempted if they are present in appreciable amount; if present in small amount, they can be precipitated with the magnesium and, like manganese, afterwards sought in the precipitate as in IV, A (p. 640).[8]

Magnesium can be separated from aluminum in the metal, and in aluminum-base alloys, by immersing the metal in 200 to 500 ml of water, adding 25-ml portions of a 30 per cent solution of sodium hydroxide at intervals

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[8] For further details, see J. I. Hoffman and G. E. F. Lundell, *J. Research NBS*, 20, 607 (1938).

until the aluminum has dissolved, and heating on the steam bath for 1 hour. The solution is then cooled and filtered, and the precipitate washed with a 1 per cent solution of sodium hydroxide.[9]

IV. METHODS OF DETERMINATION

A. DETERMINATION AS PYROPHOSPHATE

a. *General Considerations.* Magnesium is nearly always precipitated as magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, and weighed as the pyrophosphate, $Mg_2P_2O_7$. As many other elements also form insoluble phosphates, the precipitation of magnesium must be made as a rule after the usual separations by hydrogen sulfide, ammonium hydroxide, ammonium sulfide, and ammonium oxalate. It should be borne in mind that more or less magnesium may be lost during these operations (see Calcium, p. 612), particularly if much arsenic or phosphorus is present, or if single precipitations by ammonium hydroxide and ammonium oxalate were made. Magnesium can be precipitated as the phosphate in the presence of the chromate ion.

A great deal of uncertainty exists concerning the proper conditions for determining magnesium as phosphate in spite of the enormous amount of work that has been done.[10] Nearly all experimenters have aimed at getting a precipitate of normal composition by a single precipitation. This can be accomplished in a solution containing magnesium alone and in known amount, but is a false hope as regards the solutions that are obtained in the course of an analysis. These practically always contain foreign salts such as alkali chloride, ammonium chloride, and ammonium oxalate. Sodium and especially potassium salts render the precipitate impure through substitution of the alkali metal for the ammonium radical.[11] The precipitate may also be contaminated by other magnesium phosphates such as $Mg_3(PO_4)_2$ or $Mg(NH_4)_4(PO_4)_2$. Admixture of the former leads to low results. Admixture of the latter leads to high results unless the metaphosphate that is formed during the usual ignition is heated at a higher temperature until it has been converted to the pyrophosphate. All uncertainty is removed when double precipitations are made, as it is possible to create nearly ideal conditions after redissolving the first precipitate. The reprecipitation entails no significant loss of magnesium[12] and scarcely any loss of the analyst's time.

It is unnecessary to remove ammonium salts that have resulted from prior separations before making the first precipitation unless very little magnesium or an unusually large amount of oxalate is present.[13] According to our experience diammonium phosphate, $(NH_4)_2HPO_4$, is the most satisfactory precipitant. Phosphoric acid would probably serve as well if its purity were more certain. Other precipitants which have been used are microcosmic salt, $NaNH_4HPO_4$, and disodium phosphate, Na_2HPO_4. These are quite satisfactory if double precipitations are made and but *little* of the reagent is added prior to the second precipitation. If a single precipitation is made, results are appreciably higher, especially if much magnesium is present or if the precipitate has stood for only a short time, say, 4 hours. With longer standing, better results are obtained; presumably magnesium sodium phosphate is more soluble and is gradually converted to the magnesium ammonium salt.

Formerly it was thought necessary to precipitate in the presence of a very large excess of ammonium hydroxide, but this idea has been shown to be erroneous. The precipitate is practically insoluble in a solution containing 5 to 10 per cent by volume of ammonium hydroxide. Precipitates that have been digested for 12 hours are slightly less soluble than those that have stood for 2 to 3 hours.

Were it not for the necessity of examining the precipitate for impurities after ignition, a Munroe crucible (p. 101) could be used with advantage instead of a paper filter. The use of a Gooch crucible is not recommended, for some varieties of asbestos are attacked by alkaline solutions containing soluble phosphates.

The ignition of the paper and precipitate must be done slowly and at as low a temperature as possible, preferably in a muffle, until the carbon is destroyed.[14] Otherwise, the pyrophosphate is slowly reduced and phosphorus volatilized.[15] In addition, the carbon becomes partially "fireproofed" and cannot be burned out. For fear of ruining the crucible by reduction of some of the phosphate if this is incinerated in contact with the filter paper, some chemists dry the filter and its contents, separate as much of the latter as possible, and burn the paper and what adheres to it before adding the main part of the phosphate. In this treatment there is always

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[9] *Ibid.*, 18, 1 (1937).

[10] Among the contributors to the subject may be mentioned H. Neubauer, *loc. cit.*; F. A. Gooch and M. Austin, *Am. J. Sci.*, [4] 7, 187 (1899); K. Bube, *Z. anal. Chem.*, **49**, 587 (1910); K. K. Jarvinen, *ibid.*, **44**, 335 (1905); D. Balarew, *Z. anorg. Chem.*, **101–104** (1918–19); Z. Karaoglanow and P. Dimitrow, *Z. anal. Chem.*, **57**, 353 (1918).

[11] For example, in careful single precipitations in solutions containing 0.0741 g of MgO as $MgCl_2$ and 5 g of NaCl per 400 ml, an average value of 0.0766 g MgO was obtained when precipitation was made at 20° C and 0.0787 when it was made in hot solution, followed by digestion at 20° C.

[12] For example, in tests made for us by H. B. Knowles, aliquot portions of a solution of pure magnesium chloride showed an average of 0.0729 g of MgO in single, 0.0733 g in double, and 0.0734 in triple precipitations. See also Phosphorus (p. 702).

[13] For a convenient method of removing ammonium salts, see p. 133

[14] If time permits, the wet paper and precipitate can be placed in the cold muffle, gradually heated to 750° C in the course of 3 hours, and finally stepped up to 1100 to 1150° C.

[15] K. D. Jacob and D. S. Reynolds, *J. Assoc. Offic. Agr. Chemists*, 11, 128 (1928).

danger of losing a little of the fine dry precipitate; hence we prefer to take the small risk of damage to the crucible. In our experience covering thousands of analyses, only twice has a crucible been damaged by burning precipitate and filter together, and then probably through the presence of an unsuspected foreign compound.

If the precipitate is of proper composition, it need not be ignited at temperatures above 1050 to 1100° C.[16] In the ordinary case, however, and especially with large precipitates (0.5 g), ignition at such temperatures may still leave a little $Mg(PO_3)_2$ in the residue, as the result of the formation of a little $Mg(NH_4)_4(PO_4)_2$ during the precipitation of the magnesium. It may therefore be desirable, especially after single precipitations, finally to heat for 5 to 15 minutes, depending on the size of the precipitate, at 1150 to 1200° C in order to convert the $Mg(PO_3)_2$ to $Mg_2P_2O_7$. The precipitate cannot be heated to constant weight at this temperature, for $Mg_2P_2O_7$ itself slowly loses P_2O_5 (see under Phosphorus, p. 705). Small amounts of foreign phosphates, such as calcium phosphate, lower the melting point of the pyrophosphate appreciably and may lead to a fused mass at temperatures as low as 1000° C.

The practice of Fresenius and others of moistening the ignited pyrophosphate with a drop or two of nitric acid, evaporating, and again igniting, in order to obtain a perfectly white pyrophosphate rarely does any good and sometimes leads to losses. Solution of the pyrophosphate in nitric acid, followed by evaporation and ignition, is certain to lead to losses.[17] Less objectionable is the procedure recommended by some authors to dissolve the washed magnesium ammonium phosphate in nitric acid, to evaporate the solution in a weighed platinum crucible, and then to ignite. If the evaporation is carefully carried out, there is no appreciable loss of phosphorus, and, as the solution approaches dryness, a pink color affords a most delicate test for contamination by manganese. Still another "corrective" measure is a final washing with a slightly ammoniacal 10 per cent solution of ammonium nitrate. Under conditions of ignition not clearly known, one of us (W. F. H.) has often observed that the product is not wholly soluble in hydrochloric or nitric acid, even on long boiling, but that white lumps of some peculiar phosphate resist the acid attack.

b. *Precipitation and Filtration.* α. *First precipitation.* Ordinarily the case is one in which manganese, calcium, and most other elements have

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[16] As a matter of fact, conversion to $Mg_2P_2O_7$ actually takes place at temperatures as low as 250° C, but heating at the higher temperatures is necessary to expel other compounds.

[17] D. Campbell, *Phil. Mag.*, [4] **24**, 380 (1862); E. Luck, *Z. anal. Chem.*, **13**, 255 (1874); Z. Karaoglanow and P. Dimitrow, *ibid.*, **57**, 353 (1918). According to W. M. McNabb [*J. Am. Chem. Soc.*, **49**, 893 (1927)], no loss occurs if the nitric acid solution of the ignited pyrophosphate is neutralized with ammonium hydroxide before evaporating and igniting.

already been separated, and the solution is then ammoniacal and contains sufficient ammonium chloride besides ammonium oxalate and often much sodium chloride.[18]

Slightly acidify the ammoniacal solution with hydrochloric acid, and add enough diammonium phosphate, as crystals of the pure salt or as a freshly prepared 10 per cent solution, to provide at least a ten-fold excess and preferably 1 g in addition for each 100 ml of solution.[19] Stir the solution vigorously, and add ammonium hydroxide slowly, especially while the precipitate is forming, until the solution is alkaline. At this point add 10 ml more for each 100 ml of solution, and set the solution aside. If but little magnesium is present, precipitation can be hastened by stirring vigorously and by cooling to 0 to 10° C. If a glass rod is used, the sides of the vessel should not be scraped, for, wherever there is contact, an adhering crystalline deposit forms quickly.

Let the solution stand overnight, filter through paper without attempting to transfer the precipitate, and wash the vessel, precipitate, and paper five or six times with cool dilute ammonium hydroxide (5 + 95).

β. *Second precipitation.* Dissolve the precipitate in warm dilute hydrochloric acid (1 + 4), and collect the solution in the original vessel so as to dissolve what precipitate may remain in it. Clean also the stirring rod with the acid.[20] If but little magnesium is present, transfer the solution to a smaller vessel. Dilute to 50 to 150 ml, depending on the amount of magnesium present, add 0.1 to 0.3 g of diammonium phosphate, and then ammonium hydroxide, drop by drop very slowly and with constant stirring until it is in slight excess and the crystalline precipitate has formed well. At this point add 5 ml in excess for each 100 ml of solution. Let the solution stand for at least 4 hours (overnight does no harm), filter through a fresh paper, and wash the precipitate with cool dilute ammonium hydroxide (5 + 95), using this time great care to clean the vessel and stirrer from adhering precipitate.

γ. *Ignition of the precipitate.* Dry the precipitate, wrapped in its moist paper, in a weighed platinum crucible, char the paper slowly without allow-

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[18] If the amount of ammonium salts, particularly ammonium oxalate, is very large, or but very little magnesium is present, it is desirable to destroy them by evaporating and gently igniting, or by wet attack as described on p. 133, before the first precipitation is attempted.

[19] This is especially needed if the solution contains large amounts of ammonium chloride, if the amount of magnesium is small, or if the volume of the solution is large. Solutions of ammonium phosphate attack glassware, and should either be freshly prepared or made distinctly acid with hydrochloric acid before storage.

[20] If platinum has not been removed in the course of a silicate analysis, and if the solution has been treated with ammonium sulfide and not acidified before the precipitation of calcium, some platinum sulfide may separate at this stage and should be removed by filtration.

ing it to ignite, and burn the carbon off over a gradually increased flame which never heats the crucible to more than the faintest red. Finally heat for 30 minutes at 1000 to 1100° C. Cool in a desiccator, weigh as $Mg_2P_2O_7$ and repeat the heating until the weight remains constant.

c. *Removal and Determination of the Usual Contaminants in Magesium Pyrophosphate.* Experience has shown that most analysts are prone to report high results for magnesium. One of the causes of error lies in imperfect separation of other elements that accompany it. After the usual separations it is to be expected that, if originally present, barium, small amounts of strontium and calcium and, if precipitation with ammonium sulfide is omitted, most of the manganese will be precipitated with the magnesium. The precipitation of calcium and manganese is complete; that of strontium and barium is practically so if appreciable amounts of magnesium are present and the concentration of ammonium salts is not excessive. Lithium is not precipitated unless the solution is heated or evaporated. Even when all ordinary requirements have been met, small amounts of some of the elements escape removal and are weighed as phosphates with magnesium. The analyst should make tests for the commonest contaminants, if only to convince himself of the reality of the error, even after very careful work, and of the limitations of most of our methods.

α. Barium. In the usual analysis barium, in the absence of sulfates, accompanies magnesium and is finally thrown down together with it and weighed as a mixture of $Ba_2P_2O_7$ and $Ba_3(PO_4)_2$. If the magnesium pyrophosphate is tested for calcium as directed below, the barium separates as sulfate together with the calcium. Because of the uncertain composition of its phosphate and the question of its complete precipitation, barium should be removed by sulfuric acid before the final precipitation of the magnesium.

β. Calcium. The precipitation of calcium as oxalate is never quite complete, and so, if it was originally present, a very little of it will probably always be found in the magnesium pyrophosphate as a mixture of $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$. The amount of the latter is relatively small and does not cause serious error if the total amount of calcium is small and corrections are based on the normal phosphate.[21] Both barium and calcium can be determined and allowed for as described under Calcium (p. 613). The weight of lime obtained should average less than half a milligram in rock analysis, and is added to that of the lime already found, and subtracted as tricalcium phosphate from that of the magnesium pyrophosphate in order to arrive at a truer figure for magnesium. The alcoholic filtrate left after the separation of calcium can be evaporated, ignited to destroy organic matter and tested for manganese as in γ below.

A less certain way to separate the calcium that is in the pyrophosphate, but one that admits of detecting small amounts of iron and aluminum that may have escaped precipitation earlier in the analysis, is the following:

To the ignited pyrophosphate dissolved in but slight excess of hydrochloric acid, add ammonium hydroxide to alkalinity and then acetic acid, drop by drop, until the solution, which should measure 10 to 30 ml and not be hot, clears. It happens now and then that a little flocculent matter fails to dissolve. Remove this, ignite it, and subtract its weight if proved to be free from magnesium, which it often contains, from the original weight (see γ below). It is likely to consist in great part or wholly of phosphates of aluminum, iron, or manganese, and shows often a reddish color on ignition.[22] If an excess of acetic acid has been added, neutralize most of this cautiously with ammonium hydroxide, then add a drop or two of solution of ammonium oxalate, and set the small beaker aside for 12 hours if necessary. Almost invariably a small precipitate shows itself, which, if fine grained and nonadherent to the glass, may be regarded as pure calcium oxalate; otherwise it contains or may consist largely of magnesium oxalate. In that case collect, ignite, redissolve, and reprecipitate it. The operation, to be satisfactory, requires great care.

γ. Manganese. Manganese behaves like magnesium and is weighed as the pyrophosphate, $Mn_2P_2O_7$. A separation from one another of the iron, aluminum, and manganese which the flocculent precipitate mentioned under the second method in β may contain is not worth the trouble, careful prior treatment being presupposed. The first two constituents named may have been introduced since the original precipitation of the iron and aluminum, and their amount in terms of those elements is very small. But the amount of manganese it contains may be a sensible proportion of the whole of that element if it was not removed earlier in the analysis. Therefore, bring the precipitate into nitric or sulfuric acid solution, and reserve. The solution containing the magnesium may also be manganiferous and must be evaporated to dryness, ignited, and evaporated two or three times with nitric acid, or once with sulfuric acid, to remove all traces of chlorine. Unite

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[21] For example, in tests made for us, H. B. Knowles obtained the following results:

CaO Taken, g	MgO Taken, g	Mixed Phosphates, g	CaO Calculated to $Ca_3(PO_4)_2$, g	$Mg_2P_2O_7$ by Difference, g	MgO Calculated, g	CaO Recovered from Mixed Phosphates, g
0.0014	0.0492	0.1380	0.0026	0.1354	0.0490	0.0015
0.0287	0.0158	0.0958	0.0526	0.0432	0.0156	
0.0042	0.0492	0.1442	0.0077	0.1365	0.0494	0.0045
0.0070	0.0492	0.1489	0.0129	0.1360	0.0492	0.0072

[22] Iron by itself is not precipitated at all by diammonium phosphate in an ammoniacal solution containing ammonium oxalate. Aluminum is quantitatively precipitated, but more or less of it dissolves when the precipitate is washed with a 5 per cent solution of ammonium hydroxide.

this with the small solution already reserved. Now determine the manganese colorimetrically as described under Manganese (p. 451), and add its amount to that already found, unless the total has been ascertained in a separate portion of the sample. In any case its amount, if significant, is to be deducted as pyrophosphate from the gross weight of the magnesium pyrophosphate.

The distribution of the manganese over the alumina, lime, and magnesia when ammonia was employed for the precipitation of the alumina and no attempt made to remove manganese at all, is shown in the table on page 880.

B. DETERMINATION FOLLOWING PRECIPITATION WITH 8-HYDROXYQUINOLINE

A very desirable method for the determination of magnesium is that in which it is precipitated by 8-hydroxyquinoline in alkaline solution and then determined by titrating with a standard brominating solution after dissolving the precipitate in diluted hydrochloric acid, or by weighing as the dihydrate, $Mg(C_9H_6NO)_2 \cdot 2H_2O$; the anhydrous oxyquinolate, $Mg(C_9H_6NO)_2$; or the oxide, MgO; after heating at 105° C, 150 to 160° C, or 1000° C, respectively. The method, especially the volumetric modification, is more rapid than the method in which magnesium is weighed as the pyrophosphate.

A number of elements (see p. 122) are also precipitated by the reagent; the precipitation of magnesium must therefore follow their removal, as in the General Procedure (p. 855). In this procedure, the substitution of the volatile reagent 8-hydroxyquinoline, for the commonly used nonvolatile reagent, diammonium phosphate, permits determination of the alkalies in the final filtrate if they have not been introduced in other stages of the analysis.

In any procedure, interfering elements such as copper, iron, aluminum, titanium, manganese, zinc, and calcium must be removed. In the volumetric modification, interference by calcium can be avoided by converting it to the nonobjectionable calcium oxalate and then, without filtering, proceeding with the precipitation of the magnesium oxyquinolate. The following procedure illustrates the precipitation with 8-hydroxyquinoline, and its application in the routine volumetric determination of magnesium in cements containing no appreciable amounts of interfering elements, such as copper, zinc, or manganese, that are not removed by the preliminary treatment with ammonium hydroxide.[23]

PROCEDURE. Transfer a 0.500-g sample to a 400-ml beaker, mix with 10 ml of water, and then add 10 ml of hydrochloric acid. Heat gently, and grind any coarse particles with the flattened end of a glass rod until decomposition is complete. Dilute to 150 ml with hot water. Add 3 drops of methyl red indicator (0.02% alcoholic solution), and then ammonium hydroxide until the solution is distinctly yellow. Add macerated filter paper, and heat to boiling. Boil for 1 to 2 minutes, cease heating, and allow the solution to stand until the precipitate has settled. Filter without delay, and wash the precipitate thoroughly with a hot 2 per cent solution of ammonium chloride.

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[23] J. C. Redmond, *Bur. Standards J. Research*, 10, 823 (1933).

Add 5 ml of hydrochloric acid to the filtrate, and then add 25 ml of a hot 4 per cent solution of ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$. Heat to boiling, stir gently, and slowly add ammonium hydroxide until the solution is alkaline. Continue the boiling for 1 to 2 minutes, and let stand for 10 to 15 minutes as the solution cools to about 70° C.

Add 20 ml [24] of a clear 1.25 per cent solution of 8-hydroxyquinoline (25 g of the reagent dissolved in 60 ml of glacial acetic acid and diluted to 2 liters with water), and then 4 ml of ammonium hydroxide per 100 ml of solution. Stir with a mechanical stirrer for 15 minutes, and set aside until the precipitate has settled. Filter, and wash with hot dilute ammonium hydroxide (1 + 40).

Dissolve the precipitate in 200 ml of warm dilute hydrochloric acid (1 + 4). Cool to approximately 25° C, and add from a pipette 25 ml of a standard (0.2 *N*) solution of potassium bromate-potassium bromide. Stir, and let stand for about 30 seconds to insure complete bromination. Add 10 ml of a 25 per cent solution of potassium iodide, stir well, and then titrate with a standard (0.1 *N*) solution of sodium thiosulfate until the color caused by the iodine becomes faintly yellow. At this point, add 2 ml of starch solution, and titrate to the disappearance of the blue color. To calculate the weight of MgO, subtract the volume of sodium thiosulfate solution used from the volume of sodium thiosulfate solution that is equivalent to 25 ml of the bromate-bromide solution, and multiply the remainder by the MgO titer of the thiosulfate solution.

To prepare the 0.2 *N* solution of potassium bromate-bromide, dissolve 20 g of potassium bromide and 5.57 g of potassium bromate in 200 ml of water, and dilute to 1 liter. To prepare the 0.1 *N* solution of sodium thiosulfate, dissolve 25 g of $Na_2S_2O_3 \cdot 5H_2O$ in 200 ml of water, and dilute to 1 liter (see p. 196).

For the determination of the volume of the thiosulfate solution that is equivalent to a given volume of the bromate solution, see Precipitation by

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[24] This amount suffices for 0.5-g samples containing 6 per cent or less of magnesia. For cements of higher magnesia content, add proportionately more reagent. 8-hydroxyquinoline is somewhat volatile at temperatures above 60° C. In precipitations, the chief concern is to avoid undue loss of the reagent before the precipitate has formed. After the separation of the precipitate, solutions can be boiled for 1 to 2 minutes to assist in coagulating the precipitate, and in removing any reagent carried down by it. When a precipitate is dissolved in acid before titration, the temperature of the solution should be no higher than is needed to dissolve the precipitate.

8-Hydroxyquinoline (p. 125). The most satisfactory method for the standardization of the thiosulfate solution is in using a standard material of like nature, taking portions containing amounts of magnesia that are comparable with those involved in the routine determination, and carrying them through all steps of the procedure. The titer of the thiosulfate solution is then found by dividing the weight of MgO by the difference between the volume of thiosulfate solution required in the back titration and the volume of thiosulfate solution that is equivalent to the volume of the potassium bromate-potassium bromide solution that was added. This procedure leads to less calculation, and also to more accurate results if the thiosulfate solution has been properly prepared and its titer is checked at intervals of a week or so.

Theoretically, the MgO and Mg titers of 0.1 *N* solutions of either reagent should be 0.0005038 and 0.0003038, respectively, whereas those of 0.2 *N* solutions should be twice these values.

If the precipitate contains only magnesium oxyquinolate, it can be caught on a tared fritted-glass crucible and either dried at 105° C and weighed as $Mg(C_9H_6NO)_2 \cdot 2H_2O$, or at 150 to 160° C and weighed as $Mg(C_9H_6NO)_2$; the latter is preferable if 8-hydroxyquinoline was used in considerable excess. Small precipitates can be caught on paper and cautiously ignited to MgO.

C. DETERMINATION BY TITRATION

Various methods, other than that described under B, have been proposed for the volumetric determination of magnesium. The one commonly used is that of Stolba[25] as modified by J. O. Handy,[26] which is based on the reaction: $MgNH_4PO_4 + H_2SO_4 = MgSO_4 + NH_4H_2PO_4$.

The chief points in this method consist in precipitating and washing the phosphate according to the usual practice, removing the ammoniacal wash liquid, dissolving the precipitate in a measured excess of sulfuric acid (as shown by methyl orange), and then titrating with sodium hydroxide to a clear yellow color. If the solutions are equivalent, the difference in the volumes used represents the sulfuric acid required to convert the tertiary phosphate, $MgNH_4PO_4$, to the primary phosphate, $NH_4H_2PO_4$ or $Mg(H_2PO_4)_2$. The excess of the secondary phosphate precipitant and the ammoniacal wash liquid must be removed, for both would consume sulfuric acid, the former in a change to the primary salt, the latter in neutralization. Handy recommends that the washed precipitate be distributed over the lower two thirds of the filter, which is then to be turned, opened, blotted as much as possible on dry filters, and finally dried at room temperature for about 45 minutes or at not over 60° for about 15 minutes. The precipitate can be dried completely, or the drying can be stopped when the paper has dried inward one-half inch from the margin, at which time the free ammonia will have been expelled. Gooch crucibles can be used as filters, and drying is facilitated by washing the precipitate a few times with alcohol. After the drying of the precipitate, the treatment is as follows:

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[25] F. Stolba, *Jahresber.*, 985 (1876).

[26] *J. Am. Chem. Soc.*, 22, 31 (1900).

Place paper and precipitate in a suitable beaker, treat with a measured excess of normal sulfuric acid, and stir well until the paper is disintegrated and the precipitate is dissolved. Add 2 drops of a 0.1 per cent solution of methyl orange and then more acid if the solution is not decidedly pink. Dilute to 100 ml, and titrate back with 0.1 *N* sodium hydroxide solution to the appearance of a clear yellow color. One milliliter of 0.1 *N* sulfuric acid corresponds to 0.00202 g of MgO.[27]

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[27] P. J. Elving and E. R. Caley [*Ind. Eng. Chem. Anal. Ed.*, 9, 558 (1937)] point out that magnesium can be quantitatively precipitated as oxalate in 85 per cent acetic acid solution, thus permitting ignition to the oxide or titration with permanganate, as well as the determination of the alkalies in the filtrate. Drawbacks are the unpleasant nature of the solution and the bulkiness of the precipitate.

THE ALKALIES

LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, CESIUM

Chapter 42

THE ALKALIES

Lithium is almost never found in rocks in more than spectroscopic traces, although it is one of the most universally distributed of the elements. It is found in the alkali feldspars, in muscovite, beryl, and in the lithium minerals lepidolite, spodumene, petalite, amblygonite, triphylite, and lithiophylite. According to Washington [1] there is reason for the belief that it is especially prone to occur in highly sodic rocks. The more refined spectrochemical methods now available have disclosed appreciable percentages of lithium in materials not formerly suspected of containing significant amounts of this element. For example, National Bureau of Standards standard sample of flint clay no. 97 from Clearfield County, Pa., contains 0.22 per cent of Li_2O which is about twice its sodium oxide content. The analyst should therefore guard against neglecting to test for lithium when the alkalies are being determined.

Sodium is the most abundant of the alkali metals, comprising 2.75 per cent of the lithosphere.[2] In igneous rocks it is a constituent of the feldspars, of the nepheline group of minerals, and of certain pyroxenes, such as aegirite.[2] It is also abundant in rock salt and in nearly all natural waters, sea water especially.

Potassium is also an abundant metal of the alkali group, comprising 2.58 per cent of the lithosphere. It is found in many rocks, especially as a constituent of the feldspars, micas, and leucite. Nearly all terrestrial waters contain potassium.

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[1] *Manual of the Chemical Analysis of Rocks*, 4th ed., p. 31, John Wiley & Sons (1930). For a discussion of the geochemistry of lithium, see L. W. Strock, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse,* **IV**, 171 (1936). For a selective reaction for as little as a few tenths of a microgram of lithium in a single drop of solution saturated with the other alkali salts, which is based on the low solubility of the compound that lithium forms with trivalent iron and periodic acid, consult O. Pročke and R. Uzel, *Mikrochim. Acta,* **III**, 105 (1938).

[2] F. W. Clarke, The Data of Geochemistry, *U. S. Geol. Survey Bull.* 770 (1924).

Rubidium is found in lepidolite and, in minute quantities, in a number of minerals such as feldspars, beryl, micas, leucite, spodumene, and carnallite.[3]

Cesium is the rarest metal of the alkali group. It is found in pollucite, a silicate of aluminum and cesium, and, like rubidium, in lepidolite and certain other minerals.

I. GENERAL CONSIDERATIONS

In the section on the Alkalies under Rock Analysis (p. 923), the assembling of the alkali metals as chlorides free from all other elements except perhaps a very little magnesium has been described. It is possible that no one of the procedures separates quite all of the magnesium. What little of it passes into the final filtrate and is eventually weighed with the alkalies as chloride can, however, be recovered later and its weight deducted from the gross weight of the chlorides.[4] If ammonium carbonate alone was relied upon to separate calcium, the alkalies are also likely to contain a few tenths of a milligram of its chloride. In this case, the calcium should now be separated by a little ammonium oxalate and ammonium hydroxide, the filtrate evaporated to dryness, and the excess of ammonium oxalate destroyed by heat. The residue is then moistened with a drop of hydrochloric acid, this evaporated, and the weight of chlorides again determined. Not all of the lithium will be gathered with the alkali chlorides in an ordinary attack by the J. Lawrence Smith method, for some of it may be lost in the insoluble matter left after the extraction of the sintered melt with water, and some may be caught in the calcium carbonate and calcium oxalate precipitates.

In the usual case lithium is not present in determinable amount, and the analysis is done by the chloroplatinate method as in Section II. If lithium is present, the analysis can be made by the butyl alcohol-ethyl acetate method as described in Section III or by any of the methods described in Section IV. The former is used for the determination of potassium (rubidium and cesium), sodium, and lithium in successive operations; the latter are designed primarily for the isolation of lithium, followed, if need

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[3] W. R. Schoeller and A. R. Powell, *The Analysis of Minerals and Ores of the Rarer Elements*, p. 41, 2d ed., Charles Griffin and Co., London, 1940.

[4] Precipitation by means of 8-hydroxyquinoline as described under Precipitation by 8-Hydroxyquinoline (p. 122), repeated when large amounts of alkalies are present, is an excellent procedure for the separation of magnesium from the alkalies [(R. Berg, *Z. anal. Chem.*, **71**, 32 (1927); F. L. Hahn and K. Vieweg, *ibid.*, 126]. In fact, the precipitation also serves to separate many other elements, as for example iron, aluminum, titanium, and zirconium. According to L. Moser and K. Schutt [*Monatsh.*, **51**, 23 (1929)], the most satisfactory separation of magnesium from lithium is obtained by precipitating with 8-hydroxyquinoline.

be, by the determination of the accompanying alkalies. Rubidium and cesium are rarely encountered.[5] When originally present, they are to be found with the potassium that is obtained in any of the above methods and are to be determined as described in Section V. Finally, in Section VI are given the more common procedures for the determination of potassium alone.

II. THE CHLOROPLATINATE METHOD

In the chloroplatinate method, potassium (together with rubidium and cesium) is precipitated by chloroplatinic acid in a solution of the chlorides of the alkalies. The amount of sodium, as chloride, is then usually determined by subtracting the potassium chloride equivalent of the chloroplatinate precipitate that is obtained from the weight of the mixed chlorides. This is quite satisfactory when the two alone are involved, although the determination depends on the accuracy of the potassium determination and the purity of the mixed chlorides. If rubidium and cesium are present, the method fails; if these are absent and lithium is present, the subtraction of potassium chloride of course gives the weight of combined sodium and lithium chlorides, and further separations must be made.[6]

The method is the oldest and best known, and is probably still the most widely used method today. It suffers, however, from the fact that the composition of the precipitate that is obtained may vary slightly from that expressed by the formula K_2PtCl_6. Partly for this reason and partly because of the cost of the reagent, the perchlorate method has somewhat displaced the chloroplatinate method. In the long run, the saving is not much, for there need be no loss whatsoever of platinum if the precipitates and filtrates are saved and worked over from time to time.

A. DETERMINATION OF POTASSIUM

The following operations must be carried out in an atmosphere free from ammonia fumes. To the chloride solution in a small porcelain dish,[7] add sufficient chloroplatinic acid solution (Reagents, p. 42) containing 10 per cent of platinum to react with all of both the sodium and potassium.[8] The necessary amount to use is readily calculated from the known strength of the platinum solution and the weight of mixed chlorides counted as sodium chloride. The dilution of the resulting solution should be such that, when heated on the steam bath, any precipitate that may have formed dissolves wholly. This is to prevent inclusion of mother liquor in a mass of crystals suddenly formed. Evaporate until the solution is syrupy but solidifies on cooling. Do not evaporate to dryness, as this will dehydrate the sodium salt and render it less soluble in alcohol. Drench the residue with 80 per cent (by volume) alcohol,[9] filter by decantation through a small paper, wash by decantation with more of the alcohol, crushing the crystals with a small pestle or the widened and rounded end of a short glass rod. Reserve the filtrate and washings if sodium is to be determined directly. The residue should be golden yellow. An orange-red color indicates incomplete removal of the sodium salt. It is unnecessary to bring the mass of the precipitate upon the filter. Dry the dish and paper for a few moments to remove adhering alcohol. Dissolve in hot water what precipitate is on the filter, catching the solution in a weighed crucible or small dish of platinum. Evaporate to dryness and add the salt that is still in the porcelain dish. If the salt is at all lumpy, redissolve it in water, and again evaporate to dryness. Heat for an hour at 130° C in an air oven (100° suffices for very small amounts of fine-grained precipitate). It is necessary to cover the receptacle at first because the precipitate is prone to decrepitate. When

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[5] Cesium occurs as a silicate of aluminum and cesium in the rare mineral pollucite and is often found in lepidolite. Rubidium is also found in the latter, and frequently occurs in minute amounts along with potassium in iron ores [W. N. Hartley and H. Ramage, *Trans. Chem. Soc.*, **71**, 533 (1897)].

[6] Separations of potassium from lithium may not be complete in a single precipitation of the former as chloroplatinate. B. Brauner [*Collection Czechoslov. Chem. Communs.*, **2**, 442 (1930)] states that 23 per cent of the lithium was found in the potassium chloroplatinate obtained by a single precipitation in a solution containing 0.1195 g NaCl, 0.0175 g KCl, and 0.0017 g LiCl.

[7] Preferred to platinum because of the possibility of the formation of an insoluble platinous compound by an undetermined reaction. See also F. Bolm, *Z. anal. Chem.*, **38**, 349 (1899).

[8] G. F. Smith and A. C. Shead [*J. Am. Chem. Soc.*, **53**, 947 (1931)] assert that precipitates are more nearly of ideal composition and can be heated at temperatures as high as 260° C if lithium chloroplatinate is substituted for chloroplatinic acid as the precipitant.

[9] H. Fresenius and P. H. M.-P. Brinton, *Z. anal. Chem.*, **50**, 21 (1911). The solubility of potassium chloroplatinate in 80 per cent alcohol is so slight that a correction is not necessary if the volume of alcoholic filtrate and washings is kept at 50 to 75 ml, depending on the size of the precipitate. According to the data given by E. H. Archibald and his coworkers [*J. Am. Chem. Soc.*, 30, 755 (1908)], the solubility of K_2PtCl_6 in 80 per cent by volume C_2H_5OH at 20° C must approximate 10 mg per 100 ml, which represents about 1 mg of K_2O per 50 ml. The amount that is dissolved during an analysis, however, is considerably under this figure because of the presence of chloroplatinic acid and sodium chloroplatinate in the solution in which the potassium is thrown out, and because the alcohol used for washing is by no means saturated after its short contact with the salt. Moreover, any solubility loss is fairly well taken care of if potassium is found in the blank runs on the reagents.

It should be noted that potassium chloroplatinate is appreciably more soluble in methyl than in ethyl alcohol, and that the use of absolute ethyl alcohol, as sometimes recommended, may lead to decomposition of sodium chloroplatinate and precipitation of sodium chloride [J. Morozewicz, *Anz. Akad. Krakau*, 796 (1906)]. Alcohols denatured with 10 per cent of ethyl ether or of acetone can be substituted for 95 per cent ethyl alcohol in the triple acetate method for sodium or the chloroplatinate method for potassium [P. A. Webster and R. M. Crane, *Ind. Eng. Chem. Anal. Ed.*, **15**, 36 (1943)].

dry, cool and weigh as K_2PtCl_6. Calculate first the KCl equivalent of the precipitate in order by subtracting it from the weight of mixed chlorides to get that of the sodium chloride, and then the K_2O or K as desired. For such percentages of potassium as occur in rocks and most minerals, the theoretical factor 0.3067 based on the accepted atomic weight for platinum may be safely used for the conversion of K_2PtCl_6 to KCl. The use of the empirical factor 0.3056, as recommended by Fresenius, Treadwell, and others is not warranted in analyses made by the method as described.[10]

B. DETERMINATION OF SODIUM (LITHIUM)

Few minerals and perhaps no rocks carry sodium alone of the alkali metals. It is customary to separate and determine its congeners after having weighed all together, and thus to find the sodium by difference. If a check is desired, however, the sodium can be determined in the platiniferous filtrate from the potassium chloroplatinate obtained in A. First the platinum must be removed, and, of the several possible ways of doing this, the following of Bunsen's is the neatest and most satisfactory.

Evaporate the alcoholic solution in a flask of suitable size (ordinarily of 100 ml capacity) until most of the alcohol is gone, add water if need be, insert in the flask a stopper with inlet and outlet tubes, the latter of which can be closed, connect the inlet tube with a hydrogen generator, and fill the flask with hydrogen. Close then the exit without allowing any air to enter, set the flask in a warm place or in a beaker of water which can be kept warm, and leave it still connected with the generator under slight pressure until the platinum is all precipitated and the liquid is water-white. This can be determined by shaking the flask gently so that the suspended metal sinks.

Displace the hydrogen by an inert gas, filter, wash with water, evaporate the filtrate to a small volume in platinum or porcelain, transfer to a weighed platinum crucible which has a perfectly fitting cover with a projecting lip, and evaporate as nearly as possible to dryness. The attainment of this dry condition can be helped sometimes by drenching the concentrated solution at a certain stage with strong hydrochloric acid, which precipitates the salt in a fine granular state, and then continuing the evaporation very cautiously. When it is apparently dry, set the covered crucible in a triangle of platinum wire at such a height that a Bunsen burner flame, turned as low as possible and quite undisturbed by draughts, can be brought under the lip so as to heat it without the flame touching the bottom or side of the crucible. If, when it is held close to the ear, decrepitation is audible, instantly withdraw the lamp for a moment. By degrees the heat may be increased when decrepitation has ceased and no more ammonium chloride fumes escape (if a little of that salt was present) finally to a point just short of causing the salt to melt. Weigh the residue as NaCl, and test it spectroscopically for lithium if that element had not been separated.

There remains a correction to be made for any small amount of magnesium chloride which, in the analysis of certain materials carrying magnesium, may have escaped separation and is now with the sodium. This can be determined by precipitating it as magnesium ammonium phosphate, as described under Magnesium (p. 638). If a check determination of the sodium is not to be made, the filtrate from the potassium chloroplatinate, freed from its platinum as explained above, can be used directly for this magnesium test. The weight of magnesium chloride calculated from the weighed pyrophosphate is to be deducted from the gross weight of the mixed alkali chlorides.

If it is desired to weigh sodium as the sulfate, which can be safely heated to a much higher temperature than the chloride, any sodium salt of a volatile acid can be converted to sulfate by evaporating with sulfuric acid and expelling the excess of acid. Most of this can be removed over a free flame or a radiator (Fig. 5), but the last of it is tenaciously retained and needs the help of ammonium carbonate vapor to effect its complete expulsion. This salt is introduced under the cover of the crucible in small fragments, and heat is reapplied. After weighing, repeat the treatment with carbonate until the weight remains constant. Weigh as Na_2SO_4, which is slightly hygroscopic.

Sodium can also be determined directly as described in Section III.

III. THE BUTYL ALCOHOL-ETHYL ACETATE METHOD

In the butyl alcohol-ethyl acetate method,[11] the chlorides are converted to perchlorates, and sodium and lithium are separated from potassium (rubidium and cesium) by extracting with a mixture of normal butyl alcohol and ethyl acetate. The extract is then evaporated to expel ethyl acetate, and sodium is precipitated as chloride by addition of a solution of hydrochloric acid gas in butyl alcohol. Finally, the solution containing

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[10] W. J. O'Leary and J. Papish [*Ind. Eng. Chem. Anal. Ed.*, **6**, 107 (1934)] point out that potassium, rubidium, and cesium can be quantitatively precipitated and separated from large amounts of sodium, iron, aluminum, manganese, and other salts by direct precipitation with chloroplatinic acid in 60 to 70 per cent (by volume) alcohol, provided everything in the solution has previously been converted to nitrate. If the alkalies have been assembled as chlorides, immediate and quantitative precipitation can also be obtained by dissolving them in 60 to 70 per cent alcohol and adding chloroplatinic acid and then 2 to 3 drops of ethyl ether. It is maintained that chloroplatinates thus precipitated are purer than those obtained by evaporation with chloroplatinic acid to near dryness, followed by digestion with alcohol.

[11] H. H. Willard and G. F. Smith, *J. Am. Chem. Soc.*, **44**, 2816 (1922); G. F. Smith, *ibid.*, 47, 762 (1925); G. F. Smith and J. F. Ross, *ibid.*, 774, 1020.

the lithium is evaporated with sulfuric acid, and the lithium is weighed as sulfate. The solubilities of the perchlorates of the alkali and alkaline earth metals, magnesium, and ammonium are given in Table 19.

TABLE 19

Solubility of the Perchlorates of the Alkali and Alkaline Earth Metals and Ammonia[12]

	G per 100 Ml Solution at 25° C				
Perchlorate	Water	Methyl Alcohol	Ethyl Alcohol	*n*-Butyl Alcohol	Ethyl Acetate
$NaClO_4$	113.88	35.833	11.134	1.495	8.425
$LiClO_4$	47.42	89.44	79.41	49.25	63.40
NH_4ClO_4	21.91	5.268	1.488	0.0137	0.0286
$KClO_4$	2.0394	0.0830	0.0094	0.0036	0.0013
$RbClO_4$	1.328	0.0472	0.0071	0.0016	0.0014
$CsClO_4$	1.961	0.0734	0.0086	0.0048	Insoluble
$Ba(ClO_4)_2$	128.99	119.85	78.543	41.716	80.812
$Ca(ClO_4)_2$	112.34	113.68	89.551	68.419	57.377
$Sr(ClO_4)_2$	157.51	113.95	100.01	71.205	76.67
$Mg(ClO_4)_2$	73.453	37.749	18.398	44.638	54.173

PROCEDURE. Dissolve the mixed chlorides in water, transfer to a 150-ml Pyrex beaker,[13] and treat with two or three times the equivalent quantity of pure perchloric acid (not less than 1 ml of 60 to 70% acid in any case). Evaporate to dryness on the hot plate (not over 350° C), and expel any acid condensed on the side walls by brushing with a free flame. Cool, dissolve the salts in 3 to 5 ml of water, and again evaporate to dryness on the hot plate.[14] Cool, add 10 to 20 ml of a mixture of equal parts by volume of *n*-butyl alcohol and ethyl acetate (both anhydrous),[15] digest near the boiling point for 2 to 3 minutes, and cool to room temperature.

Decant the supernatant liquid into a previously ignited and weighed Gooch or, preferably, Munroe crucible,[16] and wash thrice by decantation with 5-ml portions of the alcohol-acetate mixture. Reserve the filtrate and washings.[17] Dissolve the residue in the crucible in a minimum of hot water, catch the solution in the original beaker, and again evaporate to dryness. Cool, add 10 ml of the solvent, digest and cool as before, and filter through the original crucible, which must of course have been dried. Transfer the residue to the crucible by means of a fine jet of the mixed solvent, and finally wash the crucible and contents 10 to 15 times with 0.1- to 1-ml portions from the wash bottle. Combine and reserve the filtrate and washings which should approximate 55 ml. Dry the original beaker, and brush any particles of perchlorate into the crucible. Dry the crucible and precipitate at 110° C in an oven and finally for 15 minutes in a muffle at 350° C. Cool, and weigh as $KClO_4$.[18]

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[12] H. H. Willard and G. F. Smith, *ibid.*, **45**, 293 (1923).

[13] Hot perchloric acid is said to have a solvent action on some types of laboratory glass and porcelain ware. Pyrex glass is not affected [G. F. Smith and J. F. Ross, *loc. cit.*].

[14] According to Smith and Ross, perchlorates that have been obtained from solution in perchloric acid still retain the latter after evaporation at 350° C and must be dissolved in water and again evaporated.

[15] *n*-Butyl alcohol of a boiling range of 116 to 117.7° C at 760 mm should be prepared by fractional distillation of the CP reagent (sp. gr. 25°/4° 0.8065) and preferably dried by refluxing over metallic calcium. The anhydrous ethyl acetate must be free from ethyl alcohol and have a purity of 99.7 to 100 per cent.

[16] It is desirable to arrange the filtering apparatus so that the filtrate can be caught directly in a small beaker.

Evaporate the combined filtrate and washings on a hot plate until the ethyl acetate is expelled, which is accomplished by concentrating to at least 40 per cent of the original volume. Continue the evaporation to 20 ml if the volume of the solution is greater than this. Heat to 80 to 90° C, and add, dropwise and with stirring, 2 ml of a 20 per cent solution of hydrochloric acid gas in butyl alcohol[19] and then 6 ml more. Cool to room temperature, collect the precipitate on a dry Gooch or Munroe crucible, and wash 8 to 10 times with 1- to 2-ml portions of a 6 to 7 per cent solution (sp. gr. 25°/4° 0.8425 to 0.8485) of hydrogen chloride in butyl alcohol (made by diluting 40 ml of the 20% solvent with 100 ml of butyl alcohol). Reserve the filtrate and washings for the determination of lithium. Dry the crucible and contents for a few minutes at 110° C, and then ignite for 5 minutes at 600° C in a muffle, or at a very dull red over a free flame. If it is desired to determine the sodium gravimetrically, cool in a desiccator, and weigh the crucible and impure sodium chloride. Dissolve the precipitate by means of a fine jet of water, thoroughly wash the crucible, and collect the filtrate and washings in a 150-ml beaker. Dry the crucible and insoluble residue for 1 hour at 110° C, cool, and again weigh. The loss

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[17] When sodium is absent, lithium can be completely separated from potassium by one extraction.

[18] According to Smith and Ross, a temperature of 350° C is required for the complete dehydration of $KClO_4$ that has been crystallized from its solution in water. The occluded moisture remaining after drying at 150° C may amount to as much as 0.3 per cent of the weight of the salt. The solubility of potassium perchlorate in the mixture of equal parts of *n*-butyl alcohol and ethyl acetate at 25° C is approximately 1.0 mg in 100 ml, corresponding to 0.6 mg of KCl or 0.34 mg of potassium oxide. If the total volume does not exceed 60 ml, no corrections are necessary, for the losses are offset by a correspondingly small amount of sodium and lithium perchlorates that are retained by the potassium salt. The solubility of rubidium and cesium perchlorates is about one-half that of potassium.

[19] Prepared by passing dry hydrochloric acid gas into butyl alcohol. 200 ml of a 20 per cent solution (sp. gr. 0.905) can be prepared in 2 to 3 hours.

in weight represents pure sodium chloride.[20] The value so obtained can be checked or the sodium determined without the weighing, as described by titration of the dissolved chloride as in Mohr's method (p. 732).

Dilute the filtrate and washings that were reserved for the determination of lithium with one third their volume of water, thus forming two layers. Cover with a watch glass resting on glass hooks, and evaporate on a steam bath in such a way as to avoid any condensation on the upper part of the beaker.[21] Add 5 to 10 ml of water at the end to make the removal of organic matter more nearly complete before the fumes of perchloric acid appear. When a slight brown coloration appears, remove the hooks, and rest the watch glass directly on the beaker. Heat on a wire gauze until fumes of perchloric acid appear. If a brown residue remains on the walls of the beaker, remove it by brushing the walls with a flame, if there is not enough perchloric acid to oxidize the organic matter, add a few drops more. When the brown color has been destroyed, add 0.5 ml of sulfuric acid, replace the watch glass, and heat on a hot plate or on a gauze over a low flame until dry. Cool, add 5 to 10 ml of water, wash the watch glass and inside walls of the beaker, and transfer the lithium sulfate to a platinum crucible that has been ignited and weighed with the lid. Cautiously evaporate to dryness, cover with the lid, and heat, preferably by a ring burner, until every trace of acid is removed, and then in a muffle at 600° C for 5 to 10 minutes. If the latter treatment is done over a free flame, some reduction of the sulfate to sulfide may take place. Cool, and weigh as Li_2SO_4.

According to Kallmann,[22] satisfactory determinations of lithium (and the other alkali metals) can be had by (1) obtaining the mixed chlorides by a combined J. Lawrence Smith-Berzelius attack, (2) converting the chlorides to perchlorates, (3) treating with *n*-butyl alcohol, perchloric acid, and hydrogen chloride to precipitate potassium, rubidium, cesium, and sodium, and (4) converting the lithium in the filtrate to sulfate.

IV. METHODS FOR THE DETERMINATION OF LITHIUM

The methods that are commonly used for the separation of lithium from the other alkalies are based on the greater solubility of its chloride and can be divided according to whether lithium chloride is extracted or the other chlorides are precipitated. The butyl alcohol-ethyl acetate method described in Section III is a combination of the two in that sodium and lithium are first extracted from the mixed alkalies and then sodium is precipitated in the extract. The ether-alcohol method of Palkin[23] which is described in A is a precipitation method, whereas the acetone method of Brown and Reedy described in B is an extraction method. The amyl alcohol method of Gooch[24] and the pyridine method of Kahlenberg and Krauskopf[25] have so little to commend them in point of convenience and accuracy that descriptions of them will be omitted.

The quantitative determination of lithium when present in unweighable amount is best done by means of the spectroscope.[26]

A. BY THE USE OF ETHER-ALCOHOL

The original ether-alcohol method of Rammelsberg[23] for separating lithium from sodium and potassium was an extraction method and suffered on that account. S. Palkin[23] revised it as a precipitation method and improved it greatly as follows: Dissolve the chlorides in a minimum of water (1.5 ml is ample for half a gram of salts) in a tall beaker, and add one drop of concentrated hydrochloric acid and gradually 20 ml of absolute alcohol, dropped in the center and not down the side, while rotating the beaker. The sodium and potassium chlorides should precipitate in a uniform granular condition. Then, while rotating the beaker, add 60 ml of ether (USP sp. gr. 0.716 to 0.717), and let stand 5 minutes, or until the precipitate is well agglomerated and the supernatant liquid is almost clear. Rotate the beaker occasionally. Filter through a perforated crucible into an Erlenmeyer flask under a bell jar. Rinse the beaker, and wash the precipitate and then the funnel with a mixture of one part alcohol to four or five parts ether. Detach matter adhering to the sides of the glass with a rubber-tipped rod. Set the crucible aside. Evaporate the filtrate on the

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[20] The solubility of sodium chloride in the solution of hydrochloric acid in butyl alcohol at room temperature is approximately 1.4 mg in 100 ml of solution, corresponding to 0.75 mg of sodium oxide. For this reason, the filtrate and washings should not greatly exceed 50 ml.

[21] This can be done by immersing the beaker in a copper capsule, flanged at the top and fitted to the rings of the steam bath so that condensation does not take place on the walls of the beaker or on the cover glass.

[22] S. Kallmann, *Ind. Eng. Chem. Anal. Ed.*, 16, 712 (1944).

[23] S. Palkin, *J. Am. Chem. Soc.*, **38**, 2326 (1916); C. Rammelsberg, *Pogg. Ann.*, **66**, 79 (1845).

[24] *Proc. Am. Acad. Arts Sci.*, **22**, 177 (1886); *Am. Chem. J.*, **9**, 33 (1887); *Chem. News*, **55**, 18 (1887).

[25] L. Kahlenberg and F. C. Krauskopf, *J. Am. Chem. Soc.*, **30**, 1104 (1908)

[26] See the Determination of Lithium, by W. W. Skinner and W. D. Collins, *U. S. Dept. Agr. Bur. Chem. Bull.* **153**. For a turbidimetric method for the detection and estimation of small amounts of lithium based on the formation of insoluble lithium stearate in the amyl alcohol extract, see E. R. Caley, *J. Am. Chem. Soc.*, **52**, 2754 (1930). L. B. Rogers and E. R. Caley [*Ind. Eng. Chem. Anal. Ed.*, **15**, 209 (1943)] recommend an empirical method in which lithium is precipitated as a complex periodate in an alkaline solution. Chlorides, nitrates, sulfates, or perchlorates are without effect; elements other than those of the alkali group, as well as small amounts of ammonium salts, must be removed. See also F. R. Bacon and D. A. Starks, *ibid.*, **17**, 230 (1945).

steam bath by the aid of a current of air. Take up the residue with 10 ml of absolute alcohol, and warm if necessary so that practically everything dissolves. If a film remains, remove it by scrubbing. Rotate the flask while adding 50 ml of ether, then add one drop of concentrated hydrochloric acid, rotate, and let stand half an hour with frequent rotation. When it is agglomerated, filter the small precipitate through the crucible already used, and wash with the ether-alcohol. After drying, ignite gently, weigh as the chlorides of sodium and potassium (also rubidium and cesium if present), and separate as in Section II.

Carefully evaporate the filtrate on the steam bath, take up the residue in a little water, and add a slight excess of sulfuric acid. Transfer to a weighed small platinum dish, evaporate the liquid, expel the excess of acid, ignite as in Section III, and weigh as Li_2SO_4. Repeat the treatment to constant weight.[27]

B. BY THE USE OF ACETONE

Brown and Reedy [28] state that lithium chloride is freely soluble in acetone and can readily be dissolved and separated from the chlorides of sodium, potassium, barium, and strontium which are entirely insoluble. The chlorides of rubidium, cesium, and magnesium are slightly soluble; calcium chloride is so soluble that it must be removed. The procedure is as follows: Gently evaporate the solution containing the chlorides of the alkali group to dryness in a small beaker, and heat to expel ammonium salts. Crush the crystals to a fine powder with a blunt stirring rod or a small pestle. Add about 25 ml of dry acetone and 1 drop of concentrated hydrochloric acid, and stir thoroughly. Let settle for a few seconds, and decant the clear liquid through a small filter into a weighed platinum dish. Wash the residue in the beaker and on the paper two or three times with 5-ml portions of acetone. Dissolve the residue in a small amount of water, again evaporate, and pulverize. Extract the residue with 25 ml of acetone and 1 drop of acid as before. If the weight of the combined chlorides was over 0.5 g, repeat the operation a third time.

Evaporate the combined filtrates carefully to dryness on a low-temperature hot plate or sand bath ($<50°$ C), and cautiously heat the residue to drive off organic matter. Cool, and treat with 1 to 2 ml of concentrated sulfuric acid, making sure to wet all of the chloride. Heat carefully to expel the sulfuric acid, ignite as in a, and weigh as Li_2SO_4.

According to J. I. Hoffman,[29] excellent results for lithium in a flint clay (0.22% Li_2O) were obtained when 1- to 3-g samples were decomposed

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[27] The weighing of lithium as the fluoride or phosphate has nothing to commend it. Lithium chloride is quite hygroscopic.

[28] M. H. Brown and J. H. Reedy, *Ind. Eng. Chem. Anal. Ed.*, 2, 304 (1930).

[29] Unpublished work (1940).

by digestion with hydrochloric acid in a sealed tube (p. 347) and then subjected to the following operations: (1) dilution and filtration to remove silica, (2) evaporation to small volume, treatment of iced solution with hydrochloric acid gas and ether, followed by filtration to remove most of the aluminum, (3) double precipitation with ammonium hydroxide to remove the remainder of the aluminum together with other precipitable elements, (4) treatment with ammonium oxalate and then with 8-hydroxyquinoline to remove calcium and magnesium (p. 643), (5) evaporation, ignition to chloride, and extraction with acetone (once repeated) to separate lithium, and (6) treatment with sulfuric acid and ignition to Li_2SO_4.[30]

V. METHODS FOR THE DETERMINATION OF RUBIDIUM AND CESIUM

Minerals that contain both rubidium and cesium in determinable amounts are almost unknown. This is fortunate for the analyst, for there appears to be no truly special reagent for either rubidium or cesium ions, whereby these can be quantitatively separated from potassium or from each other. Differences in the solubilities of certain of their salts serve as means for obtaining each of them pure, but the methods are in no sense quantitative. Both form insoluble chloroplatinates and perchlorates, and either one can be determined by the methods described for potassium when it occurs alone or in combination with lithium or sodium. When they occur together or in combination with potassium, further separations are in order.

A. METHOD FOR THE DETERMINATION OF RUBIDIUM AND CESIUM

The following method for the quantitative separation and determination of potassium, rubidium, and cesium is based on the use in succession of 9-phosphomolybdic, silicotungstic, and chloroplatinic acids. Precipitation with the first serves to separate rubidium and cesium from potassium; precipitation with the second serves to separate cesium from rubidium; whereas precipitation with chloroplatinic acid serves for the final precipitations of all three elements.[31] The method does not afford as clean-cut separations as might be desired, but is declared to be more reliable than those hitherto proposed.

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[30] Other extraction procedures that might be mentioned are those of (1) A. Sinka [*Z. anal. Chem.*, 80, 430 (1930)], in which lithium chloride is extracted by pure anhydrous dioxane (dimethylene dioxide) from ignited mixtures of the alkali chlorides in an extraction apparatus from which moisture is excluded as the condensed dioxane falls continuously into a suspended filtering crucible containing the mixed chlorides; and (2) E. R. Caley and H. D. Axilrod [*Ind. Eng. Chem. Anal. Ed.*, 14, 243 (1942)], in which lithium chloride is extracted from the mixed chlorides by 2-ethyl hexanol. It is asserted that no solubility corrections are needed and that the fumes of the hot solution are less bothersome than those of isoamyl alcohol.

[31] W. J. O'Leary and J. Papish, *Ind. Eng. Chem. Anal. Ed.*, 6, 107 (1934).

PROCEDURE. Obtain a sample containing not more than 0.08 g of RbCl and not more than 1.0 g of KCl. Dissolve in 100 ml of dilute nitric acid (1 + 3), heat almost to boiling, and treat with 9-phosphomolybdic acid[32] until precipitation is complete. Let settle, filter through a Munroe crucible, and wash with a 1 per cent solution of sodium nitrate. The filtrate and washings contain all of the potassium, which can be determined by precipitation as chloroplatinate as in the determination of rubidium and cesium.

Dissolve the phosphomolybdate precipitate in the least possible amount of N sodium hydroxide. Saturate the solution with hydrogen sulfide, heat to boiling, and add dilute nitric acid until slightly acid. Boil to coagulate the precipitate, filter, wash with slightly acidified hydrogen sulfide water, and discard the precipitate. If there is reason to suspect that any molybdenum still remains in solution, boil with a little bromine water, cool, again treat with hydrogen sulfide, boil, filter, wash and add the filtrate to that first obtained.

Evaporate the filtrate (or combined filtrates) to a volume of about 20 ml, add 60 ml of 95 per cent alcohol, treat with a slight excess of chloroplatinic acid and then add 2 to 3 ml of ethyl ether. Let the precipitate settle, filter through a Munroe crucible (p. 101), and wash with 80 per cent alcohol. Place a fresh receiver under the crucible, and add to the latter 5 ml of water and 2 or 3 drops of hydrazine hydrate. As soon as vigorous evolution of gas ceases, apply suction, and wash the alkali chlorides into the receiver. Cautiously add aqua regia, and boil to destroy the excess of hydrazine.

Add hydrochloric acid, evaporate to small volume, and repeat two or three times to insure *removal* of nitric acid. Take up in 50 to 75 ml of 6 N hydrochloric acid. Cool, add 0.5 to 1.0 g of solid silicotungstic acid dissolved in a few milliliters of water, and let stand for 12 hours. Filter through a Munroe crucible, and wash with 6 N hydrochloric acid. Reserve the precipitate for the determination of cesium. To the filtrate, which should contain all of the rubidium, add a little nitric acid and 5 ml of chloroplatinic acid, and then evaporate to about 10 ml. Add three times its volume of alcohol, then an excess of chloroplatinic acid, and 2 to 3 ml of ethyl ether. Filter, wash with 80 per cent alcohol, cautiously dry at 120 to 130° C, and weigh as Rb_2PtCl_6.

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[32] Prepared as follows: Heat the commercial *dodeca* acid, carefully and while stirring continuously, until the temperature reaches 300 to 350° C and the color of the dry acid turns from orange to green. Continue the heating until no orange particles remain, and then cool and extract with water. Filter if not clear, and oxidize the green solution with a little bromine water. Evaporate slowly to obtain the short, stout, yellow prisms of the luteo acid.

Dissolve the reserved precipitate in as little sodium hydroxide as possible, render faintly acid with nitric acid, and dilute to 200 ml. Cool, and add a 10 per cent solution of mercurous nitrate until precipitation is complete and the mercurous silicotungstate flocculates and settles rapidly. Filter, wash the precipitate with a 1 per cent solution of mercurous nitrate, and discard it. Oxidize the excess of mercurous nitrate in the filtrate by boiling with aqua regia. Evaporate to approximately 10 ml, and treat with three times its volume of alcohol and then with an excess of chloroplatinic acid and with ether as in the determination of rubidium. Filter, wash with 80 per cent alcohol, cautiously dry at 120 to 130° C, and weigh as Cs_2PtCl_6.

B. METHOD FOR THE DETERMINATION OF RUBIDIUM AND CESIUM (ALSO SODIUM AND LITHIUM)

The following methods were developed by Wells and Stevens[33] after unsuccessful attempts to apply existing methods for the determination of the rare alkalies in rocks and minerals. The starting point is the mixture of chlorides obtained in a preliminary attack by the J. Lawrence Smith method, and the separations are based chiefly on the use of chloroplatinic acid, absolute alcohol and ether, and ammonium sulfate. Each alkali is weighed separately, so that the initial weighing of the mixed chlorides is merely a check.

a. *Separation of the Sodium and Potassium Groups.* This is done by treating with chloroplatinic acid as described on page 648. After the chloroplatinates of potassium, rubidium, and cesium have been weighed, the alkalies are reconverted to the chlorides by dissolving in water, precipitating the platinum with hot dilute formic acid, and filtering to remove the platinum. This solution (1) is reserved for treatment as in d. The solution containing the sodium and lithium chloroplatinates is also treated with formic acid, filtered to remove platinum and the solution (2) reserved for treatment as in b.

b. *Determination of Lithium.* The separation of lithium from sodium is done by a modification of Palkin's method (p. 655) as follows: Evaporate the reserved solution (2) of sodium and lithium chlorides to dryness, preferably in a small glass-stoppered type of Erlenmeyer flask of about 30-ml capacity. Dissolve in 0.4 ml of water, warming slightly if necessary. Cool, add 0.01 ml of concentrated hydrochloric acid and 5 ml of absolute alcohol, rotate the flask, and add 15 ml of ether. Allow to stand for about 15 minutes. Filter through a weighed Jena sintered-glass or Gooch filtering crucible, wash well with a mixture of 1 part of alcohol to 4 or 5 parts of ether, and reserve the crucible and contents (3). In the usual case, a second treatment of the lithium-bearing filtrate for the recovery of sodium is

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[33] R. C. Wells and R. E. Stevens, *Ind. Eng. Chem. Anal. Ed.*, 6, 439 (1934).

unnecessary. Evaporate the filtrate with a slight excess of sulfuric acid in a weighed dish, and heat to constant weight as lithium sulfate.

c. *Determination of Sodium.* For a direct determination of sodium, weigh the reserved filtering crucible and its sodium chloride content (3) obtained in b.

d. *Separation of Rubidium and Cesium from Potassium.* Evaporate the reserved solution (1) containing potassium, rubidium, and cesium chlorides to dryness, in a 30-ml glass-stoppered type of Erlenmeyer flask, and then heat at about 106° C. Cool, add 0.4 ml of water, warm, cool again, and saturate with dry hydrochloric acid gas. Add 10 ml of absolute alcohol which has also been saturated with hydrochloric acid gas. Filter with suction through asbestos in a small funnel or through a sintered-glass filtering crucible. Wash with 2 ml of a mixture of absolute alcohol and ether. Reserve the residue (4) for possible recovery of residual rubidium as in f. Evaporate the filtrate to dryness, and ignite cautiously, finally for a moment at about 500° C. Cool and weigh as rubidium and cesium chlorides, plus 0.6 mg of potassium chloride for each extraction with alcohol and hydrochloric acid at 25° C (5). This correction is based, of course, on the assumption that the sample contained enough potassium chloride to furnish the total amount.

If the weight does not exceed 0.6 mg,[34] these elements are present in only spectrographic traces, if at all. If the weight exceeds 0.6 mg, the elements may be present. Unless appreciable amounts are present, very nearly all of the cesium is obtained in the first extract. If appreciable amounts are present, a second extraction should be made.[35] Considerable rubidium may still remain with the potassium (residue 4).

e. *Determination of Cesium.* To the dry alkali chlorides (5) obtained in d, add 0.1 ml of a 5 per cent solution of ammonium sulfate, and stir the solution until the chlorides dissolve. Stir vigorously, and add 5 ml of alcoholic ammonium sulfate[36] at a rate of about 1 drop per second for the first milliliter, and then more rapidly until all has been added. Let stand for 30 minutes, and stir the solution occasionally. Filter with mild suction through an asbestos pad, catching the filtrate, which contains the cesium, in a small weighed platinum crucible or dish. Rinse the precipitate, beaker, and filter thoroughly with three 0.5-ml portions of washing solution.[37] Reserve the residue (6) for treatment as in f. Add a small amount of ammonium sulfate to the crucible containing the filtrate and washings, evaporate on the steam bath until salts begin to crystallize, and then add a few drops of alcohol. Continue the evaporation to apparent dryness, add a few drops of absolute alcohol, and again evaporate. Cover with a glass, and heat gently in a radiator until ammonium chloride sublimes on the cover glass. Remove the glass, and increase the heat, carefully to avoid loss through spattering, until the mass begins to melt and ammonium sulfate to volatilize. When most of the ammonium sulfate is gone, gradually heat to redness as the crucible is kept in motion. Cool in a desiccator while covered with a cover glass to prevent decrepitation, and weigh as Cs_2SO_4. Repeat the heating until constant weight is obtained. As little as 0.1 mg of cesium can be confirmed with the spectroscope, by dissolving the sulfate in 2 or 3 drops of water, dipping a platinum coil in the solution, and heating in the Bunsen flame.

f. *Determination of Rubidium.* If the weight of cesium calculated to cesium chloride, plus 0.6 mg of potassium chloride for each extraction with alcohol and hydrochloric acid that was made, accounts for the weight of the chlorides (5) obtained in d, rubidium is absent. If the weight of the chlorides (5) obtained in d is greater, the difference represents the weight of RbCl (7) in the chlorides obtained in d.

A check on the weight of rubidium chloride obtained as just described can be made as follows: Dissolve the residue (6) obtained and reserved in e, evaporate to dryness in a second tared crucible, ignite, and weigh, to obtain the weight of rubidium and potassium sulfates. The amount of K_2SO_4 is then calculated from the total weight of potassium chloride to be expected in the extraction treatment, this is subtracted from the weight of the mixed sulfates, and the remainder is calculated to RbCl (8).

Any amount of RbCl indicated by either of the above calculations does not represent all of the rubidium, for some remains with the residue (4) reserved in d.

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[34] The amount of potassium chloride dissolved in a single extraction.

[35] J. C. Hillyer [*Ind. Eng. Chem. Anal. Ed.*, **9**, 236 (1937)] points out that as many as six extractions might be required if the material contains much rubidium or cesium, as for example in a pollucite containing 30 per cent of cesium oxide. In such case three procedures are open: (1) to take a small aliquot portion if the sample contains enough potassium to furnish 0.6 mg of KCl for every extraction made, or (2) if potassium is low, to substitute 10 ml of an extraction mixture made up of 1 part of concentrated hydrochloric acid and 2 parts of alcohol (which dissolves 3.1 mg of KCl instead of 0.6 mg at 25° C), or (3) if potassium is very low, to omit the extraction of cesium chloride from the mixed chlorides (solution 1) and treat them as "cesium chloride." R. C. Wells and R. E. Stevens [*ibid.*, 236] suggest also that the mixed chloroplatinates may be subjected to several fractional crystallizations to separate the bulk of the least soluble cesium, followed by their suggested procedure for separating cesium from rubidium and potassium in the soluble chloroplatinate filtrates.

[36] Prepared as follows: Dissolve 1 g of ammonium sulfate in 20 ml of water, stir, and add slowly 100 ml of 95 per cent alcohol. Filter, and add a few crystals of the sulfate to the filtrate to keep the solution saturated.

[37] Prepared in same way as the alcoholic ammonium sulfate solution, except that 0.16 g of ammonium chloride is also added to the water solution of the sulfate before addition of the alcohol.

To recover this, repeat the extraction of the reserved residue (4) with alcohol and hydrochloric acid as long as the loss in weight of the mixed chlorides exceeds 0.6 mg per extraction. Combine the extracts, and evaporate to dryness. Take up in a little water, add a slight excess of chloroplatinic acid, and evaporate nearly to dryness. Add 5 ml of 15 per cent alcohol, stir well, filter, and wash the precipitate with 95 per cent alcohol. Dry at 130° C, weigh as Rb_2PtCl_6, and calculate to RbCl (9).[38]

The weight of RbCl is then represented by the weight (9) plus the weight (7) or (8).

g. *Determination of Potassium.* If a moderate amount of potassium is present, calculate its weight after subtracting the cesium and rubidium chloroplatinate equivalents from the original weight of the mixed chloroplatinates. If the percentage is small, it is preferable to weigh the potassium as chloride or sulfate after the separation of rubidium and cesium.

VI. METHODS FOR THE DETERMINATION OF POTASSIUM ALONE

A. REDUCTION OF THE CHLOROPLATINATE PRECIPITATE

Instead of weighing the chloroplatinate a long-used alternative is to reduce and weigh the platinum in it. This procedure admits of determining the potassium in the presence of sulfates, chlorides, phosphates, nitrates, borates, dissolved silica and of salts of sodium, the alkaline earths, magnesium, iron, and aluminum. Possibly the sole interfering elements are rubidium and cesium, besides ammonium and some organic compounds. The method is especially adapted for the evaluation of potassium salts, salines, and mixed fertilizers, in which only the quantity of potassium is sought. Various reducing agents have been used, of which perhaps the most recently recommended and the simplest to use is magnesium in the form of ribbon. The procedure used by W. B. Hicks[39] for testing natural salines and borings of wells for the U. S. Geological Survey is the following:

Precipitate the potassium as chloroplatinate in the usual way, except that 5 ml of hydrochloric acid should be added before the platinum reagent which need be used in only slight excess over that required by the potassium, as the presence of sodium and other salts causes no interference. After the precipitate has been crushed and well washed with 80 to 90 per cent (by volume) alcohol, dissolve it in hot water, and add 1 ml of hydrochloric acid and approximately 0.5 g of magnesium ribbon (previously washed in water) for every 0.2 g of potassium present. Stir the solution, and hold the ribbon at the bottom of the beaker by means of a glass rod. When the magnesium is nearly gone, add a few milliliters of dilute hydrochloric acid, and allow the platinum to settle. If the reduction is complete, the liquid is clear and limpid. To make sure, add a little more magnesium, and note whether the solution darkens. Add hydrochloric acid, boil to dissolve any basic salts, filter, and wash with water until the filtrate gives no test for chlorides. Ignite, weigh the platinum, and calculate the potassium equivalent by the proportion Pt:2 K.

B. PERCHLORATE METHOD WITH BUTYL ALCOHOL

G. Frederick Smith[40] modified the original perchlorate method by using normal butyl alcohol to precipitate the potassium perchlorate and thus overcome a disadvantage under which most extraction processes labor. Only when sodium is absent, or present in very little amount, is a solubility correction (0.38 mg K_2O per 100 ml of solution) for the potassium necessary. Smith's test results by one precipitation and without solubility corrections are good, but the agreement is due to compensation of positive and negative errors. When the method was applied to mixtures of 0.14 g of potassium chloride and 0.16 g of sodium chloride, the results for the former averaged 0.2 mg low whereas those for the latter were 0.6 mg too high.

PROCEDURE. Evaporate the mixed chlorides (free from sulfate) to dryness (at not over 350° C) with an excess of perchloric acid, and repeat if the amount of chlorides is large. According as the amount of potassium is small or large, add 2 or 3 ml of water, dissolve the salts by gently swirling over a free flame, and then, according as 2 or 3 ml of water were used, add to the warm perchlorate solution, slowly and with vigorous stirring, 65 or 100 ml of boiling hot normal butyl alcohol,[41] containing 0.5 to 1 per cent of perchloric acid (70%). When all has been added, cover the vessel, boil gently for half a minute, and cool. Collect the precipitate on a Munroe or Gooch crucible[42] by the aid of some of the precipitant, and wash it eight or ten times, each time with 1 or 2 ml of the same solution. The

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[38] Any cesium that may have escaped the initial extraction would, of course, be weighed here as Cs_2PtCl_6.

[39] *J. Ind. Eng. Chem.*, **5**, 650 (1913); R. C. Wells, R. K. Bailey, and J. G. Fairchild, *ibid.*, **16**, 935 (1924).

[40] *J. Am. Chem. Soc.*, **45**, 2072 (1923).

[41] Normal butyl alcohol having a specific gravity of 0.8065 25°/4° and a boiling range of 112 to 118° C is readily obtainable on the market. Such an alcohol should be distilled and the first and last 5 per cent fractions discarded.

[42] The Gooch crucible should have holes not larger than 0.5 mm in diameter. A heavy mat of asbestos, protected by a perforated porcelain disk, is essential. Asbestos should be refluxed with the butyl alcohol mixture before use, or, as the same crucible can be used over and over, the crucible can be seasoned by two or three trial runs.

filtrate and washings should have a volume of 125 to 150 ml. Dry at 350° C, and weigh as $KClO_4$.[43]

Sodium can be determined in the filtrate but is better found by difference.

C. PERCHLORATE METHOD WITH ETHYL ALCOHOL

The following method is not so desirable as that described in B because absolute alcohol is required and the process is one of extraction instead of precipitation. A chloride solution is to be used which contains not over 1 g of mixed chlorides and no sulfates. Ammonium salts should preferably be absent, though sparing amounts may be present; chlorides of lithium, magnesium, or the alkaline earths are not objectionable. Two washing solutions are required. The first consists of absolute alcohol containing 0.2 per cent of perchloric acid (70%), and the second a solution prepared shortly before use by shaking the first solution with crystals of potassium perchlorate for 5 to 10 minutes at room temperature, allowing to settle, and pouring off the clear solution.

PROCEDURE. To the concentrated solution of the chlorides, add 1 to 2 ml of 60 per cent perchloric acid (free from sulfuric acid), and evaporate to dryness on a hot plate or over a free flame. Add 10 ml of water, again add 1 to 2 ml of the acid, and evaporate to dryness at a temperature not over 350° C. There must be complete conversion to perchlorates. Extract the residue with 20 ml of absolute alcohol containing 0.2 per cent of perchloric acid, and let stand some minutes.[44] Filter the clear solution through a Munroe or, less preferably, a Gooch crucible, and wash the container and residue once or twice with the first washing solution. Suck dry, dissolve the residue in water, add 1 to 2 ml of perchloric acid, evaporate to dryness, and extract as before. Filter, transfer the residue to a tared and dry Munroe or Gooch crucible by means of not over 100 ml of the second washing solution, and suck dry. Dry at 120 to 130° C, finally heat for a few minutes at 350° C, and weigh [45] as $KClO_4$.

D. THE LINDO-GLADDING METHOD [46]

The Lindo-Gladding method finds its chief application in the presence of sulfates, nitrates, phosphates, and magnesium, and its distinguishing

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[43] For the determination and separation of potassium as periodate, see H. H. Willard and A. J. Boyle, *Ind. Eng. Chem. Anal. Ed.*, 13, 137 (1941).

[44] G. P. Baxter and F. E. Ruppert [*J. Am. Chem. Soc.*, **42**, 2046 (1920)] showed that ethyl alcohol denatured with 5 per cent methyl alcohol (both dehydrated over lime) can be substituted for ethyl alcohol. The perchloric acid content of the alcohol is not critical, as much as 1 ml being without effect.

[45] For the thermal decomposition of the perchlorates of lithium, sodium, potassium, calcium, magnesium, iron, and aluminum, consult G. G. Marvin and L. B. Woolaver, *Ind. Eng. Chem. Anal. Ed.*, **17**, 474 (1945).

[46] *Chem. News*, **53**, 202, 296 (1886).

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feature lies in first washing the chloroplatinate precipitate with 80 per cent alcohol, then with a special ammonium-chloride wash solution, and finally with 80 per cent alcohol. The wash solution is prepared by dissolving 100 g of ammonium chloride in 500 ml of water, adding 5 to 10 g of pulverized potassium chloroplatinate, shaking at intervals for 6 to 8 hours, and filtering after the mixture has settled overnight.

E. SODIUM-COBALTINITRITE METHOD

The sodium-cobaltinitrite method is quite satisfactory for routine determinations of potassium in a given material,[47] provided the details of the procedure have been worked out for that material. See for example: (1) L. V. Wilcox,[48] who, in examinations of plant materials, developed a method in which potassium is precipitated by adding trisodium cobaltinitrite to dilute nitric instead of acetic acid solutions, and then determined by weighing as $K_2NaCo(NO_2)_6 \cdot H_2O$, or by titrating with permanganate and oxalate; (2) E. W. Koenig,[49] who recommends a semidirect method in which potassium is precipitated as the cobaltinitrite, after decomposition of silicates or silicate products in hydrofluoric and perchloric acids, and then converted to the perchlorate; (3) A. Eden,[50] who uses a photometric method for the determination of small amounts of potassium which is based on the green complex that cobalt in the precipitate forms with choline hydrochloride and potassium ferrocyanide; and (4) R. J. Robinson and G. L. Putnam,[51] who describe a colorimetric method for the determination of 0.002 to 0.40 mg of potassium in fresh waters, based on a preliminary precipitation with silver cobaltinitrite, followed by a colorimetric estimation of the nitrite content of the precipitate. These authors point out that the silver cobaltinitrite is the most sensitive of all reagents for potassium.[52] For a discussion of the cobaltinitrite method, see P. J. Van Rysselberge.[53]

F. SEPARATION OF LITTLE POTASSIUM FROM MUCH SODIUM

It is sometimes necessary or desirable when little potassium accompanies much sodium, as in mineral waters and brines, to concentrate the potassium

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[47] The composition of the potassium-sodium cobaltinitrite precipitate varies with the conditions of precipitation, especially temperature. For best results, determinations had better be corrected as indicated by runs on like material containing known amounts of potassium.

[48] *Ind. Eng. Chem. Anal. Ed.*, **9**, 136 (1937).

[49] *J. Am. Ceram. Soc.*, **22**, 164 (1939).

[50] *Analyst*, **68**, 167 (1943).

[51] *Ind. Eng. Chem. Anal. Ed.*, **8**, 211 (1936).

[52] See also L. L. Burgess and O. Kamm, *J. Am. Chem. Soc.*, **34**, 652 (1912); O. Lutz, *Z. anal. Chem.*, **59**, 145 (1920); and A. M. Ismail and H. F. Harwood, *Analyst*, **62**, 443 (1937).

[53] *Ind. Eng. Chem. Anal. Ed.*, **3**, 3 (1931).

in a solution that contains little sodium before applying methods for determining the potassium. Calcium, magnesium, etc., as chlorides or sulfates may be present.

In such case, concentrate the aqueous solution as much as possible without causing deposition of salt in an Erlenmeyer flask, set the flask in ice water, and saturate the solution with hydrochloric acid gas. The end of the tube delivering the gas should be expanded and not dip beneath the surface of the liquid. Then add 2 ml of water for every 100 ml of solution swirl, and, when the salt has settled, pour the liquid through a funnel fitted with a platinum cone, or better through a platinum-felted Gooch crucible if it is large enough to hold all of the salt. Bring the salt upon the filter with the aid of ice-cold water saturated with hydrochloric acid gas and containing the same proportion of sodium chloride as the main solution held, wash with this a few times, and suck dry at the pump.

The solution contains all the potassium, together with some sodium chloride and salts of other metals, as well as free sulfuric and boric acids if the original material held sodium sulfate or borate. Evaporate the filtrate to dryness in platinum, expel free sulfuric acid, take up the residue with a little hydrochloric acid, and apply method VI, A or D.

VII. DETERMINATION OF SODIUM ALONE

In this method, sodium is precipitated in weakly acid solution as the triple acetate, $NaZn(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O$, which can be weighed as such or dissolved and its sodium content calculated after a volumetric determination of its uranium content. The method is not suited for determinations of the highest accuracy except under exceptional conditions. It is, however, attractive for routine determinations of sodium, because the reaction is quite selective and ordinarily requires few, if any, preliminary separations.

The precipitate is quite bulky, which limits the amount of sodium that can be handled in a determination. It is also quite soluble in water. Its solubility in a solution containing an excess of the precipitant is less, but still high enough so that the volume of the solution must be kept at a minimum, and special care must be taken when the precipitate is transferred and washed.

Among the interfering substances that have been mentioned are phosphates,[54] molybdates,[55] arsenates, sulfates (in the presence of potassium), oxalates, tartrates, strontium,[56] lithium, and amounts of potassium exceeding 50 mg per ml of solution. Moderate amounts of ammonium salts, calcium, barium, and magnesium are not harmful, as is the case with hydrolyzable elements such as iron or aluminum if solutions are kept acid.

The following procedure is essentially that recommended by H. H. Barber and I. M. Kolthoff.[57]

PROCEDURE. Prepare 1 ml of a neutral or feebly acid solution, containing not more than 8 mg of sodium as sodium chloride, and free from the interfering substances that have been mentioned. Add 10 ml of zinc uranyl acetate reagent,[58] stir thoroughly, and allow to stand for not less than 30 minutes. Mechanical stirring hastens precipitation, especially with small amounts of sodium. Filter, by suction, through a weighed porous porcelain or glass-fritted crucible of medium porosity. Transfer the precipitate to the crucible, and remove most of the original solution by using 2-ml portions of the reagent. Finally, wash both precipitate and the inside of

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[54] Phosphates interfere in the feebly acid solutions obtained by adding the reagent to a solution of the mixed chlorides in water. Moderate amounts of the phosphate ion, say 2.5 mg, are apparently without effect in dilute (0.2 *N*) perchloric acid solution [E. W. Koenig, *J. Am. Ceram. Soc.*, 22, 24 (1939)]. For the removal of the phosphate ion in materials such as milk ash, O. R. Overton and O. F. Garrett [*Ind. Eng. Chem. Anal. Ed.*, **9**, 72 (1937)] proceed as follows: Prepare a solution containing 2 to 8 mg of sodium in 10 to 15 ml of feebly acid (hydrochloric) solution. Treat with an excess of powdered zinc carbonate, and let stand for 6 hours, or overnight. Filter, and wash the paper and residue thoroughly five or six times with cold water. Evaporate the filtrate and washings to a volume of 1 to 5 ml, adding a drop of acetic acid if a precipitate forms. The results must be corrected for a blank carried through all steps.

A number of other methods for removing phosphates and arsenates have been employed, such as calcium hydroxide, lead acetate, barium chloride, or zinc acetate for the former, and magnesia mixture for the latter.

[55] Interference by molybdenum, which forms a precipitate with the reagent, can be overcome by adding no more citric or tartaric acid than is needed to form a stable complex ion [C. H. Hale, *Ind. Eng. Chem. Anal. Ed.*, **15**, 516 (1943)].

[56] E. R. Caley and W. O. Baker [*ibid.*, **11**, 604 (1939)] state that salts precipitated from lithium solutions by uranyl acetate reagents for sodium are always triple acetates, analogous in composition to the triple acetates precipitated from sodium solutions by these reagents. With potassium, on the other hand, the same salt, $KUO_2(C_2H_3O_2)_3$, is precipitated from *concentrated* potassium solutions by all types of uranyl acetate reagents for sodium. For the substitution of an alcoholic cupric acetate-uranyl acetate reagent in determinations of sodium in the presence of lithium, consult E. R. Caley and L. B. Rogers, *ibid.*, **15**, 32 (1943).

[57] *J. Am. Chem. Soc.*, **50**, 1625 (1928); **51**, 3233 (1929).

[58] Prepared as follows: Dissolve 100 g of $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ and 27.8 g of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 27 ml of glacial acetic acid and 900 ml of water. Warm the solution on a steam bath or hot plate until no further solution takes place, and then cool. If a small precipitate of the sodium salt has not been formed through impurities in the reagents, add a few milligrams of sodium chloride. Let settle for 24 hours, filter, and decant as needed. It is desirable that the reagent be used at approximately the temperature prevailing at the time it was filtered. Increases in temperature of the order of a few degrees are permissible; *decreases* are not to be tolerated, for they lead to high results.

the crucible thoroughly 5 to 10 times with 2-ml portions of washing solution,[59] and then once with ether. Draw air through the crucible until the ether has been volatilized. Wipe off the outside of the crucible with a slightly moistened cloth, place in a desiccator for 10 to 15 minutes, and weigh. Correct the weight as indicated by a blank determination carried through all steps of the method, and multiply the remainder by the factor for Na_2O, 0.02015, or for Na, 0.01495.

Among volumetric treatments of the precipitate might be mentioned titration with permanganate, after solution of the precipitate in acid and reduction of the uranium to the quadrivalent state,[60] and solution of the precipitate in water, followed by titration of the uranium with sodium hydroxide.[61] A spectrophotometric method based on the orange- to red-colored compound formed by treating the triple acetate with ammonium carbonate and hydrogen peroxide is described by Eric Arnold and A. R. Pray.[62]

A number of modifications of the method have been developed in which larger amounts of sodium can be handled,[63] the volumes of the solution and reagent are increased,[64] the temperature of the solution is stepped up to 40° C,[65] and the acidity of the solution is stepped up to 4 *N* sulfuric acid [60] or 2 *N* perchloric acid (1 + 5).[66] Any marked deviation from the regular procedure is not warranted unless the analyst is confronted with

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[59] Prepared by adding 1 ml of acetic acid (30%) to 100 ml of 95 per cent ethyl alcohol, shaking with a moderate excess of the triple salt at 25° C, and filtering. As with the triple acetate reagent, the solution had better be used at the temperature at which it was saturated with the triple salt. With some materials, the use of the reagent in the transferring and the preliminary washing of the precipitate is unnecessary, and all operations can be done with the washing solution (see Koenig, footnote 54).

[60] H. V. Churchill, R. W. Bridges, and A. L. Miller, *Ind. Eng. Chem. Anal. Ed.*, **8**, 348 (1936).

[61] J. T. Dobbins and R. M. Byrd, *J. Am. Chem. Soc.*, 53, 3288 (1931).

[62] *Ind. Eng. Chem. Anal. Ed.*, **15**, 294 (1943). For a method based on the absorption of blue light by an aqueous solution of the triple acetate, see D. R. McCormick and W. E. Carlson, *Chemist-Analyst*, 31, 15 (1942).

[63] E. W. Koenig (*loc. cit.*) places the upper limit at about 12 mg of Na_2O in a solution which has a final volume of 25 ml.

[64] As for example 5 ml of solution and at least 20 ml of reagent [Koenig, *loc. cit.*].

[65] According to Koenig (*loc. cit.*), temperatures as high as 40° C are permissible if (1) the reagent is saturated with the triple acetate at the temperature used, (2) the period of precipitation is increased to 30 minutes, (3) the temperature of the solution is not allowed to change during the interval between precipitation and filtration, and (4) the temperature during these operations is controlled within a few degrees.

[66] Koenig (*loc. cit.*) points out that precipitates obtained in perchloric acid solutions containing aluminum must be transferred and given a preliminary washing with the reagent to remove aluminum perchlorate, which would be precipitated if the alcoholic washing solution is used directly.

a steady flow of samples of a special type, and has worked out the modifications that are permissible in tests of that type.[67]

Triple salts containing other bivalent elements such as copper, cadmium, mercury, manganese, nickel, cobalt, ferrous iron, and magnesium have been investigated, but only those of magnesium have been found generally useful.

Precipitation of sodium as the magnesium salt, $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O$, was advocated by E. R. Caley and C. W. Foulk,[68] who found that as much as 50 mg of sodium can be handled. The salt can be dried and weighed as such, or dissolved and its sodium content calculated after titration of the magnesium with disodium phosphate,[69] or after reduction of the uranium and titration with potassium permanganate.[70]

The necessary reagents for the Caley-Foulk method are (*a*) a solution of magnesium uranyl acetate,[71] and (*b*) a washing solution freshly prepared by saturating 95 per cent alcohol at 20° C with sodium magnesium uranyl acetate.

The procedure is as follows: Prepare a neutral solution containing not more than 25 mg [72] of sodium, preferably as the chloride. Reduce to a volume of 5 ml, or less if there is no separation of salts. Add the reagent rapidly, 100 ml if the amount of sodium is less than 10 mg and 10 ml per mg for larger amounts. Mix the solutions, partly immerse in a water bath maintained at 20 ± 1° C, and stir *vigorously* for 30 to 60 minutes, the

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[67] For the application of the uranyl-zinc acetate method to the direct rapid determination of sodium in soda-lime glasses, see F. W. Glaze, *J. Am. Ceram. Soc.*, **14**, 450 (1931); for the use of the same reagent in the direct determination of sodium in cements, see F. W. Glaze, *Rock Products*, **44**, no. 7, 42 (1941), and *ASTM Specification C114-47, Chemical Analysis of Portland Cement*, p. 31.

[68] *J. Am. Chem. Soc.*, **51**, 1664 (1929).

[69] E. R. Caley, *ibid.*, **52**, 1349 (1930).

[70] A. Nau, *Bull. soc. phar. Bordeaux*, **65**, 67 (1927); E. Kahane, *Bull. soc. chim.*, [4] **47**, 382 (1930). For potentiometric titration with potassium permanganate or ceric sulfate, see N. H. Furman, E. R. Caley, and I. C. Schoonover, *J. Am. Chem. Soc.*, **54**, 1344 (1932).

[71] Solution *a* is prepared from solutions *A* and *B* which are prepared and mixed as follows:

Solution *A*		Solution *B*	
Uranyl acetate ($2H_2O$)	90 g	Magnesium acetate ($4H_2O$)	600 g
Glacial acetic acid	60 g	Glacial acetic acid	60 g
Distilled water to	1000 ml	Distilled water to	1000 ml

Each solution is separately heated to about 70° C until all the salts are dissolved, and then the two solutions are mixed at this temperature, allowed to cool to 20 ± 1° C, held at this temperature for at least 1 hour, and then filtered through a dry filter into a dry bottle. The solution is stable if kept away from direct sunlight, and should not be allowed to cool below 20° C.

[72] With larger amounts (up to 50 mg), special precautions must be used, and, with small amounts (<1 mg), the initial volume should be reduced to 1 to 2 ml.

longer period being desirable with more than 0.2 mg of sodium. Immediately filter through a tared Gooch or a sintered-glass filtering crucible of medium porosity, using gentle suction and keeping the solution in gentle motion to prevent the precipitate from sticking to the beaker. When all of the solution has been transferred, drain, scrub the beaker, and wash the precipitate with four to six successive 5-ml portions of 95 per cent alcohol which has been freshly saturated with the triple acetate at 20° C. The alcoholic washings may cause salts to separate from the filtrate. Drain thoroughly, dry in an air oven at 105 to 110° C for 30 minutes, cool and weigh. The precipitate contains 1.53 per cent of sodium.[73]

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[73] Among the applications of the method might be cited: (1) The direct determination of sodium in calcium carbonate intended for use in the J. L. Smith method [E. R. Caley, *Ind. Eng. Chem. Anal. Ed.*, **1**, 191 (1929)]; (2) the direct determination of sodium in commercial aluminum [E. R. Caley, *ibid.*, **4**, 340 (1932)]; for separations from aluminum and chromium, see also E. R. Caley and D. V. Sickman, *J. Am. Chem. Soc.*, **52**, 4250 (1930); and (3) the determination of from 0.05 to 2.0 mg of sodium by precipitating with an alcoholic solution of magnesium uranyl acetate, followed by centrifuging and reading the volume of the precipitate in a capillary tube [E. R. Caley, C. T. Brown, and H. P. Price, *Ind. Eng. Chem. Anal. Ed.*, **6**, 202 (1934)]. E. C. Elliott [*ibid.*, **12**, 416 (1940)] states that the method can be successfully used in the presence of beryllium, cerium, lanthanum, neodymium, thallium, thorium, vanadium, and zirconium.

THE ACID-FORMING ELEMENTS

Silicon, Tungsten, Phosphorus, Sulfur, Chlorine, Bromine,
Iodine, Fluorine, Boron, Carbon, Hydrogen, and Nitrogen

Chapter 43

SILICON

Silicon comprises about 27.6 per cent of the lithosphere and is, next to oxygen, the most abundant element. It is found in quartz, tridymite, opal, and all silicates, and is the characteristic element of all important rocks except the carbonates.

I. GENERAL CONSIDERATIONS

In the usual analysis, most of the silicon is separated by dehydration in acid solution at the start of the analysis, and all, or nearly all, of the remainder is caught in the ammonia precipitate. If the preliminary separation of silica is carelessly done, and especially if the ammonia precipitate is small, appreciable amounts of silica may remain in the ammoniacal filtrate and may contaminate the oxalate and phosphate precipitates.[1] The silica that is caught in the ammonia precipitate will be counted as alumina if it is not recovered.

II. DECOMPOSITION OF ROCKS AND MINERALS CONTAINING SILICON

The decomposition of rocks and minerals containing silicon is usually carried out as described under Fluxes (p. 836). Sometimes decomposition can be effected by attack with acids, particularly with the aid of hydrofluoric acid when silica is not to be determined, and of perchloric acid when substances that form insoluble compounds with hydrochloric, sulfuric, or nitric acid are present.

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[1] Special care should be taken to remove all silica before precipitation with ammonium hydroxide if zinc is present, for otherwise zinc will be carried down as a silicate.

III. METHODS OF SEPARATION

Complete separation of silicon from other elements is rarely necessary, for its amount is usually determined by the loss in weight that occurs when the weighed and impure silica is treated with hydrofluoric and sulfuric acids, ignited, and again weighed. Impurities are therefore unobjectionable if they do not volatilize or change in weight as the result of the treatment with the mixed acids, and are not present in amounts large enough to cause difficulties in the evaporation of the mixed acids or the ignition of the residue.

Silica always carries down boron when it separates from a solution containing the two. If such a precipitate is afterwards treated with hydrofluoric and sulfuric acids, both volatilize, and high results for silica ensue.[2] Boron must, therefore, be separated before this treatment, and it is usually more convenient to make the separation before the dehydration of the silica. This is done best by volatilizing the boron as the trimethyl compound, $B(OCH_3)_3$, from a solution containing little or no water. As applied to a boric oxide melt, the procedure is as follows: Place the melt in a large porcelain or platinum dish, cover, and treat with methyl alcohol that has been saturated with hydrochloric acid gas (by passing dry hydrochloric acid gas into cooled methyl alcohol for 1 to 2 hours). When effervescence ceases, remove the cover, and heat just short of boiling, preferably on a water bath in a good hood. Cleanse the crucible in a similar manner, and add its contents to the dish. Add more reagent as necessary until disintegration is complete, boil to small volume, and evaporate to dryness on the bath. To remove the last traces of boron, evaporate to dryness at 80 to 85° C on the bath two or three times in succession, after adding small portions of the reagent and taking care to wash down the sides of the dish.

Fluorine interferes in the usual method for the determination of silica because it forms volatile silicon tetrafluoride in solutions containing strong acids. The loss is always considerably less than that called for by the amount of fluorine present[3] and can be disregarded in ordinary analyses if the amount of fluorine is under 0.3 per cent.

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[2] The same is true of arsenic if evaporations are carried on with sulfuric acid in the presence of silica and trivalent arsenic. The extent of the error caused by boron in determinations of silica is illustrated by the results 80.22 and 80.24 per cent of SiO_2 (as compared with the most probable content 80.13) which were obtained when boron was ignored in the analysis of a glass containing 12.67 per cent of B_2O_3. These determinations were made by double dehydration with hydrochloric acid and recovery of silica as usual.

[3] Silicon tetrafluoride is unstable in the presence of moisture and so some of the fluorine escapes, perhaps as hydrofluoric acid, and more is fixed in fluosilicates. The

Less silicon is lost if the platinum dish is covered with a platinum cover and the atmosphere within the dish is kept saturated with water vapor during the evaporation. Still less loss of silicon occurs if the melt is dissolved in a strong solution of boric acid and then treated as above, but this necessitates treatment of the silica for the removal of its boron content.

If fairly large amounts of silica and small amounts of fluorine are present, as in glasses containing fluorine, interference by fluorine can be minimized by fusing with boric oxide for 30 minutes at 1200° C or higher and separating silica as usual by evaporating with hydrochloric acid. With large amounts of fluorine and small amounts of silicon, as in fluorspar, this procedure gives low results, and the Berzelius method described on page 939 must be used. Fusion with a mixture of sodium carbonate and borax or with sodium carbonate followed by solution of the melt in a saturated solution of boric acid before treatment with acid is nearly as satisfactory as fusion with boric oxide. In the latter case much of the fluorine is volatilized as boron trifluoride, BF_3. In both cases, the fluorine that remains in solution is fixed as the less harmful fluoboric acid, HBF_4, during the dehydration of the silica, and the boron that is gathered by the silica must be expelled by treatment with methyl alcohol before the silica is ignited.

In the usual case, tungsten accompanies silicon, and no separation is attempted if only the latter is to be determined. The mixed oxides are ignited and treated with sulfuric and hydrofluoric acids as usual, except that the ignition of the nonvolatile residue must be done at a temperature not over 850° C because of the volatility of tungstic oxide (p. 685). No tungsten is lost through treatment with the mixed acids or even with hydrofluoric acid alone. Some tungsten is lost if the mixed oxides are heated at a temperature high enough to dehydrate the silica thoroughly. If both are to be determined in the mixed oxides, the analyst must therefore choose between getting high results for silica and low results for tungsten. Ordinarily the first choice is taken and causes less trouble, for, when the two occur

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latter, if eventually ignited with the silica, would undergo at least partial decomposition, and, on treatment with the mixed acids, the metals of the fluosilicate (presumably sodium) would be weighed eventually as sulfate if not volatilized by the heat of the ignition. According to W. T. Schrenk and W. H. Ode [*Ind. Eng. Chem. Anal. Ed.*, **1**, 200 (1929)], losses in determinations of silica in fluorspar can be largely avoided by transferring the finely ground sample to a Pyrex beaker, adding 20 per cent perchloric acid that has been saturated with boric acid at 50° C, and digesting in a Pyrex beaker until fumes of perchloric acid are given off. H. Spielhaczek [*Z. anal. Chem.*, **119**, 4 (1940)] states that satisfactory determinations of silicon in fluorine-bearing materials such as cryolite can be had by mixing 1 g of ore with 3 g of fused borax and 14 g of potassium bisulfate (all powdered) in a platinum crucible, covering, and heating cautiously at first and then until reaction is complete. The cooled melt is taken up in dilute hydrochloric acid, the solution evaporated, and the residue dried at 110° C, crushed, and reheated until hydrochloric acid is expelled. The residue is finally moistened with hydrochloric acid, treated with hot water, filtered, and washed as usual.

together, the percentage of silicon is usually relatively small. Tungsten can be dissolved and separated from silicon as described under Tungsten (p. 685), or by heating the mixed oxides in a current of hydrogen chloride. If a platinum boat is used, the gas must be dry and free from air or chlorine.[4] Under such conditions, a little tungstic oxide may be reduced to an oxide which does not form a volatile chloride. Reduction can be avoided by using a quartz boat and hydrogen chloride together with either air or oxygen. If a platinum boat is used, the reduced oxide should be reoxidized and volatilized by cooling the apparatus, expelling the hydrochloric acid with air, heating, cooling, expelling the air with hydrogen chloride, and again heating.

For the separation of small amounts of silicon from large amounts of iron, as in pure irons, the most satisfactory procedure lies in separating as much of the silica as possible by the usual dehydration with sulfuric acid, followed by dilution and filtration, and then recovering the remainder by evaporating the filtrate, heating to convert the ferric sulfate to ferric oxide, volatilizing the latter by heating at 400 to 700° C in a tube through which dry hydrochloric acid gas is passed, and working over the residue for its silica content.[5]

The separation of silicon from tin had better be done by dehydrating with hydrochloric acid, rather than with sulfuric or perchloric acids which may yield insoluble compounds of tin upon dilution, or with nitric acid which would certainly cause coprecipitation of tin.

A satisfactory separation from lead can be had by dehydrating with sulfuric acid and then extracting the lead sulfate with ammonium acetate or ammonium chloride.[6] If the acetate treatment is used, and much lead sul-

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[4] D. H. Brophy and C. Van Brunt, *Ind. Eng. Chem.*, **19**, 107 (1927); C. Friedheim, W. H. Henderson and A. Pinagel, *Z. anorg. Chem.*, **45**, 398 (1905); A. Pinagel, *Inaugural Dissertation, Bern* (1904); F. Périllon, *Bull. soc. ind. Minérale* (1884).

[5] R. M. Fowler, *Ind. Eng. Chem. Anal. Ed.*, **4**, 382 (1932).

[6] For example, by dissolving 5 g samples of bronze (88 Cu, 8 Sn, 1.5 Pb, 2 Zn, 0.2 Sb + small weighed amounts of a cast iron of known Si content) in HCl with the aid of HNO_3, treating with 15 ml of H_2SO_4, evaporating to copious fumes, and then either (1) adding 200 ml of dilute H_2SO_4 (5 + 95), filtering, and washing in turn with dilute HCl (2 + 98), hot H_2O, hot $NH_4C_2H_3O_2$ solution (equal volumes of NH_4OH and H_2O made slightly acid with $HC_2H_3O_2$) and hot H_2O; or (2) diluting with 150 ml of H_2O containing 25 g of NH_4Cl and filtering, the following results were obtained:

	Silicon	
Method	Added, %	Found, %
1	None	None
1	0.005	0.005
1	0.01	0.009
1	0.048	0.047
2	0.048	0.048
2	0.048	0.043

fate is present, it is desirable to sluice the residue into a dish, digest with the acetate solution, and again transfer to the filter.

Columbium and tantalum, when present in the original material, always accompany silicon. Occasionally precipitation is nearly complete.[7] Both remain as the quinquevalent oxides after attack with hydrofluoric and sulfuric acids and, when originally present in appreciable amount, give rise to a large nonvolatile residue that should put the analyst on guard. For the determination of silicon in the presence of columbium or tantalum, see Earth Acids (p. 602). Titanium or zirconium does not accompany silicon to any extent unless solutions have been treated so as to cause their hydrolysis, or contain notable amounts of phosphates. Neither titanium nor zirconium is lost by evaporation with the mixed acids.[8] If phosphates are present, the expulsion of sulfuric acid must be carried out at as low a temperature as possible, lest phosphoric acid be lost.[9]

IV. METHODS OF DETERMINATION

Silicon is usually weighed as silica, SiO_2, after it has been separated by dehydration in acid solution and ignited (see under Part III, p. 863). The silica that is thus obtained is usually so impure that the actual amount present is determined by noting the loss of weight that occurs when the weighed residue is treated with sulfuric and hydrofluoric acids, ignited, and again weighed.[10]

It is rare indeed that all of the silicon is recovered by one evaporation with any acid,[11] and ordinarily some remains in solution after two evapo-

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[7] For example, in single dehydrations made by fusing the oxide with Na_2CO_3, evaporating with HCl, baking at 110° C, taking up the residue in HCl and hot water, filtering, and washing with dilute HCl (1 + 99), H. B. Knowles recovered 3.6 out of 3.9 mg of Ta_2O_5 and 3.1 out of 4.3 mg of Cb_2O_5.

[8] Very little zirconium is lost if zirconia is treated with hydrofluoric acid alone and gradually heated in a well-covered crucible.

[9] W. F. Hillebrand and G. E. F. Lundell, *J. Am. Chem. Soc.*, **42**, 2609 (1920).

[10] In a careful study of the nonvolatile residues left after determinations of silica in 16 Finnish rocks, K. Rankama [*Compt. rend. soc. géol. Finlande*, **XIV**, 1 (1939)] found spectrographic evidence of Al, Ba, Be, Ca, Ce, Co, Cr, Fe, Ga, Ge, K, La, Mg, Mn, Mo, Na, Ni, Pb, (Pt), Sc, Sn, Sr, Ti, W, V, Y, Zn, and Zr, 28 elements in all.

[11] R. W. Bunsen, *Ann.*, **61**, 265 (1847); E. Ludwig, *Z. anal. Chem.*, **9**, 321 (1870); C. Meineke, *Répert. anal. chem.*, **7**, 215, 757 (1887); J. P. Gilbert, *Technol. Quart.*, **3**, 61 (1890); W. F. Hillebrand, *J. Am. Chem. Soc.*, **24**, 362 (1902); A. Cameron, *Chem. News*, **69**, 171 (1894); M. Wunder and A. Suleimann, *Ann. chim. anal.*, **19**, 45 (1914); V. Lenher and E. Truog, *J. Am. Chem. Soc.*, **38**, 1050 (1916). R. M. Fowler, *Ind. Eng. Chem. Anal. Ed.*, **4**, 382 (1932).

For example, in determinations of silica in 1-g samples of a soda-lime glass containing 74.1 per cent of SiO_2, 73.4 was obtained by evaporating once with hydrochloric acid on the steam bath and then drying for 1 hour at 110° C. Single evaporations with sulfuric and perchloric acids yielded 72.4 and 73.3, respectively.

rations with intervening filtration.[12] If the evaporations have been properly made, a third evaporation will give no more silicon, for solubility equilibrium has been reached. The silica that is still in solution is carried down by the ammonia precipitate in proportion to the size of the precipitate and the amount of silica present. If the ignited ammonia precipitate weighs more than 0.1 g and two separations of silica have been made, not more than 0.1 to 0.2 mg of silica finally remains in solution.[13] If the ammonia precipitate is small and especially if but one evaporation for silica has been made or the pyrosulfate melt of the ignited ammonia precipitate is dissolved in water instead of evaporated with sulfuric acid (p. 876), the unrecovered silica may amount to several milligrams. The silica that is caught with the ammonia precipitate is counted as alumina if the latter is obtained by difference and no recovery of silica is made. If a recovery is made, the results for silica and alumina will still be in error unless corrections for impurities in the reagents are determined as to be described. For typical recoveries of silica in the ammonia precipitate after the major portion of the silica had been separated by double evaporation and intervening filtration see Table 20.[14]

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[12] In this process, the residue left after the first dehydration is taken up in a dilute solution of the acid that was used, the solution is filtered, the impure silica washed, and the filtrate and washings again evaporated.

In analyses of 0.5-g samples of ferrosilicon and burnt refractories, the silica that remained in solution after such treatments averaged approximately 1 mg with hydrochloric acid and a trifle more with sulfuric acid (see also Table 20).

[13] The small amount of silica still in solution can be estimated satisfactorily by matching the yellow color of silicomolybdic acid produced by ammonium molybdate [2 ml of a 10% solution of $(NH_4)_2MoO_4$, and 2 drops of H_2SO_4 per 50 ml of solution containing no more than 2.5 mg of SiO_2] with an artificial standard solution of picric acid [F. Diénert and F. Wandenbulcke, *Compt. rend.*, **176**, 1478 (1923); *Bull. soc. chim.*, **33**, 1131 (1923); E. J. King and C. C. Lucas, *J. Am. Chem. Soc.*, **50**, 2395 (1928)]. For the use of solutions of potassium chromate buffered with borax as colorimetric standards in the determination of small amounts of dissolved silica by the formation of the yellow heteropoly compound, molybdisilicic acid, see H. W. Swank and M. G. Mellon, *Ind. Eng. Chem. Anal. Ed.*, **6**, 348 (1934); R. J. Robinson and H. J. Spoor, *ibid.*, **8**, 455 (1936); and M. F. Adams, *ibid.*, **17**, 542 (1945). For 0.01 to 1.0 mg of SiO_2 per 100 ml of solution, H. W. Knudson, C. Juday, and V. W. Meloche [*ibid.*, **12**, 270 (1940)] recommend development of the color by adding $(NH_4)_2 \cdot MoO_4$ in excess of a molecular concentration 12 times that of the SiO_2, adjusting the acidity to *p*H 1.6 to 2.0, letting stand for 10 minutes, and comparing against buffered chromate standards or measuring the color in a photoelectric colorimeter. Phosphate and undoubtedly other complex-forming ions interfere. The use of oxalic acid to destroy the interfering colored phosphomolybdic acid in the photometric determination of small amounts of silica (50 ppm) in treated waters is described by M. C. Schwartz [*ibid.*, **14**, 893 (1942)]. For a photometric method for the determination of as much as 1 per cent of silica in aluminous materials by the molybdenum blue reaction, consult J. A. Brabson, I. W. Harvey, G. E. Maxwell, and O. A. Schaeffer, *ibid.*, **16**, 705 (1944).

[14] For the determination of silica in the weighed ammonia precipitate by direct treatment with sulfuric and hydrofluoric acids, see under Aluminum (p. 504). According to L. R. Dawson and R. V. Andes [*Ind. Eng. Chem. Anal. Ed.*, **12**, 138 (1940)], quite satisfactory routine determinations of R_2O_3 and SiO_2 in cements can be made by combining the R_2O_3 and SiO_2 precipitates, igniting, weighing, and then treating with H_2SO_4—HF, evaporating, igniting, and again weighing.

TABLE 20

RECOVERIES OF SILICA IN THE AMMONIA PRECIPITATE AFTER DOUBLE EVAPORATION WITH ACID AND INTERVENING FILTRATION

Material	SiO_2 Present, %	Approximate Weight of Sample, g	Acid Used	SiO_2 Obtained in NH_4OH Precipitate, mg
Dolomite	0.31	10	HCl	1–1.2 *
Feldspar	66.66	1	HCl	5.6
Feldspar	66.66	0.5	HCl	0.9–1.1
Soda-lime glass	74.1	1	HCl	0.3–0.8 †
Soda-lime glass	74.1	0.5	H_2SO_4	0.6 ‡
Lead-barium glass	65.36	0.5	HCl	0.3–0.6 §
Lead-barium glass	65.36	0.5	$HClO_4$	0.4–1.1 ‖
Burnt refractory	54.7	0.5	H_2SO_4	1
Burnt refractory	32.4	0.5	H_2SO_4	0.5–0.6
Burnt refractory	20.7	0.5	H_2SO_4	0.7–0.8
Bauxite	6.32	1	H_2SO_4	0.5
Refined silicon	96.8 ¶	0.5	HCl	0.6–1
Refined silicon	96.8 ¶	0.5	H_2SO_4	1–1.5

* The precipitate obtained by acidifying the ammoniacal filtrate, adding 15 mg of Fe_2O_3 as $FeCl_3$ and treating with NH_4OH, contained no more SiO_2 than the reagents, thus indicating that SiO_2 had been completely recovered in the two dehydrations and in the regular ammonia precipitate.

† The SiO_2 obtained in the second dehydration ranged from 3.3 to 7.6 mg.

‡ 9.4 mg of SiO_2 was obtained in the second dehydration.

§ The SiO_2 obtained in the second dehydration ranged from 3 to 6 mg.

‖ The SiO_2 obtained in the second dehydration ranged from 0.6 to 0.9 mg.

¶ Si.

The dehydration of silica is usually carried out in hydrochloric acid solution because of the greater solubility of the chlorides. The choice of acid, however, must be governed by the composition of the material.[15] Sulfuric and perchloric acids both find use. Nitric acid gives satisfactory results with some materials, as for example soda-lime glass, but is not generally applicable because many nitrates are difficultly soluble in dilute acid after they have been evaporated to dryness. All require double evaporations and recovery of silica in the ammonia precipitate. Separations of silica together

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[15] For example, careful double dehydrations with intervening filtration as applied in the analysis of a glass containing the oxides of antimony (5%), lead (2%), and boron (13%), besides those of silicon, iron, aluminum, the alkaline earths, and the alkalies, gave 67.2 per cent of SiO_2 with nitric acid, 68.2 with hydrochloric acid, and 68.8 with sulfuric acid. All were based on final treatment with HF—H_2SO_4, and the last result was the most nearly correct.

with titania made by digesting with formic acid as recommended by A. Leclerc[16] are entirely unsatisfactory (L.).

If hydrochloric acid is used, the chief concern is to continue the evaporation until the residue is dry. This can be done satisfactorily on the steam bath if the crusts that form are broken up with a rod.[17] Dehydration can be made more certain, especially in the presence of magnesium or manganese, by heating the residue in a muffle or oven; but in such case the temperature should not exceed 110° C, or be prolonged over 1 hour, lest the separated silica recombine with magnesia and again dissolve.

If sulfuric acid is used for dehydration, enough should be taken to prevent the formation of a cake or paste that causes spattering or makes subsequent solution of the salts difficult. The heating should be carried to fumes of the acid, but not prolonged at a high temperature if substances, such as nickel or chromium, that form difficultly soluble sulfates are present. If considerable aluminum is present, better results are obtained if an equivalent volume of water is added while the acid is still quite hot, and the solution is then heated to boiling before further dilution with boiling water.

If perchloric acid is used, enough must be taken to insure a liquid and not a pasty or dry mass at the fuming point, and the fuming acid must be boiled gently for approximately 15 minutes to insure dehydration of the silicic acid (see Part III, p. 862).

Dehydrated silica is appreciably soluble in acid solutions[9, 18] and even in solutions containing sodium chloride or other salts.[19] The acidity of the solution in which the dehydrated silica is digested should therefore be no greater than is necessary for the solution of accompanying salts and the prevention of hydrolysis. With hydrochloric or sulfuric acid, the amount of acid need not exceed 5 to 10 per cent by volume. The period of digestion should be as short as possible, never over 15 minutes. If two evaporations with hydrochloric acid are contemplated, it is desirable to wash the first residue with hot dilute hydrochloric acid (5 + 95), and the second residue with cool dilute acid (1 + 99). The more complete removal of contaminating salts by the hot acid more than compensates for its solvent

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[16] *Compt. rend.*, **137**, 50 (1903).

[17] According to S. Shinkai [*J. Soc. Chem. Ind. Japan*, **29**, 303 (1926)], NH_4Cl transforms silica hydrosol to the hydrogel. He therefore recommends that 3 to 4 g of the salt be added after the hydrochloric acid solution of the sodium carbonate melt has been evaporated to small volume, and that the solution be then evaporated to dryness as it is frequently stirred.

[18] Wunder and Suleimann, *loc. cit.;* Lenher and Truog, *loc. cit.;* F. G. Hawley, *Eng. Mining J.*, **103**, 541 (1917). The last found that concentrated hydrochloric acid is less active than an acid of 18 to 25 per cent strength, and that the amount of silica dissolved is proportional to the amount of acid used.

[19] V. Lenher and E. Truog, *loc. cit.;* F. G. Hawley, *loc. cit.;* H. A. B. Motherwell, *Eng. Mining J.*, **103**, 1155 (1917).

action on the silica, and the cool dilute acid suffices to prevent hydrolysis and to remove impurities from the smaller amount of silica obtained by the second evaporation.

It is almost impossible to remove all of the dehydrated silica from porcelain or quartz dishes. For this reason platinum or gold dishes should be used whenever possible. If porcelain or quartz must be used, it is better to dissolve alkaline melts in dilute acid than in water, for less incrustation occurs. In any case, such dishes suffer attack during evaporation, and the silica so introduced may more than make up for that which cannot be separated from the dish by scrubbing.[20]

Great care must be exercised to prevent mechanical loss of silica when paper and silicic acid are ignited, and when the ignited silica is treated with sulfuric and hydrofluoric acids. In the first case it is best to heat slowly the wet paper containing the silica obtained in the second evaporation until the paper has charred without inflaming, then to add and heat in the same way the silica obtained in the first evaporation, next to cover the crucible partially and cautiously burn the carbon, and finally to cover tightly and keep out all drafts, especially if the final heating is done over a blast lamp or a Meker burner.[21] If the former is used, it is desirable to set the covered crucible for two thirds of its depth in an asbestos shield. The addition of water or dilute acid to the ignited residue is apt to cause dusting, and is done best from a pipette with its stem full of liquid and inserted against the side of the crucible underneath the slightly raised cover.

It is often stated that an ignition of silica at approximately 1000° C suffices to drive out all water. This seems to be true of moderate amounts of pure silica obtained in the absence of salts. With silica obtained in ordinary analyses, however, and especially with large amounts of silica, the safest procedure lies in igniting to constant weight at approximately 1200° C.[22] This temperature can be obtained by a blast lamp or a burner of the Meker type.[23] Pure dehydrated silica is not hygroscopic, but the silica that is usu-

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[20] For example, in careful analyses of soda-lime glass containing 74.1 per cent of silica, 74.1 was obtained when evaporations were made in quartz and 74.2 when made in porcelain, in spite of the fact that all of the incrusted silica could not be removed from the dishes.

[21] If the wet paper containing the silicic acid is ignited in a covered crucible, silicon carbide may be formed at temperatures as low as 950° C [K. A. Krieger and H. S. Lukens, *Ind. Eng. Chem. Anal. Ed.*, **8**, 118 (1936)].

[22] W. F. Hillebrand, *J. Am. Chem. Soc.*, **24**, 372 (1902). We have never been able to obtain any evidence that silica holds chlorine in chemical combination after dehydration in hydrochloric acid, as was asserted by E. Jordis and E. H. Kanter [*Z. anorg. Chem.*, **35**, 16 (1903) and Th. Bauer, *Thonind. Ztg.*, **37**, 89 (1913)].

[23] It must be borne in mind that some platinum crucibles lose weight steadily and very appreciably on continued heating at 1200° C, not only when new but even after long use. When a crucible suffers from this defect, the rate of loss should be ascer-

ally obtained had better be protected by a well-fitting cover and cooled over a good desiccant.

As has already been stated, the amount of silica present in the ignited residue is usually calculated from the loss of weight that occurs when it is treated with hydrofluoric acid.[24] In the usual case, sulfuric acid must also be used in order to prevent volatilization of compounds other than silicon such as zirconium and titanium. The temperature at which the nonvolatile matter is ignited should be high enough to change it to the state in which it occurred in the impure silica, but need not exceed 1000° C in the usual case. According to H. O. Hofman and W. Wanjukow,[25] some of the commoner sulfates, when heated in a slow current of air, begin to decompose at the temperatures given in Table 21. Treatment with hydrofluoric acid alone is permissible when the impurity does not volatilize or undergo a permanent change. This is the case with ferric oxide, alumina, or tungstic oxide. Boron or trivalent arsenic is volatilized with silica in any case and must be separated before silica is treated with hydrofluoric acid.[26]

TABLE 21

Temperatures at Which Certain Sulfates Decompose

Sulfate	Temperature at which Decomposition Begins, °C	Temperature at which Decomposition Becomes Energetic, °C
$FeSO_4$	167	480
$Fe_2(SO_4)_3$	530	
$Bi_2(SO_4)_3$	570	639
$Al_2(SO_4)_3$	590	639
$PbSO_4$	637	705
$CuSO_4$	653	670
$MnSO_4$	699 *	790
$ZnSO_4$	702	720
$NiSO_4$	702	764
$CoSO_4$	720	770
$CdSO_4$	827	846
$MgSO_4$	890	972
Ag_2SO_4	917	925
$CaSO_4$	1200	
$BaSO_4$	1510 †	

* According to W. Blum [*J. Am. Chem. Soc.*, **34**, 1389 (1912)], $MnSO_4$ begins to decompose slightly at temperatures from 550 to 600° C.

† Dissociation temperature is lowered by impurities such as SiO_2 or Fe_2O_3 [W. Mostowitsch, *Metallurgie*, **6**, 450 (1909)]. No doubt this is also true of the other sulfates.

Contamination of silica by alkali salts is a serious matter and can easily happen if fusions with alkali carbonate have preceded the separation of silica and the paper and residue are not thoroughly washed. Alkali salts that remain with the silica cause trouble because they volatilize in part during the ignition of the nonvolatile residue, and more or less of the remainder changes in weight. The latter is brought about because considerable decomposition of the alkali salt occurs during the intense ignition of the silica, with the formation of alkali silicate and the liberation of acid. Any silicate so formed is broken up during the hydrofluoric-sulfuric acid treatment, and the alkali is then weighed as sulfate instead of oxide, thus causing low results for silica. Any alkali chloride originally present and not decomposed or volatilized during the ignition of the silica is first weighed as chloride and then as sulfate, which of course also leads to low results. If the ignition of the nonvolatile residue is made at a temperature high enough to volatilize all of the alkali sulfate, high results for silica are obtained.

Sulfates, such as those of lead, and the alkaline earths are undesirable contaminants of silica, for these also tend to form silicates during the ignition of the silica, and cause results that are low in proportion to the amount of silicate that is formed.[27] Among other undesirable contaminants might be mentioned compounds, such as bismuth or antimony oxychlorides or stannic or antimonic acids, which undergo indefinite changes between the first and second weighings for silica. When such elements are present, the dehydration must be done with an acid that gives soluble salts.

Incorrect results for silica are also obtained as a rule if the ignited silica contains undecomposed material. This holds true, even though all of the silica in the undecomposed portion is volatilized during the treatment with hydrofluoric and sulfuric acids, because the accompanying substances rarely maintain the same weight. For example, with microcline, $KAlSi_3O_8$, volatilization of silica and ignition would leave K_2SO_4 and Al_2O_3 instead of

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tained from time to time and allowance made accordingly, or else the weight of the crucible should be taken after and not before ignition of the precipitate [see on this subject R. W. Hall, *J. Am. Chem. Soc.*, **22**, 494 (1900) and G. A. Hulett and H. W. Berger, *ibid.*, **26**, 1512 (1904)].

[24] The hydrofluoric acid must be free from nonvolatile impurities, or else corrections must be applied for the amount used, and the effect of the impurities on the rest of the analysis must be considered.

[25] *Bull. AIME*, 889 (1912), and *Met. Chem. Eng.*, 10, 172, 695 (1912).

[26] According to T. Heczko [*Z. anal. Chem.*, **77**, 327 (1929)], the excess of acids can be evaporated more quickly and probably with less spattering of the nonvolatile residue if filter paper is put into the crucible to absorb the liquid.

[27] If the separated silicic acid is contaminated by barium sulfate, no appreciable interaction between the two takes place, provided ignition temperatures do not exceed 1000° C. At 1200° C, silicon dioxide displaces sulfur trioxide in the sulfate, and causes low values for silica in determinations made by the customary treatment of the impure silica with hydrofluoric and sulfuric acids.

K_2O and Al_2O_3, whereas with talc, $H_2Mg_3(SiO_3)_4$, $MgSO_4$ would be left instead of MgO.

Corrections for impurities derived from the reagents or by attack of the containing vessels are apt to be entirely misleading if made as in the usual fashion by carrying the reagents alone through the analysis. The reason for this lies chiefly in the size of the precipitate obtained in the analysis, as compared with that obtained with the reagents. The former carries down practically all of the silica that is introduced by the reagents, attack on glassware, or other causes; the latter carries down very little. This then leads to high results for silica, and can be avoided by adding to the solution of the reagents approximately as much iron and aluminum as are contained in the sample under analysis.[28]

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[28] For example, in analyses of 0.5-g portions of bauxite, an average correction of less than 0.1 mg of silica was indicated by the reagents alone, and 0.9 mg when 0.25 g of alumina as pure aluminum chloride was added to the reagents. Corrections based on the analysis of the reagents alone would therefore have caused a plus error of 0.18 per cent of silica.

Chapter 44

TUNGSTEN

Tungsten is almost exclusively confined to the very siliceous rocks. It occurs chiefly as tungstates of iron, manganese, calcium, copper, and lead in the minerals ferberite, $FeWO_4$; hübnerite, $MnWO_4$; wolframite, $(Fe, Mn)WO_4$; scheelite, $CaWO_4$; cuproscheelite, $(Ca, Cu)WO_4$; and stolzite, $PbWO_4$. It is also found as a sulfide, tungstenite, WS_2, and in small quantity in a number of the niobates and tantalates. The ores of tungsten are by no means numerous. Wolframite is frequently found in tin ores. Tungsten is a constituent of certain metallurgical materials, and methods for its separation and determination are of considerable importance.

I. GENERAL CONSIDERATIONS

In the ordinary course of analysis, tungsten tends to separate with silica, and its presence is betrayed by the yellow color of the separated tungstic acid. Precipitation is incomplete and may not take place at all if but small amounts of tungsten are present. Much of the tungsten that separates with the silicon will be lost if ignitions are made at the customary high temperatures, for tungstic oxide begins to volatilize at about 800° C. Considerable, if not all, of the tungsten that escapes separation with the silica will be found in the ammonia precipitate in combination with iron, aluminum, and especially the alkaline earths, in spite of repeated precipitations. The tungsten so precipitated will probably survive the ignition of the ammonia precipitate and be counted as alumina if iron is determined by reduction with hydrogen sulfide or sulfur dioxide. If reduction is made by zinc or stannous chloride, the error will be distributed between both iron and alumina, provided the blue color of the reduced tungsten does not put the analyst on guard.

It is evident that the complete separation of tungsten at the start of an analysis is even more desirable than that of silicon.

II. ATTACK OF TUNGSTEN MINERALS

Most tungsten minerals are quite satisfactorily decomposed by the hydrochloric-nitric acid treatment described in IV, A, provided the mineral has been ground to at least 200 mesh. By such treatment scheelite and hübnerite are easily decomposed, ferberite is somewhat more difficult to decompose, and wolframite is the most difficult of all.

Fusion of the mineral with sodium carbonate, sodium peroxide, or sodium or potassium pyrosulfate should be avoided if possible, whenever tungsten is to be determined, for alkali salts prevent complete precipitation of tungsten by digestion with acids, and retard its precipitation by cinchonine. There is, however, no objection to such fusions if they are preliminary to the determination of other elements in the mineral, as for example the determination of iron in the residue left after the water extraction of a sodium carbonate melt.

Fusion with sodium carbonate is done by thoroughly mixing 0.5 g of the finely ground ore with 4 g of sodium carbonate in a platinum crucible and heating over a moderate flame for 30 to 60 minutes. The melt is extracted with water, the solution filtered, and the residue washed with dilute sodium carbonate solution and finally with water. The residue is ignited at a low temperature, again fused with sodium carbonate, and extracted with water. The combined water extracts contain the tungsten, molybdenum, vanadium, arsenic, phosphorus, chromium, and part, if not all, of the silicon, aluminum, antimony, tin, columbium, and tantalum. The residue contains iron, zirconium, manganese, calcium, and the like.

Attack by pyrosulfate is carried out by fusing 1 g of the finely ground ore with 5 g of pyrosulfate in a covered platinum or silica crucible at as low a temperature as possible. If the melt is dissolved in dilute sulfuric acid (5 + 95), the same result is accomplished as in an acid attack, save for less complete separation of the tungsten. If it is desirable to keep all of the tungsten in solution, this can be done by dissolving the melt in a hot 5 per cent solution of tartaric acid. In either case, the insoluble residue is filtered off, washed, ignited at a low temperature, again fused, and the melt extracted to render the decomposition more complete.

According to Travers,[1] fusion of the finely powdered material with anhydrous sodium sulfite in a porcelain crucible at bright red heat is desirable for the attack of wolframite containing tin. If the melt is extracted with boiling water, diluted to 700 ml, and then slightly acidified with an excess of not over 20 ml of normal acid, it is maintained that the tin is precipitated entirely free from tungsten.

III. METHODS OF SEPARATION

The chief method for the separation of tungsten depends on its precipitation as tungstic acid by digestion with acids, usually with the final aid of

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[1] M. Travers, *Compt. rend.*, **165**, 408 (1917).

cinchonine as described under IV, A. The precipitate is seldom pure and must be separated from contaminants as to be described.

If small amounts of tungsten are in question, it is better to separate silica by the usual dehydration with dilute hydrochloric acid,[2] then to digest the filtrate after the addition of cinchonine (p. 690), and finally to unite any precipitate so obtained with the nonvolatile residue left after the treatment of the silica with hydrofluoric and sulfuric acids. The combined residues should then be fused with as little sodium carbonate as possible, the melt dissolved in dilute hydrochloric acid and treated with cinchonine, and the solution digested for 10 hours or more.

Tungsten occurring as tungstate in an alkaline or ammoniacal solution containing considerable alkali chloride can be quantitatively precipitated as follows:[3] Dilute the solution to 100 to 200 ml, warm to 50° C, and add a fresh solution of 0.5 g of tannin. Treat with dilute hydrochloric acid until the solution is acid to litmus, and then add a little paper pulp. Stir briskly, and add, drop by drop, 5 ml of a 5 per cent solution of cinchonine in dilute hydrochloric acid (1 + 3). Allow to cool, and let stand for several hours, preferably overnight. Decant upon a no. 41 Whatman or equivalent paper. Sluice any precipitate on the paper back into the beaker, and thoroughly wash the paper with 100 ml of a cool 5 per cent solution of ammonium chloride containing a little cinchonine. Stir the precipitate, again filter, and wash the paper and precipitate thoroughly. Let drain, and transfer to a tared porcelain crucible. Heat gently until the paper chars, and then proceed with the ignition to WO_3 as described on page 692.

Tungstic oxide can be quantitatively separated from silica by volatilizing the latter with hydrofluoric acid alone or in combination with sulfuric acid. When this is done, all ignitions must be made at temperatures below 850° C because of the volatility of WO_3. This is too low a temperature for the dehydration of silica, and so a separate sample should be taken for the determination of silica if much of it is present and an accurate determination is to be made.[4] In this case the usual ignition at 1200° C should

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[2] In our hands, the use of phosphoric acid for keeping tungsten in solution during dehydration of silica by sulfuric acid has not proved entirely satisfactory.

[3] W. R. Schoeller and C. Jahn, *Analyst*, **52**, 504 (1927). Consult also D. A. Lambie, *ibid.*, **64**, 481 (1939). For the substitution of phenazone (antipyrine) for cinchonine, see *ibid.*, **70**, 124 (1945).

[4] According to J. Ciochina [*Z. anal. Chem.*, **72**, 429 (1928)], tungsten can be easily removed from silicon or tin in a mixture of their freshly precipitated acids, by washing with water until mineral acid is removed, filling the filter with a hot 25 per cent solution of sodium tungstate as the stem of the funnel is closed, letting the solution run through after a few minutes, and then washing in succession with hot water, hot dilute hydrochloric acid, and hot water. In our hands this treatment has led to the removal of some silica as well.

be made *before* the weighing of the crude silica, followed by ignition at 750 to 850° C *after* the treatment with hydrofluoric and sulfuric acids. Tungsten can be quantitatively volatilized and separated from silica by heating the mixed oxides at 700° C in a current of pure hydrochloric acid gas.[5] This treatment also causes more or less volatilization of tantalum, titanium, zirconium, and aluminum as does also heating in hydrochloric acid and oxygen, chlorine, or chloroform and oxygen.

Hydrogen sulfide produces very little precipitate in acid solutions containing tungsten alone, but appreciable amounts of the element may be carried down by molybdenum or other sulfides. Tartaric or oxalic acid prevents such precipitation. Alkali sulfides yield a deep-brown solution containing the thiotungstate except in the presence of elements such as manganese with which tungsten is partially precipitated. We do not know whether tartrate prevents the coprecipitation of tungsten in the latter case as it does in acid solution. The acidification of a solution of thiotungstate results in incomplete precipitation of the brown flocculent sulfide, WS_3, when tartrates or oxalates are absent and no precipitation when they are present.

Precipitation by α-benzoinoxime in dilute acid solution as described under Molybdenum (p. 310) precipitates tungsten as well, and serves to gather tungsten or to separate it from a number of elements. The precipitation of tungsten is complete if molybdenum preponderates, but is often incomplete if tungsten occurs alone.

Elements such as molybdenum, antimony, arsenic, and tin can be separated from tungstic acid by dissolving the impure acid or oxide in alkaline solution, adding 2 to 5 g of tartaric acid, and then precipitating the arsenic group by saturating with hydrogen sulfide and adding acid in slight excess, or by acidifying the alkaline solution and precipitating with hydrogen sulfide. Tungsten can also be separated from tin and antimony by fusing the oxides with 12 to 15 times their weight of potassium cyanide in a porcelain crucible, extracting with water, filtering to remove the metallic tin and antimony, and precipitating the tungsten in the filtrate by adding cinchonine after acidifying and boiling under a good hood.

Other methods for separating molybdenum from tungsten are those in which the wet freshly precipitated acids are digested with sulfuric acid or the ignited oxides are heated in a current of dry hydrochloric acid. The former is described under Molybdenum (p. 305). The latter depends on the fact that molybdenum is volatilized as the compound $MoO_3 \cdot 2HCl$

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[5] F. Périllon, *Bull. soc., ind. Minérale*, **1** (1884); A. Pinagel, Inaugural Dissertation, Bern (1904); C. Friedheim, W. H. Henderson, and A. Pinagel, *Z. anorg. Chem.*, **45**, 396 (1905); D. H. Brophy and C. Van Brunt, *Ind. Eng. Chem.*, **19**, 107 (1927).

when a mixture of the trioxides or their alkali salts is heated at 250 to 270° C in a current of dry hydrochloric acid gas.[6] The temperature must be carefully controlled, for tungsten can be volatilized at red heat by a similar procedure.[7] According to Marbaker,[8] as much as 0.25 g of tungsten can be separated from a like amount of molybdenum, in the form of sodium tungstate and molybdate, by diluting to 60 to 300 ml, depending on the amount of tungsten present, boiling, treating with 20 ml of stannous chloride reagent (50 g $SnCl_2 \cdot 2H_2O$ dissolved in 200 ml of concentrated HCl) for each 0.15 g of WO_3 present, and boiling for 5 minutes. The orange-colored supernatant liquid is then decanted through a filter, and the blue precipitate of W_2O_5 thoroughly washed by decantation with portions of hot dilute (1 + 20) hydrochloric acid until free from molybdenum, and finally transferred to the paper. The precipitate can be dried and ignited to WO_3.

Arsenic or phosphorus can be separated from tungsten by precipitating with magnesia mixture in an ammoniacal solution containing ammonium tartrate, as described under Phosphorus (p. 697). Because of the solubility of magnesium ammonium arsenate, it is desirable to filter without washing and to remove the tungsten more completely by dissolving the precipitate in acid and repeating the precipitation. Tungsten can be freed from small amounts of arsenic by adding sufficient sulfurous or hydrobromic acid to reduce the arsenic, and then hydrochloric acid in excess, and boiling to small volume.

Powell, Schoeller, and Jahn[9] state that tungsten can be separated from titanium by fusing the mixed oxides with sodium carbonate, extracting the melt with a 10 per cent solution of sodium hydroxide, filtering, and washing the residue with a half-saturated solution of sodium chloride. Recoveries of titanium must be made in the filtrate, and tungsten is finally precipitated with tannin and cinchonine. Zirconium can be separated from tungsten by fusing with alkali carbonate and extracting with water.

Tungsten can be separated from titanium, zirconium, columbium, and tantalum by fusing the mixed oxides with potassium carbonate, treating

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[6] E. Péchard, *Compt. rend.*, **114**, 173 (1892). P. J. Koskey, *Chemist-Analyst*, **29**, 53 (1940).

[7] F. Périllon, *Bull. soc. ind. Minérale* (1884). For the separation of very small amounts of thoria from large amounts of tungstic oxide, D. H. Brophy and C. Van Brunt (*loc. cit.*) recommend the volatilization of the latter in a current of equal parts of dry hydrochloric acid gas and oxygen at 700° C. For volatilization in an atmosphere of CCl_4-CO_2, see P. Jannasch and coworkers, *Z. prakt. chem.*, **97**, 93, 141, 154 (1918).

[8] E. E. Marbaker, *J. Am. Chem. Soc.*, 37, 86 (1915).

[9] A. R. Powell, W. R. Schoeller, and C. Jahn, *Analyst*, **60**, 506 (1935). For details of the treatments, consult the reference, or W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium*, p. 91, Chapman & Hall, London (1937).

the aqueous solution of the melt with a slightly ammoniacal solution of magnesium sulfate and ammonium chloride, filtering to remove the elements save tungsten, and then precipitating the tungsten in the filtrate by the tannin-cinchonine method. The mixed earth oxides can be recovered by dissolving the magnesia precipitate in acid, precipitating with tannin, filtering, and igniting. As a rule, these still contain a little tungsten which must be recovered by again fusing with carbonate and repeating the whole process. If uranium is present, part of it is caught in the magnesia precipitate, and the remainder is left in the filtrate after the precipitation with tannin-cinchonine.[10]

Tungsten can be separated from small amounts of elements such as tin, columbium, and tantalum by digesting the freshly precipitated tungstic acid with a moderate excess of ammonium hydroxide and filtering. The residue must, however, be carefully examined for tungsten, because some elements, notably iron,[11] carry down appreciable amounts of it. Arsenic, vanadium, and phosphorus may also be removed if present in such small amounts as can be held in the ammonia precipitate. For the separation of tungsten from large amounts of columbium or tantalum, see the Earth Acids (p. 600).

Fusion of ignited impure tungstic acid with sodium carbonate, followed by extraction with water, is not satisfactory if tin, columbium, or tantalum is present, for these will be found in both water extract and insoluble residue. Moreover, chromium, if present, will be oxidized to chromate and accompany tungsten. Small amounts of iron, titanium, and the like can be separated from tungsten by precipitating with sodium hydroxide.

IV. METHODS OF DETERMINATION

The most satisfactory method for the determination of tungsten in miscellaneous materials is in weighing it as the oxide, WO_3, after it has been separated as tungstic acid by digesting with hydrochloric or nitric acids, and finally in the presence of cinchonine. The precipitation of tungsten as mercurous tungstate, Hg_2WO_4, followed by ignition to the oxide,[12] is a quantitative procedure, but is subject to so many interfering substances, such as vanadates, chromates, and molybdates, that it serves best as a group separation as described under Vanadium (p. 455). The alkalimetric method,

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[10] For details, consult A. R. Powell, W. R. Schoeller, and C. Jahn, *loc. cit.*

[11] In fact, tungsten can be gathered, when present in minute amount, by adding an excess of a ferric salt and precipitating with ammonium hydroxide.

[12] J. J. Berzelius, *Schweigger's J.*, 16, 476 (1816); W. Gibbs, *Am. Chem. J.*, 1, 219 (1879); H. W. Hutchin, *Analyst*, 36, 398 (1911).

based on solution of tungstic acid in an excess of standard alkali and back titration with acid, is not so accurate a procedure as the gravimetric, even though the tungstic acid has been freed from all contaminants, a condition that can seldom be fulfilled. In our hands, methods based on the reduction of tungsten, followed by titration with permanganate[13] proved entirely untrustworthy, for it is difficult if at all possible to reduce tungsten to a definite stage and to remove all impurities, such as molybdenum and iron, that also undergo reduction.[14]

A. DETERMINATION BY DIGESTING WITH ACIDS AND CINCHONINE

The determination of tungsten is a simple matter when it occurs in pure materials and can be accomplished by digesting with acids alone. In mixed materials, complete separation is uncertain when acids are used, and recourse is had to final treatment with cinchonine, which forms an insoluble compound with tungsten.[15] Among the substances that interfere in the precipitation of tungsten by digestion with acid are sodium, potassium, and ammonium salts, phosphorus,[16] molybdenum, arsenic, fluorine, and organic matter such as tartaric acid. These also retard precipitation by cinchonine to some extent.

The precipitated tungstic acid is usually impure. Of the likely contaminants, some, such as silicon, tin, antimony, columbium, and tantalum, are precipitated by the treatment used to separate the tungsten; others, such as phosphorus, molybdenum, and vanadium, are carried down in combination with the tungstic acid, whereas still others, such as iron and chromium, represent the usual contamination that results in a single precipitation. Many of these contaminants are eliminated by the treatments that are specified in IV, A.

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[13] O. Frieh v. d. Pforten, *Ber.*, 16, 508 (1883); see also E. Knecht and E. Hibbert, *Proc. Chem. Soc.*, 25, 227 (1909). M. L. Holt and A. G. Gray [*Ind. Eng. Chem. Anal. Ed.*, 12, 144 (1940)] state that tungsten can be reduced to the trivalent state by liquid lead amalgam, reoxidized by ferric sulfate, and the resulting ferrous sulfate titrated with a standard solution of potassium dichromate, using diphenylamine sulfonic acid as indicator. Other easily reducible elements such as vanadium or molybdenum must, of course, be absent.

[14] For the preparation of $K_3W_2Cl_9$ by reduction with tin in concentrated hydrochloric acid solution and its use as a reducing agent, see R. Uzel and R. Pribil, *Collection Czechoslov. Chem. Communs*, 10, 7–8, 330 (1938).

[15] For example, in analyses of scheelite an average value of 58.4 per cent WO_3 was obtained by digestion with acid alone and 59.6 by the aid of cinchonine, while with ferberite the results were 62.1 and 66.0, respectively.

[16] See S. G. Simpson, W. C. Schumb, and M. A. Sieminski, *Ind. Eng. Chem. Anal. Ed.*, 10, 243 (1938).

The effect of certain substances is shown by the data given in Table 22. These were obtained by treating 1-g portions of ferberite with the contaminants as shown and proceeding as in IV, A, up to the weighing of the *impure* tungstic acid.

TABLE 22

THE EFFECT OF CERTAIN SUBSTANCES ON THE DETERMINATION OF TUNGSTEN

Contaminant	WO_3 Present, %	Impure WO_3 Obtained, %	Remarks
1% P	66.0	66.2	Contained iron and phosphorus.
10% P	66.0	66.5	
10% P	66.0	58.0	No cinchonine used in first precipitation.
3% P	66.0	65.8	Phosphorus removed with magnesia mixture after first precipitation.
5% As	66.0	65.9	
25% NH_4Cl	66.0	65.8	
25% NaCl	66.0	65.6	
25% KCl	66.0	65.7	
5% Mo	66.0	66.8	
5% Mo	66.0	65.7	No cinchonine used in first precipitation and precipitate contained molybdenum.
25% V	66.0	65.7	
5% Bi	66.0	66.0	
25% Cu	66.0	65.8	
50% Pb	66.0	65.7	
8.7% Mn	73.1	73.0	

The proper ignition of tungstic acid is a difficult matter, for a temperature of 750° C is needed for complete dehydration of the acid, while the oxide begins to volatilize at 800° C. The rate of volatilization is slow at temperatures below 900° C, however, and so a range of 750 to 850° C is quite safe. Pure ignited WO_3 is not hygroscopic.

PROCEDURE. Grind the sample of ore or mineral in an agate mortar until all of it is of 200 mesh or finer. Transfer 1 g to a 400-ml beaker, add 5 ml of water, and gently whirl the beaker so as to break up the material and distribute it evenly on the bottom. Add 100 ml of hydrochloric acid, cover the beaker, and heat for 1 hour at a temperature not exceeding 60° C and with occasional stirring to prevent the formation of crusts or cakes on the bottom of the beaker. Now raise the cover on glass hooks, increase the heat, and boil to a volume of about 50 ml. Stir the material on the bottom of the beaker until all caked residue is broken up, and then add 40 ml of hydrochloric acid and 15 ml of nitric acid. Cover until danger of spattering is past, then remove the cover, and continue the boiling until the volume of the solution has been reduced to about 50 ml. Add 5 ml of nitric acid, break up all caked matter, and boil until the volume has been reduced to 10 to 15 ml. Add 150 ml of hot water, stir thoroughly

and gently simmer the solution for one-half hour. Add 5 ml of cinchonine solution,[17] and digest the solution on a hot plate or water bath at a temperature short of boiling for at least 30 minutes.

Let the precipitate settle, decant the supernatant liquid through a 9-cm paper containing some ashless paper pulp, and wash the precipitate three or four times by decantation with hot cinchonine wash solution.[18] Transfer the precipitate, so far as possible with moderate scrubbing, to the paper, and wash the beaker, paper, and precipitate thoroughly. Add cinchonine solution to the filtrate and washings (*A*), mix thoroughly, and set aside to make sure that recovery of tungsten is complete. Transfer the washed precipitate to the original beaker by means of a jet of water; no more than about 25 ml should be used. Add 6 ml of ammonium hydroxide (enough to give a slight excess), cover the beaker, and warm gently for a few minutes. Wash the inside of the beaker with warm dilute ammonium hydroxide (1 + 9) containing 10 g of ammonium chloride per liter. Stir the solution well, filter through the same paper as was used before, collect the filtrate in a 400-ml beaker, and wash the original beaker, the filter, and the residue with the warm dilute solution of ammonium hydroxide. Reserve the residue (*B*). Evaporate the filtrate, or gently boil it until most of the ammonia has been expelled. Add 20 ml of hydrochloric acid and 10 ml of nitric acid, and boil to a volume of 10 to 15 ml. Dilute to 150 ml with hot water, add 10 ml of cinchonine solution, stir the solution thoroughly, digest at 80 to 90° C for at least 30 minutes, and then allow to cool. Add paper pulp, transfer the precipitate completely to a 9-cm paper, and wash thoroughly with the hot cinchonine wash solution. This is the main precipitate and is to be ignited together with any additional tungsten obtained as to be described. Thoroughly mix the filtrate and washings (*C*), and set aside to make sure that precipitation was complete.

If the material is completely decomposed, any tungsten held in the reserved residue (*B*) is usually combined with iron or alumina, and can be dissolved by digesting the residue with warm dilute hydrochloric acid (1 + 9), filtering, and washing in turn with small amounts of a hot 0.5 per cent solution of ammonium chloride and the ammonium hydroxide wash solution. The tungsten (recovery 1) is then precipitated by further treatment with acid and cinchonine as with the boiled ammonium hydroxide extract, with which it should not be combined.

The residue (*D*) still left after the treatments with dilute acid and ammonium hydroxide is usually free from tungsten. It may contain silica or

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[17] Made by dissolving 125 g of cinchonine in a mixture of 500 ml of hydrochloric acid and 500 ml of water.

[18] Made by diluting 25 ml of the cinchonine solution and 30 ml of hydrochloric acid to 1 liter with hot water.

undecomposed silicates, cassiterite, and minerals containing columbium and tantalum[19] and can be tested as described under the Earth Acids (p. 601), or as follows: Ignite the paper and residue (*D*) at a low temperature in a porcelain crucible (because of a possible tin content), transfer the ash to a platinum crucible, and volatilize silicon by evaporation with hydrofluoric and sulfuric acids. Fuse the residue with as little sodium carbonate as possible, cool, and extract with water. Filter, acidify the filtrate with hydrochloric acid, boil to expel carbon dioxide, and test for tungsten by adding 5 ml of cinchonine reagent and digesting the solution at the side of the steam bath for 30 minutes, and then at room temperature for several hours, preferably overnight. If a precipitate appears in this solution or in the two reserved filtrates and washings (*A* and *C*), filter all through the same paper, and wash the combined precipitates with cinchonine wash solution. Extract with ammonium hydroxide, precipitate, and wash as in the preceding recovery (recovery 2).

Transfer the papers containing the main precipitate and the recoveries (1 and 2) to a large weighed platinum crucible, and heat at a low temperature until all carbon has been destroyed. Cool, moisten the precipitate with a little hydrofluoric acid, evaporate to dryness to expel any silica, and then ignite at 750 to 850° C. Cool in a desiccator, weigh as impure WO_3, and repeat the ignition until constant weight is obtained.

The tungstic oxide that is obtained must be examined for contaminants such as molybdenum,[20] silver, iron, and phosphorus as follows: Fuse with as little sodium carbonate as possible, extract the melt with water, filter, and wash any residue with a warm 1 per cent solution of sodium carbonate and then with hot water. Reserve the filtrate. Ignite the paper and residue, and repeat the operation. Combine the filtrates, and set aside. Ignite the well-washed paper and residue, cool, weigh, and correct the weight of tungstic oxide for the oxides found. In the rare event that silver is present,

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[19] Columbium and tantalum are precipitated very slowly by cinchonine when alone.

[20] Molybdenum is carried down by tungstic acid, no matter whether precipitation is done by digesting with acid or by treating with cinchonine. If cinchonine is not used, the contamination is less, but precipitation of the tungsten is incomplete. For example, in analyses of 1-g samples of ferberite containing 65.8 per cent of WO_3 and 5 per cent of added MoO_3, the weighed WO_3 contained 0.8 per cent of MoO_3 when cinchonine was used and 0.36 per cent when it was omitted. In the former case, all of the tungsten was precipitated; in the latter, 0.4 per cent escaped precipitation. In analyses of 1-g samples of ferrotungsten containing 75.2 per cent W and 0.24 per cent Mo, the weighed tungstic oxide contained 0.002 g of MoO_3 or approximately one half of the molybdenum. Tungstic oxide cannot be freed from molybdenum by heating at temperatures that do not also cause volatilization of tungsten.

Molybdenum tends to retard precipitation of tungsten with cinchonine. When appreciable amounts of molybdenum are present, as in Mo-W tool steels, the solution should be allowed to stand for 30 to 40 hours before filtration in order to obtain quantitative precipitation of tungsten.

digest the first insoluble residue with ammonium hydroxide, filter, wash the residue, and then proceed with the ignition and refusion with sodium carbonate. Treat the ammoniacal filtrate with ammonium sulfide, recover any precipitate, and ignite it with that obtained in the combined water extracts.

Acidify the water extracts, boil to expel carbon dioxide, and then add ammonium hydroxide in excess. Ordinarily no precipitate should remain, if one does, it must be recovered by filtration, washed, and ignited, and the weight deducted from that of the tungstic oxide. Add 3 to 5 g of tartaric acid to the clear ammoniacal solution, saturate with hydrogen sulfide, add sulfuric acid until 1 per cent by volume excess, digest for 1 hour at 40 to 60° C, and filter. Wash the precipitate with hydrogen sulfide water containing 5 g of tartaric and 5 ml of sulfuric acid per liter. Reserve the filtrate if tests for phosphorus and vanadium are deemed desirable. As the sulfides may still contain tungsten, dissolve the precipitate in hot dilute nitric acid containing a little bromine, boil to expel the latter, add 1 to 2 g of tartaric acid, and render the solution ammoniacal. Again treat with hydrogen sulfide, and proceed as before. Finally ignite very carefully at a temperature not over 600° C, cool, weigh, and correct the tungstic oxide for the oxides found.[21]

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[21] The use of anti-1,5-di-(*p*-methoxyphenyl)-1-hydroxyl-amino-3-oximino-4-pentene for the precipitation of the tungstate ion in 0.2 *N* hydrochloric acid solution is described by J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 45 (1944). For a colorimetric method for the determination of tungsten in low-grade ores based on the yellow color produced when weakly alkaline tungstate solutions are treated with thiocyanate and stannous chloride, consult F. S. Grimaldi and V. North, *ibid.*, **15**, 652 (1943) and E. B. Sandell, *ibid.*, **18**, 163 (1946).

For a colorimetric method for the determination of moderate amounts of tungsten in alloys based on the color produced by hydroquinone in strong sulfuric acid solution, see G. Bogatski, Z. *Anal. Chem.*, **114**, 170 (1938). Titanium and columbium give similar reactions, cf., C. M. Johnson, *Iron Age,* **157**, no. 14, 66–69 (1944).

Chapter 45

PHOSPHORUS

Phosphorus is found in greatest abundance in the more basic igneous and metamorphic rocks and is practically never entirely absent. It affects especially those rocks that are high in lime and iron rather than in magnesia. With one or two minor exceptions, it exists in the mineral kingdom only in the form of phosphates, of which a large number are known. Its chief mineral occurrence is in apatite, though it may be found in xenotime and monazite. An iron phosphide occurs in meteorites.[1] Phosphorus is an essential constituent of living matter. It is present in a great number of ores and metallurgical products and methods for its correct determination are of considerable importance.

I. GENERAL CONSIDERATIONS

In ordinary analyses, silica obtained by dehydration with acids may be contaminated by phosphates if the material under test contains elements, such as titanium, zirconium, thorium, or tin, associated with phosphorus. Some of the phosphorus so caught will be lost and counted as silica if, in the volatilization of silica, much sulfuric acid is added with the hydrofluoric acid and then volatilized at elevated temperatures.[2] The phosphorus that remains may again be precipitated if the nonvolatile residue left after the treatment of the silica is fused with sodium carbonate and the melt taken up in acid. In such case the phosphorus had better be removed by extracting the melt with water and filtering, before an attempt is made to dissolve the bases and to add them to the filtrate from the silica. The aqueous extract of the carbonate melt may then contain other elements, such as tin, tungsten, or columbium, besides phosphorus, and it should therefore be carefully examined. When the filtrate from the silica is treated with ammonium hydroxide, any phosphorus that is present will accompany the iron, aluminum, and titanium. If it is preponderant, it will cause precipitation of the alkaline earths; in extreme cases it may cause their complete precipitation. If no provision is made for its effect, the determination of aluminum will be in error. If alkaline earths are carried down, the error will extend to their determinations as well, if these are made in the filtrate from the ammonia precipitate.

Losses of phosphorus during analysis are occasioned chiefly by the neglect or improper treatment of insoluble compounds which may be obtained. These frequently contain phosphorus, as for example silica as just cited, metastannic acid that is obtained by digesting with nitric acid, or tungstic acid that is separated by boiling with acid. A common cause of small losses of phosphorus lies in discarding filters that are apparently clean. If ammonium phosphomolybdate has been precipitated in solutions containing titanium, zirconium, or tin, it is an easy matter to lose from 0.1 to 1 mg of phosphorus as an invisible phosphate left on the filter after extraction of the ammonium phosphomolybdate by ammonium hydroxide, or the subsequent solution of the first magnesium ammonium phosphate precipitate in acid.

II. SOLUTION OF COMPOUNDS CONTAINING PHOSPHORUS

All methods for the determination of phosphorus in minerals, rocks, ores and metallurgical products call for its presence as orthophosphate. Meta- or pyrophosphates must be converted to the ortho by appropriate treatments such as fusion with alkali or digestion with hot strong acid. Aside from certain phosphides in meteorites and a doubtful pyrophosphate, the only known compounds in which phosphorus occurs in the mineral kingdom are orthophosphates. Furthermore, the usual methods for decomposing metallurgical products yield the orthophosphate. The analyst is therefore fortunate in that he will not ordinarily have to deal with other acids of phosphorus except as the result of special treatments of his own, such as ignitions of primary or secondary orthophosphates or prolonged fusions of these with alkali pyrosulfate at high temperatures.

Cases where the material can be dissolved in water are few and are practically confined to chemicals. The use of hydrochloric or sulfuric acid is not desirable except where direct precipitation with magnesia mixture follows, or where the acid must be added to aid solution. In the latter case, as little as possible should be used. With metallurgical materials, a strong oxidizing attack is necessary, lest phosphorus be lost as phosphine. Nitric acid is generally employed and preferably alone. If hydrofluoric acid is used, it should afterwards be removed by evaporation or, if present in small amount, rendered harmless by the addition of boric acid.

Minerals that are insoluble in acids or residues that are obtained during analysis are usually fused with sodium carbonate or peroxide (in some cases after the addition of silica), the melt is extracted with water, the solution filtered, and the residue washed with a 1 per cent solution of

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[1] F. W. Clarke, The Data of Geochemistry, *U. S. Geol. Survey Bull.* 770, 18 (1924).

[2] W. F. Hillebrand and G. E. F. Lundell, *J. Am. Chem. Soc.*, 42, 2609 (1920).

sodium carbonate. When much phosphorus is involved, these operations are usually repeated.

Compounds that contain phosphorus must not be subjected to protracted fusions with pyrosulfate in open crucibles or at unnecessarily high temperatures, nor should they be heated with sulfuric acid at high temperatures or to complete expulsion of the acid.[2] No losses occur when evaporations with sulfuric acid are made at low temperatures and are stopped as soon as fumes of the acid appear, nor do losses occur when nitric, hydrochloric, or hydrofluoric solutions are evaporated to dryness. Negligible losses occur in short fusions with pyrosulfate if crucibles are tightly covered and only sufficient heat for proper fusion is used. Such fusions may, however, give rise to meta- or pyrophosphates which must then be converted to orthophosphate by boiling with dilute sulfuric acid (1 + 9) for at least 2 hours.[2]

As a general rule, compounds of phosphorus mixed with organic matter should not be ignited in platinum unless good oxidizing conditions are maintained.

III. METHODS OF SEPARATION

By all odds the most important method for the separation of phosphorus from other elements prior to its determination is that in which it is precipitated as ammonium phosphomolybdate from nitric acid solution as described in IV, A. The method can be almost universally applied, and can serve as well for the removal of phosphorus from solutions in which it is not wanted.

Very small amounts of phosphorus in the presence of large amounts of elements such as copper, nickel, or sexivalent chromium are best gathered by adding a decigram or two of aluminum or iron as an appropriate salt, precipitating with ammonium hydroxide in slight excess, filtering, and dissolving the precipitate in dilute nitric acid before attempting precipitation with molybdate.[3] Small amounts of phosphorus can also be gathered by precipitation with zirconium as follows: Add an excess of zirconium chloride to a hydrochloric acid solution of the orthophosphate, evaporate to dryness, dissolve the residue in 30 ml of hydrochloric acid and 10 ml of hydrobromic acid, and boil to expel arsenic. Evaporate to dryness, bake, take up in dilute hydrochloric acid (1 + 1), evaporate to 20 ml, and dilute with 500 ml of hot water. Digest at 50° C, filter, ignite the residue, and recover the phosphorus by fusing with sodium carbonate and extracting the melt with water.[4] The same reaction can also be used for the removal of part or all of the phosphorus from a solution containing large amounts of it. In the former case, prepare a solution containing 10 to 20 ml of hydrochloric or sulfuric acid, heat to about 50° C, slowly add the zirconium solution as long as a precipitate forms, let settle, and filter. In the latter case, treat the filtrate with enough zirconium solution to insure a slight excess, heat to boiling, and add ammonium hydroxide, slowly and with stirring until in slight excess. Add macerated paper, filter, and proceed with such determinations as those of the alkaline earths, magnesium, or the alkalies.

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[3] The method of gathering phosphorus by digesting with tin and nitric acid, fusing the ignited residue with cyanide, and extracting the melt in water is no longer widely used because the recovery of phosphorus is rarely complete, even though the initial ratio of tin to phosphorus was as high as 20 to 1.

[4] T. R. Cunningham, Union Carbide & Carbon Research Laboratories (private communication).

Phosphorus is easily separated from elements such as iron, nickel, cobalt, titanium, zirconium, or trivalent chromium by precipitating them, twice if need be, with sodium hydroxide (p. 84). The same end is usually obtained by fusing with alkali carbonate or peroxide, dissolving the melt in water, and filtering. Such separations leave phosphorus still associated with elements such as vanadium and arsenic if these were originally present. Further separations or special treatments are then in order as to be described.

The separation of iron, cobalt, zinc, and the like from phosphorus by precipitating with ammonium sulfide (p. 64) is of limited application, for elements such as the alkaline earths and magnesium must be absent. Elements such as zirconium, titanium, and thorium, however, are not precipitated in phosphate solutions containing both ammonium sulfide and ammonium tartrate.

Members of the hydrogen sulfide group, save possibly molybdenum, are separated by precipitation with hydrogen sulfide in acid solution as described on page 60. The separation of molybdenum from phosphorus is best done by the addition of acid to a solution of the two in ammonium sulfide, or by repeated precipitation of the phosphorus by magnesia mixture as described in IV, A (p. 702).

Arsenic can also be separated by reducing it to the trivalent condition and then boiling with either hydrochloric acid or hydrofluoric acid. Such treatments also serve for the removal of quadrivalent germanium. A fairly satisfactory separation of phosphorus from tungsten, quinquevalent vanadium, or molybdenum can be obtained by precipitating with magnesia mixture in ice-cold ammoniacal solution containing tartrate.[5]

Other separations that should be mentioned in passing are those based on the deposition of iron, copper, nickel, chromium, molybdenum, and the

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[5] In such case, add no more tartaric acid than is required to hold the bases in solution, warm to about 50° C, and add NH_4OH in slight excess and then a 10- to 25-fold excess of magnesia mixture. Add glass beads, chill the solution, shake violently, and then add 10 ml of NH_4OH per 100 ml of solution. Again chill, shake violently, and keep the solution cold for at least 12 hours. Complete separation is somewhat difficult as indicated by the results 0.1589 and 0.1587 as against the actual value 0.1579 g of $Mg_2P_2O_7$ obtained in double precipitation of a mixture of 0.2 g of W as Na_2WO_4 and approximately 0.04 g P as $(NH_4)_2HPO_4$.

like in a mercury cathode (p. 138), precipitation with cupferron in strong sulfuric or hydrochloric acid solution (p. 116), and extraction with ether (p. 134).

IV. METHODS OF DETERMINATION

Phosphorus is nearly always determined in a separate sample, and practically all methods require its preliminary separation as ammonioum phosphomolybdate; $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 2HNO_3 \cdot H_2O$ is the ideal composition.[6] It is difficult to get this composition under the conditions that usually obtain in the determination of phosphorus. Numerous procedures for the subsequent treatment of the phosphomolybdate precipitate have been proposed. These can be divided into two classes—those requiring a reasonably pure precipitate of any composition and those based on a pure precipitate of definite composition. There are but few methods of the first type, and the only one that is in common use is that calling for final weighing as magnesium pyrophosphate.[7] Methods that require a pure phosphomolybdate of ideal composition include such as involve the weighing of the dried[8] or ignited precipitate,[9] the reduction of the molybdenum and subsequent titration with standard permanganate,[10] and the titration of the precipitate with a standard solution of alkali.[11] All of these methods can give good results in experienced hands, but only the last is now in general use.[12]

If citric acid is added and a goodly excess of magnesia mixture is used, phosphorus can be precipitated directly as magnesium ammonium phosphate

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[6] F. Hundeshagen, *Z. anal. Chem.*, 28, 141–172 (1889).

[7] This method was originally proposed by F. L. Sonnenschein [*J. prakt. Chem.*, 53, 339 (1851)] and since modified by many others.

[8] C. Rammelsberg, *Ber.*, 10, 1776 (1877); R. Finkener, *ibid.*, 11, 1640 (1878); G. P. Baxter, *Am. Chem. J.*, 28, 298 (1902). According to the last, the best conditions are as follows: Prepare a solution containing about 0.1 g of P_2O_5 per 50 ml, and, if much HNO_3 is present, remove most of it by evaporation. Pour the solution, with vigorous stirring, into at least 50 ml more molybdate reagent than is theoretically required, both solutions being at room temperature. Let stand 16 hours, filter through a Gooch crucible, wash the precipitate with a 10 per cent solution of NH_4NO_3, heat at 300° C for at least 2 hours, and weigh as $(NH_4)_3PO_4 \cdot 12MoO_3$. The precipitate always contains a little more MoO_3 than is indicated in the formula.

[9] C. Meineke, *Chem. Ztg.*, 20, 108 (1896); R. Woy, *ibid.*, 21, 441 (1897). This ignition is made at 300 to 400° C and yields the compound $P_2O_5 \cdot 24MoO_3$.

[10] F. A. Emmerton, *Trans. AIME*, 15, 93 (1887); A. A. Blair, *The Chemical Analysis of Iron*, 8th ed., p. 87, J. B. Lippincott Co. (1918).

[11] H. Pemberton, *Chem. News*, 46, 4 (1882); *J. Am. Chem. Soc.*, 16, 278 (1894); *ASTM Methods of Chemical Analysis of Metals*, p. 88 (1950).

[12] Routine determinations of phosphorus can also be made by noting the volume occupied by the precipitate after it has settled or has been centrifuged in a graduated tube [V. Eggertz, *J. prakt. Chem.*, [1] 79, 496 (1860); G. W. Goetz and H. Wedding, *Stahl u. Eisen*, 7, 118 (1887); W. E. Baulieu, *Ind. Eng. Chem.*, 17, 908 (1925)].

in the presence of elements such as calcium, iron, aluminum, titanium, zirconium, vanadium, and tin.[13]

A. PRECIPITATION OF PHOSPHORUS AS AMMONIUM PHOSPHOMOLYBDATE AND TREATMENT OF THE PRECIPITATE

a. *Precipitation as Ammonium Phosphomolybdate.* For the precipitation of ammonium phosphomolybdate, an excess of molybdate reagent is required. In the usual case 1.3 g of MoO_3 per 100 ml of solution should be present in excess of that required by the phosphorus (56 mg MoO_3 per 1 mg P). A larger excess does no harm, excepting that the precipitate may be slightly richer in MoO_3. Under some conditions, twice the above concentration may be required to effect complete precipitation, as, for example, if much titanium, zirconium, chloride, or sulfate is present. From 5 to 10 per cent of ammonium nitrate is needed for rapid and complete precipitation. The amount of nitric acid can be varied between 5 and 10 per cent (by volume). Higher concentrations lead to incomplete precipitation unless the concentration of ammonium nitrate and molybdate reagent is also increased. Moderate concentrations of perchloric acid (1 + 20) or ammonium perchlorate (10%) are without harmful effect.

Precipitation takes place more rapidly if the solution is warm (40 to 50° C) and vigorously shaken. Precipitates formed at temperatures above 50° C contain excessive amounts of MoO_3 and suffer greater contamination by substances such as arsenates, vanadates, and silica. In pure solutions precipitation may be complete in 10 minutes. More time must be allowed if precipitations are made in cool solution or if retarding substances such as quadrivalent vanadium are present. In analyses of the highest accuracy, it is well to let the solution stand for 12 hours. No significant change in the composition of the precipitate takes place during the longer period.

Among the substances that may retard precipitation or contaminate the precipitate should be mentioned sulfuric, hydrochloric, or hydrofluoric acid, the ammonium salts of these acids, arsenic, vanadium, selenium, tellurium, tungsten, silicon, titanium, zirconium, and some organic compounds. In analyses of the highest accuracy, the three mineral acids should be avoided. Moderate concentrations of hydrochloric acid (1 + 9) or sulfuric acid (1 + 20) are not objectionable in routine analyses if more ammonium nitrate and molybdate reagent are added and a longer precipitation period is allowed. The same is true of hydrofluoric acid (1 + 20) if it is converted to fluoboric acid, HBF_4, by the addition of boric acid in excess. If time allows, it is desirable first to drive out most of the hydrofluoric acid by evaporating once or twice with nitric acid.

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[13] G. E. F. Lundell and J. I. Hoffman, *Ind. Eng. Chem.*, 15, 44, 171 (1923); J. I. Hoffman and G. E. F. Lundell, *J. Research NBS*, 20, 607 (1938).

Arsenic is undesirable because it not only retards the precipitation of ammonium phosphomolybdate but it also reacts with molybdate reagent to form an insoluble arsenomolybdate. Precipitation may be complete at 75 to 100° C; very little is precipitated at 20 to 25° C. If much arsenic is present, it had better be removed at the start by reducing it and distilling with hydrochloric acid (p. 260), or by precipitating with hydrogen sulfide (p. 262). If small amounts of arsenic are present and precipitation is made at room temperature, the contamination can be ignored in any but the most accurate work. If phosphorus is to be reprecipitated as magnesium ammonium phosphate, any arsenic in the phosphomolybdate will be precipitated as magnesium ammonium arsenate. In such case, it is customary to dissolve the precipitate in hydrochloric acid and to reprecipitate with magnesia mixture after removing the arsenic by treating with hydrogen sulfide or, less certainly with large amounts, by reducing with sulfurous or hydrobromic acid and boiling with dilute hydrochloric acid (1 + 1).

Vanadium in the quinquevalent state also retards precipitation and contaminates the precipitate. Its precipitation may be complete if phosphorus is in considerable excess. Quadrivalent vanadium retards precipitation somewhat, but is not carried down by ammonium phosphomolybdate if precipitation is made at 10 to 20° C.[14]

Both quadrivalent and sexivalent selenium or tellurium compounds interfere seriously in precipitations of phosphorus by molybdate reagent, for they retard precipitation of the phosphorus and contaminate the precipitate that is formed. For complete precipitation, the solution should be allowed to stand at least 4 hours, and the determination must be completed by precipitating as magnesium ammonium phosphate in the presence of citrate.

Tungsten is carried down by ammonium phosphomolybdate and must be removed before precipitation is attempted, except possibly in case the amount of tungsten is small and the molybdate-magnesia method is to follow. The removal of tungsten is accomplished by digesting with nitric and hydrochloric acid and filtering. The filtrate must then be evaporated with nitric acid to expel most of the hydrochloric acid, and the tungstic acid must be examined for its phosphorus content, preferably by dissolving it in ammonium hydroxide containing ammonium citrate and precipitating with magnesia mixture in ice-cold solution as described on page 706.

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[14] J. R. Cain and F. H. Tucker, *J. Ind. Eng. Chem.*, **5**, 647 (1913). If the amount of phosphorus equals or exceeds that of vanadium^{V} and is large, all of the phosphorus is precipitated in 2 hours. If the amount is small, more time must be allowed. If the amount of vanadium^{V} exceeds that of phosphorus, precipitation is seriously retarded, never complete in 2 hours, and with little phosphorus not in 24 hours, if at all. In all cases, the retarding effect of vanadium^{V} can be overcome to some extent by using more molybdate.

Silicon is apt to retard precipitation and to be carried down by the precipitate as ammonium silicomolybdate. If much is present, it may clog the filter. It is therefore preferably removed by dehydration, or by evaporation with hydrofluoric and nitric acids before precipitating the phosphorus.

Titanium and zirconium usually cause trouble before the precipitation with molybdate is reached because of the insolubility of their phosphates. If they are present in appreciable amount, much of the phosphorus may be precipitated and lost in the preliminary operations unless the insoluble residues are fused with sodium carbonate and the phosphorus is extracted with water. If zirconium or titanium is present when molybdate is added, more of the latter should be used, and more time should be allowed, at least 12 hours. The elements are then usually thrown down in part, and their presence is afterwards revealed if the phosphomolybdate precipitate is dissolved in ammonium hydroxide. If their amount is not too large, the condition can be remedied by using a little citrate with the ammonium hydroxide. If a residue still remains, it must be ignited, fused with sodium carbonate, the melt leached with water, and the water extract added to the ammoniacal solution. In the presence of moderate amounts of titanium (0.025 g), more complete precipitation of phosphomolybdate is obtained in dilute nitric acid solution (2 + 1) to which one half of its volume of molybdate solution is added.

Organic matter is usually destroyed, as a matter of precaution by boiling with a slight excess of potassium permanganate and then reducing the excess before the molybdate reagent is added.

α. In the absence of vanadium. Prepare 100 to 200 ml of solution containing 5 to 10 per cent by volume of nitric acid, 5 to 15 per cent of ammonium nitrate, and not much over 0.05 g of phosphorus entirely present as the ortho compound. Heat in an Erlenmeyer flask to 40 to 50° C, add a 15- to 25-fold excess of molybdate reagent (see under Reagents, p. 41), stopper, and shake vigorously for 5 to 10 minutes. If the amount of phosphorus is small, or substances that retard the precipitation are present, use a larger excess of the reagent, which will do no harm in any case.

In accurate analyses in which precipitation as magnesium ammonium phosphate is to follow, allow the solution to stand overnight. In routine analyses, let the precipitate settle for 10 to 30 minutes. Filter through a paper of close texture. If the alkalimetric method is to follow, filtration through asbestos or paper pulp can be substituted and suction applied to promote more rapid filtration and more efficient washing. The choice of a washing medium will necessarily vary according to the further treatment of the phosphomolybdate. If precipitation as magnesium ammonium phosphate is to follow, wash the precipitate moderately with a 5 per cent solution of ammonium nitrate. If the alkalimetric method is to be used, wash with a 1 per cent solution of potassium nitrate until free acid is removed. The precipitate is slightly soluble in the latter solution but not sufficiently so as to seriously disturb the results if a fixed procedure is used.

β. In the presence of vanadium. Prepare the solution as in α, cool to 10 to 20° C, and add sufficient ferrous sulfate to reduce the vanadium and then a few drops of sulfurous acid. If the solution does not contain iron, it is well to add at this point about 1 g of iron as ferric nitrate that is free from phosphorus, in order to prevent subsequent reduction of the molybdenum. Add a 20- to 30-fold excess of cool molybdate reagent, and shake the solution for 5 minutes. Allow the solution to stand overnight or, if the alkalimetric method is to follow, for at least 30 minutes. Proceed with filtration as in α.

b. *Treatment of the Ammonium Phosphomolybdate Precipitate.* Of the various procedures for the further treatment of the phosphomolybdate precipitate, the two that are in most common use are those in which (1) the phosphorus is reprecipitated as magnesium ammonium phosphate after solution of the ammonium phosphomolybdate in ammonium hydroxide, and (2) the so-called alkalimetric method in which the phosphomolybdate is dissolved in an excess of a standard solution of sodium hydroxide which is then determined by titration with standard acid in the presence of phenolphthalein.[15]

α. Gravimetrically by precipitation as magnesium ammonium phosphate and ignition to the pyrophosphate. The number of compounds that interfere in the precipitation of phosphorus as magnesium ammonium phosphate is so large that the precipitation must usually follow its preliminary separation as the phosphomolybdate. There is no difficulty in obtaining the ideal composition, $MgNH_4PO_4 \cdot 6H_2O$, and this method is recommended for all accurate analyses, particularly when the amount of phosphorus is large. In the rare cases where direct precipitation can be made, the procedure is the same as that used after the solution of the phosphomolybdate. It is practically impossible to obtain accurate results by a single precipitation of magnesium ammonium phosphate in either hot or cold solution containing alkali phosphate alone and in approximately known amount. When the approximate amount is unknown or foreign substances are present, a single precipitation can only give correct results through compensating errors. Double precipitations should therefore be the rule.[16] The first precipitation is preferably carried out by adding magnesia mixture to an acid solution of the phosphate and then slowly adding ammonium hydroxide until the solution is alkaline. The addition of magnesia mixture to an ammoniacal solution of the phosphate is not so desirable. The second precipitation *must* be made by the slow addition of ammonium hydroxide to the acid solution of the first precipitate to which a very little magnesia mixture has been added.

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[15] The results that can be expected in determinations of phosphorus by the alkalimetric (A), molybdate-single precipitation as magnesium ammonium phosphate (B), and molybdate-double precipitation as magnesium ammonium phosphate (C) methods, are illustrated by the following results obtained by representative analysts who cooperated in the analysis of a sample of phosphate rock containing 31.33 per cent of P_2O_5.

A % P_2O_5	B % P_2O_5	C % P_2O_5
31.76	31.41	31.29
30.68	31.44	31.30
31.42	31.56	31.35
31.75	31.51	31.34

For the first precipitation, a 3- to 4-hour precipitation period is sufficient for comparatively pure solutions containing appreciable concentrations of the orthophosphate. A 12-hour period is desirable in exact analysis and is necessary in cases where the concentration of phosphorus is very low or where the solution contains considerable amounts of dissolved salts. Special precipitation procedures, such as precipitation in boiling solution, have not been found necessary or even helpful by us. Contamination by elements such as tin, vanadium, iron, titanium, and zirconium can be entirely prevented if the precipitation is done in the presence of ammonium citrate as described on page 706.[17]

Selenic acid does not interfere in the determination of phosphorus by double precipitation as magnesium ammonium phosphate. Selenious acid interferes slightly, and tellurous and telluric acid interfere seriously. None of these interfere if 1 g of citric acid is added before the first precipitation of the phosphate. For example, in double precipitations of phosphorus equivalent to 0.2423 g of $Mg_2P_2O_7$, 0.2424 was obtained when 0.1 g of H_2SeO_4 was added, and 0.2436 when 0.1 g of H_2SeO_3 was added. Tellurites and tellurates give white precipitates with magnesia mixture. In double precipitations in which 1 g of citric acid was added before the first precipitation, results were 0.2420, 0.2424, 0.2424, and 0.2421 in determina-

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[16] The loss of phosphorus through repeated precipitation is negligible [G. E. F. Lundell and J. I. Hoffman, *J. AOAC*, 8, 188 (1924)]. In analyses of six aliquot portions of a standard solution of pure diammonium phosphate (without preliminary precipitation as the phosphomolybdate), 0.2367 and 0.2368 g of $Mg_2P_2O_7$ were obtained by single, 0.2370 and 0.2368 g by double, and 0.2366 and 0.2368 g by triple precipitations. An average of less than 0.03 mg of P_2O_5 was lost in each precipitation as shown by careful recovery of the phosphorus in the combined filtrates and washings from 10 of the 12 precipitations. The agreement between the results obtained in single and double precipitations is exceptional and was due to the fact that the latter were carried through first, the amount of magnesia mixture needed to give a 2-ml excess calculated, and the single precipitations then made in a solution containing this excess as well as the amount of hydrochloric acid used to dissolve the first precipitate in the other determinations.

[17] G. E. F. Lundell and J. I. Hoffman, *Ind. Eng. Chem.*, 15, 44, 171 (1923).

tions involving 0.1-g portions of H_2SeO_3, H_2SeO_4, H_2TeO_3, and H_2TeO_4, respectively.

PROCEDURE. 1. *In the absence of arsenic and appreciable amounts of elements such as tin or iron.* Dissolve the phosphomolybdate precipitate obtained as in IV, A, in dilute ammonium hydroxide (1 + 2), and then wash the filter successively with hot water, dilute hydrochloric acid, and finally again with ammonium hydroxide. Treat the ammoniacal solution with 0.5 g of citric acid, and filter if the solution is not clear. If the filtrate remains cloudy, add a little macerated paper, boil, and refilter. When turbid solutions are encountered, and, even in their absence in exact analyses, ignite the well-washed paper, fuse the small ash with a pinch of sodium carbonate, extract the melt with water, filter, and add the acidified extract to the main solution.

Render the solution, preferably of a volume not to exceed 100 ml, slightly acid, cool, add 10 ml of magnesia mixture (see Reagents, p. 42), and then 0.1 ml more for every mg of P_2O_5 that is expected. A greater excess will do no harm. Next add dilute ammonium hydroxide (1 + 1), slowly and with constant stirring. When the white crystalline phosphate begins to appear, stop the addition, stir until no further precipitation ensues, add a few drops of ammonium hydroxide, stir, and so continue. When the solution is alkaline, add 10 ml of the dilute ammonium hydroxide per 100 ml of solution, and set the solution aside for 4 hours or preferably overnight.

If only a single precipitation is contemplated, filter, transfer the precipitate to the paper, wash with dilute ammonium hydroxide (1 + 20) until free from chloride, and ignite as to be described. If a second precipitation is to be made, filter without attempting to transfer the precipitate, and wash the vessel, residue, and paper a few times with the dilute ammonium hydroxide. Dissolve the precipitate in 25 ml of dilute hydrochloric acid (1 + 1), catching the solution in the original beaker containing the bulk of the precipitate. Wash the filter thoroughly with dilute hydrochloric acid (1 + 20),[18] dilute the solution to 50 to 100 ml, and add 1 to 2 ml of magnesia mixture. Add dilute ammonium hydroxide slowly and with constant stirring as before and finally in 10 ml excess. Allow the solution to stand for at least 2 hours or preferably overnight.

Filter, transfer the precipitate to the filter, and wash with dilute ammonium hydroxide (1 + 20) until free from chlorides. Transfer the paper and precipitate to a weighed platinum crucible, dry, and heat carefully, preferably in a muffle, until the paper chars without inflaming. Burn the carbon at the lowest possible temperature. All of the carbon must be burned out before the precipitate is heated to 900° C, for otherwise the pyrophosphate is slowly reduced and phosphorus volatilized.[19] Finally ignite at 1050 to 1100° C to constant weight. Weigh as $Mg_2P_2O_7$.

If the precipitate is of proper composition, ignition at 1000° C until constant weight is obtained is sufficient. At temperatures above 1100° C, the precipitate gradually loses weight, probably through a slow dissociation of the $Mg_2P_2O_7$ into $Mg_3(PO_4)_2$ and P_2O_5.[20]

Treatment of the pyrophosphate precipitate with a drop or two of nitric acid and reignition do no harm and rarely any good. Solution of the pyrophosphate in nitric acid, followed by evaporation and ignition, leads to low results, for it is impossible to prevent volatilization and even popping of the residue. According to W. M. McNabb,[21] the operation succeeds, however, if the nitric acid solution is neutralized with ammonium hydroxide before evaporating and igniting. The same is true if the acid solution of the pyrophosphate is treated with 2 to 3 ml of magnesia mixture and then with ammonium hydroxide and finally filtered and washed as usual. It is also permissible to dissolve the magnesium ammonium phosphate in nitric acid and then to evaporate and ignite.

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[18] Ordinarily there is no need for saving this paper. As a matter of precaution, however, in very accurate analyses, and always, if the original material contained appreciable amounts of elements such as zirconium or titanium, burn the paper in platinum, fuse the ash with 0.2 g or less of sodium carbonate, extract the melt with water, filter the solution, and add the acidified filtrate to the main filtrate.

[19] K. D. Jacob and D. S. Reynolds, *J. Assoc. Offic. Agr. Chemists*, 11, 128 (1928).

[20] This is illustrated by the following data obtained by heating approximately 0.25 g of $Mg_2P_2O_7$ (obtained by double precipitation of pure $(NH_4)_2HPO_4$ as described) in a platinum crucible that showed no loss in weight when heated over a blast lamp for 1 hour. After the usual ignition at 1000° C, the weight was 27.3394. Further heating changed the weight as follows: one-half hour at 1000° C, 27.3392; another half hour, 27.3391; another half hour, 27.3392; one hour at 1100° C, 27.3392; one-half hour over a strong blast, 27.3386; another hour, 27.3382; and half an hour longer, 27.3380. In other tests, a similar precipitate when finally heated over the blast lamp for four one-half-hour and three one-hour periods showed an average loss of approximately 0.4 mg per hour and lost as much in the fifth hour as it did in the fourth. The slightly greater rate of loss obtained when the precipitate was first heated over the blast might well have been caused by the presence of a small amount of $Mg(PO_3)_2$ that had been formed from a corresponding amount of $Mg(NH_4)_4(PO_4)_2$ in the original precipitate. The conversion of the metaphosphate to the pyrophosphate, which is desirable in the determination of magnesia (p. 638), of course increases the error when phosphorus is in question. In experiments in which the $Mg_2P_2O_7$ was obtained by preliminary precipitation as the phosphomolybdate, followed by double precipitation as $MgNH_4PO_4 \cdot 6H_2O$, precipitates weighing 0.2835, 0.2824, and 0.2826, after ignition to constant weight at 1000° C, lost 0.4, 0.3, and 0.1 mg, respectively, when heated for one hour at 1100° C. It is not at all unlikely that these losses represented in large part molybdenum still held by the phosphates in spite of the double precipitations. This is also indicated by the fact that the average loss in weight of these precipitates over the blast lamp was 0.7 mg per hour during the second and third hours. For a study of the precipitation and ignition of magnesium ammonium phosphate, see J. I. Hoffman and G. E. F. Lundell, *J. Research NBS*, 5, 279 (1930).

[21] *J. Am. Chem. Soc.*, 49, 893 (1927).

2. *In the presence of arsenic.* Proceed as in 1 until the first precipitate of magnesium ammonium phosphate has been dissolved in dilute hydrochloric acid. If the amount of arsenic is known to be small, add 0.5 to 1 g of ammonium bromide, carefully boil the solution to near dryness, and take up the residue in 25 ml of dilute hydrochloric acid (1 + 1). If much arsenic is present, the treatment of the hydrochloric acid solution with bromide and boiling must be repeated two or three times or, better, the arsenic removed by treating the acid solution with hydrogen sulfide and filtering. In the latter case, the filtrate should be boiled to expel hydrogen sulfide and to reduce the volume to 50 to 100 ml. After either of these separations proceed as in 1.

3. *In the presence of moderate amounts of iron, aluminum, vanadium, zinc, tin, selenium, tellurium, titanium, or zirconium.* To 100 ml of the acid solution containing the orthophosphoric acid, add 3 to 5 g of citric acid and a 25- to 50-fold[22] excess of magnesia mixture. Precipitate as in 1, and let the solution stand at room temperature for 12 to 24 hours. Filter, wash, dissolve the precipitate as in 1, and recover any phosphate left on the paper. Add 0.2 to 0.5 g of citric acid and 3 to 4 ml of magnesia mixture, and continue as in 1 except that the solution should be left for at least 6 hours before filtration.[23]

β. Volumetrically by dissolving the ammonium phosphomolybdate precipitate in a standard solution of alkali. The alkalimetric method is by far the most important and widely used method for the rapid, routine determination of phosphorus. It is based on the assumption that the washed phosphomolybdate precipitate has the composition $(NH_4)_3PO_4 \cdot 12MoO_3$, and that this compound yields normal salts of molybdic acid R_2MoO_4 and secondary salts of phosphoric acid, R_2HPO_4, upon titration with sodium hydroxide in the presence of phenolphthalein as indicator. The reaction

can be expressed by an equation such as the following: $(NH_4)_3PO_4 \cdot 12MoO_3 + 23NaOH = 11Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + 11H_2O$.

The equation holds quite well for phosphomolybdate that is precipitated at 20 to 45° C, no matter whether the solution is filtered after 15 minutes or after 15 hours. The advantage in starting at approximately 40° C lies in more rapid precipitation. Under no circumstances should the solution be heated *after* the molybdate reagent has been added.

If conditions have not been carefully governed, the ratio of sodium hydroxide to phosphorus is usually higher than 23 to 1. Causes of higher ratios are: (1) precipitation at temperatures above 45° C, which gives a precipitate higher in molybdic acid; (2) incomplete washing of the precipitate, which leaves free acid; (3) boiling of the phosphomolybdate with an excess of sodium hydroxide, which drives out ammonia and leads to the ratio 26 to 1; (4) undue exposure or agitation of the alkaline solution of the phosphomolybdate (particularly when the precipitate is large), which causes slow volatilization of ammonia; and (5) presence of carbon dioxide, which causes consumption of sodium hydroxide.

The foregoing concerns conditions that obtain in pure solutions. Other difficulties are introduced by substances that retard the precipitation of ammonium phosphomolybdate in the short period that is commonly used in the alkalimetric method or, like arsenic, selenium, or tellurium, contaminate the precipitate and afterwards consume alkali.[24]

Phenolphthalein is not an ideal indicator for the titration because of its sensitiveness to carbonic acid and its lack of sensitiveness to ammonium hydroxide. No other indicator has, however, proved so satisfactory. Carbonic acid can be avoided by proper preparation of the alkali solution. The liberation of some ammonia is unavoidable and would be expected to cause high results for phosphorus. Its effect, however, is to compensate for normal minus errors when results are calculated on the 23 to 1 basis.

As regards the proper method of obtaining the phosphorus titer of the sodium hydroxide solution, the authors prefer to standardize the solution (free from carbonate) against benzoic acid or acid potassium phthalate (p. 178), and to calculate its phosphorus titer on the basis of the 23 to 1 ratio. This procedure involves reasonable adherence to the directions to be described. If these are not to be followed, the safest plan is to adopt some other definite procedure and then to standardize the sodium hydroxide

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[22] If larger amounts of citric acid are used, more magnesia mixture must be added, particularly if vanadium is present.

[23] The efficacy of the treatment is shown by the following data (G. E. F. Lundell and J. I. Hoffman, *loc cit.*).

$Mg_2P_2O_7$, g Expected	$Mg_2P_2O_7$, g Found	Contaminant, g
0.1048	0.1048	None
	0.1048	None
	0.1044	0.005 Fe
	0.1049	0.005 Al
	0.1044	0.005 Ti
	0.1048	0.005 Ti
	0.1043	0.005 Zr
0.0105	0.0107	0.005 V
	0.0104	0.020 Sn
	0.0107	0.250 Zn

[24] For example, alkalimetric determinations of phosphorus in a steel containing 0.096 per cent of phosphorus showed 0.167 when 0.1 g of H_2SeO_4 was added, 0.109 when 0.1 g of H_2TeO_3 was added, and 0.116 when 0.1 g of H_2TeO_4 was added. H_2SeO_3 gave a copious precipitate with molybdate alone. In the four cases cited, 0.0973, 0.0971, 0.0971, and 0.0970 were obtained by allowing 4 hours for the precipitation of the molybdate and then precipitating twice as magnesium ammonium phosphate as described.

solution by applying the procedure to material which is similar to that under test and of known phosphorus content.

PROCEDURE. 1. *Absence of vanadium.* Precipitate the phosphomolybdate as in IV, a, α (p. 701) but at a temperature of 30 to 45° C. The solution may be heated directly *before* the addition of molybdate reagent or, more simply, by the addition of a definite amount of ammonium hydroxide to a definite excess of nitric acid. After the solution has been shaken for 5 to 15 minutes and allowed to settle for 10 to 15 minutes, filter upon an 11-cm paper of close texture, leaving as much of the precipitate in the flask as possible. Asbestos or paper pulp and suction can be substituted if desired. Wash the flask and precipitate five times with 15-ml portions of a 1 per cent solution of potassium nitrate,[25] and then wash the paper five times with like portions of the same solution. The paper should be carefully washed each time from the rim downward and then allowed to drain completely before washing with the next portion of solution. The wash solution and all others subsequently used must be free from carbon dioxide. Return the paper and precipitate to the flask, and add enough 0.1 *N* sodium hydroxide to decompose the precipitate and to leave approximately 2 ml in excess. Dilute with 25 ml of water, stopper, and shake until the precipitate has dissolved. Dilute to approximately 150 ml with water, add 6 drops of a 1 per cent solution of phenolphthalein, and discharge the pink color with standard acid which is exactly equivalent to the alkali solution. Finish the titration by adding standard alkali until the reappearance of the pink color. Subtract the volume of acid used from the total volume of alkali used, and multiply the remainder by the phosphorus titer of the alkali solution.

2. *Presence of vanadium.* If vanadium is present, precipitate as in IV, a, β (p. 702). Let the solution stand for at least 30 minutes, and then proceed with filtration, etc., as above.

B. DIRECT PRECIPITATION OF PHOSPHORUS AS MAGNESIUM AMMONIUM PHOSPHATE

The conditions that govern the direct precipitation of phosphorus as magnesium ammonium phosphate are illustrated in the following procedure for the determination of phosphorus in a phosphate rock containing no appreciable amounts of compounds of phosphorus that are insoluble in the acid attack.[26]

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[25] If there is danger of hydrolysis, as with tin in phosphor bronze, wash the precipitate at first with small portions, not over 50 ml in all, of dilute nitric acid (1 + 49).

[26] J. I. Hoffman and G. E. F. Lundell, *J. Research NBS*, 19, 59 (1937). Moderate amounts of calcium do not interfere in the precipitation of phosphate ion by magnesia mixture. For example, 0.01 g of CaO added to either the solution or the magnesia mixture causes no contamination of the precipitate in single precipitations, and 0.1 g of CaO added to the original solution causes no difficulty in double precipitations [G. E. F. Lundell and J. I. Hoffman, *J. Assoc. Offic. Agr. Chem.*, 8, 188 (1924)].

PROCEDURE. Transfer 0.5 g of a sample that has been dried at 105° C to a 300-ml Erlenmeyer flask, and add 15 ml of hydrochloric acid and 3 ml of nitric acid. Place a small cover glass over the mouth of the flask, and boil gently for 30 minutes. Rinse and remove the cover glass, and, without filtering, add 30 g of ammonium citrate, 10 ml of hydrochloric acid, and 100 ml of *strong* magnesia mixture.[27] Neutralize the solution with ammonium hydroxide, using litmus paper as indicator, and add 3 ml of ammonium hydroxide in excess. Dilute the solution to 225 to 250 ml with water, add a few glass beads, stopper the flask tightly, shake on a shaking machine for about one-half hour, and allow to stand overnight. Filter through a paper of close texture, and wash the flask and paper once with a small quantity of dilute ammonium hydroxide (1 + 19). Discard the filtrate.

Dissolve any magnesium ammonium phosphate remaining in the flask in about 50 ml of warm dilute hydrochloric acid (1 + 4), and pour the solution through the paper to dissolve the phosphate that was transferred to the filter and to separate any insoluble residue that may have remained after the acid attack. Wash the paper and flask with more of the same acid, and add 0.3 g of citric acid and 1 ml of magnesia mixture to the solution, which should have a volume of about 100 ml. While stirring, slowly add ammonium hydroxide until the solution is alkaline to litmus, and then add 5 ml in excess. Stir occasionally during one-half hour, and allow to stand for 4 hours or overnight.

Collect the precipitate on a 9-cm paper of close texture, wash with cool dilute ammonium hydroxide (1 + 19), and transfer the paper and precipitate to a weighed platinum or porcelain crucible. Char the paper without flaming, burn off the carbon below 900° C, and finally ignite to constant weight, preferably in a muffle, at 1050 to 1100° C.

The time of standing in the first precipitation can be reduced to 3 hours and in the second to 2 hours, if the solutions are chilled before shaking or stirring and then allowed to stand in ice water or in a refrigerator at 5 to 10° C. With small quantities (less than 10 mg of P_2O_5), the longer time of standing is essential, and even then it is best to chill and shake alternately two or three times.[28]

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[27] Prepare the *strong* magnesia mixture as follows: Dissolve 400 g of $MgCl_2 \cdot 6H_2O$ and 300 g of ammonium chloride in 1500 ml of warm water. When solution is complete, add ammonium hydroxide until the solution is alkaline to litmus. Allow to stand for about 1 hour, filter, and add hydrochloric acid to the filtrate until the solution is acid to litmus. If properly prepared, the volume of the solution is almost exactly 2 liters.

[28] For the analysis of mixtures of ortho-, pyro-, meta-, and polyphosphates consult L. F. Audrieth and R. N. Bell, *Inorganic Syntheses*, Vol. III, p. 91, McGraw-Hill Book Co. (1950); R. N. Bell, *Anal. Chem.*, 19, 97 (1947); and L. T. Jones, *ibid.*, 14, 536 (1942).

C. COLORIMETRIC METHODS

Small amounts of phosphorus can be determined colorimetrically by (1) converting to the blue complex that phosphorus forms with molybdenum that has been reduced by stannous chloride and then comparing with standards in an ordinary or in a photoelectric colorimeter,[29] or (2) converting to the yellow complex that phosphorus forms with quinquevalent vanadium and sexivalent molybdenum and then measuring the transmittance at 450 mμ in a spectrophotometer.[30] The latter method is also being applied to materials containing considerable amounts of phosphorus, for example, phosphate rock and basic calcium phosphate.[31]

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[29] For a spectrophotometric study of the molybdenum blue reaction, consult J. T. Woods and M. G. Mellon, *Ind. Eng. Chem. Anal. Ed.*, 13, 760 (1941), and R. E. Kitson and M. G. Mellon, *ibid.*, 16, 466 (1944). See also C. W. Eddy and F. Deeds [*ibid.*, 9, 12 (1937)], who apply the method in determinations of as little as 0.001 mg of phosphorus; S. R. Dickman and R. H. Bray [*ibid.*, 12, 665 (1940)], who apply the method in hydrochloric acid solutions of soils, waters, and plants; and J. L. Hague and H. A. Bright [*J. Research NBS*, 26, 405 (1941)], who measure the transmittancy of the colored solution with a photoelectric colorimeter and a Corning Lantern Shade yellow filter no. 349 in determinations of phosphorus in cast irons or steels. Interference by the fluoride ion in the formation of the blue complex can be avoided by adding boric acid [L. T. Kurtz, *Ind. Eng. Chem. Anal. Ed.*, 14, 855 (1942)].

[30] For a method in which iron is decolorized and silica is removed by treatment with perchloric acid before the phosphovanadomolybdate color is developed in analyses of iron ores, consult H. H. Willard and E. J. Center, *Ind. Eng. Chem. Anal. Ed.*, 13, 81 (1941). For a spectrophotometric study of the method, especially as applied to steels, consult R. E. Kitson and M. G. Mellon, *ibid.*, 16, 379 (1944).

[31] Allen Gee and V. R. Deitz, *Anal. Chem.* (1953).

Chapter 46

SULFUR

Sulfur is found native and in many sulfides and sulfates. Essential rock-forming minerals containing sulfur in the oxidized condition are limited to haüynite and noselite, minerals that are found chiefly in the more basic rocks, and especially those high in soda. In the sulfide condition, the element is of very wide distribution, both as pyrite and pyrrhotite, less often as chalcopyrite and possibly other sulfides, also in the mineral lazurite, and here too in greater abundance in the basic rocks. It is a very common error of most chemists to report the sulfur in silicate and carbonate rocks, clays, etc., as SO_3 instead of S. Now and then it may occur in both states, but much more often only in the sulfide condition.

I. GENERAL CONSIDERATIONS

In ordinary analyses sulfur causes no difficulties unless it is associated with elements such as barium, lead or strontium that form insoluble sulfates, or is present in large amount together with calcium. In the former case, particularly with barium, an insoluble sulfate is precipitated and caught with the silica. Its presence is then revealed by the character of the precipitate and by the size and appearance of the nonvolatile residue that is left after the treatment of the impure silica with sulfuric and hydrofluoric acids. If the latter treatment is omitted, the results for silica will of course be high; if it is carried out, the results will be low, for some of the barium sulfate reacts with silica to form barium silicate during the intense ignition that is necessary to dehydrate the silica before the first weighing, and the barium silicate so formed is reconverted to the sulfate by the hydrofluoric-sulfuric acid treatment prior to the second weighing.

The amount of sulfate that comes down with the silica depends on the solubility of the sulfate. Precipitation is never complete, and further precipitation of the sulfate usually occurs, especially with calcium, when the solution is made alkaline with ammonium hydroxide, because of its reduced solubility in alkaline solution. In such case, the result for aluminum, if calculated by difference, will be high in proportion to the amount of sulfate that is precipitated, whereas the result for the alkaline earths will be correspondingly low. If the nonvolatile residue left from the silica is weighed with the ammonia precipitate, the case is still worse.

II. DECOMPOSITION OF MINERALS

Especial care must be taken to avoid oxidation of sulfide minerals during the preparation of the sample. Fine grinding of material such as pyrite causes slight losses of sulfur as the dioxide and appreciable formation of sulfate.[1] Both lead to a low result for total sulfur; the latter leads to false conclusions as to its condition as well. For most purposes it is sufficient to crush the sulfide to 60 to 80 mesh, and the crushing should be by concussion rather than by grinding (p. 809).

Care must also be taken during the decomposition of sulfur minerals to avoid contamination by sulfur compounds in the atmosphere, and to use reagents that either are free from sulfur or contain so little that corrections can safely be made on the basis of blank determinations. Although contamination may be caused by the exposure of solutions to an atmosphere containing such compounds as hydrogen sulfide or sulfur dioxide, it is more often the result of ignition or fusion over flames that are fed by gases containing sulfur. Such contamination can be avoided well enough for most purposes by protecting the work by means of an asbestos shield (p. 26) from direct contact with the products of combustion. In analyses of the highest accuracy, heating must be done electrically, as for example in a muffle furnace, or over an alcohol burner.

Certain sulfides can be completely oxidized by attack with fuming nitric acid at 125° C in a sealed tube.[2] According to Allen and Bishop,[1] the decomposition of pyrite and the preparation of the solution for analysis is best done as follows: Transfer 1.3736 g of pyrite, that has been ground to 80 mesh and dried at 100° C, to a dry 300-ml Jena beaker, add 10 ml of a mixture of two parts by volume of liquid bromine and three parts of carbon tetrachloride (both free from sulfur), and cover with a glass. Let stand 15 minutes at room temperature with occasional shaking, add 15 ml of nitric acid, and allow the mixture to stand 15 minutes longer at room temperature and with occasional shaking. Next place the beaker on an asbestos board on top of the steam bath, and let stand until all action ceases and most of the bromine is gone. Finally place directly over the bath, raise the glass cover on bent glass rods, and evaporate the solution to dryness. Add 10 ml of hydrochloric acid, mix thoroughly, and again evaporate to dryness under the raised glass. Dehydrate silica by heating in an air bath at 100° C, preferably overnight. Drench the dried mass with 4 ml of hydrochloric acid, after 5 minutes add 100 ml of hot water, and rinse the glass, supports, and inside of the beaker thoroughly with hot water. Replace the supports and cover, boil gently for 5 minutes, let cool somewhat for 5 minutes, add 0.2 to 0.3 g of powdered aluminum and gently shake until the solution becomes colorless. Cool, remove and rinse the cover and supports with cool water, and filter into a 2500-ml tall-form beaker. Wash the beaker, paper, and residue nine times with hot water. Add 6 ml of hydrochloric acid to the filtrate, and enough cool water to bring the volume to 1600 ml. Stir well and precipitate as in IV, C.[3]

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[1] E.T. Allen and J. Johnston, *Ind. Eng. Chem.*, 2, 196 (1910); W. S. Allen and H. B. Bishop, *8th Intern. Congr. Applied Chem.*, 1–2 [I–II], 48, 1912. The latter showed that no appreciable error is occasioned if pyrite is ground not finer than 100 mesh, and that a sample so ground suffers no oxidation at 100° C, even though heated at this temperature for 16 hours. The preliminary drying of wet samples should be carried out at 50 to 75° C.

[2] E. T. Allen and J. Johnston (*loc. cit.*) used 4 ml of fuming nitric acid for the oxidation of 0.5 g of pyrite. For the oxidation of sulfur compounds that give rise to stable sulfones, V. C. Rogers and G. Dougherty [*J. Am. Chem. Soc.*, 50, 1232 (1928)] recommended the use of a little NaCl or KCl with the fuming nitric acid. Most organic compounds containing sulfur can be broken up by means of the sodium peroxide-sugar explosion method (p. 839).

In the following procedure the pyrite is oxidized and iron completely removed without the use of nonvolatile reagents:[4] Transfer approximately 0.5 g of the sample, ground to pass 80 mesh to a 250-ml beaker, and treat with 12 ml of a mixture of three parts of nitric acid and one part of hydrochloric acid to which 4 or 5 drops of bromine have been added. Cover the beaker with a well-fitting watch glass, let the reaction proceed at room temperature for half an hour, and then transfer the beaker to a steam bath. Heat gently until all apparent action has subsided, raise the cover, and evaporate the liquid to dryness. Add 5 ml of hydrochloric acid, replace the cover, and heat until effervescence ceases. Raise the cover, wash it and the sides of the beaker with water, and again evaporate to dryness. Treat the residue with 25 ml of hot water, and stir until it is disintegrated. The insoluble residue will not contain sulfur unless barium or appreciable amounts of lead, calcium, or strontium are present and need not be filtered

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[3] The following modification of Allen and Bishop's method was used with success for the solution of stibnite by J. A. Scherrer of the Bureau of Standards: Transfer a factor weight of the sample to a casserole, cover with a glass, and add through the lip 10 ml of a 10 per cent solution of bromine in carbon tetrachloride. Next add 5 ml of bromine, slowly and with frequent shaking, and allow to stand with occasional shaking for 30 to 60 minutes. Partially immerse the casserole in a beaker of cold water, add 15 ml of strong nitric acid, and allow to stand for 15 to 30 minutes with occasional shaking. Add 15 ml of hydrochloric acid, let stand at room temperature for 15 to 30 minutes, warm slowly to drive off the carbon tetrachloride, and then evaporate to syrupy consistency (do not allow to dry). Add 10 ml more acid, evaporate to a syrup, and again add 20 ml of acid. Heat until all soluble matter is in solution, and transfer to a 500-ml Erlenmeyer flask. Keep the volume under 100 ml. Add 5 g of ingot iron drillings, let stand for 1 to 2 hours, filter, wash thoroughly, and proceed as in IV, C.

[4] A. M. Smoot, *Eng. Mining J.*, **94**, 412 (1912).

off. Transfer the solution to an electrolyzing cell and deposit iron in a mercury cathode as described in Section III.

For material containing but little sulfur, it is generally preferable to fuse with thoroughly mixed sodium carbonate and niter (12 + 1) in a platinum crucible set in an asbestos shield (p. 26). After thorough fusion, finally for a few moments over the blast, the melt is extracted with water containing a drop or two of alcohol to reduce manganates, the solution filtered and sulfur determined in the filtrate as in IV, B, after the addition of a slight excess of hydrochloric acid to the cool solution. Ordinarily there is no need to repeat the fusion and extraction or to separate silicon, though the latter can be done by evaporating the solution to dryness on the steam bath, drenching with a little hydrochloric acid, diluting with water, and filtering.

Evaporation of sulfates in perchloric acid solution can be carried to dryness without loss of sulfuric acid, provided the solution contains a relatively large excess of an element, such as calcium, which forms a difficultly soluble salt and the evaporation is made at as low a temperature as possible.[5]

An interesting method for the decomposition of sulfates as well as the liberation of sulfur in certain materials, particularly those containing tungsten or molybdenum, is that of C. M. Johnson,[6] in which the finely powdered compound is heated at approximately 1000° C in a tube through which hydrogen that has been bubbled through hydrochloric acid is passed. By this treatment, a sulfate such as barium sulfate can be entirely decomposed with the formation of barium chloride and the liberation of all of the sulfur as hydrogen sulfide.

III. METHODS OF SEPARATION

Iron, and other elements that are precipitable by ammonium hydroxide without formation of basic sulfates, can be separated from the sulfate ion by double precipitation, preferably in a hydrochloric acid solution, with an excess of ammonium hydroxide as described under Molybdenum (p. 305).[7] The ammonium chloride that is formed can be removed by acidifying the combined filtrates with hydrochloric acid, evaporating to small volume, digesting with nitric acid (p. 133), and finally evaporating with hydrochloric acid on the steam bath to remove the nitric acid. The decomposition of ammonium nitrate by repeated evaporation with hydrochloric acid (p. 134), or of ammonium sulfate by evaporation with aqua regia (p. 134), does not proceed so easily, but is satisfactory for the purpose here in question.

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[5] For example, H. B. Knowles found no loss when a soda-lime glass containing 0.41 per cent of SO_3 was so treated, whereas a solution of Na_2SO_4 corresponding to 0.1005 g of $BaSO_4$ gave but 0.0912 g of $BaSO_4$ after evaporation with 10 ml of 60 per cent $HClO_4$.

[6] C. M. Johnson, *Chemical Analysis of Special Steels*, 3d ed., p. 122, John Wiley and Sons (1920).

[7] For an example of such a separation, see E. Hintz and H. Weber, Z. *anal. Chem.*, 45, 31 (1916).

Electrolysis with a mercury cathode in dilute acid solution (p. 138) was recommended by A. M. Smoot[4] as a satisfactory procedure for the separation of bases such as iron, copper, chromium, molybdenum, and nickel, preliminary to the precipitation of barium sulfate. In the case of pyrite, an initial attack by reversed aqua regia and bromine, followed by evaporation on the steam bath as in Section II, leaves sufficient sulfuric acid. Hydrochloric or perchloric acid can be employed in small amount. Electrolysis is carried out at 0.8 to 1 ampere for 5 to 6 hours or with a weaker current overnight. After the separation is complete, wash down the sides of the cell, decant the electrolyte as closely as possible into a 300-ml beaker, wash the cell and mercury with small portions of water decanted into the main solution, and finally free this solution from suspended matter by filtering and washing.

If it is not feasible to remove iron, much better results will be obtained if it is reduced to the bivalent state before precipitation of barium sulfate is carried out. This can be done with aluminum as described in Section II, with zinc, or with pure iron. These also serve for the removal of certain reducible compounds, such as lead or antimony.

For the separation of sulfates from magnesium and the alkaline earths, the simplest procedure is in fusing with sodium carbonate, extracting the melt with water, filtering, and washing the residue with a hot 1 per cent solution of sodium carbonate. The operation must be repeated one or more times for complete recovery of the sulfate, and the filtrates and washings must be combined.

Members of the hydrogen sulfide group can be removed, or ferric chloride can be reduced, by treatment with hydrogen sulfide in dilute hydrochloric acid solution,[8] but this procedure would appear to be unreliable because of the possibility of oxidizing sulfide ions.

IV. METHODS OF DETERMINATION

The literature on the determination of sulfur as barium sulfate is very voluminous, and the difficulties attending an exact determination have become well recognized. Most of the researches have had to do with the determination of sulfur under conditions where the precipitate of barium sulfate

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[8] G. von Knorre, *Chem. Ind.*, 28, 9 (1905).

was large, as in the analysis of the commercially important mineral pyrite. In such cases it is only when the precipitation is made under well-defined conditions that the result is good, and then through compensation of considerable plus and minus errors.

A determination of the sulfate ion by precipitation with barium chloride in a solution containing only sulfuric acid is subject to a minus error caused by the solubility of the precipitated barium sulfate in the solution and in the wash water, and to a plus error caused by the coprecipitation of barium chloride. These errors may be of about equal magnitude (1 to 2 mg) when precipitation is made by the slow addition of a moderate excess of barium chloride to a hot dilute solution of the sulfuric acid which is then allowed to stand for several hours.[9] Corrections for both errors must be made in analyses of the highest accuracy. It is safer to make no corrections at all than to correct for solubility alone as is so often done.

When the sulfate ion is precipitated in a solution containing sulfates of the alkalies, two other sources of error, both minus, are introduced: one caused by the coprecipitation of alkali sulfate, the other by the coprecipitation of acid alkali sulfate. The former causes a low result through the substitution of a lighter element for barium in the weighed precipitate; the latter through the same cause and, in addition, through loss of sulfuric acid when the precipitate is ignited. When ammonium salts are present, these errors are greater, for both base and acid are volatilized. It is evident that the loss of sulfuric acid through volatilization will be counteracted by any barium chloride that is coprecipitated with the impure barium sulfate, and that the ignited precipitate may contain very little, if any, barium chloride if much acid sulfate or ammonium sulfate was carried down. In such case the solubility loss is not counteracted by the presence of barium chloride in the ignited precipitate, and so uncorrected determinations of the sulfate ion in solutions containing sulfates or chloride are usually low.[10]

The solubility of barium sulfate varies directly with the acidity of the solution and the amount of wash water that is used. It is increased very little by the presence of chlorides. The coprecipitation of barium chloride varies directly with the acidity of the solution, the concentration of the sulfate, and the rapidity of the precipitation; it is greater when the sulfate is poured into the chloride than when the chloride is poured into the sulfate. The coprecipitation of alkali or ammonium sulfates varies directly with the concentration of alkali chlorides and inversely with the speed of precipitation and time of digestion. The coprecipitation of acid sulfates varies directly with the acidity and with the concentration of alkali or ammonium chlorides, and inversely with the speed of precipitation and time of digestion. Greater contamination results with potassium than with sodium salts.

If the solution contains other substances than those that have been discussed, the case is worse. With some, as for example nitrates, marked occlusion occurs; with others, such as chromium sulfate,[11] complete precipitation is a matter of doubt; with others, such as ferric sulfate, coprecipitation results in subsequent loss of sulfuric acid and contamination by the base, whereas with others, such as zirconium sulfate, hydrolysis sets in if the acidity is kept at reasonable limits and causes serious coprecipitation of the base. The analyst must therefore endeavor to remove all heavy metals and prepare a solution containing either sulfuric acid alone or else

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[9] For example, T. W. Richards and H. G. Parker [*Proc. Am. Acad. Arts Sci.*, **31**, 67 (1895–96)], in precipitations of 10.2107- and 10.2189-g portions of a dilute solution of pure sulfuric acid, obtained 0.7804 and 0.7821 g of $BaSO_4$, 0.0011 and 0.0017 g of $BaSO_4$ as the correction for solubility, and 0.0005 and 0.0017 g as the correction for coprecipitated $BaCl_2$. The final corrected results therefore showed 3.213 and 3.215 per cent of H_2SO_4 in the solution. The average, 3.214, was exactly that found by careful alkalimetric determination.

[10] The extent of the errors caused by the solubility of barium sulfate and by the coprecipitation of sodium sulfate or acid sulfate was studied by E. T. Allen and J. Johnston [*J. Am. Chem. Soc.*, 32, 588 (1910)]. In every case enough of a solution of pure sodium sulfate to give approximately 2 g of $BaSO_4$ was weighed out, treated with the appropriate reagents, diluted to 350 ml, heated to boiling, and precipitated with a 1- to 1.5-ml excess of a 10 per cent solution of $BaCl_2$, slowly added in a very thin stream flowing down the side of the beaker. The solution was then allowed to stand for 18 hours and filtered through paper, and the precipitate washed with water till 25 ml of washings showed no more than 0.005 mg of chlorides, then dried in a platinum crucible, and very carefully ignited to constant weight. The losses due to the solubility of $BaSO_4$ in the filtrate and 350 ml of washings were found to be 0.9, 1.50, 3.3, 3.9, 12.0, and 36.0 mg of $BaSO_4$, respectively, after precipitations in solutions containing 0.2, 1, 5, 10, 20, and 100 ml of HCl in 350 ml. The average deficit in terms of mg of $BaSO_4$ caused by coprecipitation of the Na_2SO_4 was found to be 8.1 when the solution of sodium sulfate contained 0.2 ml of HCl, and 11.4 when the solution also contained 10 g of NaCl. The average deficit in terms of mg of $BaSO_4$ caused by volatilization of sulfuric acid from coprecipitated sodium acid sulfate was found to be 0.5 when the solution of sodium sulfate contained 0.2 ml of HCl and 8.8 when the solution contained 0.2 ml of HCl and 10 g of NaCl.

[11] Better precipitation in the presence of trivalent chromium results if the solution is allowed to stand for 12 hours or longer. For the determination of sulfates in the presence of chromates, obtain approximately 1 g of chromate in 100 ml of solution containing 2 ml of hydrochloric acid, add 20 ml of a 1 per cent solution of barium chloride, and allow to digest. Filter, wash the precipitate moderately, ignite, and fuse the residue with a little sodium carbonate. Extract the melt with water, filter, acidify the filtrate with hydrochloric acid, and reduce the chromate with alcohol. Adjust the acidity and precipitate with barium chloride as usual. Quicker, and quite satisfactory results can be obtained by reducing all of the chromate to the trivalent state, and precipitating with barium chloride in an acetic-hydrochloric acid solution [H. H. Willard and R. Schneidewind, *Trans. Am. Electrochem. Soc.*, **56**, 333 (1929)].

a solution containing sodium sulfate and no impurity other than sodium chloride.

Precipitates are usually caught in paper as a matter of convenience or of ease in examining the weighed residue. Gooch or Munroe crucibles can be used when subsequent operations permit.

The washing of a barium sulfate precipitate should not be unduly prolonged, for its solubility, 2.4 mg per liter at 20° C, is appreciable. In accurate analyses the washing should not be carried beyond the point at which 25 ml of washings give but a faint opalescence with silver nitrate.

Care must be taken during ignitions of barium sulfate in paper first to char the paper without inflaming, and then to burn off the carbon slowly and at a low temperature. Material will surely be carried out of the crucible if the ignition is hurried. The precipitate is not reduced when ignited in paper if an oxidizing atmosphere is maintained in the crucible and carbon is burned at temperatures below 600° C.[12] Final ignition of the precipitate should not be done at a temperature above 350° C if the precipitate has been obtained from pure sulfuric acid and correction for occluded barium chloride is to be made; at higher temperatures the barium chloride is broken down in part. If the precipitate has been obtained from a solution of sodium sulfate and corrections for free acid and occluded sodium sulfate are to be made, the preliminary heating must be done at approximately 105° C and the final heating at 1000° C (see footnote 15) to make sure that all of the occluded acid sulfate has been converted to the normal sulfate. If no corrections are contemplated, ignitions had better be made at approximately 900° C, although the precipitate suffers no appreciable dissociation at temperatures up to 1400° C if it is pure and is heated in pure dry air.[12] If impurities such as silica or iron oxide are present, decomposition sets in at about 1000° C with the liberation of sulfur trioxide. Treatment of the ignited residue with sulfuric acid is unnecessary and of course prevents subsequent correction for occluded barium chloride.

Three methods of analysis will be given. The first is intended for the determination of the sulfate ion in solutions containing only sulfuric acid, and for the accurate analysis of solutions containing no other substances than alkali sulfates or alkali sulfates and chlorides. Corrections must be made as specified in accurate analyses of sulfuric acid and in all analyses of solutions containing alkali salts. If no corrections are contemplated, analysis of solutions containing moderate amounts of the sulfate ion in the presence of alkali or ammonium salts had better be done by method B, in which the normal tendency toward low results is offset by greater occlusion of barium chloride. Method C is designed primarily for the determination of large amounts of the sulfate ion in solutions containing considerable iron, as with pyrite, and moderate amounts of other substances such as aluminum, zinc, or calcium.

A. FOR SOLUTIONS CONTAINING ONLY SULFURIC ACID

Prepare a solution that contains no more than 0.5 g of the acid, and dilute with water so that it contains approximately 0.002 g of sulfuric acid per ml. Heat to boiling, add a 1- to 2-ml excess of a 10 per cent solution of barium chloride, dropwise and with constant stirring, from a burette or precipitation bulb drawn out to a capillary tip, and let the solution stand for 18 hours before filtering.[13] Filter on paper, and wash with warm water until 25 ml of the washings show a barely perceptible opalescence with silver nitrate. Dry the wet paper and precipitate in a tared platinum crucible, char the paper without inflaming, and carefully burn the carbon in a good oxidizing atmosphere. Finally heat at approximately 375° C to constant weight.

As has already been stated, the result will be in error if the barium chloride that is carried down by the precipitate does not compensate for the loss of barium sulfate in the filtrate and washings. In accurate analyses the proper corrections for these two errors must be determined as described in footnote 15.

Solutions containing only alkali sulfate or alkali sulfates and chlorides can be treated in the same way after the addition of 0.05 ml of hydrochloric acid in excess per 100 ml of solution. As already noted, the results obtained with such solutions are usually low[14] and accurate analyses require that all four corrections cited in the succeeding footnote be made.[15]

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[12] W. Mostowitsch, *Metallurgie*, **6**, 450 (1909); *Chem. Zentr.*, 80, II, 1038 (1909); *C. A.*, **5**, 841 (1911).

[13] E. J. Bogan and H. V. Moyer [*Ind. Eng. Chem. Anal. Ed.*, 14, 849 (1942)] state that the precipitate can be flocculated and filtered within 30 minutes after precipitation, if 1 to 2 ml of a solution of agar-agar containing 1 mg per ml (prepared by suspending 0.5 g of USP agar-agar in 50 ml of cold water, adding this to 450 ml of near boiling water, and stirring constantly as the solution is heated to boiling) is added a drop at a time while the suspension is stirred rapidly for 10 seconds after each drop.

[14] This is illustrated by the following weights of $BaSO_4$ that were obtained by treating 100-ml portions of a standard sulfuric acid solution with 10 g of the specified salt; no addition 0.5992, NaCl 0.5883, $FeCl_3$ 0.5896, NH_4Cl 0.5849, and NH_4NO_3 0.6113. Somewhat better but still incorrect results are obtained by digesting the unignited $BaSO_4$ with HCl, diluting or neutralizing to the proper acidity, and adding a little more $BaCl_2$. Such treatment gave the following results: NaCl 0.5896, $FeCl_3$ 0.5950, NH_4Cl 0.5872 and NH_4NO_3 0.6014. The last is high because of the coprecipitation of barium nitrate.

[15] The correction for solubility can be made as follows: Evaporate the filtrate and washings to dryness in a platinum basin, take up the residue in a little water or, if necessary, in very dilute hydrochloric acid, filter on a small paper, wash to remove chlorides, and combine the recovery with the main precipitate. The correction for

B. FOR SOLUTIONS CONTAINING MODERATE AMOUNTS OF SULFATES IN THE PRESENCE OF ALKALI OR AMMONIUM SALTS[16]

PROCEDURE. Prepare a water or hydrochloric acid solution containing not more than 0.025 g of sulfur as sulfate per 100 ml and preferably no other salts than those of sodium, potassium, or ammonium. Add methyl orange, neutralize, and then add 1 ml of hydrochloric acid for each 100 ml of solution. Heat to incipient boiling. Take enough of a 10 per cent solution of barium chloride to provide an excess of 7 to 8 ml over what is required to precipitate the sulfate, dilute to 100 ml, heat to boiling, and quickly pour into the hot sulfate solution as it is vigorously stirred. Let stand at the side of the steam bath for 30 minutes, and decant the clear solution through a filter. Wash the precipitate three times by decantation with hot water, transfer to the paper, and continue the washing until a test for chloride gives no more than a faint opalescence. Place the wet paper in a weighed crucible, heat carefully until dry, char the paper without inflaming, carefully burn the carbon under good oxidizing conditions, and finally heat at approximately 900° C to constant weight. The precipitate

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the barium chloride content of the precipitate can be made by either of the following procedures: (1) Fuse the precipitate with sodium carbonate, extract the melt with water, precipitate with silver nitrate after acidification with nitric acid, and calculate the weight of $BaCl_2$ from the weight of silver chloride obtained; or (2) dissolve the precipitate in warm sulfuric acid, catch the evolved hydrochloric acid in a solution of silver nitrate, and proceed as in (1) [G. A. Hulett and L. H. Duschak, Z. *anorg. Chem.*, **40**, 196 (1904)]. The correction for alkali sulfate is obtained as follows: Dissolve the precipitate in about 15 ml of sulfuric acid in a platinum dish, cool, and pour the solution, slowly and with vigorous stirring, into about 350 ml of water. Warm to facilitate filtering, filter without washing, and evaporate the clear filtrate to fumes of sulfuric acid and finally until all acid is expelled. Dissolve the residue in water, filter through a small paper into a tared platinum dish, evaporate the solution to dryness, heat carefully to redness, and weigh. By this procedure approximately 90 per cent of the occluded sulfate is recovered. The remainder can be recovered by repeating the operation or its amount empirically assumed to be 10 per cent. The determination of the correction for free acid is the most difficult of all and must be made on the unignited precipitate. Allen and Johnston (*loc. cit.*) proceeded as follows: Dry the precipitate at 105° C, transfer it to a weighed platinum boat, and place in a platinum combustion tube. Connect one end of the tube with a source of pure dry air and the other end with two Liebig potash bulbs in series and containing a 1 per cent solution of 30 per cent hydrogen peroxide. Start a slow current of air, and gradually heat the tube to approximately 1000° C. Cool and weigh the boat. Combine the two solutions, evaporate to expel hydrogen peroxide, precipitate with barium chloride, and calculate the weight of sulfuric acid. To make all corrections on a precipitate, perform the operation just described to obtain the volatilization loss of sulfuric acid and the weight of the impure barium sulfate, then determine the chloride by volatilization of hydrochloric acid from a hot sulfuric acid solution of the impure sulfate, and finally determine the occluded alkali sulfate in the sulfuric acid solution.

[16] Essentially the method of E. Hintz and H. Weber, Z. *anal. Chem.*, **45**, 31 (1906).

can of course be caught in a Gooch or Munroe crucible, or the heating done in a muffle.[17]

C. FOR SOLUTIONS CONTAINING LARGE AMOUNTS OF SULFATES IN THE PRESENCE OF IRON AND THE LIKE

PROCEDURE. Prepare a clear solution having a volume of approximately 1600 ml and containing 10 ml of hydrochloric acid. Cool to 20 to 25° C, cover with a glass, and add, from a precipitating cup (Fig. 28) and without stirring, 125 ml of a 5 per cent solution of barium chloride, dropwise at the rate of 5 ml per minute. When all of the solution has been added, stir gently, and allow the precipitate to settle, preferably overnight. Filter through a tared 35-ml Gooch or fritted-glass crucible under suction in the filtering arrangement shown in Fig. 29. Nearly fill the crucible with water

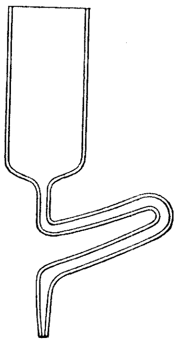

FIG. 28. Precipitating cup. Capacity 130 ml and adjusted to deliver 5 ml per minute.

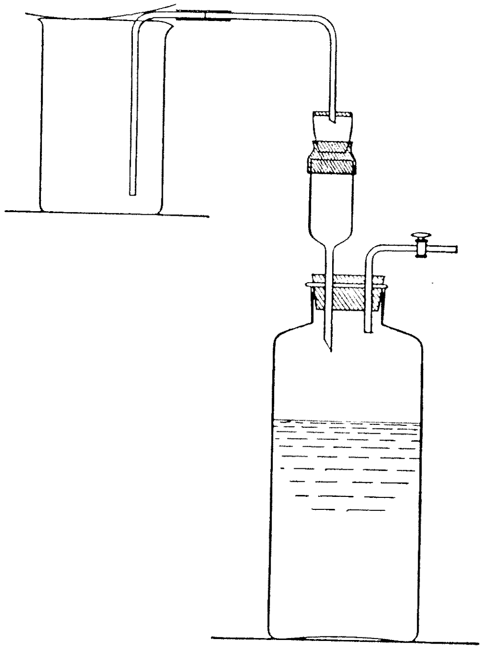

FIG. 29. Apparatus for filtering large amounts of solution.

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[17] In routine determinations of sulfur in the same kind of material by a method of this kind, more accurate results are obtained with very little extra labor by preparing a correction graph. This is done by running a series of determinations to cover the sulfur range, in which known amounts of the sulfate ion are precipitated according to the chosen method in solutions having exactly the same compositions as obtain in the routine analysis. The weights of barium sulfate found are plotted against the calculated weights and the corrected results read off directly thereafter. See C. E. Waters, Sulphur in Petroleum, *Bur. Standards Tech. Paper* 177, 25.

before the cork and siphon are placed in position, exhaust the air in the bottle, and continue the filtration until most of the solution has siphoned over. Remove and wash the siphon and cork, transfer the precipitate to the crucible by sluicing and scrubbing with as little water as possible, and finally wash the precipitate six times with cold water, dry carefully, and heat, preferably in an oven at about 900° C for 30 minutes. Cool in a desiccator, and weigh.

D. VOLUMETRIC METHODS

Among the volumetric methods for the determination of sulfur should be mentioned the benzidine, barium chromate, and evolution methods. The first can be used for large amounts of sulfur as in pyrite, the second for moderate amounts as in coal, and the third preferably for small amounts of sulfur as in steel. All are best suited for routine analyses.

In the preferred modifications of the first,[18] the sulfate ion is precipitated by benzidine hydrochloride in neutral or slightly acid solution (*p*H 4), and the solution filtered, the precipitate of benzidine sulfate washed with five 3-ml portions of water and titrated at 50° C with a standard solution of sodium hydroxide and with phenolphthalein as indicator.[19] The method can be applied in the presence of bivalent iron, copper, cobalt, zinc, nickel, manganese, and aluminum. It is subject to interference by compounds such as trivalent iron.

In the barium chromate method,[20] the sulfate is precipitated in very dilute hydrochloric acid solution by the addition of an excess of a hydrochloric acid solution of barium chromate. The barium sulfate and the excess of barium chromate are filtered off after the solution is rendered ammoniacal, and the soluble chromate equivalent of the sulfate originally present is determined by titration with thiosulfate after the addition of potassium iodide and acid to the filtrate.

This method is subject to interference by appreciable amounts of calcium, nitrates, or ammonium chloride.

The so-called evolution method[21] is employed for the determination of sulfur occurring in a sulfide that quantitatively yields hydrogen sulfide on treatment with acid. The liberated hydrogen sulfide is generally absorbed in an ammoniacal solution of cadmium chloride or zinc sulfate and then oxidized by a standard solution of iodine or iodate after the addition of acid.

If the sulfide is absorbed in cadmium solution, it is very important that the solution be kept out of direct sunlight, for otherwise reactions take place that cause results that are much too low.[22] Zinc sulfide is affected very little if at all.

E. TURBIDIMETRIC AND COLORIMETRIC METHODS

Small amounts of soluble sulfates are best determined in a nephelometer (p. 27), by comparing, under like conditions, the turbidities produced by barium chloride in solutions of the unknown and of standards.[23] Very small amounts of sulfur (such as 0.001 mg) occurring as easily decomposed sulfide, are conveniently determined colorimetrically by comparing stains produced on lead acetate paper with those produced by a standard.[24]

A photometric method for the determination of sulfur in metals is described by C. L. Luke.[25]

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[18] W. Müller, *Ber.*, 35, 1587 (1902); F. Raschig, *Z. angew. Chem.*, 16, 617, 818 (1903); C. Friedheim and O. Nydegger, *Z. angew. Chem.*, 20, 9 (1907); *Chem. Ztg.*, 52, 318 (1928); G. v. Knorre, *Chem. Ind.*, 28, 2 (1905); *Chem. Ztg.*, 34, 405 (1910).

[19] According to W. B. Meldrum and I. G. Newlin [*Ind. Eng. Chem. Anal. Ed.*, 1, 231 (1929)], the solubility of benzidine sulfate per 1000 g of solution at 25° C is 0.098 g in water, 0.542 g in 0.239 *N* HCl, 0.942 g in 0.53 *N* HCl, and 1.253 g in 1.009 *N* HCl. At 3.5 *N*, the solubility of benzidine hydrochloride is less than that of the sulfate.

[20] C. W. Hinman, *Am. J. Sci.*, [3] 14, 478 (1877); J. D. Pennock and D. A. Morton, *J. Am. Chem. Soc.*, 25, 1265 (1903); M. Holliger, *Z. anal. Chem.*, 49, 84 (1910).

[21] Evolution methods are best suited for the determination of small amounts of sulfur, as in steels, and are described in detail in texts dealing with the analysis of ferrous metals. [See, G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, *Chemical Analysis of Iron and Steel*, John Wiley & Sons (1931).] For a method in which stannous chloride is used to prevent oxidation of hydrogen sulfide by higher oxides during the solution of materials such as cement, see H. A. Bright, *J. Research NBS*, 18, 137 (1937).

[22] For example, samples of steel containing 0.092 per cent of sulfur showed, when run by the evolution method in direct sunlight, 0.046 after the hydrogen sulfide was absorbed in ammoniacal cadmium chloride, 0.063 when ammoniacal cadmium acetate was used, and 0.090 when the absorbent was ammoniacal zinc sulfate. Further experiments showed that the effect was caused by the action of sunlight on the cadmium sulfide and not on the absorbing solution itself.

[23] Cf. R. B. Rudy, Determination of Sulphuric Anhydride in Portland Cement by Means of the Wagner Turbidimeter, *J. Research NBS*, 16, 555 (1936).

[24] W. A. Drushel and C. M. Elston, *Am. J. Sci.*, [4] 42, 155 (1916); C. E. Lachele, *Ind. Eng. Chem. Anal. Ed.*, 6, 200 (1934).

[25] *Anal. Chem.*, 11, 1369 (1949). The metal is dissolved in HCl + HNO_3. Sulfate is reduced to sulfide with HI, distilled as H_2S, and the transmittancy of lead sulfide sol in the distillate measured at 370 mμ.

Chapter 47

CHLORINE, BROMINE, AND IODINE

Chlorine is present most abundantly in rocks that are high in soda, and especially when so low in silica that nephelite is present, though it is also found sometimes in nephelite-free rocks and in a few cases in quartz-bearing ores.[1] It is an essential component of rock-forming minerals such as sodalite (also noselite) and the scapolites. It is commonly found as sodium chloride in sea water and rock salt and is also found in a variety of minerals of greater or lesser importance, as for example in carnallite, cerargyrite, and a few apatites. When present in rocks its amount rarely exceeds 0.2 or 0.3 per cent, but in sodalite rocks it may exceed 1 per cent.

Bromine is never found in the free state in nature. It usually occurs in combination with the alkalies and alkaline earths, and is therefore present in sea water, in many salt springs, and in salt deposits. Lesser occurrences are in coal, in saltpeter, and in the minerals bromyrite, and embolite, bromide, and chlorobromide of silver, respectively.

Iodine is the least abundant member of the halogen group. It is found in sea water, in certain mineral springs and in a few rare minerals, notably the iodides of silver, copper, and lead. Lautarite, an iodate of calcium, occurs in the Chilean nitrate beds.[2]

I. GENERAL CONSIDERATIONS

The halides rarely cause difficulties in the ordinary methods of analysis. Exceptions are analyses of materials that also contain elements, such as lead or silver, that form insoluble chlorides, or mercury or antimony that form volatile compounds. In such cases special treatments are required as noted in Section II.

II. DECOMPOSITION OF HALOGEN COMPOUNDS

For the decomposition of rocks and minerals containing chlorine, see Part III (p. 936).

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[1] H. S. Washington, *Chemical Analysis of Rocks*, 3d ed., p. 20, John Wiley & Sons (1919).

[2] For the determination and occurrence of iodine in phosphate rock, consult W. L. Hill and K. D. Jacob, *J. Assoc. Offic. Agr. Chemists*, 16, 128 (1933).

Insoluble chlorides must be broken up by appropriate digestion or fusion. Lead chloride is digested with sodium or potassium bicarbonate, silver chloride is fused with sodium or potassium carbonate and the melt extracted with water, whereas mercurous chloride is digested with sodium or potassium hydroxide. Compounds that contain chlorine wholly or partly in the nonionized state must be broken up, as for example perchlorates by careful ignition, or mercuric chloride by digestion in a solution of sodium carbonate.

In the analysis of a glass, the sample was decomposed and the chlorine successfully determined by one of us (L.) by treating the glass with a solution of silver sulfate in hydrofluoric and perchloric acids, warming gradually, and then evaporating until fumes of perchloric acid just appeared. The solution was then cooled, diluted, and filtered, and the silver chloride purified by dissolving in ammonium hydroxide and reprecipitating with nitric acid. Possibly a similar attack could be used on certain minerals.

In general, methods for the decomposition of minerals containing bromine or iodine follow those given for chlorine.

For a general method for the determination of halogens in organic compounds based upon the oxidation of the substance by fuming sulfuric acid and distillation of the halogen in an all-glass apparatus, consult J. J. Thompson and U. O. Oakdale.[3] A simplified lime ignition method, in which the sample is weighed in a gelatin capsule, ignited in a Pyrex tube filled with hydrated lime, and the halogens are determined by dissolving the residue in nitric acid and titrating as in the Caldwell-Moyer modification of the Volhard method (p. 732), is described by R. H. Kimball and L. E. Tufts.[4] F. E. Beamish[5] states that substituted halogens in diphenyl, and diphenylbenzene compounds can be completely converted to sodium halide by means of the sodium peroxide-sugar explosion method (p. 839).

According to Schwenk, Papa, and Ginsberg,[6] many aliphatic, aromatic, alicyclic, and heterocyclic compounds can be dehalogenized by treatment with a nickel-aluminum alloy in an alkaline-hydroxide solution. A method, tested on 36 different organic halogen compounds, in which the sample is decomposed by vaporizing it into a stream of combustible gas which is then burned at a jet, is described by Winter.[7]

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[3] *J. Am. Chem. Soc.*, 52, 1195 (1930).

[4] *Ind. Eng. Chem. Anal. Ed.*, 10, 530 (1938).

[5] *Ibid.*, 6, 352 (1934).

[6] E. Schwenk, D. Papa, and H. Ginsberg, *ibid.*, 15, 576 (1943).

[7] P. K. Winter, *ibid.*, 15, 571 (1943).

III. METHODS OF SEPARATION

The chief separation of the chloride ion is that based on its precipitation as silver chloride. Substances that interfere are (1) iodides, bromides, cyanides, and thiocyanates that are also precipitated by silver nitrate, (2) chlorides such as those of tin or antimony that hydrolyze in neutral or feebly acid solutions, (3) chlorides such as platinic chloride that are carried down by silver chloride, and (4) chlorides such as those of chromium or mercury that are incompletely precipitated.

Tin can be separated from chlorine by diluting the solution to 200 to 300 ml, rendering it just alkaline to methyl orange, boiling for 1 to 2 minutes with 2 to 3 g of ammonium nitrate, filtering, and washing the precipitate with a 1 per cent solution of the nitrate. Solutions of platinic chloride are preferably evaporated with a slight excess of sodium carbonate, the residue heated until it just fuses, and the melt extracted with water. Elements such as chromium and aluminum are best separated by repeated precipitation with ammonium hydroxide. Antimony or mercury are best separated by precipitation with hydrogen sulfide. If chlorine is to be determined after the separation of the sulfide group, the precipitation with hydrogen sulfide should be done in a diluted solution which is saturated with the gas and allowed to digest for some time, for some sulfides tend to carry down chlorine. After filtration, most of the hydrogen sulfide can be removed by passing carbon dioxide through the solution and the rest conveniently destroyed by making the solution ammoniacal and oxidizing the hydrogen sulfide by means of hydrogen peroxide or potassium percarbonate that contains no chloride. The solution is then boiled to remove the excess of the oxidizing agent, rendered just acid with nitric acid, and treated as in IV, A (p. 730).

Iodides are usually separated from chlorides by oxidizing with a proper reagent in dilute sulfuric acid solution and volatilizing the liberated iodine. The oxidizing agent commonly used is nitrous acid or ferric sulfate.[8] To carry out the separation, transfer not more than 0.5 g of the mixed halides to a 1000-ml Erlenmeyer flask, dissolve in 400-ml of water, add 10 ml of dilute sulfuric acid (1 + 1), and then oxidize the hydriodic acid by the addition of 2 g of sodium nitrite if pure, otherwise by nitrous acid generated in a separate flask. Insert a funnel with short stem in the neck of the flask, and boil the solution until it is colorless and the escaping steam gives no gray-blue color on red litmus paper upon exposure for 2 minutes. If ferric sulfate is preferred, 2 g of it (as ferric alum or ferrous sulfate oxidized in concentrated solution by 0.3 ml of nitric acid), together with

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[8] F. A. Gooch and F. W. Mar, *Am. J. Sci.*, [3] **39**, 293 (1890).

3 ml of nitric acid, are added instead of the nitrite, the iodine is expelled as before, and then again tested for complete expulsion of iodine after the addition of another milliliter of nitric acid.

Bromine (and chlorine) is usually separated from iodine by Gooch's method[9] as follows: Prepare a neutral solution containing not more than 0.25 g of each of the halogens as fixed salts, and preferably no other salts. Dilute to 700 ml in a 1000-ml Erlenmeyer flask, add 2 to 3 ml of dilute sulfuric acid (1 + 1) and then 2 to 3 g of sodium nitrite that is free from the halogens. Insert a short-stemmed funnel in the mouth of the flask, and boil until all iodine has been expelled. This should not require more than 45 minutes, and the volume of the liquid should not be reduced below 500 ml. If desired, the operation can be carried out in a closed flask fitted with a glass stopper carrying an inlet tube reaching to the bottom of the flask and an outlet tube, and the iodine quantitatively caught as follows:[10] Connect the outlet tube with cooled flasks or tubes containing equal volumes of 5 per cent sodium hydroxide and 3 per cent hydrogen peroxide (both free from halogen), and pass a slow current of steam through the reaction flask as the solution is boiled. When all iodine has been expelled, combine the alkaline solutions, add 50 ml more of peroxide to oxidize all nitrite, and then boil to expel the excess of peroxide. Cool, acidify the solution with dilute sulfuric acid, and treat with sulfurous acid to convert all free iodine to iodide.

Precipitation with palladous chloride in a slightly acidified mixture of the alkali halides as described on page 734 serves quite satisfactorily for the gravimetric separation of iodine from chlorine or bromine. Another desirable method for the separation of iodine in mixtures of the three halides is that based on precipitation with silver nitrate and oxidation of the mixed silver halides with sulfuric and chromic acids as described on page 735.[11]

Spitzer[12] points out that bromine, but not iodine, reacts with formic acid or formates as indicated in the equations:

$$\mathrm{HCOOH} + \mathrm{Br_2} = \mathrm{CO_2} + 2\mathrm{HBr}$$

$$\mathrm{HCOONa} + \mathrm{Br_2} = \mathrm{CO_2} + \mathrm{HBr} + \mathrm{NaBr}$$

and that the reactions can serve for the determination of bromine and iodine in the presence of each other, and of iodide in the presence of

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[9] F. A. Gooch and J. R. Ensign, *ibid.*, [3] **40**, 145 (1890).

[10] P. Jannasch and K. Aschoff, *Z. anorg. Chem.*, **1**, 144, 245 (1892).

[11] For the separation and determination of iodine in natural waters, see H. W. Brubaker, H. S. Van Blarcom, and N. H. Walker, *J. Am. Chem. Soc.*, **48**, 1502 (1926); P. A. Meerburg, *Z. physik. Chem.*, 130, 105 (1927). For the determination of traces of iodine in organic matter, see J. F. McClendon, *J. Am. Chem. Soc.*, **50**, 1093 (1928).

[12] L. Spitzer, *Ind. Eng. Chem. Anal. Ed.*, **8**, 465 (1936).

bromide. In the first case, two aliquot portions of the solution are titrated with thiosulfate, one after treatment with potassium iodide ($Br_2 + I_2$) and the other after treatment with sodium formate (I_2 only). In the second case, a solution of bromine in potassium bromide is added to liberate the iodine, which is titrated with thiosulfate after the excess of bromine has been destroyed by sodium formate.

The quantitative separation of bromides from chlorides is a more difficult matter. F. A. Gooch and H. I. Cole [13] recommended oxidation of hydrobromic acid by the use of telluric acid as follows: Transfer 0.5 g of the mixed halides and 1 g of telluric acid to a small distillation flask fitted with a ground-in stopper carrying a small separatory funnel. Add 40 ml of water, and then 10 ml of dilute sulfuric acid (1 + 1). Pass a slow current of carbon dioxide through the flask, and boil the solution to a volume of 17 to 18 ml.[14]

The separation of bromine from chlorine can also be accomplished by oxidation as follows: [15] Prepare 50 ml of solution containing not more than 0.25 g of each of chloride and bromide, and transfer to a flask such as described in the separation of iodine. If the solution left after the separation of iodine there described is to be used, add sodium hydroxide until just alkaline, and evaporate to a volume of approximately 50 ml. Cool, neutralize with diluted *pure* acetic acid (1 + 2), add 65 ml in excess, and then 1 to 1.5 g of potassium permanganate. Connect the flask with absorption tubes filled and cooled as in the separation of iodine. Pass a slow current of steam into the flask until all bromine has been expelled, approximately 1 hour, combine the alkaline solutions, and proceed as in the separation of iodine.

According to L. W. Andrews,[16] small amounts of chlorine are best separated from large amounts of bromine by oxidation with potassium biiodate, $KH(IO_3)_2$, in dilute nitric acid solution as follows: Transfer the mixed bromides and chlorides to a Kjeldahl flask of 400 to 500 ml capacity and having a neck 20 to 25 cm long. Add the calculated amounts of 0.2 *N* iodate solution and 2 *N* nitric acid,[17] and dilute to 200 to 250 ml. Rest the flask over a hole about 2.5 inches in diameter in a square of asbestos board, and incline it at an angle of 30° from the vertical. Heat to gentle boiling with a Bunsen burner, boil for 5 minutes, and let stand overnight. Again heat, and boil so that the volume is reduced to about 90 ml in 30 to 40 minutes. Add 100 ml of water, continue the boiling until 50 ml have passed off, and then pass the escaping steam, with the help of a clean rubber stopper and narrow bent tube, into a test tube containing 10 ml of a 2 per cent solution of potassium iodide feebly acidified with 0.1 *N* hydrochloric acid. If the liquid shows no yellow color in about 40 seconds, the bromine has been expelled. When this occurs, add, without interrupting the boiling, 1 to 1.5 ml of a 25 per cent solution of phosphorous acid. Continue the boiling until all iodine is driven off (about 5 minutes) as shown by the color and then 5 minutes longer. At no time may the volume be allowed to become less than 90 ml. Cool the solution, add a moderate excess of a 0.05 or 0.02 *N* solution of silver nitrate and then a fragment of filter paper, and shake violently. Filter, wash moderately with dilute nitric acid (1 + 100), and titrate the excess of silver by Volhard's method as described under Silver (p. 207).

Small amounts of bromide in the presence of large amounts of chloride can be recovered by oxidizing with chromic acid in cool dilute sulfuric acid (1 + 3) solution, passing a current of air through the solution, and catching the liberated bromine in a measured volume of a standard solution of sodium arsenite containing bicarbonate.[18]

Cyanides and chlorides are usually not separated from each other because the combined chloride and cyanide can be determined by Volhard's method as described on page 731 and then the cyanide in a second portion of sample by titration with a standard solution of silver nitrate.

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[13] *Am. J. Sci.*, [4] **37**, 257 (1914).

[14] H. I. Cole [*Am. J. Sci.*, [4] **38**, 265 (1914)] extended the use of telluric acid to cover first the expulsion of iodine and then the expulsion of bromine from a mixture of the three halides. See R. F. Newton and E. R. Newton, *Ind. Eng. Chem. Anal. Ed.*, **6**, 213 (1934), for a method for the determination of bromide in the presence of a large excess of chlorides and of moderate amounts of iodides, in which bromine is liberated by chlorine water added in moderate excess, collected in sodium sulfite solution, and titrated potentiometrically with a standard solution of potassium bromate after air oxidation of the excess sulfite.

[15] P. Jannasch and K. Aschoff, *Z. anorg. Chem.*, **5**, 8 (1894).

[16] *J. Am. Chem. Soc.*, **29**, 275 (1907); S. Bugarszky, *Z. anorg. Chem.*, 10, 387 (1895).

[17] For the determination of chloride in crude potassium bromide the amounts of sample and reagents are as follows:

KCl Present, %	Weight of Sample, g	Volume of 0.2 *N* KIO_3 Solution, ml	Volume of 2 *N* Nitric Acid, ml
5–10	0.6	36	20
1.5–5	1.8	96	26
0.25–1.5	3.6	186	35

[18] B. S. Evans, *Analyst*, **56**, 590 (1931).

For a volumetric method for the determination of minute amounts of bromide (0.003%) in the presence of much chloride, as in sodium chloride, which is based on conversion of the bromide to bromate by hypochlorite, destruction of the excess of hypochlorite by sodium formate, reduction of the bromate with iodide, and titration of the liberated iodine with thiosulfate, see I. M. Kolthoff and H. Yutzy, *Ind. Eng. Chem. Anal. Ed.*, **9**, 75 (1937).

IV. METHODS OF DETERMINATION

A. CHLORINE

By far the most important method for the determination of the chloride ion is the gravimetric method in which it is weighed as silver chloride. Less accurate, but entirely satisfactory for anything but the most refined analyses, is the volumetric method in which the chloride is precipitated by a slight excess of a standard solution of silver nitrate and the excess determined, after filtration, by titration with thiocyanate. Titration with silver nitrate in a neutral solution containing potassium chromate as indicator is a valuable routine method but is of restricted application and the least accurate of the three.

a. *By Weighing as Silver Chloride.* Some of the substances that interfere in the determination of chlorine by precipitation as the chloride, and corrective measures that can be applied are described in Section III. In addition, the determination is subject to error through solubility of the chloride in the solutions in which it is precipitated and washed, and through contamination of the chloride by other compounds in the solution. The solubility can be reduced by adding a proper excess of silver nitrate to a dilute solution of chloride or hydrochloric acid which has been freed from disturbing compounds and contains little or no nitric acid. Corrections for solubility can be calculated from solubility data and nephelometric determination as directed under Silver (p. 206). As regards contaminants, excessive amounts of compounds such as silver nitrate and alkali or alkaline earth nitrates should be avoided, for these contaminate the silver chloride and also increase its solubility.[19]

When silver chloride is exposed to light during precipitation, chlorine is liberated and then largely changed back to chloride ions. If the solution contains an excess of silver nitrate (as in the standardization of a solution of hydrochloric acid), these ions cause further precipitation of silver chloride, and positive errors ensue. If silver nitrate is not present (as in the standardization of a solution of silver nitrate), the chloride ions remain in solution, and negative errors are obtained. The positive error is always greater than the negative error for the same degree of exposure. In the standardization of 0.1 *N* solutions the errors approximate 1 part per 1000 in the precipitation of silver nitrate and 2 parts per 1000 in the precipitation of hydrochloric acid, if operations are performed with reasonable speed in bright light (not sunlight or reflected sunlight). Light has very little effect on dry silver chloride. The error, if any, is negative and becomes greater if the dried precipitate is moistened before exposure or if the precipitate is exposed before drying.[20]

PROCEDURE. In the succeeding operations, the precipitate should be protected from light as much as possible.

Prepare 200 ml of a solution containing approximately 0.1 g of chlorine, preferably as hydrochloric acid or sodium chloride, and none of the interfering substances that have been mentioned. Gradually and with stirring add a 5 per cent solution of silver nitrate containing 1 ml of nitric acid per liter, until the precipitate coagulates and no more precipitate is formed. Avoid a large excess.[21] If substances that tend to hydrolyze are present, add 1 to 2 ml of nitric acid. Heat the solution to approximately 60° C, let the precipitate settle, and add a few more drops of silver nitrate. Repeat the operation if a precipitate appears. When precipitation is complete, set the flask aside in the dark for a few hours or preferably overnight. Decant the clear solution through a tared Gooch or Munroe crucible (p. 101), and wash by decantation with a solution containing 0.05 g of silver nitrate per liter. Finally, transfer the precipitate to the crucible, wash with a very little dilute nitric acid (1 + 99) to remove the silver nitrate and then twice with water to remove the nitric acid. Dry and ignite as described under Silver (p. 206), and weigh as $AgCl$.[22]

b. *By Precipitation with Silver Nitrate and Titration with Thiocyanate.* The determination of chlorides by precipitation with an excess of a standard solution of silver nitrate, followed by titration of the excess by Volhard's method as described under Silver (p. 207), is entirely satisfactory for most purposes and more rapid than the gravimetric method. The method is of more general application than Mohr's method, which is described on page 732, for operations can be carried out in nitric acid solution.

It is desirable to add but a small excess of silver nitrate, for this leads to less error through occlusion and the subtraction of the silver nitrate equivalent of the thiocyanate solution. Silver chloride must be removed before titration is attempted, for it reacts with thiocyanic acid and leads to low

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[19] Thallic nitrate, contrary to published statements, has no solvent action on silver chloride, according to A. S. Cushman [*Am. Chem. J.*, **26**, 508 (1901)] and A. J. Berry [*Proc. Cambridge Phil. Soc.*, **22**, 367 (1923–25)].

[20] For further details, see G. E. F. Lundell and J. I. Hoffman, *J. Research NBS*, **4**, 109 (1930).

[21] With pure solutions the most desirable concentration of silver nitrate in the solution and in the preliminary washing solution is 0.05 g per liter [G. P. Baxter and F. A. Hilton, Jr., *J. Am. Chem. Soc.*, **45**, 698 (1923)]. Such a solution dissolves 0.05 mg of $AgCl$ per liter at 20° C.

[22] In analyses of the highest accuracy the weight of chloride must be corrected by the amount of silver chloride that is unprecipitated or later dissolved in the washing solutions. In addition, the slight moisture content of the dried chloride must be expelled by fusion. For such refinements, consult such references as T. W. Richards and R. C. Wells, *Carnegie Inst. Wash. Pub.*, p. 25 (1905), or G. P. Baxter and F. A. Hilton, Jr., *J. Am. Chem. Soc.*, **45**, 694 (1923).

results.[23] Iodides, bromides, cyanides, and thiocyanates interfere because they are also precipitated by silver nitrate, while bivalent mercury and palladium must be removed because they are precipitated by thiocyanate. Nitrous acid and oxides of nitrogen must be excluded for they attack thiocyanic acid and cause a premature red coloration of the solution.[24]

PROCEDURE. For solutions that are required, see under Silver (p. 208). It is desirable, though not absolutely necessary in routine analyses, that the silver nitrate solution be standardized against weighed portions of pure dry sodium chloride.

Prepare 100 to 200 ml of a dilute nitric acid solution (1 + 99) containing approximately 0.1 g of chlorine, preferably as hydrochloric acid or alkali chloride, and none of the interfering substances that have been listed. Add a 1- to 3-ml excess of the standard 0.1 *N* solution of silver nitrate, coagulate the silver chloride by vigorous shaking in a stoppered flask that is protected from the light, and filter through paper, asbestos, or platinum felt. Wash the flask, precipitate, and paper with dilute nitric acid (1 + 99) that is free from nitrous acid. Titrate as described under Silver (p. 209). From the volume of silver nitrate added, subtract the volume of silver nitrate that is equivalent to the volume of thiocyanate required, and multiply the remainder by the chlorine titer of the silver nitrate solution.[25]

c. *Mohr's Method.* Mohr's method[26] is based on the fact that silver chromate is much more soluble than silver chloride in neutral or feebly acid solutions. No permanent precipitate of red silver chromate can there-

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[23] G. Drechsel, *Z. anal. Chem.*, **16**, 351 (1877); M. A. Rosanoff and A. E. Hill, *J. Am. Chem. Soc.*, 29, 269 (1907). In tests made by the latter, a solution of sodium chloride containing 2.324 g of chlorine per liter by gravimetric test showed 2.276 g when the silver chloride was left in solution and 2.328 when it was removed before titration. J. R. Caldwell and H. V. Moyer [*Ind. Eng. Chem. Anal. Ed.*, **7**, 38 (1935)] state that it is not necessary to remove the silver chloride by filtration if 1 ml of nitrobenzene is added for each 0.05 g of chloride before precipitating with silver nitrate. The nitrobenzene forms an insoluble layer over the silver chloride and reduces its rate of solution to such an extent that it does not interfere in the thiocyanate titration. In addition, it lessens adsorption of silver nitrate by the silver chloride and inhibits its darkening in light.

[24] Chlorine in thallic chloride, $TlCl_3$, cannot be determined by Volhard's method, for trivalent thallium oxidizes thiocyanic acid in nitric acid solution and thereby causes increased consumption and low results [A. S. Cushman, *loc. cit.*]. Mohr's method, however, is applicable if ammonium acetate is first added [A. J. Berry, *loc. cit.*].

[25] L. A. Reber and W. M. McNabb [*Ind. Eng. Chem. Anal. Ed.*, **9**, 529 (1937)] point out that the excess of silver nitrate can also be determined by titrating with a standard solution of potassium iodide in the presence of ceric ammonium sulfate and starch, after filtering to remove the precipitated silver chloride or bromide. J. F. Matejczyk [*Chemist-Analyst*, **28**, 54 (1939)] states that silver iodide must also be removed before titrating the excess of silver nitrate.

[26] C. F. Mohr, *Liebig's Ann.*, **97**, 335 (1856). For a study of the method, consult A. J. Berry and J. E. Driver, *Analyst*, **64**, 730 (1939).

fore be obtained in solutions containing chromate and chloride until all of the latter has been precipitated. Mineral acids, which dissolve silver chromate, must be absent or removed either by neutralizing with calcium carbonate, or by neutralizing most of the acid by ammonium hydroxide and then adding an excess of ammonium acetate.[27]

Among the substances that interfere may be mentioned (1) iodides, bromides, thiocyanates, phosphates, carbonates, and hydrogen sulfide that also form precipitates with silver nitrate; (2) cyanides and thiosulfates that dissolve the precipitate; and (3) organic or other compounds that reduce silver nitrate in neutral solution. Lead, bismuth, barium, and iron are preferably also excluded, for they form insoluble chromates and require the addition of excessive amounts of indicator.

PROCEDURE. Standard approximately 0.1 *N* solutions of silver nitrate and sodium chloride and a 1 per cent solution of potassium chromate (free from chloride) are required. All must be neutral, and the first two should be equivalent. The silver nitrate solution should be standardized against weighed portions of dry, pure sodium chloride treated as in the method to be described.

Prepare 100 ml of a neutral or weak acetic acid-ammonium acetate solution containing approximately 0.1 g of chlorine and none of the interfering substances that have been mentioned. Transfer the solution to a porcelain dish, add 1 ml of a 1 per cent solution of potassium chromate (free from chloride), and then slowly add the standard neutral solution of silver nitrate while stirring vigorously. Toward the end of the reaction, proceed very slowly until a permanent red tint is obtained. Now add an equivalent solution of sodium chloride, drop by drop and with vigorous stirring, until the red color is just destroyed.[28] Deduct the volume of solution so employed from the volume of the silver nitrate solution added, and multiply by the titer of the solution.

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[27] For the use of dichlorofluorescein as an adsorption indicator (pink tint, on silver halide precipitate) instead of chromate, in titrations of halides in neutral or weakly acid solutions, see I. M. Kolthoff, W. M. Lauer, and C. J. Sunde, *J. Am. Chem. Soc.*, 51, 3273 (1929); for titrations of organic hydrochlorides in alcoholic solutions, consult K. Bambach and T. H. Rider, *Ind. Eng. Chem. Anal. Ed.*, **7**, 165 (1935). W. T. Burg [*Chemist-Analyst*, 28, 52 (1939)] recommends titration to a violet-red color of the precipitate in 75 ml of solution containing 50 ml of methyl alcohol, 1 ml of 0.5 *N* nitric acid, and 1 drop of a 1 per cent solution of eosin.

[28] After the reading is made, it is convenient to add a few drops extra of the sodium chloride solution and then set the solution aside for use as a comparison solution in succeeding titrations. According to W. B. Meldrum and J. C. Forbes [*J. Chem. Education*, **5**, 205 (1928)], the end point can be easily judged if the titration is made as follows: Dissolve 0.4 g of the chloride in 75 ml of H_2O, add methyl orange, then dilute HNO_3 until just acid, and next just enough 1 per cent $NaHCO_3$ to turn the indicator yellow. Add 5 drops of molal K_2CrO_4 solution, titrate with $AgNO_3$ to a faint end point, boil for 5 minutes, cool in ice water, and finish the titration.

B. BROMINE

Silver bromide is less soluble in water than is the chloride, 0.107 mg of the former per liter at 21° C[29] compared with 1.54 mg of the latter,[30] and so methods for the determination of bromine are practically the same as those used for chlorine. Protection from light is more essential with the bromide than with the chloride because of its greater sensitiveness. For the titration of bromides in mixtures of the halides see under IV, C (p. 736).

a. *By Precipitation as Silver Bromide.* Proceed as described under Chlorine (p. 730), except that the solution should be more dilute and especial care should be taken to wash all nitric acid from the precipitate.[31]

b. *By Precipitation with Silver Nitrate and Titration with Thiocyanate.* Proceed as described under Chlorine (p. 731). There is less need of filtering before titration than with chlorine, and this step can be omitted in anything but the most exact work.

C. IODINE

a. *By Weighing as Silver Iodide.* Silver iodide is the least soluble of the silver halides; 1 liter of water dissolves but 0.0035 mg at 21° C.[32] It is prone to carry down silver nitrate and other compounds present in solution, and these are more difficult to remove than in the case of silver chloride. Precipitation should therefore be made by adding a very dilute solution, say 0.05 *N*, of silver nitrate, slowly and with stirring, to an equally dilute ammoniacal solution of the iodide until precipitation is complete and then adding nitric acid in 1 per cent by volume excess. The precipitate can be safely washed with dilute nitric acid of this strength, but the final washing must be done with water to remove the nitric acid which would otherwise attack the iodide during drying. Water must be sparingly used, however, because it tends to render the chloride colloidal. For other details of the determination, see Chlorine (p. 730).[33]

b. *By Precipitation as Palladous Iodide.*[34] Palladous iodide is insoluble in water and in dilute hydrochloric acid (1 + 99), but is slightly soluble in solutions containing excessive amounts of saline salts. Substances, such as alcohol, that cause reduction to metallic palladium must be absent, as must precipitable compounds such as sulfides or cyanides. Quadrivalent palladium forms insoluble precipitates with chlorides in the presence of potassium or ammonium salts; it is not likely, however, that the quadrivalent compound will be present in the reagent or be formed in a solution that is suitable for the determination of iodides. The iodide can be weighed as such, or as metallic palladium after ignition in a current of hydrogen. The latter is preferable because the iodide slowly loses iodine when it is heated at 100° C.

[29] F. Kohlrausch, Z. *physik. Chem.*, **50**, 356 (1904).

[30] G. S. Whitby, Z. *anorg. Chem.*, **67**, 108 (1910).

[31] For an example of the procedure followed in the most exact analyses, consult such references as G. P. Baxter, *Proc. Am. Acad.*, **42**, 201 (1906–07).

[32] F. Kohlrausch, Z. *physik. Chem.*, **50**, 355 (1904).

[33] For descriptions of methods that are used in analyses of the highest accuracy, consult such references as G. P. Baxter, *op. cit.*, **40**, 419 (1904); **41**, 73 (1905); and *J. Am. Chem. Soc.*, **32**, 1591 (1910). Silver iodide gradually loses iodine when heated above its melting point [G. P. Baxter and A. C. Titus, *ibid.*, **62**, 1826 (1940)].

[34] J. L. Lassaigne, *J. Chem. Med.*, **1**, 57 (1835); R. Strebinger and I. Pollak, *Mikrochemie*, **3**, 38 (1925).

PROCEDURE. Prepare a solution of the alkali halides containing approximately 1 per cent of hydrochloric acid by volume, no reducing agents such as alcohol, and preferably no other bases. Add a solution of palladous chloride as long as a precipitate forms. Let the solution stand for 24 to 48 hours at 20 to 30° C, filter on a weighed Gooch crucible, wash with warm water, and finally with a very little alcohol. Dry at 90 to 95° C for 1 hour and weigh as PdI_2 or, preferably, heat gradually to about 1000° C in an atmosphere of hydrogen and weigh as metallic palladium. In the latter case, stop the current of hydrogen as soon as the flame is removed, and cool. Moisten with alcohol, light, and allow to burn off. Cool in a desiccator, and weigh.

c. *By Oxidation of the Silver Halides with Sulfuric and Chromic Acids.* Perhaps the most desirable method for the separation and determination of iodine and the estimation of chlorine and bromine in mixtures of the three halides is Bekk's[35] modification of Baubigny's method.[36] This is carried out as follows: Divide the solution into two equal parts, and treat each with silver nitrate, filter, and wash as described under Silver (p. 207). Dry one precipitate to constant weight at 180° C, and weigh the mixed halides.[37] Treat the second washed precipitate (preferably not over 0.4 g of mixed halides) with a solution of 2 g of potassium bichromate in 30 ml of sulfuric acid, and heat for 30 minutes at 95° C to liberate all chlorine and bromine and to convert the iodide to iodate. Toward the end of the operation, blow air through the solution. Dilute to 300 to 400 ml, filter, and reduce the iodate in the filtrate by adding a concentrated solution of sodium sulfite until a faint odor of sulfur dioxide is perceptible after the solution has stood for 10 minutes. A large excess may cause reduction of silver iodide. Filter the solution and wash, dry and weigh the silver iodide. Precipitate the silver in the filtrate and washings as silver iodide, filter, and wash and weigh. From the weights of AgCl + AgBr + AgI, the AgI derived from

[35] J. Bekk, *Chem. Ztg.*, **39**, 405 (1915).

[36] H. Baubigny, *Compt. rend.*, **127**, 1219 (1898); **128**, 51 (1899).

[37] The weighed silver salts can be used instead of working with the moist halides obtained in a separate portion, but in this case the digestion with acid chromate must be continued for 2 hours.

the iodate, and AgI obtained from the silver originally bound to the chlorine and bromine, the weights of the three halogens are easily calculated.

d. *Volhard's Method.* Iodides can be determined by Volhard's method as described under Chlorine (p. 731), except that ferric alum is not added until all of the iodide has been precipitated, the silver solution must be added very slowly and with vigorous stirring to a dilute solution, and there is no need of filtering before titration with thiocyanate.

e. *Other Methods.* The determination of iodide in a mixture of the halides can be made in dilute sulfuric acid solution by potentiometric titration with a standard solution of potassium permanganate.[88]

According to R. Berg,[39] iodide, bromide, or combined iodide, bromide, and chloride can be determined by adding cyanide, carefully adjusting the acidity in accordance with the halogen in consideration, oxidizing to ICN, BrCN, or ClCN by a standard solution of potassium bromate, and titrating with a standard solution of sodium thiosulfate after the addition of potassium iodide. Willard and Greathouse[40] describe methods for the determination of iodide and bromide based on their oxidation by a standard solution of periodate added in excess (in neutral solution with iodide and in acid solution with bromide), followed by titration of the excess of the periodate with arsenite.

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[88] R. Behrend, *Z. physik. Chem.*, **11**, 466 (1893); W. S. Hendrixson, *J. Am. Chem. Soc.*, **43**, 14 (1921); I. M. Kolthoff and E. J. A. H. Veryzl, *Rec. trav. chim.*, **42**, 1055 (1923); H. H. Willard and F. Fenwick, *J. Am. Chem. Soc.*, **45**, 623 (1923); and F. L. Hahn and G. Weiler, *Z. anal. Chem.*, **69**, 417 (1926).

[39] *Z. anal. Chem.*, **69**, 1, 369 (1926); see also N. McCulloch, *Chem. News*, **60**, 259 (1889); C. Meineke, *Z. anorg. Chem.*, **2**, 157 (1892); T. Ewan, *J. Soc. Chem. Ind.*, **25**, 1130 (1906); R. Lang, *Z. anorg. Chem.*, **144**, 75 (1925); G. Alsterberg, *Biochem. Z.*, **166**, 1 (1925); and I. M. Kolthoff, *Chem. Zentr.*, **97** (1), 1858 (1926).

[40] H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, **60**, 2869 (1938).

Chapter 48

FLUORINE

Washington said:[1] "Fluorine as a component of apatite, biotite, etc., seems to have no special preference as to magma, though, on the whole, it is found more frequently in silicic than in ferric (ferromagnesian) rocks. It is, however, most apt to be met with as fluorite and some other rare fluorine-bearing minerals in rocks that contain nephelite, as foyaites and tinguaites. It is an essential constituent of fluorite and most apatite, and as an integral part of the last mineral is almost universally present.[2] It also occurs in small amount in biotites and other micas, in some hornblende and augite, as well as in tourmaline, topaz, chondrodite, etc."

In rocks, fluorine is usually found in amounts under 0.1 per cent, but, freedom of the weighed calcium fluoride from contamination being assured, the reported amount is invariably too low because of the inaccuracy of the method for its separation.

It is interesting to record that Armand Gautier and P. Clausmann[3] believed that fluorine is indispensable to the living cell and stated that it occurs, together with phosphorus, in all animal and vegetable tissues.

Determinations of fluorine are of increasing importance, in natural waters, in plant materials, in ores such as fluorspar, cryolite, and phosphate rock, and in ceramic materials such as opal glasses and enamels.

I. GENERAL CONSIDERATIONS

The presence of fluorine causes considerable trouble in the course of an ordinary analysis. In the case of rocks rich in the element, strict accuracy requires the separation of silica to be made after the separation of fluorine, as in some such procedure as the Berzelius method (p. 939), but in practice it is not often necessary to resort to this tedious procedure, for the amount of fluorine is usually small, and it could by no possibility cause a loss of much more than three fourths of its own weight of silica if it were all to volatilize as silicon tetrafluoride when the sodium carbonate melt is

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[1] H. S. Washington, *The Chemical Analysis of Rocks*, 4th ed., p. 22, John Wiley & Sons (1930).

[2] See also K. D. Jacob and D. S. Reynolds, The Fluorine Content of Phosphate Rock, *J. Assoc. Offic. Agr. Chemists*, **11**, 237 (1928).

[3] *Compt. rend.*, **162**, 105 (1916).

dissolved and evaporated with hydrochloric acid. The loss is not so great as this, however, for the tetrafluoride is unstable in the presence of moisture. Some of the fluorine therefore escapes, perhaps as hydrofluoric acid, and more is fixed in fluosilicates. These, if eventually ignited with the silica, would undergo at least partial decomposition, and, on treatment of the ignited silica with hydrofluoric and sulfuric acids, the metal of the fluosilicate (presumably sodium) would be weighed as sulfate if not volatilized by the heat of the ignition.

Any fluorine that is left in the filtrate from the silica will render the precipitation of aluminum very incomplete.[4] The sometimes incomplete precipitation of aluminum by ammonium hydroxide from sulfate solutions after a rock has been attacked with hydrofluoric and sulfuric acids and the solution evaporated to fumes of the latter is due, no doubt, to failure to expel the hydrofluoric acid completely.[5] No loss of aluminum occurs during evaporation of aluminum fluoride with hydrofluoric acid and subsequent careful ignition.

In addition to causing trouble with aluminum, fluorine causes more or less precipitation of calcium as calcium fluoride during the precipitation with ammonium hydroxide. This of course tends to offset the loss of aluminum at the expense of calcium. In such an event, the determination of calcium will be in error, not only because of its partial inclusion in the ammonia precipitate, but also because some calcium may be thrown down as fluoride instead of oxalate by any fluorine still remaining in solution.

It is not difficult to detect fluorine in material, such as apatite or fluorite, that contains appreciable amounts of the element. In such cases the etch test, the hanging drop test, or the flame test are all satisfactory. On the other hand, these methods will not reveal fluorine with certainty when applied directly to material, such as rocks, containing but little of the element. Although in some rocks as little as 0.1 per cent of fluorine can be detected with ease, in rocks of another class much larger amounts may fail to show.[6]

The etch test is well known and depends on the etching action on glass of the hydrofluoric acid that is liberated when the material is heated with

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[4] F. P. Veitch, *J. Am. Chem. Soc.*, 22, 246 (1900); F. W. Hinrichsen, *Ber.*, 40, 1497 (1907), and *Z. anorg. Chem.*, 58, 83 (1908); and H. Cavaignac, *Compt. rend.*, **158**, 948 (1914).

[5] E. Selch, *Z. anal. Chem.*, **54**, 395 (1915).

[6] A. Gautier and P. Clausmann [*Compt. rend.*, **154**, 1670 (1912); **158**, 1389, 1631 (1914); and **162**, 105 (1916)] published a series of fine papers on the occurrence and determination of fluorine in waters, minerals, and other materials, and described an elaborate and seemingly extraordinarily delicate method of test that is especially suitable for very small amounts. The authors' summary of the method is given in the last reference. Space does not allow presenting here a description of the method and of the apparatus employed.

sulfuric acid or fused with an acid flux such as sodium metaphosphate. If silicon or boron is present, silicon tetrafluoride or boron trifluoride is also formed and weakens the test, for these compounds do not etch glass. If the percentage of fluorine is low in proportion to that of silicon or boron, no etching at all takes place. In such case the fluorine must first be separated as calcium fluoride as in the Berzelius method (p. 939), and the final washed product subjected to the test.[7]

The hanging drop test is based on the turbidity produced in a drop of water by silicon tetrafluoride that has been formed by the action of sulfuric acid on a dry mixture of a fluoride and powdered silica or silicate. The turbidity is caused by silicic acid formed in accordance with the following equation:

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6$$

This test is more satisfactory than the etching test when applied to siliceous material containing very little fluorine. As in the etching test, relatively large amounts of boron may cause a negative result, for boron trifluoride may not render the water turbid.[8]

The flame test takes its name from the green color caused by boron trifluoride when a bead containing acid flux, fluoride, and borosilicate is fused in the Bunsen flame.[9]

II. METHODS OF DECOMPOSITION

Some silicates and fluorides yield all of their fluorine as silicon tetrafluoride when mixed with finely powdered silica and treated with sulfuric acid as described in IV, A.

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[7] A. G. Woodman and H. P. Talbot [*J. Am. Chem. Soc.*, **28**, 1437 (1906)] gave detailed descriptions of an etching method which is stated to be sensitive to 1 part in 5,000,000 if no silica whatever is present.

[8] The test is usually carried out by mixing approximately 0.5 g of the fine and thoroughly dried material with 0.1 g of dried precipitated silica and transferred to a small test tube fitted with a one-hole stopper that is slightly notched and carries a small piece of glass tubing which is sealed at one end and open at the other. A drop of water is placed in the open end and the tube adjusted so that the open end extends 2 to 3 mm below the stopper. One or two milliliters of sulfuric acid are next poured on the mixed powder, the stopper is inserted loosely, and the test tube gently heated in a water bath for 30 minutes. If appreciable amounts of fluorine were present, a ring of gelatinous silicic acid is found at the mouth of the tube.

[9] According to F. B. Wilson [*Chemist-Analyst*, **24**, 23 (1918)], the test is best made as follows: To 2 parts by weight of $KHSO_4$ add 1 part of a borosilicate such as axinite or borosilicate glassware. Pulverize finely, and mix well. Mix 1 part of the substance to be tested with 3 parts of the above flux, make a semifused bead of the mix on a platinum loop, and hold the bead just outside of the lower margin of a Bunsen flame. Or, make a semifused bead of the flux alone, roll while hot in some of the powder to be tested, and hold in the flame. A transient green coloration of the flame, due to the liberation of boron trifluoride, indicates fluorine. Barium also gives a green flame.

If the silicate cannot be decomposed by sulfuric acid, the fluorine can be converted to soluble sodium fluoride by fusion of the silicate with sodium carbonate at as low a temperature as possible.[10] If the fluoride is refractory, it should be mixed with silica, which facilitates the decomposition. The melt is then extracted with water, and substances such as sodium silicate, carbonate, and phosphate separated from the fluorine as described in the Berzelius method (p. 939). If appreciable fluorine is present or a large residue remains after extraction of the melt with water, two or three fusions and extractions may be necessary. Very little, if any, fluorine is lost during the evaporation or boiling of neutral or ammoniacal solutions of sodium fluoride.[11]

Because of the great preponderance of lime, direct fusion of carbonate rocks with sodium potassium carbonate and silica is of somewhat doubtful practicability. Probably the following treatment will afford the best results: Dissolve the powder in dilute acetic acid, as far as this may be possible without boiling, filter, and wash with hot water. To the filtrate add a solution of sodium carbonate until in some slight excess, boil, and treat the precipitate of calcium carbonate and possible fluoride as described in the Berzelius method (p. 939). Most of the fluorine that may have been dissolved by the acetic acid will thus be found. Fuse the insoluble matter with sodium-potassium carbonate, and proceed as directed in the method.

Fluorspar can be satisfactorily decomposed by fusing with potassium hydroxide in a gold crucible or potassium carbonate and niter in a platinum crucible, followed by solution of the melt in water or in cool dilute nitric acid. Melts so obtained dissolve more readily than those made with the corresponding sodium salts. If fluorine is not to be determined, fluorspar may be decomposed by heating the fine powder with sulfuric or perchloric acid,[12] or by digesting with diluted hydrochloric acid (1 + 1) containing boric acid.

For the decomposition of organic compounds containing fluorine (and boron), D. J. Pflaum and H. H. Wenzke[13] recommend that the compounds be weighed in gelatin capsules and decomposed by combustion in a Parr bomb with an oxidizing mixture of sodium peroxide, potassium chlorate, and sugar.

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[10] According to F. G. Hawley [*Ind. Eng. Chem.*, **18**, 573 (1926)], sulfides, as for example pyrite, cause a loss of fluorine which can be partially overcome by the addition of niter or peroxide to the sodium carbonate. Possibly roasting after the addition of lime, as in IV, A, might overcome the difficulty.

[11] W. H. Adolph, *The Quantitative Methods for Fluorine*, thesis, p. 12, University of Pennsylvania (1915); *Z. anal. Chem.*, **55**, 395 (1916).

[12] G. E. F. Lundell and J. I. Hoffman, The Analysis of Fluorspar, *Bur. Standards J. Research*, **2**, 671 (1929).

[13] *Ind. Eng. Chem. Anal. Ed.*, **4**, 392 (1932).

III. METHODS OF SEPARATION

In quantitative analyses, fluorine is usually separated by precipitating it as calcium fluoride, CaF_2, or volatilizing it as silicon tetrafluoride, SiF_4, or hydrofluosilicic acid, H_2SiF_6. The former is not an ideal procedure because of the solubility of the salt and the necessity for removing a number of compounds such as phosphates, chromates, and sulfates that also form insoluble salts with calcium. These separations are described in detail in the Berzelius method (p. 939). The separation of fluorine by volatilization is based on attack with sulfuric or perchloric acid. Direct attack is seldom entirely successful, for most of the fluorine minerals occurring in rocks are attacked incompletely, if at all, by strong sulfuric or perchloric acid. The separation may fail, even with decomposable fluorides, if amorphous silica or silicates are used.[14] Best results are obtained with finely powdered quartz, but recent work indicates that, if distillation is continued sufficiently long, complete separation of fluorine can be obtained by volatilization, even if gelatinous silica is present.[15]

O. Ruff and E. Schiller[16] asserted that fluorine can be quantitatively separated from columbium and tantalum as follows: Precipitate with ammonium hydroxide, let settle, decant, and reserve the clear liquid. Dissolve the precipitate in a little warm dilute nitric acid, again precipitate, decant, and repeat the operation a third time. Determine the fluorine in the combined filtrates and the earth acids in the final precipitate.

For the elimination of fluorine from solutions in which it is not wanted, the chief separation is that based on its volatilization as hydrofluoric acid or, if silica be present, as silicon tetrafluoride or hydrofluosilicic acid. The complete decomposition of fluorides is sometimes difficult.[17]

For the complete elimination of fluorine by the use of more volatile acids, such as nitric, A. A. Noyes[18] recommended the addition of finely divided

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[14] K. Daniel, *Z. anorg. Chem.*, **38**, 257 (1904).

[15] H. H. Willard and O. B. Winter, *Ind. Eng. Chem. Anal. Ed.*, **5**, 7 (1933).

[16] *Z. anorg. Chem.*, **72**, 329 (1911).

[17] For example, after treating 1 g of calcium sulfate with hydrofluoric and sulfuric acids as in a silica determination, R. C. Wells [*J. Am. Chem. Soc.*, **44**, 2188 (1922)] was unable to expel all fluorine by evaporating to dryness and igniting, even though the residue was ignited four times, twice after intervening additions of water and sulfuric acid and twice after additions of 5-ml portions of sulfuric acid. The fluoride is more easily decomposed, however, if the residue is thoroughly broken up and triturated in the sulfuric acid, as was found by H. A. Bright, who thus obtained complete expulsion of fluorine in two treatments with 2-ml portions of sulfuric acid. A similar treatment completely removed all fluorine from 1 g of fluorspar.

[18] *Technol. Quart.*, **16**, 101 (1903); A. A. Noyes and W. C. Bray, *Qualitative Analysis for the Rarer Elements*, p. 25, Macmillan Co. (1927).

silica to the solution to supplement the action of the acid. Possibly boric acid would serve as well. Complete removal without the introduction of sulfuric acid can also be accomplished by evaporation with perchloric acid (see Reagents, p. 39). When this acid is used, evaporation had better be carried to dryness and, in most cases, repeated. The resultant perchlorates can then be converted to chlorides or basic chlorides by cautiously heating until no further effervescence takes place.

IV. METHODS OF DETERMINATION

The most commonly used methods for the determination of fluorine in rocks or minerals are perhaps those of Berzelius[19] and Steiger.[20] In the former, the fluorine is precipitated and weighed as calcium fluoride, CaF_2; in the latter the amount of fluorine is judged by its bleaching effect on a peroxidized solution of titanium. The Berzelius method is used when appreciable amounts of fluorine are in question and gives results that are almost certain to be too low, and even negative if the method is applied in solutions containing less than 1 mg of fluorine per 100 ml. For amounts of fluorine under 10 mg, the indirect method is preferable. The preliminary attack of material such as rocks and the subsequent treatments in both methods are described under Fluorine, Part III (p. 938).

At present there is a tendency on the part of analysts to separate fluorine from interfering substances by distilling it from sulfuric or perchloric acid solutions. The procedure to be followed for final determination of the fluorine in the distillate depends on the amount. For quantities between 0.01 and 0.10 g, the lead chlorofluoride method is convenient, and, for traces up to 50 mg, titration with thorium nitrate is usually employed. The latter procedure is especially useful in determining very small amounts. These methods are described in the succeeding sections.

A. THE EVOLUTION METHOD FOR FLUORINE

a. *By Distillation as Hydrofluosilicic Acid and Titration with Thorium Nitrate.* In this method, as originally proposed by Willard and Winter,[15] an aqueous solution of a soluble fluoride or silicofluoride is treated with zirconium-alizarin mixture, diluted with an equal volume of alcohol, titrated with a standard solution of thorium nitrate until the pink color of the zirconium-alizarin lake reappears, and the results are corrected as indicated in a blank run.

If interfering substances are present, fluorine is volatilized as hydrofluosilicic acid by distilling from a flask containing pieces of glass and either sulfuric or perchloric acid, the final temperature being held at approximately 135° C by adding water from a dropping funnel. Insoluble compounds are fused with sodium carbonate, and the melt is taken up with a little hot water before transferring to the distilling flask. If much silicic acid is present, it must be removed by treatments with zinc perchlorate and carbonate before attempting to distil.[21]

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[19] J. J. Berzelius, *Schweigg J.*, 16, 426 (1816); H. Rose, *Ann.*, 72, 343 (1849).

[20] G. Steiger, *J. Am. Chem. Soc.*, 30, 219 (1908); H. E. Merwin, *Am. J. Sci.*, [4] 28, 119 (1909).

Certain substances interfere in distillation or titration. Among the former are high concentrations of aluminum salts which may prevent complete volatilization, or gelatinous silica which may retard the volatilization of fluorine. Substances that interfere in titrations include any ion that forms a precipitate or a nondissociated salt with fluorine or thorium. Among these may be mentioned sulfate, phosphate, arsenate, chloride, nitrate, perchlorate, hypochlorite, and, to a lesser extent, alkali, borate, and sulfide ions. Arsenite, chlorate, and silicate ions are without effect.

Numerous modifications of the original method have been proposed, as follows: Armstrong[22] recommends the use of sodium alizarin sulfonate alone, the use of an aqueous rather than an alcoholic solution, and the addition of silver perchlorate before distilling to hold back hydrochloric acid; Hoskins and Ferris[23] point out that more satisfactory end points are obtained with a concentration of 4×10^{-5} per cent of the indicator in 50 ml of solutions buffered at *p*H 3.5, as by the use of monochloroacetic acid; Churchill, Bridges, and Rowley[24] state that interference by phosphate can be avoided by a preliminary distillation with sulfuric acid at 150° C, followed by redistillation of the distillate with perchloric acid at 135° C; and Gilkey, Rohs, and Hansen[25] distil by leading superheated steam into a sulfuric acid solution in a distilling flask which is heated at 145° C in a copper vessel containing boiling tetrachloroethane, and fitted with a return condenser; perchloric acid cannot be used because of the danger involved, should the flask break.

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[21] For studies of the distillation of fluoride ion from sulfuric, perchloric, or phosphoric acid solutions, consult D. Dahle and H. J. Wichmann, *J. Assoc. Offic. Agr. Chemists*, 19, 313, 320 (1936); 20, 297 (1937). In general, low volumes of liquid in the distilling flask and high temperatures (especially with $HClO_4$ and H_3PO_4) give better recovery of fluorine per milliliter of distillate. In the presence of considerable aluminum a preliminary distillation with H_2SO_4 at 162 ± 2° C, followed by neutralization with alkali, concentration to small volume, and redistillation with H_2SO_4 at 137 ± 5° C, is desirable. Perchloric acid should be free from volatile acids.

[22] W. D. Armstrong, *J. Am. Chem. Soc.*, 55, 1741 (1933), and *Ind. Eng. Chem. Anal. Ed.*, 8, 384 (1936). R. J. Rowley and H. V. Churchill [*ibid.*, 9, 551 (1937)] state that as much as 50 mg of fluorine can be handled in an aqueous as against 20 mg in an alcoholic solution.

[23] W. M. Hoskins and C. A. Ferris, *ibid.*, 8, 6 (1936).

[24] H. V. Churchill, R. W. Bridges, and R. J. Rowley, *ibid.*, 9, 222 (1937).

[25] W. K. Gilkey, H. L. Rohs, and H. V. Hansen, *ibid.*, 8, 150 (1936).

The method can be illustrated by the following modified procedure developed by Reynolds and Hill[26] for the analysis of phosphate rock.

PROCEDURE. Transfer 0.5 g of sample and 15 ml of dilute perchloric acid (2 + 1) to a steam-distillation flask, and distil at 125 to 150° C until 150 ml of distillate has been obtained.[27] If the material is pyritiferous, moisten the sample in the distilling flask with 2 to 3 ml of a saturated solution of potassium permanganate, and increase the concentration of the added perchloric acid accordingly. Add a few drops of phenolphthalein to the distillate and then 1 *M* sodium hydroxide until just alkaline. Dilute to exactly 250 ml, and take a 50-ml aliquot portion. Add 5 drops of alizarin indicator (0.1 per cent aqueous solution of sodium alizarin sulfonate) and then 0.1 *M* hydrochloric acid until the pink color of the alizarin is discharged. Now add 2.5 ml of monochloroacetic acid (0.4 *M*), sodium hydroxide (0.2 *M*) buffer solution, and titrate with a 0.04 *N* solution of thorium nitrate.

The solution of thorium nitrate had better be standardized against known amounts of fluorine in the form of specially purified sodium fluoride or standardized fluorine-bearing material of like composition, which cover the range of the amounts of fluorine involved in the analysis and have been carried through all steps of the method.[28]

B. THE LEAD CHLOROFLUORIDE METHOD

The determination of fluorine as lead chlorofluoride has been attempted by a number of investigators.[29] The method is based on the precipitation

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[26] D. S. Reynolds and W. L. Hill, *ibid.*, 11, 21 (1939).

[27] D. S. Reynolds [*J. Assoc. Offic. Agr. Chemists*, 18, 108 (1935)] points out that a coating of precipitated silica, which tenaciously retains fluorine, gradually accumulates on the walls of the distillation flask in analyses of slag, phosphate rock, and calcined phosphate. If it is allowed to accumulate, serious errors may arise when the flask is used successively in the analysis of samples containing widely differing quantities of fluorine. The coating can be removed by hot concentrated alkali solution. F. J. McClure [*Ind. Eng. Chem. Anal. Ed.*, 11, 171 (1939)] states that, if it is desired to reduce the volume of the distillate by rendering it alkaline and evaporating before the titration, the evaporation must be done in platinum and not in glass or porcelain, because low results are obtained if glass or porcelain is used.

For a multiple-unit distilling apparatus in which steam is led into a distilling flask heated by a Nichrome coil in a transite board box, see D. S. Reynolds, J. B. Kershaw, and K. D. Jacob, *J. Assoc. Offic. Agr. Chemists*, 19, 156 (1936).

[28] Pure sodium fluoride can be prepared by treating pure sodium carbonate or bicarbonate with an excess of pure hydrofluoric acid, evaporating the excess hydrofluoric acid, and finally heating the residue at about 600° C in an atmosphere of dry nitrogen or air. For purification of the hydrofluoric acid, see J. I. Hoffman and G. E. F. Lundell, *Bur. Standards J. Research*, 3, footnote page 582 (1929).

[29] G. Starck, *Z. anorg. Chem.*, 70, 173 (1911); F. G. Hawley, *Ind. Eng. Chem.*, 18, 573 (1926). See also W. H. Adolph, *loc. cit.*, and L. D. Hammond, *Ind. Eng. Chem.*, 16, 938 (1924); J. I. Hoffman and G. E. F. Lundell, *Bur. Standards J. Research*, 3, 581 (1929).

of the compound PbClF, which can be weighed as such or titrated as in Volhard's method (p. 731), and its fluorine content calculated from the amount of chlorine found. A desirable feature of the gravimetric method is the low conversion factor for fluorine; the volumetric method on the other hand can be applied in the presence of other precipitated substances, provided they do not contain chlorine. Either procedure gives excellent results when applied to solutions of pure fluorides.

The precipitation is carried out in a solution having a *p*H value in the range *p*H 3.6 to 5.6, depending on the conditions. The presence of as little as 0.5 mg of aluminum causes low results, as do excessive amounts of boron (>0.05 g) and ammonium (>0.5 g), sodium, or potassium salts (>10 g). Iron also interferes, but in practice it is always removed by preliminary treatments. If the precipitate is to be weighed, the precipitation must be made in a solution that is free from substances, such as carbon dioxide or phosphates, that are precipitated by lead chloride, or hydrolyze at the hydrogen ion concentration employed. In the volumetric procedure small amounts of silica are without effect on the reaction but tend to clog the filter if present in quantities in excess of 0.05 g. Small amounts of phosphates or sulfates (10 mg or less) do not interfere. The former may cause the filtrate from the PbClF to be cloudy, but this can be ignored.

The precipitate is appreciably soluble in water, 0.325 g dissolving in 1 liter at 25° C. It is less soluble in ice water and is insoluble in a saturated solution of lead chlorofluoride.[30] If the precipitate is to be weighed, it should be caught on a Gooch or Munroe crucible and dried at 120 to 150° C.

PROCEDURE. Prepare a neutral or alkaline solution containing 0.01 to 0.1 g of fluorine and none of the interfering substances that have been discussed. For the preparation of such a solution in the analysis of rocks and minerals see under Fluorine (p. 944). The following operations can be carried out in glass if desired.

Add 2 drops of bromphenol blue indicator[31] to the solution, treat with 3 ml of a 10 per cent solution of sodium chloride, and dilute the solution

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[30] Corrections for the solubility of the precipitate cannot be based on data given in solubility tables. Tests made by J. I. Hoffman showed that no more than 0.002 g of PbClF (equivalent to 0.15 mg of fluorine) is dissolved when 0.5 g of PbClF is washed as described in the method. These experiments also indicated a solubility of 0.320 g of PbClF per liter in pure water at 21° C which agrees well with the value given by Starck. However, when 0.5 g of PbClF was washed on a 9-cm S. & S. no. 589 blue-band paper by directing 10-ml portions of water on the precipitate so as to agitate it thoroughly at every washing, only 0.260 g of PbClF was found in a liter of washings. When the same precipitate was washed with a jet of water directed along the rim of the paper and without agitating the precipitate, the amount dissolved dropped to 0.220 g per liter.

[31] Prepared by grinding 0.4 g of the dry powder with 6 ml of 0.1 *N* NaOH and diluting to 100 ml.

to 250 ml. Add dilute nitric acid until the color changes to yellow, and then add dilute sodium hydroxide until the color just changes to blue. Treat with 2 ml of dilute hydrochloric acid (1 + 1) and then with 5.0 g of lead nitrate, $Pb(NO_3)_2$, and heat on the steam bath. Stir gently until the lead nitrate has dissolved, and then immediately add 5.0 g of sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$. Stir vigorously, and digest on the steam bath for one-half hour. Stir occasionally. Let stand at room temperature overnight, and filter on a no. 589 blue-band S. & S. or a no. 42 Whatman filter paper. Wash the precipitate in the beaker and on the paper once with cold water, then four or five times with a saturated solution of lead chlorofluoride,[32] and finally once more with cold water. Transfer the precipitate and paper to the beaker in which the precipitation was made, stir the paper to a pulp, add 100 ml of dilute nitric acid (5 + 95), and heat on the steam bath until the precipitate has dissolved (5 minutes is ample). Next add a slight excess of a standard 0.2 *N* solution of silver nitrate, digest on the steam bath for 30 minutes, and cool to room temperature while protected from the light. Filter, wash with cold water, and titrate the silver nitrate in the filtrate with a standard solution of potassium thiocyanate as described under Silver (p. 207). Subtract the amount of silver found in the filtrate from that originally added. The difference represents the amount of silver that was required to combine with the chlorine in the PbClF precipitate, and from this the fluorine can be calculated. One milliliter of 0.2 *N* silver nitrate is equivalent to 0.00380 g of fluorine.[33]

C. COLORIMETRIC METHODS

Numerous colorimetric methods for the determination of small amounts of fluoride in materials such as natural waters, sea water, grains, and foods have been developed. Among these may be mentioned those based on the fading effect of the fluoride ion on the (1) yellowish-red zirconium-quinalizarin lake;[34] (2) reddish-violet zirconium-alizarin lake;[35] (3) pink purpurin-zirconium oxychloride lake;[36] (4) red ferric thiocyanate;[37] (5) green-colored "ferron" (7-iodo-8-hydroxyquinoline-5-sulfuric acid)-ferric complex;[38] and (6) yellow-colored peroxidized titanium.[39]

Spectral methods, visual and photographic, are described by Petrey,[40] a photronic colorimetric method, based on the use of ferric-acetylacetone reagent, by Wilcox,[41] and a colorimetric-titration method in which the color of the thorium-alizarin lake in the unknown is matched by titration of a blank, treated exactly as the unknown, with a standard solution of sodium fluoride, by Dahle and his associates.[42]

D. OTHER METHODS

Other methods for the determination of fluorine that might be mentioned are the volumetric method carried out by titration with ferric chloride[43] and the gravimetric method in which the fluorine is precipitated as thorium fluoride, ThF_4.[44] The former is applicable to soluble fluorides and is based on the formation of "iron" cryolite, Na_3FeF_6. The titration is carried out in a solution that is neutral to phenolphthalein and contains ammonium thiocyanate as indicator, sodium chloride and alcohol to decrease the solubility of the precipitate, and ether to render the end point more distinct. Potassium chloride can be substituted for sodium chloride and the titration can be made potentiometrically.[45] Boron interferes.

The precipitation of fluorine as thorium fluoride is not so satisfactory as the foregoing. The precipitate is never pure, being contaminated perhaps by compounds such as Na_2ThF_6; it is quite soluble in an excess of the thorium reagent; and it must be ignited to the oxide, ThO_2. As much

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[32] To prepare the PbClF wash solution, dissolve 10 g of lead nitrate in 200 ml of water, and pour the solution into 100 ml of a solution containing 1.0 g of sodium fluoride and 2 ml of hydrochloric acid. Mix thoroughly, let settle, decant the supernatant liquid, and wash the precipitate four or five times by decantation with 200-ml portions of water. Add 1 liter of water to the precipitate, stir occasionally, let stand for 1 hour, and filter. More wash solution can be prepared as needed by treating the precipitate with fresh portions of water.

[33] For an application of this procedure to the distillate obtained by the Willard and Winter distillation (p. 742), consult J. I. Hoffman and G. E. F. Lundell, The Analysis of Phosphate Rock, *J. Research NBS*, **20**, 607 (1938).

[34] O. M. Smith and H. A. Dutcher (natural waters), *Ind. Eng. Chem. Anal. Ed.*, **6**, 61 (1934).

[35] T. G. Thompson and H. J. Taylor (sea water), *ibid.*, **5**, 87 (1933); J. M. Sanchis (natural waters), *ibid.*, **6**, 134 (1934); and O. B. Winter (alfalfa), *J. Assoc. Offic. Agr. Chemists*, **19**, 362 (1936).

[36] I. M. Kolthoff and M. E. Stansby, *Ind. Eng. Chem. Anal. Ed.*, **6**, 118 (1934). The authors describe a simple distillation method and state that the method is sensitive to 0.005 mg of F in 1 ml.

[37] J. G. Fairchild (rocks), *J. Wash. Acad. Sci.*, **20**, 141 (1930); H. V. Churchill, *Ind. Eng. Chem.*, **23**, 996 (1931); and M. D. Foster, *Ind. Eng. Chem. Anal. Ed.*, **5**, 234 (1933). For a review of various methods, consult H. V. Smith, *ibid.*, **7**, 23 (1935).

[38] J. J. Fahey (rocks and minerals and natural waters), *ibid.*, **11**, 362 (1939).

[39] H. J. Wichmann and D. Dahle (fruits and vegetables), *J. Assoc. Offic. Agr. Chemists*, **16**, 612, 619 (1933); D. Dahle, *ibid.*, **20**, 505 (1937).

[40] A. W. Petrey, *Ind. Eng. Chem. Anal. Ed.*, **6**, 343 (1934).

[41] L. V. Wilcox, *ibid.*, 167.

[42] D. Dahle, R. U. Bonnar, and H. J. Wichmann, *J. Assoc. Offic. Agr. Chemists*, **21**, 459, 468 (1938).

[43] P. Guyot, *Compt. rend.*, **71**, 274 (1870); A. Greeff, *Ber.*, **46**, 2511 (1913); I. Bellucci, *Ann. chim. applicata*, **1**, 441 (1914); L. D. Hammond, *loc. cit.*

[44] E. Deladrier, *Chem. Weekblad*, **1**, 324 (1904); M. F. Pisani, *Compt. rend.*, **162**, 791 (1916); F. A. Gooch and M. Kobayashi, *Am. J. Sci.*, **45**, 370 (1918).

[45] A. F. Köhl, thesis 446, Technische Hochschule, Zurich (1926), and W. D. Treadwell and A. F. Köhl, *Helv. Chim. Acta*, **9**, 470 (1926).

as 0.1 g of fluorine per liter may escape detection entirely.[46] Organic fluorine compounds can be quantitatively analyzed for fluorine by determining the loss in weight of a tared Pyrex flask caused by the etching action of the generated hydrofluoric acid. The sample is completely destroyed by heating with small amounts of potassium nitrate in sulfuric acid solution.[47]

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[46] According to L. Domange [*Compt. rend.*, 213, 31 (1941)], precipitation of fluorine as bismuth fluoride, BiF_3, offers certain advantages in that it has a high molecular weight, is stable in aqueous solution, is less soluble than CaF_2, and is easy to filter and wash.

[47] Dirk H. Brauns, *J. Research NBS*, 27, 105 (1941).

Chapter 49

BORON

Boron, usually as a constituent of tourmaline, is most apt to occur in highly siliceous rocks and is common in many contact-metamorphic schists. It is also an essential constituent of several other silicates, notably datolite. Its compounds are obtained commercially from borates, such as borax, ulexite, and colemanite, or from the native orthoboric acid, sassolite, which is found in the waters of certain volcanic springs. Some alkaline lakes or lagoons, especially in California and Tibet, yield boron in large quantities.[1]

No doubt boron occurs occasionally in rocks in amounts superior to those of some of the other constituents that are habitually determined. But the lack of accuracy of the methods that are at all applicable to mineral substances not directly soluble in acids, other than hydrofluoric acid, is accountable for the fact that no one has ever sought to apply these methods to rocks, unless boron was supposed to be present in appreciable amount.

I. GENERAL CONSIDERATIONS

The detection of very small amounts of boron in rocks is not a simple test. E. T. Wherry and W. H. Chapin[2] found the limit of sensibility of the direct flame test to be 0.2 per cent. The test is made by mixing the mineral powder with potassium bisulfate and calcium fluoride and introducing it on a clean platinum wire into the nonluminous Bunsen burner flame. A green color imparted to the flame, appearing only as evanescent flashes toward the lower limit of sensitiveness, is indicative of boron if no other elements are present that might give a green color.

Applied to distillates as obtained in Section IV, the color imparted to the flame of burning alcohol by its boric ester affords a much more delicate test, as shown by C. Mannich and H. Priess,[3] V. Lenher and J. S. C. Wells,[4] and others. Barium interferes in a direct test with alcohol and acid.[5]

The turmeric paper test as carried out by W. H. Low[6] gave Wherry

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[1] F. W. Clarke, The Data of Geochemistry, *U. S. Geol. Survey Bull.* 770, 14 (1924).

[2] *J. Am. Chem. Soc.*, 30, 1684 (1908).

[3] *Chem. Ztg.*, 32, 314 (1908).

[4] *J. Am. Chem. Soc.*, 21, 417 (1899).

[5] F. Krauss, *Chem. Ztg.*, 51, 38 (1927).

[6] *Ibid.*, 28, 807 (1906).

and Chapin a distinct positive test for boron in a mineral carrying 0.08 per cent B_2O_3. Low's procedure is as follows: In the boric solution acidified with hydrochloric acid and contained in a shallow dish (not glass of the borosilicate type) is placed a piece of turmeric paper. The solution is then evaporated to complete dryness in a desiccator. Boron imparts a pinkish-red color to the paper if no interfering element, such as titanium or too much hydrochloric acid, is present. The test is not applicable directly to the solution of a mineral, but only to distillates obtained as described in Section IV.

The turmeric test is the most delicate of all when made with the precautions taken by G. Bertrand and H. Agulhon,[7] for which reference must be made to the original publications. These authors applied the tests for amounts of boric oxide ranging from 0.1 down to 0.0005 mg. Specially prepared reagents must be used. E. T. Allen and E. G. Zies[8] used the method with success. The basis of the test is the length of coloration imparted to small strips of turmeric paper dipping into like volumes of the test solution and of several standard solutions contained in small graduates. The solutions drawn up by capillarity evaporate at the exposed ends of the strips, and after some hours these appear colored for different lengths according to the amounts of boron present in the different solutions. With a sufficient number of standard solutions, the test yields fairly accurate quantitative results. Application of ammonia turns the color blue.

Cassal and Gerrans[9] maintained that (1) the intense magenta-red color obtained with curcumin provides a more delicate test than does turmeric; (2) the color is permanent for at least 10 hours; (3) the coloring matter is soluble in alcohol and ether without alteration; and (4) an intense blue color is obtained on treatment with alkali. The test in materials such as milk or other food products is usually made on the ash as follows: Treat the ash with a few drops of (1) dilute hydrochloric acid, (2) a saturated solution of oxalic acid, and (3) an alcoholic solution of curcumin. Dry on the water bath, and take up in a little alcohol. If the amount of boric acid is very small, the sample should be made alkaline with a solution of barium hydroxide before evaporation and incineration. Caustic soda or potash and large amounts of sodium or potassium salts are objectionable.

Boron causes trouble in the course of an ordinary analysis. In the first place, it is likely to accompany silica, and, when this occurs, it is volatilized by the hydrofluoric acid treatment and causes high results for silicon. It also interferes in precipitations of iron or aluminum by ammonium hydroxide, for it cannot be entirely removed by as many as three precipitations.

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[7] *Compt. rend.*, **157**, 1433 (1913); *Bull. soc. chim.*, [4] **7**, 90, 125 (1910); **13**, 396 (1913).

[8] *J. Am. Ceram. Soc.*, **1**, 739 (1918).

[9] C. E. Cassal and H. Gerrans, *Chem. News*, **87**, 27 (1903).

The boron that remains is weighed with the ammonia precipitate and is finally reported as aluminum. So far as we know, moderate amounts of boron, as for example a 5 per cent solution of boric acid, cause no difficulties in the determination of calcium or magnesium.

II. DECOMPOSITION OF MINERALS

Care must be exercised in the preparation of solutions for the determination of boron; otherwise appreciable losses may occur in such operations as evaporation, drying, ignition, and, under certain conditions, fusion with alkali carbonate. The losses that can occur during evaporation of solutions containing free boric acid are illustrated by experiments carried out by Tchijewski,[10] who found that two solutions containing 0.603 and 0.0095 g of B_2O_3 lost 0.0522 and 0.0071 g of B_2O_3, respectively, when evaporated to dryness on a water bath. He also noted considerable losses of boron when the dry acid was heated to prepare the oxide.

There seems to be some question as to the volatility of borax when heated at moderate temperatures. I. M. Kolthoff[11] was unable to detect any loss as a result of heating borax for 2 hours at 800° C in an electric oven. H. V. A. Briscoe and P. L. Robinson,[12] on the other hand, asserted that borax loses sodium oxide when fused for several hours at 700 to 800° C in an electrically heated silica muffle. S. Waldbott[13] stated that borax is lost as such when it is heated over the blast lamp, and V. Dimbleby and W. E. S. Turner[14] found that boron is volatilized during sodium carbonate fusions of glasses containing more than 10 per cent of boric oxide. To overcome this difficulty, they recommend the use of a small sample and the addition of pure silica before fusing.

Allen and Zies,[8] in tests of Chapin's method (IV, A) as applied to material containing no fluorine, found no appreciable contamination of the solution by boron as a result of operations in a borosilicate (Jena) glass. Nevertheless, all operations had better be carried out in platinum or quartz if very small amounts of boron are in question or extreme accuracy is sought. In all cases the reagents must be carefully tested, for the amount of boron present may be appreciable, as was shown by Allen and Zies, who found 0.6 mg of B_2O_3 in the reagents entering into a single test.

If the mineral is not soluble in hydrochloric acid, it can be fused with sodium carbonate alone or with potassium carbonate, and then dissolved

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[10] P. Tchijewski, *Arch. Phys. Nat.*, [3] 12, 120 (1884).

[11] *J. Am. Chem. Soc.*, 48, 1449 (1926).

[12] *Nature*, 118, 374 (1926); see also the same authors with G. E. Stephenson, *J. Chem. Soc.*, 127, 150 (1925).

[13] *J. Am. Chem. Soc.*, 16, 410 (1894).

[14] *J. Soc. Glass Technol.*, 7, 76 (1923).

in hydrochloric acid at 15 to 30° C. In this event it is convenient to weigh the flux to within a milligram, so that the proper amount of acid to use in the solution of the melt can be determined in advance.[15]

Jannasch and Noll[16] carried out the preliminary decomposition by first fusing 2 g of anhydrous Na_2HPO_4 and 1 g of HPO_3 in a platinum crucible, then adding 0.5 g of the finely powdered mineral, and slowly heating until the whole mixture is in complete fusion. If necessary, the covered crucible can be heated for a few minutes over a blast lamp. The tightly covered crucible is then partly immersed, while still hot, in ice water, and the loosened cake transferred to the distillation flask (see Section IV). Any substance adhering to the crucible is removed by heating with syrupy phosphoric acid; this is added to the flask as well as 10 ml more of phosphoric acid and a few pieces of cracked porcelain. The flask is then connected with the condenser and heated until the water has distilled over and a homogeneous solution is obtained. This is then treated with methyl alcohol, and the boric ester distilled.

For the decomposition of organic compounds containing boron (and fluorine) see under Fluorine (p. 740).

III. METHODS OF SEPARATION

The chief separation of boron, and the one of the greatest interest to the analyst, is that based on the fact that all of the boron is volatilized as methyl borate, $B(OCH_3)_3$, when alkali or alkaline earth borates are acidified, treated with methyl alcohol, and boiled. This reaction serves as well for the isolation of boron prior to its determination as for its removal from solutions in which it is not wanted. The procedure adopted in the first case is indicated in detail under IV, A. Here the prime requisite is the recovery of all of the boron with as little contamination by acid as possible, and the use of a dehydrating agent such as calcium chloride or syrupy phosphoric acid is permissible. Dehydrating agents cannot ordinarily be used when the object is to get rid of the boron. In this case, the solution is evaporated to dryness, the residue treated with 25 ml of absolute methyl alcohol or methyl alcohol saturated with hydrochloric acid gas, and the solution again carefully evaporated to dryness after being covered with a glass. From two to four treatments are necessary to remove all of the boric acid. Imperfect separations of boron are usually obtained if dilute aqueous solutions are employed.

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[15] For the decomposition of certain metals containing boron, as for example steel, consult N. Tschischewski [*Ind. Eng. Chem.*, **18**, 607 (1926)], who recommended attack with dilute sulfuric acid under a reflux condenser, oxidation with 30 per cent H_2O_2, neutralization of most of the acid, electrolysis with a mercury cathode (p. 138), and titration with sodium hydroxide, first in the presence of methyl orange and then phenolphthalein as in Section IV.

[16] P. Jannasch and F. Noll, *J. prakt. Chem.*, **99**, 1 (1919).

Boron can also be volatilized and completely removed from solutions in which it is not wanted by evaporating to dryness with hydrofluoric acid[17] or to fumes with a mixture of sulfuric and hydrofluoric acids.[18]

Aluminum[19] and possibly also iron, titanium, zirconium and the like can be quantitatively separated from boron by precipitating with 8-hydroxyquinoline in ammoniacal solution (p. 125).

IV. METHODS OF DETERMINATION

Most of the methods for the determination of boron are based on its volatilization as methyl borate. In the volumetric method described in A, the volatilized ester is caught and saponified in alkaline solution, the alcohol expelled, and the boric acid finally titrated with a standard solution of sodium hydroxide. In the gravimetric method described in B, the ester is saponified and the boric acid fixed in a weighed amount of lime which is then again weighed. The volumetric method is to be preferred.

A. BY TITRATION WITH SODIUM HYDROXIDE

An aqueous solution of boric acid cannot be titrated directly with a standard solution of sodium hydroxide, for no indicator is known that gives a sufficiently sharp color change at the neutralization point, which occurs at approximately *p*H 11. If, however, polyhydric alcohols are added, as for example glycerine or mannite, compounds of much stronger acid properties are formed, and the titration can be carried out successfully by the use of such indicators as phenolphthalein or α-naphtholphthalein. Mannite gives a somewhat sharper end point than glycerine[20] and is to be preferred for this reason as well as for the fact that it requires no special precautions and does not materially increase the volume of the solution that is to be titrated. Glycerine which is cheaper can be used in ordinary work.

In the usual case, a borate and not boric acid is obtained at the start of the analysis. The first problem, therefore, is to liberate all of the boron as boric acid in a solution containing no other free acid. This is accom-

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[17] For example no residue whatever was left after treating 0.2 g of B_2O_3 with 20 ml of HF in a platinum crucible, evaporating, and igniting gently.

[18] For the separation and determination of small amounts of boron in tungsten, see D. H. Brophy, *J. Am. Chem. Soc.*, 47, 1856 (1925).

[19] G. E. F. Lundell and H. B. Knowles, *Bur. Standards J. Research*, 3, 91 (1929).

[20] J. A. M. Van Liempt, *Z. anorg. u. allgem. Chem.*, **111**, 151 (1920); M. G. Mellon and V. N. Morris, *Ind. Eng. Chem.*, **16**, 123 (1924).

plished by titrating with hydrochloric acid in the presence of an indicator that undergoes a definite color change at a hydrogen ion concentration slightly greater than that of the boric acid solution alone (*p*H 6.5 to 7) and does not cause interference in the final titration through its color. The use of methyl orange and titration to an orange-red color (approximately *p*H 4) answers these requirements quite well. In the method to be described, paranitrophenol (*p*H 7 at the end point chosen) is used as indicator because the first titration is made in methyl alcohol in which methyl orange gives an unsatisfactory end point. This indicator is not insensible to boric acid in high concentrations as was pointed out by Strecker and Kannappel[21] and in such cases will cause low values if the final titration is made with a sodium hydroxide solution, the B_2O_3 titer of which has been obtained by calculation from its sodium hydroxide content. This difficulty, as well as the effect of traces of carbonate in the sodium hydroxide solution, can be overcome by standardizing the solution against portions of pure dry boric oxide that are approximately equal to those sought and are treated exactly as in the method.

No matter what indicators are used, some alkali will be consumed in passing from the first end point to the second in a solution containing no boric acid. For example, Allen and Zies[8] found that 0.08 ml of 0.1 *N* solution, corresponding to 0.3 mg of B_2O_3, was used in passing from the paranitrophenol end point to that of phenolphthalein. This correction is included in the blank test on the reagents which must always be made.

The following method is that perfected by Chapin and the most important references that relate to its development are given in the footnote below.[22]

a. *Reagents.* α. *Paranitrophenol.* One gram dissolved in 75 ml of neutral ethyl alcohol and made up to 100 ml with water.

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[21] W. Strecker and E. Kannappel, Z. *anal. Chem.*, **61**, 378 (1922).

[22] In 1893, R. T. Thomson [*J. Soc. Chem. Ind.*, 12, 432 (1893)] introduced a volumetric method in which boric acid is set free by treating with hydrochloric acid in the presence of methyl orange, and then titrated with sodium hydroxide after the addition of glycerol and of phenolphthalein as indicator. G. W. Sargent [*J. Am. Chem. Soc.*, **21**, 859 (1899)] applied the Thomson method after distilling the boron as the ester and obtained satisfactory results in the analysis of tourmaline. Later M. F. Schaak [*J. Soc. Chem. Ind.*, **23**, 699 (1904)] introduced the modification of passing methyl alcohol vapor through the solution during distillation, whereas W. H. Low [*J. Am. Chem. Soc.*, **28**, 807 (1906)] further improved the method by adding anhydrous calcium chloride to the solution of the borate to prevent the hydrolytic action of water on the methyl ester and by performing the final expulsion of carbon dioxide under reduced pressure. Finally W. H. Chapin [*ibid.*, **30**, 1691 (1908)] extended the application of Low's method to the analysis of minerals and showed that the boric ester can be volatilized directly from the acidified solution of the carbonate melt. For a modification of the Chapin method applicable to organic materials containing less than 5 parts of boron per million, see L. V. Wilcox [*Ind. Eng. Chem. Anal. Ed.*, **2**, 358 (1930)].

β. *Phenolphthalein.* One gram dissolved in 100 ml of ethyl alcohol and made up to 200 ml with water.

γ. *Hydrochloric acid, 0.1 normal.* The water should be boiled to remove carbonic acid.

δ. *Dilute hydrochloric acid* (1 + 1). A dropping bulb should be filled with this acid when it is needed in accurate small amounts.

ε. *Sodium hydroxide, "0.5" and "0.1" normal.* These solutions must not be stored in contact with borosilicate glass, and should preferably be free from carbon dioxide (p. 178), and standardized as follows: Fuse pure boric acid in a platinum dish. While still warm, break the melt up, and place the fragments quickly in a weighing tube. Dissolve 1.741 g in 250 ml of hot, recently boiled water, cool, and dilute the solution to 500 ml. This solution is 0.1 *N*, and each milliliter should require approximately 1 ml of the 0.1 *N* solution of sodium hydroxide after a measured appropriate volume of the solution has been treated exactly as in the method to be described.

ζ. *Mannite or glycerol.* The former is to be preferred.

η. *Methyl alcohol.* A good grade of methyl alcohol should be distilled over lime after it has been heated for some hours in contact with the lime under a reflux condenser. The more nearly anhydrous the alcohol is the better. If volatile organic acids are left in the alcohol, high results for boron will of course ensue.

θ. *Calcium chloride.* This should be granular, anhydrous, and free from boron.

b. *Apparatus.* The main setup of the apparatus required is shown in Fig. 30.

PROCEDURE. Use not more than half a gram of mineral powder and not less unless the percentage exceeds 10. When the percentage is high, it is best to so limit the weight of the sample that the amount of B_2O_3 shall not exceed 0.1 g. If a flux is used, it should be weighed to within a milligram or two; then the amount of acid required to take up the melt can be measured out at once, and there is no danger of using too great an excess.

If the mineral is soluble in hydrochloric acid, transfer 1 g of it to the flask *B*, without letting any adhere to the neck, and treat with not more than 5 ml of hydrochloric acid (1 + 1). Heat gently on a water bath until solution is complete.

If the mineral is not soluble, add to it exactly six times its weight of sodium carbonate or of an equimolecular mixture of sodium and potassium carbonates, mix, and fuse in the usual manner. Without removing from the crucible, decompose the melt with 1 + 1 hydrochloric acid in calculated amount added by degrees. While this is being done, the crucible should rest in a casserole, and the lid should be kept in place as much as possible. Toward the end it may be necessary to heat a little, but care should be taken not to boil, for boric acid would be lost with the steam. Pour the solution into the flask *B* and rinse the crucible with a very little water.

Then add pure anhydrous calcium chloride, using about 1 g for each milliliter of solution and running it through a paper funnel to keep the neck of the flask clean. Twirl the flask a little to allow the chloride to take up the water, connect it with the rest of the apparatus, raise the casserole beneath it until the flask rests in the water but does not touch the

bottom, and then begin the distillation of the alcohol from flask *A*, taking care that the open end of the capillary "boiling tube" is free from alcohol and that the U tube attached to the receiver is trapped with water.

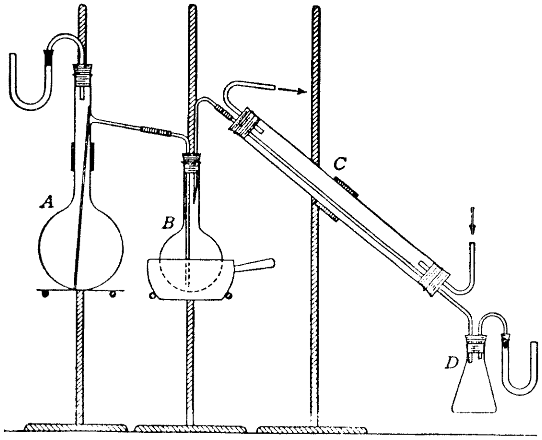

FIG. 30. Distilling apparatus for boron.

- *A*. Flask of 500 ml capacity for methyl alcohol, having a U tube containing a little mercury as a safety trap, and a capillary "boiling tube" 3 mm in bore, the bore closed at 1 cm from the lower end.
- *B*. Flask of 250 ml capacity, supported in a casserole of water but not touching the bottom. The outlet tube of *B* should be not less than 12 cm in vertical height and of rather wide bore. The end inside the flask should be jagged to allow condensed liquid to drop back instead of jumping up the tube.
- *C*. Glass condenser, 40 cm long, of tubing 3 cm wide.
- *D*. Receiving flask of 250 ml capacity. Two or three of these flasks should be at hand, with necks of the same size, so that the receiver can be changed without interrupting the distillation. The small U tube attached contains a little water to prevent the escape of any uncondensed methyl borate.
- *E*. (Not shown.) A second glass condenser like *C*, connected on the one side to a flask exactly like *B*, which, however, has a stopper with only one hole and rests completely within a large bath. The flask carries also a "boiling tube." On the other side is a receiver like *D*, but without the U trap. This apparatus is used for distilling off the alcohol after the preliminary titration.
- *F*. (Not shown.) Filter pump. At the end of the side tube is an elbow tube connected to a rubber stopper with two holes and of a size to fit the flask mentioned in connection with *E*. The second hole of the stopper is closed by a glass plug, which can be withdrawn to break the vacuum. Midway between pump and stopper is a small safety bottle, to prevent the tap water from sucking back into the flask.

The decomposition flask *B* is not heated until about 25 ml of alcohol have condensed in it. After that, the water bath is heated by a small flame and the flask thus kept hot enough to prevent further condensation of alcohol. The distillation should not be so rapid as to permit escape of methyl borate from the system.

When a distillate of about 100 ml has collected, the receiver is exchanged for a fresh one, and the collection of a second distillate is proceeded with. The contents of the trap tube are added to the first receiver, and a preliminary titration is made as follows: Add a drop of paranitrophenol solution, and run in the standard sodium hydroxide until the indicator shows that the free mineral acid is neutralized. Next, add 0.2 ml of the phenolphthalein solution, and continue the titration until the color of that indicator begins to appear. The end point will not be sharp, but the amount of alkali used between the two end points indicates approximately the amount of boric acid in the distillate. If the mineral is likely to contain more than 3 or 4 per cent of B_2O_3, use the 0.5 *N* solution, the object being to keep the distillate as free from water as possible and thus facilitate the dehydration later on.

After completing the titration, add to the distillate twice as much alkali as was used between the two end points, transfer the distillate to the second distilling apparatus, and boil off the alcohol. The addition of the indicated amount of alkali prevents loss of boron by converting unstable $NaBO_2$ to stable Na_3BO_3.

In the meantime the second distillate of 100 ml will have collected. Unless the alcohol contained water or insufficient calcium chloride was used, this second distillate will contain the remainder of the boron.[23] Therefore, before removing the receiver, stop the distillation. Treat the second distillate exactly like the first, and then add it to the first.

If the amount of alkali used for titrating the second distillate is less than 1 ml of the 0.1 *N* solution, the distillation may be regarded as complete.

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[23] In accurate analyses, especially if the amounts of boron and silica are high, the residue in the flask must be filtered off, washed moderately with water, ignited, fused, carried through the method, and the result corrected for the blank on the reagents. The amounts of boron thus recovered in analyses of a 1-g portion of the National Bureau of Standards sample no. 92 (approximately 75% SiO_2 and 0.7% B_2O_3) represented from 0.05 to 0.09 per cent of B_2O_3. One-half gram samples of sample no. 128 (69.51% SiO_2 and 1.52% B_2O_3) and of sample no. 93 (80.60% SiO_2 and 12.76% B_2O_3) yielded recoveries representing from 0.04 to 0.07 per cent of B_2O_8 and 0.06 to 0.08 per cent of B_2O_3, respectively.

When the liquid from which the alcohol is being distilled no longer boils in the steam bath, remove it to a casserole, rinsing the flask once or twice with water, and heat over a direct flame, rotating the casserole while doing so, until the little remaining alcohol has been boiled out. The residue should now be small—about 25 ml if 0.1 *N* alkali was used and much less if 0.5. If the volume is less than 25 ml, make up to that extent.

Return the solution to the flask, and add, drop by drop with constant twirling, hydrochloric acid (1 + 1) from a dropping bulb, until the color of both indicators is discharged, taking care not to add a drop too much. Now put in the "boiling tube," heat the flask in the steam bath for a minute or two, then attach to the filter pump, and boil under reduced pressure until the liquid is nearly cold and only an occasional bubble appears. All carbon dioxide being thus removed, break the vacuum, cool if necessary under the tap, and proceed to the final titration.

First neutralize the excess of hydrochloric acid by running in carefully 0.5 *N* sodium hydroxide until the yellow of paranitrophenol just appears. Bring back to acid reaction with 0.1 *N* hydrochloric acid and then to the appearance of a faint yellow with 0.1 *N* alkali. The solution is now exactly neutral, as the indicator itself shows this color in a neutral solution. Make sure that the end point is reached exactly. One drop of 0.1 *N* acid should discharge the color entirely.

Now add 1 g of mannite,[24] read the burette, and continue titrating to the end point for phenolphthalein. Add another gram of mannite, and, if this causes a disappearance of the end color, add more alkali until it reappears.

The number of milliliters of alkali used corrected for the blank on the reagents and multiplied by its equivalent in terms of B_2O_3 gives the amount of the latter contained in the solution. If the solution of alkali is exactly 0.1 *N*, this equivalent is 0.00348.

The changes of color that take place during the titration need mention. When the mannite (or glycerol) is added to the solution, the yellow color due to the paranitrophenol disappears at once. This is due to the fact that the combination of these reagents with the boric acid forms an acid of sufficient strength to affect the indicators, although boric acid alone does not. As the titration proceeds, the color reappears and grows stronger, becoming very intense just before the phenolphthalein end point appears. The latter will be noticed as a faint brownish tinge, and then another drop

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[24] If glycerin is to be used instead of mannite, add 40 ml of glycerin at this point. Commercial glycerin contains fatty acids and should be treated as follows: For each 500 ml of glycerin add 50 ml of water, then 5 ml of phenolphthalein solution, and finally 0.5 *N* sodium hydroxide until the pink color of the indicator just begins to appear. If the solution becomes colorless on standing, again treat with 0.1 *N* alkali before it is added to the test.

of the 0.1 *N* alkali changes it to an intense brownish red, which is the real end point.[25]

Compared with the time required for gravimetric determinations, that necessary to carry out this method is not excessive. After apparatus and reagents are ready, a series of four determinations may be run easily in 8 hours.[26]

E. T. Allen and E. G. Zies [8] tested the Chapin method very fully in its application to the determination of boron in glasses and regard it as far superior to other methods, even though it is subject to a slight but very uniform correction of 1 mg or less, to be determined by a blank run. The correction seems to be due always in part to a boron content of the reagents used and in part to a titration error. The fact that such correction is unavoidable makes the method of uncertain value for determining the very small amounts of boron that rocks may be presumed to carry, but the constancy of results is so great that a consistent excess found over what the blank affords is strong evidence that boron is actually present.

Allen and Zies also found that the presence of as much as 1 per cent of acetone in the methyl alcohol is not objectionable and that as much as 10 mg of arsenious oxide causes no error if no more than 0.5 ml of hydrochloric acid in excess is present in the distillation flask. Larger amounts of arsenious acid had better be converted to arsenic acid, which is without effect, by oxidizing with hydrogen peroxide after making the solution distinctly alkaline with sodium hydroxide. It was also found that relatively large amounts of fluoride (0.2 g NaF) affect the accuracy of the method but do not seriously impair its usefulness for ordinary work. Chapin found that a smaller amount of fluoride (0.1 g KF) gave no trouble.

B. BY TITRATION WITH SODIUM HYDROXIDE FOLLOWING EXTRACTION

The following method involves a special application of Henry's law—the so-called "partition law," and is based on the titration of the boric acid that can be extracted by ether from an aqueous solution containing boric acid, hydrochloric acid, and alcohol.[27] It is well suited for the routine determination of boron (in the range 0.3 to 16% of B_2O_3) in glass. Silicon, calcium, barium, magnesium, aluminum, sodium, lithium, iron, zinc, lead,

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[25] Strecker and Kannappel (*loc. cit.*) asserted that the end point is sharper if α-naphtholphthalein is used instead of phenolphthalein. In this case the end point tint is green as a result of superimposing the blue color of this indicator on the yellow color of methyl orange or paranitrophenol.

[26] In three tests of the method on synthetic mixtures containing 0.0350 g of B_2O_3 and various other substances, Chapin obtained 0.0348, 0.0351, and 0.0352 g. The precision that can be expected is shown by analyses made by Allen and Zies (*loc. cit.*), who found 26.02, 26.06, and 26.06 per cent of B_2O_3 in a glass relatively high in this constituent, and 0.64, 0.67, and 0.69 in one that was relatively low.

[27] F. W. Glaze and A. N. Finn, *J. Research NBS*, **16**, 421 (1936); **27**, 33 (1941).

and arsenic do not interfere, in the amounts likely to be found in glasses. Fluorine causes low values.

The method as applied in the determination of boric oxide in glass is as follows:

PROCEDURE. Grind 0.5000 g of glass and 1 g of sodium carbonate intimately together in a mortar and transfer to a platinum crucible. Fuse at as low a temperature as possible and only as long as is necessary to effect complete decomposition. Cool, wash the lower surface of the lid, catching the washings in the crucible, and wash down the inside of the crucible with hot water. Disintegrate the melt by warming on the steam bath and stirring with a platinum wire. Concentrate the solution to about 5 ml. Cool, and cautiously neutralize most of the alkali with sulfuric acid (approximately 5.8 *N*), guarding against loss by spattering. Add 2 drops of *p*-nitrophenol,[28] complete the neutralization by adding the acid dropwise, and then add 1 ml of sulfuric acid (approximately 11.6 *N*).

Transfer the contents of the crucible to a calibrated 100-ml glass-stoppered cylinder. Dilute to 25 ml, and add 25 ml of absolute ethanol and 50 ml of ether.[29] Shake intermittently for 20 minutes, and note the final temperature. Allow the layers to separate, record their volumes, and pipette off a 50-ml sample of the ether layer. Transfer to a 250-ml Erlenmeyer flask, add 2 drops of *p*-nitrophenol, and titrate to the *p*-nitrophenol *end point* with 0.5 *N* sodium hydroxide which is free from carbon dioxide and boron, and has been stored in a container free from boron. Read the burette, add 1 ml of phenolphthalein,[30] and continue the titration to the phenolphthalein end point. Add a volume of the 0.5 *N* sodium hydroxide equal to three times that used between the two end points, and shake the flask vigorously. Wash down the inside with water, and bring the water volume to 40 to 50 ml. Boil to expel the ether and ethanol as quickly as

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[28] One gram dissolved in 75 ml of ethanol (95%) and made up to 100 ml with distilled water. According to P. A. Webster and A. K. Lyle [*J. Am. Ceram. Soc.*, 23, 235 (1940)], 1 drop of a 0.04 per cent solution of bromcresol purple can be substituted for *p*-nitrophenol in this and in the subsequent operations. Neutralization is then carried to a blue instead of a yellow color.

[29] The ether must be tested as follows: Mix approximately 50 ml of ether with 5 ml of 0.5 *N* sodium hydroxide and about 50 ml of water, and treat exactly as a sample would be treated for the removal of ether and ethanol. Dilute to 35 ml, and neutralize with 0.5 *N* hydrochloric acid to the *p*-nitrophenol end point. No color should develop if the ether is satisfactory. If a color does develop, cool a supply of the ether, agitate with asbestos impregnated with alkaline permanganate (5 ml of saturated $KMnO_4$ to 15 ml of a 33 per cent solution of NaOH), then slowly siphon in a very fine stream through a column of the impregnated asbestos into a bottle containing the impregnated asbestos, and store in a cool dark place.

[30] One gram dissolved in 100 ml of ethanol (95%) and made up to 200 ml with distilled water.

possible,[31] first on a water or steam bath, and finally over a free flame to remove the last traces of ether and ethanol.

Adjust the volume of 35 to 45 ml by adding water, cool, and then make just acid with 0.5 *N* hydrochloric acid. Warm on a steam bath for about 1 minute, put under reduced pressure to boil and to remove carbon dioxide. Let cool, and titrate to the *p*-nitrophenol end point with 0.1 *N* barium hydroxide. Record the burette reading, add mannitol, and titrate the B_2O_3. One milliliter of 0.1 *N* barium hydroxide is equivalent to 0.00348 g of B_2O_3. Correct as determined by a blank determination made on a glass that is known to be free from boron.

Calculate the percentage of B_2O_3 in a 0.5-g sample by the use of the equation:

$$\text{Percentage of } B_2O_3 = 4(B_2O_3)_{50\mathrm{Et_2O}} \left[V_{\mathrm{Et_2O}} + \frac{V_{\mathrm{H_2O}}}{k} \right]$$

where $(B_2O_3)_{50\mathrm{Et_2O}}$ represents the grams of B_2O_3 found in the 50-ml aliquot portion taken for analysis, and $V_{\mathrm{Et_2O}}$ and $V_{\mathrm{H_2O}}$ are the volumes of the ether layer and the water layer, respectively. The value of k in above is found from the equation[32]

$$k = 0.417 - 0.00232t$$

C. BY WEIGHING AS CALCIUM BORATE

The following method is that perfected by Gooch and Jones. The most important references that relate to its development are given in the footnote below.[33]

The apparatus is shown in Fig. 31 and consists essentially of a retort, paraffin bath, condenser and receiving flask. The retort is made from a 200-ml pipette with tube of at least 0.7 cm inner diameter. The tube is bent at one end to a right angle and at the other to a gooseneck. To the

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[31] Long standing on a water or steam bath yields a colored acid solution which tends to mask the *p*-nitrophenol end point in the final titration.

[32] k represents the ratio of the concentration of boric acid in the ether and in the water layers ($k = C_{\mathrm{Et_2O}}/C_{\mathrm{H_2O}}$), and is affected by temperature and by the amount of flux. It is practically independent of the quantity of B_2O_3 present.

[33] The first quantitative methods based on the saponification of methyl borate and weighing the boric acid after its fixation in alkaline solution were those of F. A. Gooch [*Am. Chem. J.*, **9**, 23 (1887)] and T. Rosenbladt [*Z. anal. Chem.*, **26**, 21 (1887)], which appeared simultaneously. The former used lime for binding the boron; the latter, magnesia. Later Gooch and L. C. Jones [*Am. J. Sci.*, [4] **7**, 34 (1899)] perfected the method. For a useful modification in the way of collecting the ester in ammonium hydroxide before bringing in contact with the lime, see S. L. Penfield and E. S. Sperry, *Am. J. Sci.*, [3] **34**, 222 (1887); also H. Moissan, *Compt. rend.*, **116**, 1087 (1893), and *Bull. soc. chim.*, [3] **11**, 955 (1894), who modifies the Gooch distilling apparatus in certain respects.

former is fused a glass funnel tube fitted with a stopcock. The end of the gooseneck passes through a rubber stopper into the upper end of a condenser, which in turn is connected with a small Erlenmeyer flask by means of a small thistle tube and rubber stopper grooved to permit free passage of air. Lime is used in the flask to retain the boric oxide. Before a determination is started, approximately 1 g of the pure oxide is ignited in the crucible in which the final evaporation of the distillate is to be made, carefully weighed, then transferred to the Erlenmeyer flask, and finally slaked with a little water. The crucible with any lime adhering to it is placed in a desiccator and reserved.

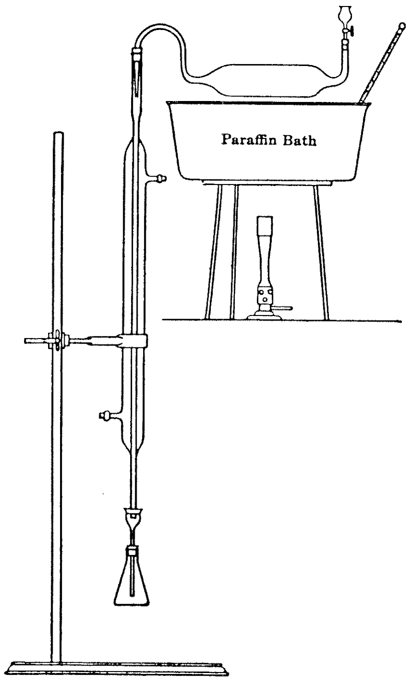

FIG. 31. Gooch apparatus for the distillation of boron.

For the determination of boron in a mineral, fuse with carbonate as in A, extract the melt with water, and evaporate to small volume. Render the solution faintly acid with hydrochloric acid, then just alkaline with sodium hydroxide, and finally acid to litmus by the addition of acetic acid. Transfer the solution to the retort through a funnel tube, taking care not to fill the bulb more than half full. Close the stopcock, and start water through the condenser. Heat the paraffin bath to 130 to 140° C, and carefully lower the retort, keeping it inclined so that only the rear end is at first submerged in the paraffin and no sudden expulsion of liquid into the gooseneck can take place. Finally completely submerge the retort, and heat until all of the liquid has passed to the distillate. Raise the retort, cool, and drench the dry residue with 10 ml of methyl alcohol (free from acetone and preferably absolute). Again submerge the retort carefully and heat till the alcohol is distilled. Repeat this treatment three times. Moisten the residue with 2 to 3 ml of water, and discharge the blue color of the litmus (caused by the hydrolytic decomposition of the acetate) by the addition of a drop or two of acetic acid. Repeat the treatment with methyl alcohol three times, and raise the retort so that it will not be broken when the paraffin solidifies. Remove the Erlenmeyer flask, stopper, shake thoroughly, and let stand 1 to 2 hours. Transfer the liquid as completely as possible to a 200-ml platinum dish, and let the alcohol evaporate slowly below its

boiling point, so as to avoid mechanical loss of the solution. When the alcohol has been expelled, heat the dish carefully over a free flame, and finally ignite gently to destroy the calcium acetate that is always present. Cool, and transfer the residue by means of a little water to the crucible in which it was originally weighed. Remove any material clinging to the Erlenmeyer flask or the platinum dish by the use of a little nitric acid, and wash into the crucible. Evaporate the contents of the crucible to dryness on the water bath, and then, with the cover on, ignite at first gently and finally more strongly until the weight remains constant. The increase in weight represents the amount of B_2O_3.[34]

D. OTHER METHODS

Wherry's method,[35] as modified by Sullivan and Taylor,[36] is suited for routine control but not for accurate analyses because of the retention of boric acid in the residues. As applied to the analysis of glass the procedure is as follows: Fuse 0.5 g of glass with 3 g of sodium carbonate for 1 to 2 minutes after the mass is liquid. Decompose the melt with 20 to 30 ml of hot water, filter, and wash the residue. Transfer the filtrate and washings to a 250-ml, round-bottomed flask, add about 7 ml of hydrochloric acid, heat nearly to boiling, and add dry precipitated calcium carbonate in moderate excess. Connect with a return condenser, boil vigorously for about 10 minutes, filter by suction through a small Büchner funnel, and wash several times with hot water. Keep the volume below 100 ml. Return the filtrate to the flask, add a pinch of calcium carbonate, heat to boiling, connect with a filter pump through a splash trap, remove the flame, and continue the suction until boiling has nearly ceased. Cool to room temperature, filter if the residue has a red color, add 4 or 5 drops of phenolphthalein, and run in slowly 0.1 *N* sodium hydroxide solution until the liquid is pink in color. Add 1 g of mannite, shake, continue the titration to a pink color, add another gram of mannite and, if necessary, more alkali until a permanent pink color is obtained.

Boric acid can also be determined rapidly and accurately by potentiometric titration[37] if the acid has been quantitatively separated from such

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[34] The precision that can be expected in this method is shown by the following results obtained by Gooch and Adams:

B_2O_3 Taken, g	B_2O_3 Found, g
0.2065	0.2062
0.2067	0.2070
0.2077	0.2075
0.1791	0.1795

[35] E. T. Wherry and W. H. Chapin, *J. Am. Chem. Soc.*, **30**, 1687 (1908).

[36] E. C. Sullivan and W. C. Taylor, *J. Ind. Eng. Chem.*, **6**, 897 (1914).

[37] J. H. Hildebrand, *J. Am. Chem. Soc.*, **35**, 861 (1913).

substances as would interfere in the titration with alkali. Interesting titration methods in which an acidified carbon dioxide-free solution of a borate is titrated to a given *p*H, treated with mannitol, and again titrated to the same *p*H have been described. The titration can be followed potentiometrically [38] or colorimetrically.[39] In the former, titrations are carried to about *p*H 7.3; in the latter, phenol red is used as indicator and titrations are carried to about 7.6. Such methods are based on the extraordinary difference between the strength of boric acid by itself and the acid that boric acid forms when treated with mannitol. The former is so weak that its salts are almost completely hydrolyzed at *p*H values as high as 7.3, whereas the latter yields salts that are stable. The error introduced by the partial neutralization of boric acid at *p*H 7.3 (about 12%) can be taken care of by standardizing the alkaline solution against similar amounts of boric acid carried through the procedure. It is, of course, necessary that the solution should not be highly buffered or contain bases or other acids that are affected by mannitol. These conditions are met by most natural waters and soil extracts. The behavior of fluorides or considerable amounts of silica or phosphates has not been studied.

For the detection and colorimetric determination of the small amounts of boron found in soils and plants, K. C. Berger and E. Truog [40] make use of the color, pink changing to a bluish hue, which boron yields with quinalizarin in a solution containing 93 per cent (by weight) of sulfuric acid. Under proper conditions as little as 0.0001 mg of boron can be detected. Fluorides, germanium, nitrates, ferricyanides, and other oxidizing agents interfere.[41]

For the determination of small amounts of boron in plant material, K. L. Robinson [42] uses ortho-phosphoric acid as a dehydrating agent in the methyl alcohol distillation and estimates the boron in the distillate by the color developed with turmeric extract. All reagents must be of low-boron content, and all parts of the apparatus or equipment that come in contact with solutions or the distillate must be of quartz or boron-free glass. The determination is made essentially as follows:

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[38] L. V. Wilcox, *Ind. Eng. Chem. Anal. Ed.*, **4**, 38 (1932); **12**, 341 (1940).

[39] F. J. Foote, *ibid.*, **4**, 39 (1932).

[40] *Ind. Eng. Chem. Anal. Ed.*, **11**, 540 (1939).

[41] Alizarin-S gives a color that can be matched more easily than the quinalizarin color [D. Dickinson, *Analyst*, **68**, 106 (1943)].

[42] K. L. Robinson, *Analyst*, **64**, 324 (1939); see also J. A. Naftel, *Ind. Eng. Chem. Anal. Ed.*, **11**, 407 (1939). The distillation-titration method for the determination of boron in steel and cast iron is described by J. L. Hague and H. A. Bright [*J. Research NBS*, **21**, 125 (1938)].

(*a*) Place 10 ml of the diluted distillate in a 3-inch porcelain dish, and add 5 ml of 0.1 *N* calcium hydroxide suspension.[43] If the boron content is known to be high, less distillate may be used; if the boron content is low, a larger aliquot may be taken. The contents of the dish must be alkaline; if not, sufficient calcium hydroxide suspension must be added to make the solution alkaline. Evaporate to complete dryness on a steam bath. Remove from the steam bath, and cool to room temperature. Add 1 ml of freshly prepared oxalic acid reagent.[44] Manipulate the dish so as to bring the oxalic acid reagent into contact with all the residue in the dish. Then add 2 ml of turmeric extract,[45] and twirl the dish to mix thoroughly. Place in a water bath or a constant-temperature bath which is kept at 55° C ± 3° C until just dry; then dry for 30 minutes longer. The heating period is rather critical, and the 30 minutes must not be exceeded. Remove from the bath, cool, and add about 5 ml of ethyl alcohol (95%) from a wash bottle. Stir the residue with a rubber-tipped stirring rod, and transfer the alcoholic solution to a 15-ml centrifuge tube. Rinse the dish with ethyl alcohol (95%), and transfer the washings to the centrifuge tube. Centrifuge for about 10 minutes at 1700 rpm. Pour the clear liquid into a 25-ml graduate, and fill to the mark with ethyl alcohol (95%), and mix.

(*b*) The transmittancy of the test solution may be measured conveniently with a Fisher Electrophotometer using a 525 mμ filter or with a Coleman spectrophotometer at 540 mμ. First set the instrument at 100 per cent transmission on a solution obtained by carrying 5 ml of $Ca(OH)_2$ suspension through all the steps described in *a*. Then measure the transmittancy of the test solution, and calculate the boron content from a transmittancy-concentration curve prepared from measurements made on solutions obtained by carrying varying amounts of standard boric acid solution,[46] (0.5 μg to 2 μg) through all steps described in *a*. Correct the amount of boron found by a blank carried through all steps of the procedure.

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[43] Grind a boron-free (high-grade) calcium oxide, conveniently made from boron-free or low-boron calcium, in an agate mortar. Add 2.8 g to 1 liter of distilled water. Store in a boron-free container.

[44] Oxalic acid reagent. Mix 20 ml HCl (sp. gr. 1.18) and 80 ml of a 20 per cent solution of oxalic acid. (If the oxalic acid has crystallized, warm the solution until the crystals are dissolved. Prepare the reagent each day just before using.)

[45] Turmeric extract. Prepare a 1 per cent turmeric extract in 95 per cent ethyl alcohol by placing 1 g of turmeric powder in a boron-free flask, adding 100-ml ethyl alcohol (95%), and stirring 2 to 3 hours with a quartz or Corning no. 728 glass rod. Filter, and preserve in a stoppered boron-free container.

[46] Standard solution of boric acid (1 ml = 2 μg of boron). Transfer 5.72 mg of boric acid to a 500-ml volumetric flask, dilute to the mark with previously boiled water, mix, and store in a boron-free container.

Chapter 50

CARBON AND HYDROGEN

In the mineral kingdom, carbon is found crystallized as graphite and diamond, amorphous in coal, and as hydrocarbons in natural gas, petroleum, and bitumen. Carbon dioxide is a normal constituent of atmospheric air. Carbonic acid and carbonates exist in most natural waters, and great rock masses are composed of carbonates of calcium, magnesium, and iron. Carbon is found in a few silicates, but of these cancrinite is the only species having petrographic importance.

Hydrogen occurs almost everywhere in nature. The free gas is present in very minute amounts in the atmosphere and in certain granite and other rocks.[1] In a majority of all mineral species, and therefore in practically all rocks, it is found either as nonessential hydrogen, as for example absorbed moisture, or essential hydrogen, such as that present as hydroxyl (see under Water, Part III, p. 814). All organic matter contains hydrogen, and hence it is an essential constituent of such derived substances as natural gas, petroleum, asphaltum, and coal.

I. GENERAL CONSIDERATIONS

The following discussion has to do with the general phases of the determination of carbon and hydrogen, especially as applied to rocks. For the determination of these elements in special cases, as for example carbon in steel, other texts must be consulted.[2]

Carbonates or carbonaceous matter do not cause serious difficulties in ordinary analyses, though of course carbon dioxide must be excluded in certain determinations such as the precipitation of iron by ammonia in a solution of limestone. Provision must occasionally also be made for carbonaceous matter, as by roasting before fusing with sodium carbonate or employing an oxidizing flux in dry attacks, or by fuming with nitric and sulfuric acids or oxidizing with permanganate in wet attacks. Carbonaceous matter also causes trouble in analyses of certain materials containing elements in their lower valencies, as for example the determination of bivalent iron in carbonate rocks (p. 907).

Free hydrogen occurs in such small amounts in rocks that it does not cause significant errors in the determination of water. That which occurs as water of crystallization or combined as hydroxyl is of importance as regards its behavior during the preparation of the sample before analysis (see Part III, p. 816). Hydrogen that occurs in organic matter is involved with the latter in its effect on the determination of elements, such as iron, in their lower valencies.

II. ATTACK OF CARBONACEOUS MATERIAL

In the usual case, carbon that is present as carbonate is determined by attack with dilute hydrochloric acid as in IV, A, whereas total carbon is found by direct combustion as in IV, B. In special cases, other methods of attack may be desirable, as for example the preliminary separation of carbon in steel by solution of the latter in copper potassium chloride, or the direct combustion of carbon in aluminum by attack with sulfuric and chromic acids as in IV, C. For determinations of constituents such as halides, sulfur, phosphorus, and nitrogen in organic materials, samples can be oxidized by the action of fuming nitric acid at high temperatures and pressures in sealed glass tubes.[3]

In analyses of inorganic materials, the hydrogen that is present in nonessential water or in volatile organic matter is usually driven off at some temperature between 100 and 110° C for the purpose of reporting it as "moisture" or of starting the analyses with the material in a definite condition.[4] That which remains as essential water or nonvolatile organic matter is then usually driven off by heating at higher temperatures and included in the result reported for "Loss on Ignition."

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[1] A. Gautier, *Compt. rend.*, **131**, 647, 1276 (1900); **132**, 58 (1901); *Ann. chim. phys.*, [7] **22**, 5 (1901); F. W. Clarke, The Data of Geochemistry, *U. S. Geol. Survey Bull.* **770**, 17, 48 (1924).

[2] For example, Hans Meyer, *Analyse und Konstitutionsermittelung organischer Verbindungen*, Julius Springer, Berlin; Houben and Weyl, *Die Methoden der organischen Chemie*, Georg. Thieme, Leipzig; L. Gattermann and W. B. Schober, *Practical Methods of Organic Chemistry*, Macmillan Co., New York; G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, *Chemical Analysis of Iron and Steel*, John Wiley & Sons, N. Y. (1931); *ASTM Methods of Chemical Analysis of Metals*, American Society for Testing Materials (1950); and *ASTM Spec. D 271–48*, Laboratory Sampling and Analysis of Coal and Coke, ASTM Standards, Part 5, p. 583 (1949).

[3] L. Carius and J. Houben, *Die Methoden der organische Chemie*, Vol. I, pp. 59–63, Georg. Thieme, Leipzig (1925). For modifications of the method designed to minimize danger of explosions, consult C. L. Gordon, *J. Research NBS*, **30**, 107 (1943), and L. A. Greenberg, *Ind. Eng. Chem. Anal. Ed.*, **16**, 308 (1944).

[4] With materials containing essential hydrogen present as hydroxyl, it may be difficult to obtain a definite condition at 110° C. For example, in the standardization of a sample of bauxite it was necessary to dry portions of the sample for 2 hours at 140° C in order to reproduce samples consistently for analysis, whereas with pyrolusite a temperature of 120° C was necessary.

III. METHODS OF SEPARATION

Separations of organic matter are not usually necessary and are confined to special cases such as the separation of organic matter in shale as described in Part III (p. 935).

IV. METHODS OF DETERMINATION

A. DETERMINATION OF CARBON PRESENT AS CARBONATE

The determination of carbon that is present as carbonate is done best by liberating the carbon dioxide through attack by acid and absorbing it in soda asbestos. Hydrochloric acid is preferable for the solution of the material, in spite of its volatility, because of the solubility of chlorides. In special cases, the use of dilute perchloric acid might be desirable. The carbon dioxide that is liberated must be freed from other gases that are absorbed by soda asbestos, it must be quantitatively driven into the absorbent by a current of air that has been freed from carbon dioxide, and the unabsorbed gas must not undergo a permanent change in moisture content. These requirements are met sufficiently well for most purposes by the arrangement shown in Fig. 32.

In this chain, use is made of a small condenser to condense most of the water and hydrochloric acid, followed by (1) a tube containing sulfuric acid to bear the brunt of the dehydration; (2) a tube containing anhydrous copper sulfate to remove hydrochloric acid, chlorine, and hydrogen sulfide; (3) a tube containing the final desiccant, say, $Mg(ClO_4)_2 \cdot 3H_2O$; (4) the CO_2-absorption tube containing soda asbestos and the desiccant used in 3; and (5) a second weighed CO_2 absorption tube to act as a guard and to indicate when tube 4 is beginning to fail. It should be noted that the end of the separatory funnel in *E* is bent upward to prevent escape of bubbles of carbon dioxide through the tube. The seals are all made with mercury as shown. With such seals, pressure is better than suction for drawing the gases through the train. Other absorbents can be substituted, as for example a solution of silver arsenite (Reagents, p. 46) for the copper sulfate, and anhydrone for the magnesium perchlorate trihydrate. For liquid absorbents, tubes of the type pictured in Fig. 33 permit easy removal of the exhausted solution and refilling.

PROCEDURE. Transfer 1 to 5 g of the sample to the flask, and cover with water. Insert the stopper carrying the separatory funnel and condenser, and connect the latter with *D*, *C*, and *B*. Pass air that is free from carbon dioxide through the system until it is judged that all carbon dioxide has been removed. Close the stopcock in the separatory funnel, and insert the weighed bulbs *A* and *A* in the train. Half fill the separatory funnel with dilute hydrochloric acid (1 + 1), replace the stopper carrying the air, and see that there is free passage for gases through the train. Open the stopcock in the separatory funnel and run acid into the flask, slowly if there is much carbon dioxide, rapidly if there is but little. When effervescence diminishes in the former case, at once in the latter, start a flow of water through the condenser, and heat the flask slowly so as to secure steady but quiet ebullition. When it is judged that carbon dioxide has been boiled out of the solution, remove the flame, increase the current of air, and sweep

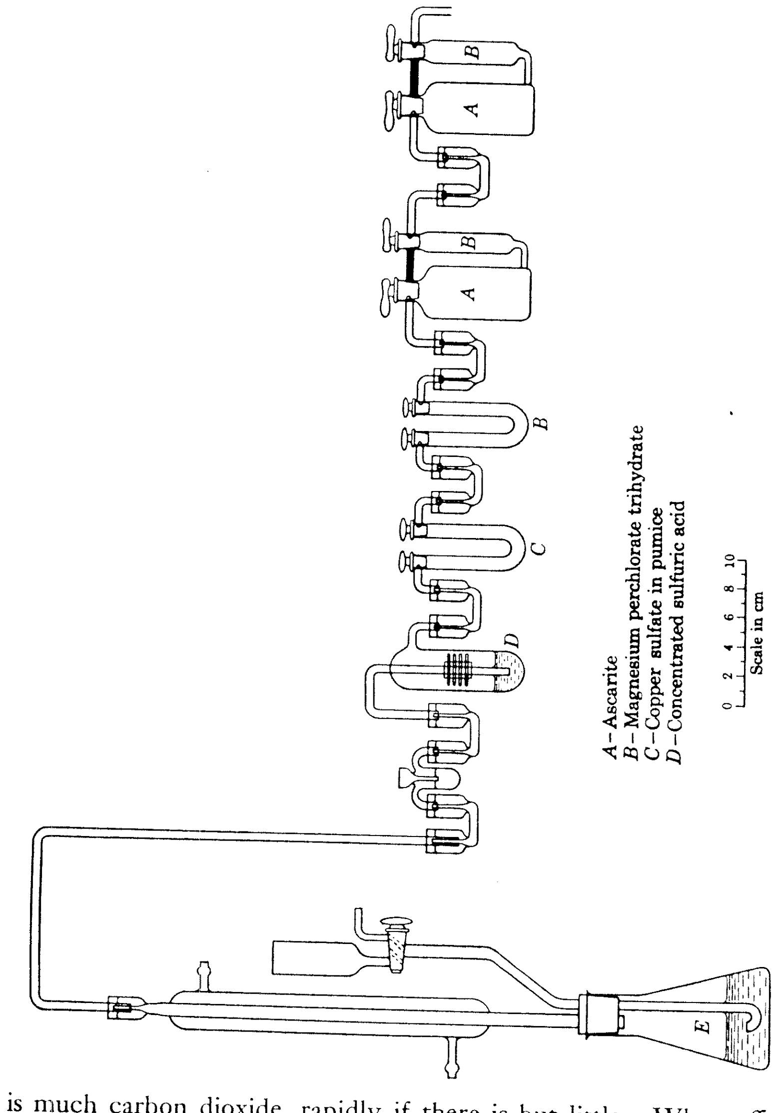

FIG. 32. Absorption train for carbon dioxide. As actually used, the tubes are compactly arranged along the edge of a 6″ x 9″ board which is supported 5″ from the table-top upon a tripod base.

out all carbon dioxide. Disconnect the weighed bulbs, close the inlet and outlet tubes, and place them in the balance case. When cool, open the stopper momentarily, and weigh against a similar tube used as a counterpoise.

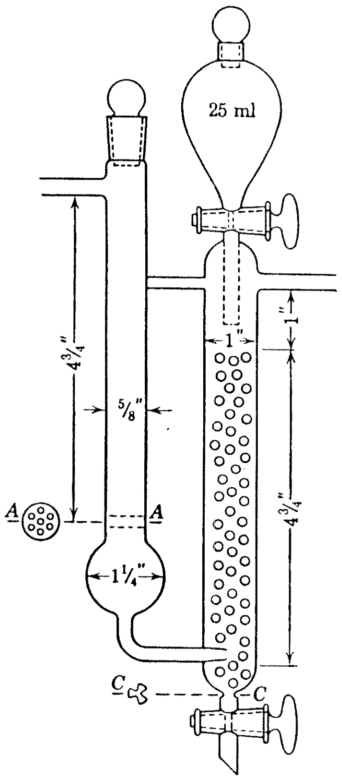

Fig. 33. Absorption bulb for oxides of sulfur.[5]

B. DETERMINATION OF TOTAL CARBON AND HYDROGEN BY DIRECT COMBUSTION

In a determination of total carbon and hydrogen by direct combustion, care must be taken that combustion is complete; that no carbon dioxide is fixed and held in the ash; that no carbon monoxide is unburned; that all of the carbon dioxide and water is driven into the weighed absorbers; that halides, oxides of sulfur and nitrogen, and other compounds than carbon dioxide that would be absorbed by the absorbers are removed; that the moisture content of the gas is the same when it leaves the weighed system as when it entered; and that the air introduced into the apparatus be freed from carbonaceous matter, carbon dioxide, hydrogen, and water.

a. *In Rocks and Minerals.* With rocks and minerals, combustion is facilitated, and sulfur and halides are fixed by fusion with granulated lead chromate.

PROCEDURE. Intimately mix 1 to 5 g of sample with a mixture of 10 parts of ignited and powdered lead chromate and 1 part of potassium chromate. Transfer to a porcelain boat. Place in a combustion tube that is loosely packed with granulated lead chromate as described on page 774, and connect the exit end of the tube with a tube containing magnesium perchlorate trihydrate to dry the gas. Pass purified air through the system until all carbon dioxide is expelled, and then attach a weighed carbon dioxide absorber and guard tube as in A. With a slow current of air passing, heat the lead chromate in the exit end to 300 to 400° C, and then gradually heat that nearest the boat as hot as can be without fusing. Finally heat the section of the tube under the boat at full heat. Shut off the heat when combustion is judged to be complete, and continue the current of air until all carbon dioxide has been swept out of the apparatus. Stopper and remove the weighed absorber, and weigh as in A.

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[5] As used in the determination of carbon in steels by direct combustion in oxygen, the left arm is loosely packed with asbestos, and the right arm contains sulfuric acid that has been saturated with chromium trioxide.

In case nitrogenous compounds are present, a reduced copper spiral must be placed in the exit end of the tube as described on page 775. The heating is at first conducted with the air current shut off until the combustion is practically finished and the reduced copper spiral has been allowed to cool somewhat. Air is then introduced and the combustion finished as in a.[6]

b. *In Organic Compounds.* Methods for the determination of total carbon (and hydrogen) in organic compounds by direct combustion must necessarily vary according to the composition of the material under test and its volatility. Substances that contain halogens, sulfur, or nitrogen require the use of special reagents in the combustion tube, whereas those that volatilize readily must be weighed and heated with special care.

In the simplest case, that of a nonvolatile compound containing carbon, hydrogen, and oxygen, the procedure is as follows:

α. *Preliminary operations.* For a furnace 75 cm long,[7] procure a combustion tube 90 to 95 cm in length, 10 to 15 mm in internal diameter and 2 mm in wall thickness.[8] Prepare three compact copper-gauze rolls that fit loosely in the tube, two 1 to 2 cm in length, and the other 10 to 15 cm long and provided with a loop to permit easy removal. Hold one of the short rolls 10 cm from one end of the tube (afterwards to be called the exit end), pour in sufficient coarse copper oxide, prepared from copper wire or gauze, to form a 45-cm layer, and then hold it in place with the second small roll.[9] Place the tube in the furnace so that the exit end extends 10 cm outside of the furnace, and insert a one-hole stopper carrying a piece of glass tubing of the same outer diameter as the side arm of the absorption tube for water. The tubing must be flush with the stopper on the inside of the tube and extend 5 cm on the outer side.[10] In the inlet end

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[6] For a discussion of the difficulties that attend a determination of carbon in rocks and minerals, and a description of a wet combustion method based on the use of phosphoric and chromic acids, consult B. E. Dixon, *Analyst*, **59**, 739 (1934). See also C. J. Schollenberger, *J. Ind. Eng. Chem.*, **8**, 1126 (1916).

[7] A three-unit split electric furnace is very convenient, for different sections of the tube can be heated at will, and the progress of the combustion can be easily followed.

[8] For compact, micro and semimicro trains for the determination of carbon and hydrogen in which 2.5 to 70 mg of sample can be burned within 40 to 55 minutes, see S. Natelson, S. S. Brodie, and E. B. Conner, *Ind. Eng. Chem. Anal. Ed.*, **10**, 276, 609 (1938).

[9] The copper oxide must be free from the chlorides of copper, the alkalies, and alkaline earths.

[10] It is desirable to draw out the end of the exit tube to permit direct attachment of the absorption tube, if the analyst is sufficiently skilled to do this without spoiling the tube or making the walls of the drawn out portion too thin. For the use of metal combustion tubes, copper for carbon and hydrogen, and nickel for nitrogen determinations, see S. Avery and D. Hayman, *Ind. Eng. Chem. Anal. Ed.*, **2**, 336 (1930).

of the tube, insert another stopper carrying a tube with a glass stopcock. Protect the stoppers by slipping asbestos plates with a circular hole in the center along the tube until they rest against the ends of the furnace. To prevent overheating during the combustion, the stoppers can be cooled by strips of wet cloth wound around the ends of the tube and kept saturated by letting the ends dip into water placed directly underneath.

Next prepare the tubes for the absorption of water and carbon dioxide and also the purifying and guard tubes. For the absorption of water, magnesium perchlorate trihydrate, phosphorus pentoxide, or sulfuric acid (p. 46), can be used in any glass tube that is light, permits good contact with the gases, and can be closed to the air when it is detached from the absorption chain. To spare the absorbent, it is desirable that the tube have an empty bulb in the side next the furnace, in which most of the water can be condensed. For carbon dioxide, soda asbestos (p. 45) is the most satisfactory absorbent, and it can be used, together with magnesium perchlorate trihydrate or phosphorus pentoxide in a tube such as is shown in Fig. 32 (p. 769), or in special tubes such as the modified Fleming. The purifiers must contain the same absorbents, and of course in the same order as the absorption chain. To spare these as much as possible, they may be preceded by less efficient and cheaper reagents, as for example strong potassium hydroxide solution (p. 44), before the soda asbestos, and calcium chloride before magnesium perchlorate trihydrate. If oxygen is used or there is any possibility that the air contains hydrocarbons (as from a compressor), the gas should be passed through a tube containing copper oxide heated to approximately 700° C in a small furnace before it enters the purifiers. A guard tube at the end of the weighed absorbing tubes is not necessary except in most accurate work or in very slow or long-continued combustions. In such cases a glass-stoppered U tube containing magnesium perchlorate trihydrate at the inlet and soda asbestos at the outlet end is satisfactory.

To prepare the combustion tube and contents for a determination, insert the long copper roll as far as the copper oxide, connect the inlet end of the tube with the purifiers, pass a slow current of air through, and gradually heat to dull redness. Drive off any water collected in the exit end by brushing the tube with a small blue flame, shut off the heat except under the exit end of the copper oxide, and let the forward part of the tube cool. While the tube is being heated and cooled, weigh the tubes that are to be used for the absorption of water and carbon dioxide. These should be weighed against like tubes used as tares, and, of course, after they have been filled with the gas that is to be used in the combustion and have cooled to the temperature of the balance.

If the substance is solid and nonvolatile, weigh 0.15 to 0.3 g in a porcelain, quartz, or platinum boat that has been previously heated strongly, cooled in a desiccator, and weighed. If it is likely to burn with extreme difficulty, mix it with 100- to 200-mesh copper oxide that has been ignited and cooled in a desiccator.[11]

β. The combustion. When the inlet end of the combustion tube is cool, withdraw the long copper roll by means of a hooked wire, and take care to prevent contamination during its removal. Insert the boat and contents as far as the coarse copper oxide, and then the copper roll to within 1 cm of the boat (see Fig. 34). Immediately connect the tube with the purifiers and with the weighed absorbents and guard tube. All connections must be made end to end by means of thick-walled seamless rubber tubing that fits tightly.[12] Start a slow current of air, 1 to 2 bubbles per second, through the apparatus, and increase the heat at the exit end so that the copper oxide is heated at about 600° C while the section of tube covering the boat is still quite cool. Gradually advance the heat toward the boat, and at the same time start heating the section of tube at the inlet end. This is the most difficult part of the analysis. No volatilization or combustion should take place until the copper oxide in the exit end is red hot, and at no time must combustion be very rapid. The part of the tube under the boat is now gradually heated to 600 to 800° C and oxygen admitted if it seems that combustion will be extremely slow or incomplete. When combustion is finished, turn off the source of heat, and drive over into the absorption tube any water that has condensed in the exit end of the tube or in the connecting tube, by brushing the tubes with a small blue flame. Continue the current of air or oxygen until it is judged that all water and carbon dioxide have been swept into the absorption tubes and these have been

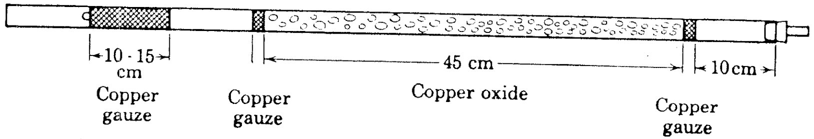

FIG. 34. Tube for the combustion of compounds containing carbon, hydrogen, and oxygen.

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[11] J. Meyer and H. Tischbierek [*Z. anal. Chem.*, **80**, 241 (1930)] state that admixture with vanadium pentoxide aids in the burning of difficultly combustible carbon-bearing substances. Powdered metallic copper or freshly prepared Pb_3O_4 (free from C or CO_2) serves the same purpose.

[12] For a discussion of an analytical combustion apparatus for accurate determinations, on a macro scale, of carbon and hydrogen in hydrocarbons or in compounds containing carbon, hydrogen, and oxygen, and of the precision and accuracy attained in combustion of a highly purified benzoic acid, see D. D. Wagman and F. D. Rossini, *J. Research NBS*, **32**, 95 (1944), and W. H. Smith, Charles Proffer Saylor, and H. J. Wing, *Bur. Standards J. Research*, **10**, 479 (1933).

filled with the same gas as at the start. Disconnect and stopper the weighed absorbers, cool in the balance case, and weigh against the tares originally used, after opening momentarily to equalize the pressure. The amount of hydrogen is calculated from the increase in weight of the water absorber and the amount of carbon from the increase in weight of the carbon dioxide absorber.

γ. *For substances that volatilize or sublime, greater precautions must be taken.* If the substance is difficultly volatile, it may be weighed in a boat and the section of combustion tube surrounding the boat heated with still greater care. Moderately volatile substances can be weighed in a very small glass-stoppered bottle which is placed in an inclined position in the boat and opened just as the boat is pushed into the tube. Easily volatile liquids must be weighed in small glass bulbs with fine capillary stems. These are cleaned, dried, weighed, and then filled by warming the bulb, immersing the stem in the liquid as it cools, and repeating the operation if insufficient liquid is drawn up. The capillary is then freed from liquid and sealed and the bulb again weighed. Finally, when everything is in readiness, the copper oxide in the exit end red hot, and the inlet end cool, the bulb is inclined in the boat, the stem broken, the boat quickly pushed in the tube, and the roll and stopper immediately inserted. With substances that sublime, care must be taken lest some of it sublime near the stopper at the inlet end. This can be avoided by pushing the boat as far away from this end as possible, heating the section of copper roll nearest the cork as hot as possible before the boat is heated, and using a somewhat more rapid current of air.[13]

δ. *Substances that contain halogens or sulfur.* Substances that contain sulfur or halogens give rise to compounds that are not completely retained by copper oxide at red heat. Substitution of granulated ignited lead chromate for copper oxide leads to satisfactory results, provided the chromate nearest the boat is not heated so hot that it fuses down and that nearest the exit end is not heated over 300 to 400° C. In such determinations, the material should be mixed with finely powdered ignited lead chromate either in a large boat or in the tube itself.[14]

ε. *Substances that contain nitrogen.* Nitrogenous materials give rise to oxides of nitrogen which cause high results for carbon unless they are reduced before they leave the furnace. This is easily done by using a reduced copper roll in the exit end and modifying the charge in the combustion tube and the manner of burning the sample. To make room for the reduced copper roll, the length of the copper oxide layer is shortened from 45 cm to 35 cm, leaving 20-cm open space at the exit end. In this is placed a 10- to 15-cm compact and snugly fitting copper roll which has been made from fine copper gauze and reduced as follows: Put 1 ml of methyl alcohol in a test tube that is large enough to hold the roll, and loosely clamp the tube in an upright position. Grasp the roll with crucible tongs, heat to glowing in a large roaring blast flame, and drop it as quickly as possible into the test tube. As soon as reduction is complete, cover snugly with a small beaker, and, when cool, withdraw and heat gently by passes through a blue flame until dry.

In order to prevent oxidation of the roll, no air is admitted during the first part of the combustion. For this reason it is necessary to mix thoroughly the substance under test with considerable finely powdered and ignited copper oxide.[15] Toward the end of the combustion, the section of tube around the reduced roll can be allowed to cool and the combustion finished in a current of air or oxygen.

C. DETERMINATION OF TOTAL CARBON BY WET COMBUSTION

Oxidation of organic matter by heating with sulfuric and chromic acids[16] is less used now than before compressed oxygen could be so easily obtained. The method, however, finds occasional use in spite of the difficulty in obtaining complete decomposition without undue liberation of sulfur trioxide. An improvement in the process is the use of an electrical pre-

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[13] For a rapid method in which the organic compound is burned in a calorimetric bomb containing compressed oxygen and a known amount of a standard solution of barium hydroxide, consult H. D. Wilde, Jr., and H. L. Lochte, *J. Am. Chem. Soc.*, **47**, 440 (1925). For the absorption of volatile, explosive, or easily carbonizable organic liquids in kieselguhr prior to combustion, see M. G. Sevag, *Ind. Eng. Chem. Anal. Ed.*, **1**, 16 (1929).

[14] According to R. de Roode [*Am. Chem. J.*, **12**, 226 (1890)], a mixture of lead chromate and lead oxide which is quite infusible can be prepared as follows: Make a slurry of finely powdered lead chromate, and then thoroughly mix with one-fourth its weight of red oxide of lead. Transfer the mixture to a filter under slight suction, and draw into a compact mass. While still moist, withdraw pea-sized portions with a spatula, and heat to redness in a porcelain crucible. Cool, break up to the size of wheat grains in a porcelain mortar, and sieve out the fine material which should be crushed still finer for mixing with the sample. Heat both fine and coarse material to 150° C, and cool in a desiccator. Under ordinary conditions, a charge of chromate can be used for three or four combustions. See also E. Beryl and others, *Ber.*, **61b**, 83 (1928).

[15] This can be done in a large copper boat or directly in the open space in front of the column of copper oxide in the tube. The boat is filled as follows: Heat sufficient 200-mesh copper oxide in a porcelain crucible, and cool in a desiccator. Place a small agate mortar on a sheet of black glazed paper, pour in a little oxide, and next the weighed sample, and then cover with more oxide. Mix carefully by stirring without pressure with the pestle. Avoid loss by dusting. Transfer the contents of the mortar to the boat and dry-wash the mortar, pestle, and paper with more copper oxide. If the sample is to be poured directly into the tube, it can be mixed with oxide in a stoppered tube having a neck that will fit in the combustion tube, carefully poured into the tube, and the bottle dry-washed with more oxide.

[16] R. E. Rogers and W. B. Rogers, *Sill. Am. J.*, [2] **6**, 110 (1848); C. Brunner, *Pogg. Ann.*, **95**, 379 (1855).

cipitator as recommended by Oschwald[17] for holding back sulfur trioxide. In this precipitator the gases pass through tubes in which a high tension field is maintained between copper gauze on the outside and a copper wire on the inside, by means of an induction coil. Inasmuch as some carbon monoxide may be formed, it is also desirable to pass the gases through a combustion tube heated at 800 to 900° C and filled with copper oxide. If the precipitator is used, connections must be made by mercury seals instead of rubber because of the ozone. Air is used for washing out the carbon dioxide unless hydrogen is evolved, as in the direct solution of some alloys, when nitrogen must be substituted. As for the rest of the apparatus, a flask of the Corleis type[18] with long neck, ground-in stopper carrying an inner water condenser is preferable, and purifiers and absorbers such as have been listed in the preceding sections must be used as needed.

PROCEDURE. To prepare for the determination, place 60 ml of a 50 per cent solution of chromium trioxide, CrO_3, and 200 ml of dilute sulfuric acid (1 + 1) in the flask, and connect with the purifiers and furnace. Heat the furnace to 800 to 900° C, start the electrical precipitator and the water in the condenser, and boil the solution for 30 minutes as a slow current of air is maintained. Insert the carbon dioxide absorber, continue the boiling and the passage of air for 30 minutes, remove the absorber, cool, and weigh. Again insert in the train, continue the boiling and the passage of air for 2 hours, and again weigh. The gain in weight represents the blank which should not exceed 0.5 mg.

Cool the solution in the flask, insert the absorber in the chain, transfer the sample to the flask, and start water through the condenser and a slow current of air through the apparatus. Heat gradually, and finally boil the solution for at least 1 hour after solution of the sample is complete. Remove the absorber, again weigh, and subtract the blank from the gain in weight.[19]

D. OTHER METHODS FOR THE DETERMINATION OF CARBON

Instead of absorbing carbon dioxide in a dry, weighed absorbent as in A, B, or C, some analysts prefer to absorb the gas in a solution of barium hydroxide and then (1) weigh the washed and ignited barium carbonate,[20]

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[17] F. Oschwald, *Beitr. Bestimmung Kohlenstoffes Aluminum*, Eidgenössischen Technischen Hochschule, Zürich, p. 31 (1923).

[18] E. Corleis, *Stahl u. Eisen*, 14, 581–591 (1894).

[19] For the determination of total carbon in soils by a modification of the method in which a special apparatus is used and carbon is determined by titration after the carbon dioxide has been absorbed in an excess of a standard alkaline solution, see J. E. Adams, *Ind. Eng. Chem. Anal. Ed.*, 6, 277 (1934).

[20] Fresenius-Cohn, *Quantitative Chemical Analysis*, Vol. 1, p. 482, John Wiley & Sons (1904); Chemists U. S. Steel Corp., *Sampling and Analysis of Carbon and Alloy Steels,*

or (2) dissolve the washed carbonate in an excess of standard acid, and titrate with standard alkali in the presence of methyl orange,[21] or (3) determine the barium hydroxide that is left by titration with acid in the presence of phenolphthalein[22] or by measuring the electrical resistance change of the solution in relation to its concentration.[23] In such methods great care must be used to exclude contamination by carbon dioxide from the atmosphere. In the second procedure, it is not necessary to free the carbon dioxide from substances such as sulfur trioxide or hydrochloric acid.

The volumetric determination of carbon dioxide as in gas analysis[24] can seldom be carried out in the analysis of inorganic substances other than gases, because the volume of carbon dioxide obtained is usually very small in comparison with that of the oxygen, air, or nitrogen that is required to collect it.

Determinations of carbon monoxide are seldom required except in tests concerned with safety of atmospheric conditions for breathing by humans or animals. By the use of a silica gel impregnated with a palladium and a molybdenum solution 1 part of carbon monoxide in 500,000,000 parts of

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p. 54, Reinhold Publishing Corp., New York (1938). J. McFarlane and A. W. Gregory [*Chem. News*, 94, 133 (1906)] preferred to convert the carbonate to sulfate after the carbon dioxide has been absorbed in a *cool* ammoniacal solution of barium chloride (50 g of $BaCl_2 \cdot 2H_2O$ and 250 ml of dilute NH_4OH (sp. gr. 0.88, per liter). The reaction yields barium carbamate, $Ba(NH_2CO_2)_2$, which is soluble in moderate concentrations. Partial conversion to the insoluble barium carbonate takes place in concentrated solutions, and complete conversion occurs if the solution is *boiled* for 1 minute. The chief advantages in the use of the solution are that less of it is required because the chloride is more soluble than barium hydroxide, and no special precautions are needed during filtration and washing of the carbonate. When the solution is to be used, it is boiled for 1 minute to precipitate any carbon dioxide already absorbed, filtered through asbestos while still hot, caught in the absorption flask which has been swept free from carbon dioxide, and cooled before absorption is started. When absorption is complete, the current of air free from carbon dioxide is continued and the solution quickly heated to boiling and boiled for 1 minute. It is then cooled and filtered, and the tube, flask, and residue are washed with cold and then with hot water. The small amount of carbon dioxide absorbed from the air during filtration and washing remains in solution. Finally, the residue, together with any precipitate adhering to the tube or flask, is dissolved in hydrochloric acid and the barium precipitated by sulfuric acid (p. 630) as usual.

[21] J. R. Cain, *J. Ind. Eng. Chem.*, 6, 465 (1914); J. R. Cain and L. C. Maxwell, *ibid.*, 10, 520 (1918).

[22] W. Brady, *J. Ind. Eng. Chem.*, 6, 843 (1914); *Methods of the U. S. Steel Corporation, loc. cit.*, p. 56; J. Linder [*Z. anal. Chem.*, 72, 135 (1927)] stated that this method gives slightly high results.

[23] E. L. Bennet, J. H. Harley, and R. M. Fowler, Conductometric Method for Determination of Carbon in Steel, *Anal. Chem.*, 22, 445 (1950); K. Gardner, W. J. Rowland, and H. Thomas, Method for the Estimation of Small Amounts of Carbon in Steel, *Analyst*, 75, 173 (1950).

[24] L. M. Dennis and M. L. Nichols, *Gas Analysis*, Macmillan Co., N. Y. (1929).

air can be detected. The gel can determine physiologically significant amounts in approximately 1 minute and will detect 0.001 per cent by volume in less than a minute. The color of the gel turns decisively from bright yellow to bright greens, and finally to bluish greens. For laboratory or field use, the gel is conveniently used in small glass tubes, and colorimetric determinations are made by comparison with similar tubes exposed to known quantities of carbon monoxide. Even more convenient is the use of a standard color chart.[25]

E. DETERMINATION OF HYDROGEN IN ROCKS AND MINERALS

Methods for the determination of hydrogen in rocks and minerals include those that give (1) nonessential hydrogen, (2) essential hydrogen, (3) hydrogen present in organic compounds, and (4) total hydrogen. The first two are discussed in the section on Water (p. 823 and p. 827), the third in the section on Rocks (p. 936), and the fourth in IV, B (p. 770).

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[25] For details, see Martin Shepherd, Rapid Determination of Small Amounts of Carbon Monoxide, *Ind. Eng. Chem. Anal. Ed.*, **19**, 77 (1947).

Chapter 51

NITROGEN

Nitrogen is the predominating element in the atmosphere, in which it is uncombined. It is also abundant in organic matter in such derived substances as coal. Nitrates are present in the soil; in some arid regions they exist in enormous quantities. Nitrogen, though found in but small relative amount in the free state in the earth's crust, is comparatively abundant and easily detectable as ammonia or ammonium salts in certain classes of rocks.

I. METHODS OF DETERMINATION

The standard procedure for the determination of nitrogen is that first recommended by Dumas[1] in which the substance is mixed with copper oxide, burned in an atmosphere of pure carbon dioxide in a tube containing copper oxide and metallic copper, and the nitrogen measured after the absorption of the rest of the gases in a solution of alkali hydroxide contained in a nitrometer. This method is applicable to all nitrogenous compounds.

For most compounds, the determination of nitrogen by the simpler Kjeldahl method or its numerous modifications[2] suffices. Determinations can be made quickly and simply by microanalytical modifications of both methods. If the material is of sufficiently uniform composition to permit the use of small samples, these methods should be adopted whenever material is limited or much routine work is to be done.[3] Very small amounts of nitrogen occurring as ammonium hydroxide or nitrates are best determined colorimetrically.

A. BY DUMAS' METHOD

The chief difficulties in this method lie in maintaining an atmosphere of pure carbon dioxide during the whole operation, and in collecting and measuring all of the nitrogen.

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[1] J. B. Dumas, *Ann. chim. phys.*, **2**, 198 (1831).

[2] J. Kjeldahl, *Z. anal. Chem.*, **22**, 366 (1883); J. W. Gunning, *ibid.*, **28**, 188 (1889); H. Wilfarth, *Chem. Zentr.*, **56**, 17, 113 (1885).

[3] For detailed outlines of such methods, consult Fritz Pregl and H. Roth, *Quantitative Organic Microanalysis*, translated by E. B. Daw, P. Blakiston's Son and Co., Philadelphia (1937); A. Steyermark, *Quantitative Organic Microanalysis*, Blakiston Co., Philadelphia (1951).

An atmosphere of carbon dioxide was formerly obtained by using a tube closed and filled at one end with magnesite, from which the necessary gas was obtained by heating at the start and at the end of the analysis. In later modifications of the method, a tube open at both ends was used, and the carbon dioxide was generated outside by mixing a saturated solution of sodium or potassium carbonate with dilute sulfuric acid (1 + 1) in a suitable generator.[4] A still more convenient arrangement is one recommended by M. S. Kharasch [5] in which the removal of air is facilitated by alternately evacuating the tube and filling with carbon dioxide from any reasonably pure source, and finally made certain by the use of pure carbon dioxide generated from sodium bicarbonate within the system [6] (see Fig. 35).

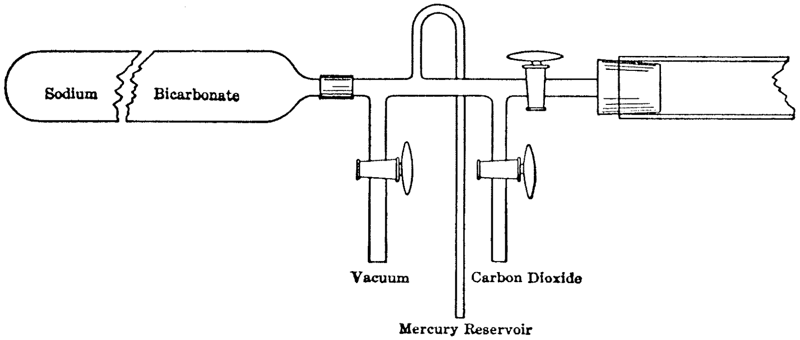

FIG. 35. Fore part of apparatus for the determination of nitrogen by the Dumas method.

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[4] For a detailed description of such a method, consult P. H. M.-P. Brinton, F. M. Shertz, W. G. Crockett, and P. P. Merkel, *J. Ind. Eng. Chem.*, 13, 636 (1921).

[5] Private communication.

[6] This is accomplished by putting stopcocks on the exit and inlet ends of the combustion tube and connecting the inlet end with a tube which is in turn connected with: (1) a tube leading to a source of carbon dioxide (a cylinder of the gas or a Kipp generator), (2) a bent tube of sufficient length and dipping into mercury to act as a manometer, (3) a tube leading to a vacuum pump, and (4) a large tube at the extreme end and filled with pure sodium bicarbonate (free from nitrogen). With such an arrangement, the exit end is closed, the system evacuated, and residual air drawn out by filling with carbon dioxide from the cylinder or generator, evacuating, and repeating the operation several times. The final washing and the filling of the tube with carbon dioxide is done with gas generated by heating the tube containing sodium bicarbonate. When connection has been made with the filled nitrometer and the system contains only carbon dioxide, the heating of the bicarbonate is stopped and the stopcock on the inlet end closed. The combustion is then carried out as usual until no bubbles are given off for 2 minutes. The bicarbonate is then again heated until carbon dioxide bubbles vigorously through the mercury in the manometer. The stopcock on the inlet end is then slowly opened and a slow stream of carbon dioxide maintained until the nitrogen is entirely washed out. Numerous schemes for utilizing Dry Ice as a source of carbon dioxide in determinations of nitrogen by the Dumas method have been proposed. For these, see W. S. Ide, *Ind. Eng. Chem. Anal. Ed.*, 7, 442 (1935); W. H. Hamill and J. A. Alicino, *ibid.*, **9**, 290 (1937), and F. Shea and C. E. Watts, *ibid.*, **11**, 333 (1939).

The arrangement of the combustion tube and the treatment of the sample is the same as described under Carbon and Hydrogen (p. 773). The weight of the sample, however, must be calculated in advance to make sure that no more nitrogen will be given off than can be caught in the nitrometer, and the sample must be well mixed with sufficient copper oxide to insure complete decomposition, for no air or oxygen can be admitted during the combustion.[7] The exit end of the combustion tube is attached directly to a nitrometer of the Schiff type, having a mercury seal extending halfway between the inlet and the leveling bulb arms, and a leveling bulb filled with a 50 per cent solution of potassium hydroxide (see Fig. 36). The nitrom-

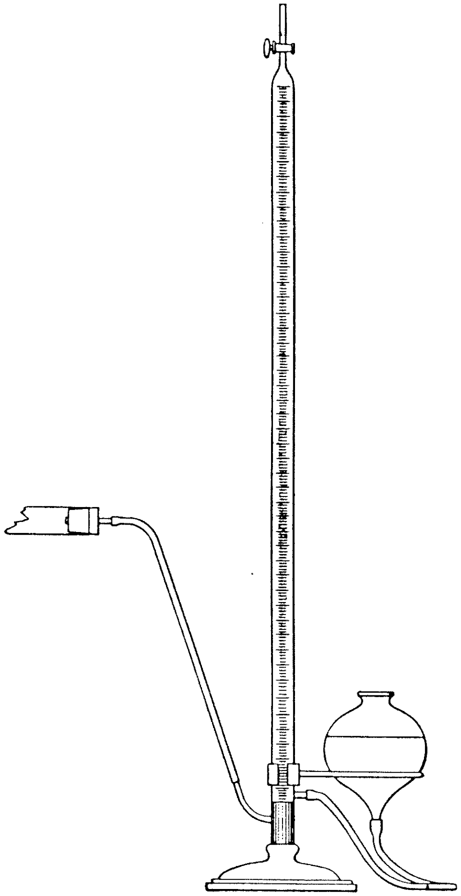

FIG. 36. Exit end of apparatus for the determination of nitrogen by the Dumas method.

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[7] For the burning of relatively unstable liquid compounds, consult F. Shea and C. E. Watts, *Ind. Eng. Chem. Anal. Ed.*, **11**, 333 (1939), and for the combustion of compounds that are resistant to combustion, see J. R. Spies and T. H. Harris, *ibid.*, **9**, 304 (1937).

TABLE 23

The Vapor Pressure of Liquid Water from 15 to 35° C

In mm Hg *

t° C	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
15	12.788	12.870	12.953	13.037	13.121	13.205	13.290	13.375	13.461	13.547
16	13.634	13.721	13.809	13.898	13.987	14.076	14.166	14.256	14.347	14.438
17	14.530	14.622	14.715	14.809	14.903	14.997	15.092	15.188	15.284	15.380
18	15.477	15.575	15.673	15.772	15.871	15.971	16.071	16.171	16.272	16.374
19	16.477	16.581	16.685	16.789	16.894	16.999	17.105	17.212	17.319	17.427
20	17.535	17.644	17.753	17.863	17.974	18.085	18.197	18.309	18.422	18.536
21	18.650	18.765	18.880	18.996	19.113	19.231	19.349	19.468	19.587	19.707
22	19.827	19.948	20.070	20.193	20.316	20.440	20.565	20.690	20.815	20.941
23	21.068	21.196	21.324	21.453	21.583	21.714	21.845	21.977	22.110	22.243
24	22.377	22.512	22.648	22.785	22.922	23.060	23.198	23.337	23.476	23.616
25	23.756	23.897	24.039	24.182	24.326	24.471	24.617	24.764	24.912	25.060
26	25.209	25.359	25.509	25.660	25.812	25.964	26.117	26.271	26.426	26.582
27	26.739	26.897	27.055	27.214	27.374	27.535	27.696	27.858	28.021	28.185
28	28.349	28.514	28.680	28.847	29.015	29.184	29.354	29.525	29.697	29.870
29	30.043	30.217	30.392	30.568	30.745	30.923	31.102	31.281	31.461	31.642
30	31.824	32.007	32.191	32.376	32.561	32.747	32.934	33.122	33.312	33.503
31	33.695	33.888	34.082	34.276	34.471	34.667	34.864	35.062	35.261	35.462
32	35.663	35.865	36.068	36.272	36.477	36.683	36.891	37.099	37.308	37.518
33	37.729	37.942	38.155	38.369	38.584	38.801	39.018	39.237	39.457	39.677
34	39.898	40.121	40.344	40.569	40.796	41.023	41.251	41.480	41.710	41.94
35	42.175	42.409	42.644	42.880	43.117	43.355	43.595	43.836	44.078	44.320

* *International Critical Tables*, III, 212 (1928).

eter is not filled with the solution until practically all of the air has been expelled, and the combustion of the sample is not started until the whole system is entirely free from gases that are not absorbed in the potassium hydroxide solution. Once started, the combustion is carried out as usual, all of the nitrogen being finally driven into the nitrometer by a slow current of carbon dioxide. The carbon dioxide used for this purpose must of course be free from gases that are not absorbed by the alkaline solution.

The nitrogen that has been collected is finally transferred to a water-jacketed nitrometer, the volume carefully read, the temperature and barometric pressure noted, and the weight of nitrogen calculated by reference to tables giving the weight of a cubic centimeter of moist nitrogen at different temperatures and pressures or by the use of the formula

$$x = 0.04493 \frac{v(B - w)}{(273 + t)a}$$

in which x represents the percentage of nitrogen, v the volume of nitrogen obtained, B the barometric pressure, w the tension of water vapor measured in millimeters of mercury (see Table 23), t temperature and a the weight of the sample.[8]

B. KJELDAHL METHOD

In the simplest application of the Kjeldahl method, the sample is decomposed and the nitrogen fixed as ammonium sulfate by boiling with sulfuric acid. Free halogens or oxygenated halogen compounds may cause losses in Kjeldahl digestions and should be avoided. The nitrogen is then determined by boiling with sodium hydroxide, absorbing the ammonia in an excess of standard sulfuric acid, and titrating the excess. There is no modification of the method that is applicable to all nitrogenous compounds. Decomposition of the sample by sulfuric acid is usually aided by the addition of mercuric oxide and potassium sulfate. With some compounds, these are unnecessary. A number of substitutes for mercuric oxide, potassium sulfate, and even sulfuric acid have been recommended.[9]

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[8] Illustrative of the accuracy of the method are the results obtained by Brinton and his students, *loc. cit.*, in the analysis of specially purified picric acid and dinitrobenzene. For these, average values of 18.45 and 16.70 per cent N were obtained as against the theoretical contents 18.35 and 16.64 per cent.

[9] The molecular equivalent of sodium sulfate can be substituted for potassium sulfate in most cases where the latter is used [R. B. Deemer, *J. Assoc. Offic. Agr. Chemists*, **3**, 303 (1920); T. D. Jarrell, *ibid.*, 304; W. L. Latshaw, *J. Ind. Eng. Chem.*, **8**, 586 (1916)]. According to O. M. Shedd [*J. Assoc. Offic. Agr. Chemists*, **10**, 507 (1927)], the digestion period can be materially shortened by using 18 g of Na_2SO_4, together with 0.7 g of Hg, and heating strongly. I. K. Phelps and H. W. Daudt [*J. Assoc. Offic. Agr. Chemists*, **3**, 306 (1920); **4**, 72 (1920)] found, however, that the substitution was not satisfactory in the decomposition of pyridine zinc chloride, nicotinic acid, and hydroxyquinoline, as was also the case when potassium sulfate was replaced by compounds such as Na_2HPO_4, $Na_4P_2O_7$, $CuSO_4$, $NiSO_4$, $KAl(SO_4)_2$, $ZnCl_2$, $MnCl_2$, MnO_2, H_2WO_4, H_2MnO_4, H_2TiO_3, or HVO_4. Substitution of other oxidizing agents such as $CuSO_4$, $KMnO_4$, and H_2O_2 have also been recommended. Copper sulfate is satisfactory if a longer digestion period is used. $KMnO_4$ is unsatisfactory and leads to low results unless it is added 2 minutes after heating has stopped [W. Frear, W. Thomas, and H. D. Edmiston, *J. Assoc. Offic. Agr. Chemists*, **3**, 220 (1919)]. According to F. C. Koch and T. L. McMeekin [*J. Am. Chem. Soc.*, **46**, 2066 (1924)], decomposition is facilitated and no nitrogen is lost in an attack with 30 per cent H_2O_2 and H_2SO_4; whereas H. H. Willard and W. E. Cake [*J. Am. Chem. Soc.*, **42**, 2646 (1920)] recommended the addition of a moderate excess of dry, ammonia-free $K_2S_2O_8$ to the charred and cooled solution of organic matter. B. Mears and R. E. Hussey [*Ind. Eng. Chem.*, **13**, 1054 (1921)] stated that rapid decomposition is obtained by the use of 25 ml of H_2SO_4, 1 g of $CuSO_4$, and 2 ml of $HClO_4$. The substitution of H_3PO_4 for part of the H_2SO_4 does not have any marked advantage. M. F. Lauro [*Ind. Eng. Chem. Anal. Ed.*, **3**, 401 (1931)] states that complete decomposition of organic matter proceeds much more rapidly if selenium or selenium oxychloride is used as catalyst. A solution containing 10 g of either sodium or potassium sulfate, 25 ml of sulfuric acid, and 0.1 to 0.2 g of selenium is recommended,

The absorption of ammonia in a 50-ml portion of a 4 per cent solution of boric acid instead of a standard acid has been recommended by various investigators[10] because such a solution need not be measured out carefully and no standard alkali is required. If a suitable indicator such as bromphenol blue is used (preferably in artificial light) and the blank is carefully determined, the method gives excellent results. H. H. Willard and W. E. Cake[11] have recommended that instead of distilling the ammonia, the solution be rendered slightly alkaline, treated with an excess of standard hypobromite and the excess determined by adding acid and iodide and titrating with thiosulfate.

a. *Procedure in the Absence of Nitrate, Nitrites, Azo, Hydrazine, Cyanide, or Other Compounds Noted in the Succeeding Sections.* Place 0.35 to 3.5 g, according to the nitrogen content, of the 30-mesh or finer sample in a 500- to 600-ml Kjeldahl flask, add 10 g of powdered potassium sulfate, 0.5 to 0.7 g of mercuric oxide [prepared in the wet way (p. 84), but not from mercuric nitrate], or 0.6 to 0.65 g of mercury, and 20 to 25 ml of sulfuric acid. Shake until the contents are well mixed; place the flask on a hole in an asbestos board, and incline the neck at an angle of about 60°. The hole must be of such size that the flame never plays on the flask above the surface of the liquid at any time during the digestion. Heat below the boiling point of the acid until frothing ceases. Extreme frothing can be prevented by the addition of a small piece of paraffin. Gradually increase the heat until the acid boils briskly, and continue the boiling for 15 to 30 minutes after the solution becomes colorless or it is judged that decomposition is complete (about 1 to 1.5 hours). Decrease the heat so that the solution boils very gently, and heat for 1 to 3 hours longer. Add sulfuric acid as required to keep the volume of acid above 20 ml during the digestion. Cool; carefully dilute with about 200 ml of water; add a few pieces of pumice stone, granulated zinc, or cracked porcelain, if necessary, to prevent bumping, and then, carefully and with shaking, 25 ml of a solution containing 80 g of sodium thiosulfate or 40 g of either sodium or potassium sulfide per liter. This is to fix the mercury and can be omitted in its absence. Next add sufficient sodium hydroxide solution to make the solution strongly alkaline (50 ml is usually enough), pouring the solution down the side of the flask so that it does not mix at once with the acid solution.[12] Place the flask in an upright position, attach a Kjeldahl bulb or other suitable scrubber to prevent contamination by sprayed sodium hydroxide, and connect with a vertical condenser, preferably lined with tin. In an Erlenmeyer flask put enough of a measured solution of a standard sulfuric acid to react with the ammonia that is to be evolved, and place the flask so that the end of the condenser just dips in the acid. Mix the contents of the Kjeldahl flask by gentle shaking, heat to boiling, and distil until all ammonia has passed over into the standard acid. From 150 to 200 ml of distillate is sufficient. Lower the Erlenmeyer flask, remove the flame, and rinse the condenser with water. Add methyl red or cochineal to the distillate, and titrate with an alkaline solution that is equivalent to the acid solution. Subtract the volume of the alkali required from the volume of acid taken, and correct the difference by the volume of acid required in a blank run on 1 g of a nitrogen-free organic compound, such as sugar. One milliliter of 0.5 N acid corresponds to 0.007 g of nitrogen.[13]

b. *In the Presence of Nitrates.* The preceding method fails in the presence of nitrates. If these are present, the special modification given in α can be

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and no sulfide need be added before distillation. R. B. Bradstreet [*ibid.*, 10, 696 (1938)] maintains that the digestion time can be shortened by using 0.25 g each of selenium and ferrous sulfate. Larger amounts of selenium lead to losses of nitrogen and must be avoided. See also A. Sreenivasan and V. Sadasivan, *ibid.*, 11, 314 (1939), who declare that the addition of mercuric oxide offers no advantages and leads to complete oxidation of selenium to selenic acid in the concentrated sulfuric acid solution.

[10] L. W. Winkler, *Z. angew. Chem.*, **26**, 231 (1913); F. M. Scales and A. P. Harrison, *J. Ind. Eng. Chem.*, **12**, 350 (1920); H. D. Spears, *J. Assoc. Offic. Agr. Chemists*, **5**, 105 (1921); and K. S. Markley and R. M. Hann, *ibid.*, **8**, 455 (1925); J. L. Hague, R. A. Paulson, and H. A. Bright, "Determination of Nitrogen in Steel," *J. Research NBS*, **43**, 201 (1949). A. Eisner and E. C. Wagner [*Ind. Eng. Chem. Anal. Ed.*, **6**, 473 (1934)] state that 4 per cent solutions of boric acid undergo no change when stored in Pyrex glass.

[11] *Loc. cit.*

[12] For a convenient apparatus for adding the sodium hydroxide solution and aerating the solution during distillation, see I. K. Phelps and H. W. Daudt, *J. Assoc. Offic. Agr. Chemists*, **3**, 312 (1920). The use of aeration in a slightly modified apparatus is also described by W. B. Meldrum, R. Melampy, and W. D. Myers [*Ind. Eng. Chem. Anal. Ed.*, **6**, 63 (1934)]. Distillation by steam instead of by heating with gas or electricity is preferred by F. T. Adriano [*Philippine Agr.*, **17**, 509 (1929)], by J. Green [*Ind. Eng. Chem. Anal. Ed.*, **3**, 160 (1931)], and by J. M. Fife, [*ibid.*, **8**, 316 (1936)]. For an efficient modification of the Kjeldahl trap, see G. H. W. Lucas, *Ind. Eng. Chem. Anal. Ed.*, **1**, 140 (1929).

[13] By this method, I. K. Phelps and H. W. Daudt (*loc. cit.*) obtained excellent results in the analysis of compounds such as monomethylamine, trimethylamine, glucosamine hydrochloride, tetramethyl-ammonium iodide, cholin hydrochloride, isatin, atropine, cocaine, nicotine zinc chloride, nicotinic acid, β-eucaine hydrochloride, hydroxyquinoline, cinchonidine, strychnine, brucine, papaverine, narcotine, morphine, hydrastinine, caffeine, lophine, amarine, histidine dihydrochloride, quinoxaline hydrochloride, 2-methyl 4-quinazolon, 2-methyl 3-phenyl 4-quinazolon. Unsatisfactory results were obtained with azo and hydrazine compounds. For the behavior of certain organic substances in a different attack, consult P. Fleury and H. Levaltier, *J. pharm. chim.*, **30**, 265 (1924); *Bull. soc. chim.*, **37**, 330 (1925); *C. A.*, **18**, 1625 (1924); **19**, 2002 (1925). For a review of methods that have been recommended for Kjeldahl digestions, and the reduction of the time of digestion to 30 minutes by the use of sulfuric acid to which mercury, dipotassium phosphate and ferric sulfate have been added, see F. M. Stubblefield and E. E. De Turk, *Ind. Eng. Chem. Anal. Ed.*, **12**, 396 (1940).

used, although the determination can be done more rapidly and accurately by Devarda's method as given in β. The nitrometer method,[14] in which the nitrate is decomposed by ferrous chloride in hydrochloric acid solution and the volume of nitric oxide that is given off is measured, gives results that are low unless based on results obtained with pure salts and is not recommended except for routine control work.

α. *Sulfuric-salicylic acid.*[15] Dissolve 10 g of the nitrate in water, dilute to exactly 500 ml, and take a 25-ml portion for analysis. Transfer to a 650-ml Kjeldahl flask, and evaporate to dryness at 90 to 100° C. Add 35 ml of salicylic-sulfuric acid (40 g of salicylic acid dissolved in 1000 ml of sulfuric acid), rinsing down the neck of the flask. Shake frequently, and warm at a temperature no hotter than the hand can bear until solution is complete and reaction begins. Let stand at least 1 hour with occasional shaking. Add 5 g of sodium thiosulfate, heat at a low temperature until frothing ceases (about 5 minutes), and then add 10 g of sodium or potassium sulfate and 1 g of mercuric oxide, and proceed as in a,

β. *Devarda's method.* Devarda's method[16] is not a modification of the Kjeldahl method but is given here because of its use for the determination of nitrogen in nitrates. It is based on the reduction of nitrates by aluminum and zinc in alkaline solution. An alloy containing 50 Cu, 45 Al, 5 Zn is ordinarily used, the copper giving a more brittle and easily powdered alloy and also tending to prevent bumping in the final distillation. The method is not applicable in the presence of nitrogenous organic matter.[17] Ammonium salts if originally present can be distilled from the alkaline solution before adding the alloy. The procedure is as follows:

Dissolve a 10-g sample of the nitrate in water, dilute to exactly 1000 ml, and transfer exactly 50 ml of the solution to a 600-ml Erlenmeyer flask. Mix with 60 ml of water, 5 ml of alcohol, and 40 ml of potassium hydroxide solution (sp. gr. 1.3). Add 2 to 2.5 g of finely powdered Devarda alloy, and immediately connect with a trap and a condenser, dipping into a

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[14] J. J. Schlosing, *Compt. rend.*, **37**, 858 (1853); *Jahresber.*, 654 (1854); F. Tiemann, *Ber.*, **6**, 1041 (1873); P. Wagner, *Chem. Ztg.*, **7**, 1710 (1883); **8**, 475 (1884); G. Lunge, *Technical Methods of Chemical Analysis*, Vol. I, Part I, p. 309, Gurney and Jackson, London (1908).

[15] O. Förster, *Chem. Ztg.*, **13**, 229 (1889); **14**, 1674 (1890); H. C. Moore, *J. Ind. Eng. Chem.*, **12**, 669 (1920); *J. Assoc. Offic. Agr. Chemists*, **8**, 411 (1924–25).

[16] A. Devarda, *Chem. Ztg.*, **16**, 1952 (1892); *Z. anal. Chem.*, **33**, 113 (1894); *J. Assoc. Offic. Agr. Chemists*, **8**, 410 (1924–25).

[17] For the determination of total nitrogen in solutions containing organic and nitrate nitrogen, B. S. Davisson and J. T. Parsons [*Ind. Eng. Chem.*, **11**, 306 (1919)] obtained excellent results by first reducing the nitrate with Devarda's alloy in dilute alkaline solution, absorbing the ammonia in sulfuric acid, and then decomposing the organic matter as in a.

measured volume of standard acid. Gently heat for 30 minutes, and then distil, very gently at first.[18]

Correct the result as determined by a blank run, which must be made on each new lot of alloy.[19]

c. *In Presence of Azo Compounds.*[20] Dissolve 0.2 to 0.4 g of the compound in 20 ml of alcohol, add 5 ml of a solution of 40 g of stannous chloride in 100 ml of hydrochloric acid, and heat at the boiling point under a return condenser until the solution is bleached and then for an additional 7 minutes (at least 15 minutes in all). Cool, add an equal volume of water and 30 ml of sulfuric acid, and carefully heat until water is expelled and foaming has ceased. Add 0.7 g of mercuric oxide and 10 g of potassium sulfate, and proceed as in a (p. 784). If so much sulfuric acid volatilizes that stannous sulfate causes bumping, add 5 to 10 ml more acid.

d. *In Presence of Hydrazine Compounds.* Hydrazine and semicarbazid compounds are not broken up by the preceding treatments. According to Phelps and Daudt,[20] hydrazine, phenylhydrazine, phenyl methyl hydrazine, and similar compounds are broken up by treating an alcoholic solution of the compounds with formaldehyde, zinc dust, and concentrated hydrochloric acid, heating at the boiling temperature for 30 minutes or more

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[18] According to Devarda, the whole operation can be finished in 1 hour. The accuracy of the method is indicated by the values 13.88 and 16.46 as against the theoretical values 13.86 and 16.46 obtained by Devarda in analyses of chemically pure potassium and sodium nitrates. The performance of the method as compared with the sulfuric-salicylic acid method is shown by the following average results obtained by 20 chemists [*J. Assoc. Offic. Agr. Chemists*, **8**, 415 (1924–25)]:

Method		Impure $NaNO_3$	Impure KNO_3	"High Potash Nitrate"
Devarda	....	15.55	12.49	15.13
Sulfuric-salicylic and mercury fixed by	Na_2S	15.55	12.45	15.08
	$Na_2S_2O_3$	15.57	12.48	15.17

According to M. B. Donald [*Analyst*, **61**, 250 (1936)], the optimum conditions for the reduction of 1 g of nitrate is 3 g of alloy and 2 g of caustic soda in about 250 ml of water. For a modified method in which magnesium oxide is substituted for sodium or potassium hydroxide, and ammonia and nitrate nitrogen are determined in the same solution, consult J. Davidson and A. Krasnitz, *Ind. Eng. Chem. Anal. Ed.*, **6**, 315 (1934).

[19] According to A. Seyewetz [*Bull. soc. chim.*, [4], **45**, 463, (1929)], nitrogen that is present as nitrate, nitrite, sulfonitrate or nitrated cotton can be determined by treating with impalpable aluminum powder (dull gray, and not the bright powder used in varnishes, etc.), slowly adding a solution of sodium hydroxide (35° Bé), and absorbing the ammonia in a standard solution of sulfuric acid.

[20] I. K. Phelps and H. W. Daudt, *J. Assoc. Offic. Agr. Chemists*, **3**, 306 (1920). According to these authors, the procedure was applied successfully to azobenzene, hydroxyazobenzene, amidoazobenzene, toluene azo-*p*-toluidine, methyl red, diethyl red, dipropyl red, benzene azo-β-naphthylamine, Ponceau 4R, and Congo Red.

under a return condenser, and adding a little stannous chloride after 15 minutes to hasten the reaction between the zinc and acid. The solution is finally diluted with an equal volume of water and treated as in the preceding method. The zinc dust must be very finely divided and at least 90 per cent pure.

C. PRECIPITATION AS NITRON NITRATE

Nitron, the commercial name for 1,4-diphenyl-3-5-endo-anilodihydrotriazol,[21] is a basic compound which forms rather insoluble salts with certain acids. The more important of these, in order of their solubilities, and starting with the most soluble, are bromide, nitrite, chlorate, chromate, thiocyanate, iodide, nitrate, perchlorate, and picrate. Oxalic and citric acids are also said to form more or less insoluble salts.

Nitron has found its chief use in determinations of nitric, perchloric, and picric acids; organic nitrates, nitric esters; nitro compounds; and oxides of nitrogen.[22]

Noninterfering substances that have been mentioned are dextrin, gelatin, sucrose, iodate, aluminum, magnesium, or ammonium sulfates, potassium phosphate, and magnesium chloride. Sulfuric, hydrochloric, phosphoric, boric, formic, acetic, benzoic, and tartaric acids form soluble salts.

Interfering substances are the acids that form insoluble salts, peptone, ferro- and ferricyanic acids, and large amounts of chlorides.

PROCEDURE. Prepare a solution containing not over 0.1 g of nitrate ion and free from the interfering substances that have been listed. Dilute to 80 to 100 ml, add 0.5 to 0.75 ml of dilute sulfuric acid (2 + 3) or 1 ml of glacial acetic acid, and heat to boiling. Add at one stroke 10 to 12 ml of the nitron reagent,[23] stir, let stand for 30 to 45 minutes, and then cool in

ice water for 1.5 hours. Filter through a weighed filtering crucible under moderate suction, using the filtrate for transferring the precipitate, and washing out the beaker. Finally wash the precipitate with five 2-ml portions of ice water. To make sure that precipitation is complete, heat the filtrate to boiling, add a little more of the reagent, and cool as before. Dry the crucible and precipitate at 105° C for 1 hour, cool in a desiccator, and weigh. The empirical factor for HNO_3 in the precipitate is 0.1679.

Results for "NO_3" are apt to be a little low.[24]

D. OTHER METHODS

For the determination of total nitrogen in calcium cyanamide, K. Scherrer[25] recommended that 1 g of sample be moistened with water in a digestion flask, mixed with 1 g of powdered copper, and carefully treated in cooled solution with 30 ml of cold 50 per cent sulfuric acid. The solution is then digested for 1 hour at a low temperature, then for 30 to 60 minutes at a higher one, and finally distilled as usual.[26]

According to K. Kürschner,[27] excellent results for nitrogen in substances such as phenylhydrazine hydrochloride, antipyrine, brucine, *m*-dinitrobenzol, calcium cyanamide, and nitrates are obtained by proceeding as follows: Transfer 0.15 g of sample to a dry Kjeldahl flask, dissolve in 5 ml of water, and add an intimate mixture of 7 g of iron filings, or powder, with 1 g of cupric oxide. Mix thoroughly by shaking for 1 minute so that all of the iron settles to the bottom of the flask. Add 20 ml of well-cooled dilute sulfuric acid (1 + 1), and again shake thoroughly. If vigorous reaction takes place, cool the flask. Let stand for 1 hour, add 30 ml of sulfuric acid, heat gently for 15 minutes and then as usual for 1 to 3 hours, depending on the ease with which the compound is decomposed. A colorless solution does not necessarily denote complete decomposition. A residue of sulfur, undecomposed iron, and sulfates of copper and iron is of no consequence.

W. A. Drushel and M. M. Brandegee[28] maintained that the nitrogen of aliphatic nitrites, cyanogen substituted esters, amides, and imides can be quantitatively fixed as ammonium chloride by heating with an excess of hydrochloric acid in sealed tubes for 2 to 3 hours at about 200° C. The nitrogen in glycocol is fixed quantitatively at this temperature only after 3 to 4 hours. After the attack, the solution can be evaporated to dryness

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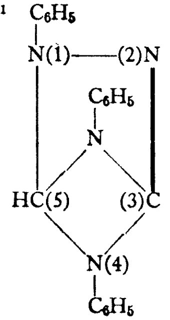
[21]



or $C_{20}H_{16}N_4$. Nitron nitrate has the formula $C_{20}H_{16}N_4 \cdot HNO_3$.

[22] For its use in the determination of rhenium, see p. 320. For a detailed discussion of the uses of "nitron" in analyses of inorganic and organic materials, see W. C. Cope and J. Barab, *J. Am. Chem. Soc.*, **39**, 504 (1917).

[23] Made up as needed as follows: Dissolve 1 g of "nitron" in 10 ml of 5 per cent acetic acid, filter through a filtering crucible, transfer to an amber bottle, and store in a cool place.

[24] For a study of the method, consult J. E. Heck, H. Hunt, and M. G. Mellon, *Analyst*, **59**, 18 (1934).

[25] *Chem. Ztg.*, **49**, 237, 243 (1925).

[26] For the determination of urea and nitrate nitrogen in the presence of cyanamide, consult E. G. Fox and W. J. Geldard, *Ind. Eng. Chem.*, **15**, 743 (1923), and K. D. Jacob, *ibid.*, 1175.

[27] *Z. anal. Chem.*, **68**, 209 (1926).

[28] *Am. J. Sci.*, [4] **39**, 398 (1915).

on the water bath, heated in an oven for 5 minutes at 110 to 112° C to expel all hydrochloric acid,[29] and the nitrogen calculated after titration of the chloride with a standard neutral solution of silver nitrate as in Mohr's method (p. 732).

According to H. ter Meulen,[30] all of the nitrogen of many organic compounds can be transformed into ammonia by heating in a current of hydrogen and passing the mixture of gases over nickelized asbestos.

E. DETERMINATION OF MINUTE AMOUNTS OF NITROGEN OCCURRING AS AMMONIA OR NITRATE

For the determination of very small amounts of ammonia or nitrates, as for example potable water, recourse must be had to colorimetric methods,[31] such as the Nessler method[32] for the former and the phenolsulfonic method[33] for the latter.

a. *Determination of Minute Amounts of Free Ammonia.* First prepare Nessler reagent as follows: Dissolve about 13 g of potassium iodide in 25 ml of water, and add, with constant stirring, a cold saturated solution of mercuric chloride until the precipitate at first formed no longer redissolves. Do not let crystals of mercuric chloride fall into the solution, and avoid the formation of more than a very little permanent precipitate. Finally filter, and treat with a solution of potassium hydroxide obtained by dissolving 55 g of potassium hydroxide in 150 ml of water, letting stand in a corked flask until clear and then decanting the clear solution. Dilute the solution to 250 ml, mix, and add a saturated solution of mercuric chloride, drop by drop and with constant stirring, until a slight yellowish permanent precipitate is formed. Let stand in a stoppered flask until clear, decant into a bottle, and keep stoppered and in a dark place. The reagent so prepared should have a yellow color, should give a brown tint in 1 minute when 0.5 ml is added to 10 ml of distilled water containing 0.5 ml of standard ammonium chloride solution (0.00001 g nitrogen as NH_3 per ml) and must not give a turbidity when 0.5 ml is added to 10 ml of water containing 8 ml of the ammonium chloride solution.[34]

PROCEDURE. Place 50 ml of water in a thoroughly clean retort, add 2 ml of a saturated solution of sodium carbonate, connect with a vertical condenser, distil off 30 ml, and then catch 10 ml in a Nessler tube. Cool to room temperature, add 0.5 ml of the Nessler reagent, and let stand 5 minutes. If no color develops, the apparatus is free from ammonia; if the solution turns yellow, more water must be added to the retort and the distillation repeated until ammonia is gone. Then add 100 ml of the sample, distil at a rate of 10 ml per 2 minutes, and collect the 10-ml distillates in 10-ml Nessler tubes. After five 10-ml portions have been obtained, catch a sixth, add Nessler reagent, and stand in warm (30 to 40° C) water. If no yellow color results, stop the distillation; otherwise collect a total of eight fractions. Let the distillates cool to room temperature, and add to each 0.5 ml of Nessler reagent, beginning with the distillate last obtained. If a deep color appears in the third distillate, the first and second will probably contain too much ammonia for direct test. In this case, dilute the second distillate to exactly 50 ml, mix, and test 10 ml of the solution. If the color is still too dark, dilute 10 ml of the already diluted solution to 50 ml. Treat the first distillate in like fashion, and determine the quantity of ammonia in each fraction as follows: Prepare a series of color standards by adding to a series of 10-ml Nessler tubes 0.5-, 1-, 2-, 3-, 4-, and 5-ml portions of an ammonium chloride solution containing 0.00001 g of nitrogen per ml. Fill to the mark with ammonia-free water, add 0.5 ml of Nessler reagent to each tube, mix thoroughly, and, after 5 minutes, compare with the distillates. All solutions must have the same temperature. Tubes containing equal amounts of ammonia of course have the same intensity of color.

b. *Determination of Minute Amounts of Nitrates.* α. *Phenoldisulfonic acid method.* The phenoldisulfonic reagent must not contain monosulfonic acid and is prepared as follows: Dissolve 25 g of pure white phenol in 150 ml of pure concentrated sulfuric acid, add 75 ml of fuming sulfuric acid (13% SO_3), stir well, and heat for 2 hours at about 100° C. Two milliliters of this reagent suffice for 50 parts of nitrate per million of water.

PROCEDURE. Measure into an evaporator 100 ml of the sample or, if nitrates are high, such a volume as will contain from 0.01 to 0.05 mg of nitrate nitrogen. Add sufficient 0.04 *N* or 0.02 *N* sulfuric acid to not quite

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[29] Drushel and Brandegee found that 1.2377 g of NH_4Cl lost but 0.0002 g in weight when heated for 10 minutes at 110 to 112° C, and but 0.0005 g in one-half hour at 105 to 108° C.

[30] *Rec. trav. chim.*, 43, 643 (1924); 44, 271 (1925).

[31] For detailed descriptions of these methods, consult such references as *Standard Methods for the Examination of Water and Sewage,* 9th ed., American Public Health Association, Boston (1946), or *Official and Tentative Methods of Analysis of Association of Official Agricultural Chemists,* 7th ed., Washington, D. C. (1950).

[32] W. A. Miller, *Z. anal. Chem.*, 4, 459 (1865); J. Nessler, *ibid.*, 7, 415 (1868); E. Frankland and H. E. Armstrong, *J. Chem. Soc.*, [2] 6, 77 (1868); H. Trommsdorff, *ibid.*, 8, 356 (1869).

[33] H. Sprengel, *Pogg. Ann.*, 121, 188 (1864); A. Grandval and H. Lajoux, *C. r.*, 101, 62 (1885); E. M. Chamot and D. S. Pratt, *J. Am. Chem. Soc.*, 31, 922 (1909), 32, 630 (1910), and with H. W. Redfield, *ibid.*, 33, 366, 381 (1911).

[34] A. P. Vanselow [*Ind. Eng. Chem. Anal. Ed.*, 12, 517 (1940)] recommends that the reagent be prepared as follows: Dissolve 45.5 g of mercuric iodide and 34.9 g of potassium iodide in as little water as is needed, add 112 g of potassium hydroxide (140 ml of an almost saturated solution, sp. gr. 15°/4° = 1.538), dilute to 1 liter, and let stand for 1 week before using. In the test, 5 ml are added per 100 ml of final volume, and the solutions are allowed to stand 30 minutes before being compared with standards.

neutralize all the alkalinity, and then a volume of standard solution of silver sulfate (free from nitrate and containing 4.3969 g per liter) which will precipitate all but about 0.5 mg of the chlorine as previously determined in a separate sample. The removal of the chloride can be omitted if the sample contains less than 30 parts of chloride per million. Heat to boiling, add a little "aluminum cream,"[85] filter and wash with small amounts of water. Evaporate the filtrate to dryness, add 2 ml of the disulfonic acid reagent, rubbing with a glass rod to insure intimate contact. If the residue is compact or vitreous in appearance, place the dish on the water bath for a few minutes. Dilute with distilled water, and slowly add a strong solution of 10 to 12 *N* potassium hydroxide until the maximum color is developed. Transfer to a colorimeter cylinder, filtering if necessary, and compare with potassium nitrate standards.[86] Nitrites interfere if present in excess of 1 part of nitrite nitrogen per million. They should be converted to nitrates by heating the sample a few moments with repeated additions of a few drops of hydrogen peroxide (free from nitrates) and a correction applied for the nitrate so formed.

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[85] Prepared by precipitating $Al(OH)_3$ from a solution of aluminum sulfate by means of a very slight excess of NaOH, filtering, washing, dissolving in HCl, and again precipitating and washing.

[86] These can be made as follows: Dissolve 0.72 g of pure recrystallized KNO_3 in 1 liter of water. Evaporate 10 ml of this solution to dryness on the water bath. Moisten the residue quickly and thoroughly with 2 ml of the phenoldisulfonic acid, and dilute to 1 liter. One milliliter of this solution represents 0.001 mg of nitrate nitrogen. The comparison standards can be made as needed by adding 2 ml of potassium hydroxide solution to various amounts (as for example 0, 0.5, 1.0, 1.5, 2.0, 4.0, 6.0, 8.0, 10.0, 15.0, 20.0, and 40.0 ml) and diluting to 50 ml in Nessler tubes. Such standards keep for several weeks without deterioration.

PART III

SILICATE ROCK ANALYSIS

I. INTRODUCTION

1. Importance of Complete and Thorough Analyses

The composition of the ultimate ingredients of the earth's crust—the different mineral species that are found there, of many of which its rocks are made up—was the favorite theme of the great workers in chemistry of the earlier half of the nineteenth century, and, for the painstaking care and accuracy of Berzelius, Wöhler, and others, the mineralogists and geologists of today have reason to be thankful. Considering the limited facilities at their disposal in laboratory equipment and quality of reagents, the general excellence of their work is little short of marvelous. As an outgrowth of the analysis of minerals and closely associated with it came the analysis of the more or less complex mixtures of them—the rocks. To aid the petrographer and geologist in the study of rocks, a host of chemists, for many decades, have annually made hundreds of analyses of all grades of quality and completeness. With the growth and extraordinary development of the so-called organic chemistry, inorganic chemistry gradually fell into a sort of disfavor. In many, even the best, European laboratories the course in mineral analysis, although maintained as a part of the curriculum of study, became but a prelude to the ever-expanding study of the carbon compounds, which, multiplying rapidly and offering an easy and convenient field for original research and possible profit, proved more tempting to young chemists than the often worked-over and apparently exhausted inorganic field. For one student devoting his time to higher research in inorganic chemistry fifty perhaps were engaged in erecting the present enormous structure of carbon chemistry. The instruction afforded to the student in mineral analysis was confined to the ordinary separations of the commoner ingredients occurring in appreciable quantities, with little regard to supposed traces and with still less attempt to find out if the tabulated list really comprised all that the mineral or rock contained.

With the introduction of improved methods of examination by the petrographer, especially as applied to thin rock sections, and the use of heavy solutions, whereby, on the one hand, the qualitative mineral composition of a rock could be preliminarily ascertained with considerable certainty, and, on the other hand, chemical examination of the more or less perfectly separated ingredients was made possible, a great help and incentive was afforded to the few chemists engaged in rock analysis. The microscope often obviated in part the necessity for tedious and time-wasting qualitative tests, and the heavy solutions, by permitting the concentration and separation of certain components, facilitated the detection of elements whose existence had long been overlooked.

Meanwhile, in the progress of chemistry, new methods and reagents for qualitative detection and quantitative separation and estimation were gradually being devised and discovered. The belief that some well-established methods were adequate was shown to be unwarranted; some had to be discarded altogether; others were still utilizable after modification. In the light thus shed, it became possible to explain many hitherto incomprehensible variations in the composition of some rock species or types, as shown in earlier analyses, and in not a few cases it appeared that the failure to report the presence of one or more elements had obscured relations and differences which more thorough examination showed to exist (see pp. 796–797). Consequently there arose a feeling of distrust of much of the older work in the minds of those chemists and petrographers who were best fitted to judge of its probable qualities. This and the incompleteness of nearly all the earlier work (and some of that of today, unfortunately), as shown by the largely increased list of those elements now known to enter into the normal composition of rocks, are rendering the old material less and less available to meet the increasing demands of the petrographer.[1]

And yet these demands were, with few exceptions, by no means so exacting as they should have been. Frequently the analysis was intrusted to a student without other experience than that gained by the analysis of two or three artificial salts and as many comparatively simple natural minerals, and with a laboratory instructor as adviser whose experience in rock analysis might be little superior to his own. In other words, one of the most difficult tasks in practical analysis was given to a tyro, and his results were complacently accepted and were published broadcast without question. Even to those who are thoroughly familiar with the subject, rock analysis is a complex and often a trying problem. Although long practice may have enabled one to do certain parts of the work almost mechanically, perplexing questions still arise which require trained judgment to meet and answer properly, and there is yet room for important work in some of the

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[1] H. S. Washington [*U. S. Geol. Survey Profess. Papers* **99** (Chemical Analyses of Igneous Rocks, published from 1884 to 1913, with a critical discussion of the character and use of analyses) and **28** (The Superior Analyses of Igneous Rocks from Roth's Tabellen, 1869 to 1884, arranged according to the quantitative system of classification)] did a most important work in sifting the great mass of data accumulated in the thousands of analyses published since 1869. After a systematical critical examination, he assigned to each analysis a certain value on a scale of 5. Many of these values may be incorrect, but most of them undoubtedly give a fairly true measure of the weight to be attached to the respective analyses.

supposedly simplest quantitative determinations. If the results are to have any decided value for purposes of scientific interpretation and comparison, they must be the outcome of the work of one who is able to find his way through the intricacies of an analysis in which 15 to 25 components are to be separated and estimated with close approach to accuracy, and this a beginner cannot hope to do. The conscientious chemist should have a live interest in this matter. He should work with a two-fold purpose in view—that of lightening the labors of those who come after him by enabling them to use his work with less supplementary examination, and that of enhancing his own reputation by meriting encomiums on work that has stood the test of time.

How little understood may be the principles underlying the treatment of bodies so complex, and the accurate separation and determination of their constituents, even when these are comparatively few, have been strikingly shown in the work of committees of chemists charged with the investigation of the methods employed in various branches of technical chemistry involving the analysis or assay of zinc ores, slags from the smelting of copper ores, argillaceous limestones, glasses, refractories, and cements. In all cases a most woeful inability to obtain accordant results is apparent, not only among those less experienced but among those supposed to be most expert in each of the particular fields as well. Some improvement in commercial silicate analysis has resulted from the investigations set on foot and the recommendations made by these committees, and further improvement may be expected. A more marked improvement has been shown in the quality of analyses made for scientific study, but the art of analysis still stands in great need of more thorough treatment in our educational institutions.

The petrographer, again, should seek to have his analyses made as complete as possible, and not, as was often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalies, and water. The latter course, it is true, is entirely justifiable at times and may serve the immediate purposes of the analyses, but their incompleteness may, on the other hand, not only conceal points fruitful of suggestion to the attentive mind, but, what is of still greater importance, they may be actually misleading. Enough instances of totally inaccurate conclusions to be drawn from them have fallen under our observation to fully justify this plea in favor of greater completeness in rock and mineral analysis made for purely scientific purposes.[2]

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[2] For further presentation of this subject from the viewpoint of an experienced petrographer, see H. S. Washington, *Manual of the Chemical Analysis of Rocks*, pp. 7–17 (1919).

The importance of the points indicated in the foregoing paragraph is shown by the difference between the analyses given in Table 24A. The specimens were taken and analyzed at widely separated times and by different persons, it is true, but they were unquestionably from the same rock mass, in which, however much the relative proportions of the different mineral constituents might vary within certain limits, there can be no reason to doubt the general distribution of all the elements shown by the second analysis.

Another instance of similar kind is given in Table 24B. Here, again, certain differences are explainable by natural variations in the proportions of the constituent minerals, but it can hardly be doubted that TiO_2, BaO, SrO, P_2O_5, and SO_3 were present in both specimens in approximately the same amounts. In the earlier analysis, determinations of some supposedly unimportant constituents were purposely omitted or made only qualitatively, with results that cannot be otherwise than fatal to a full comprehension of the mineralogic nature of the rock.

F. W. Clarke has shown that the combined percentages of titanic and phosphoric oxides in rocks of the earth's crust, averaged from hundreds of analyses, amount to 0.8 per cent. When the determination of these is neglected, the error falls on the alumina. If the alumina is then used as a basis for calculating the feldspars, it is easy to see that a very large average error in the latter may result, amounting to several per cent of the rock.

In order to emphasize more strongly the importance of completeness in analysis, a few facts brought out by the hundreds of rock analyses made in the U. S. Geological Survey laboratory may be cited. It has been demonstrated most conclusively that barium and strontium are almost never-failing constituents of the igneous rocks of the United States and of many of their derivatives. The amounts are usually below 0.1 per cent for each of the oxides of those metals, but higher amounts are by no means uncommon. Furthermore, the weight of barium is almost without exception in excess of that of strontium; but a still more important point is that the igneous rocks of the Rocky Mountain region, so far as examined, show much higher average percentages of both metals than the rocks from the eastern and the more western portions of the United States. The following examples serve to illustrate certain types of Rocky Mountain igneous rocks: Of seven rocks forming a Colorado series, six held 0.13 to 0.18 per cent of BaO, whereas in the seventh the percentage was 0.43. The SrO ranged from 0.07 to 0.13 per cent for six and was 0.28 for that one highest in BaO. Of 13 geologically related rocks from Montana, embracing basic as well as acidic and intermediate types, the range of BaO was 0.19 to 0.37 per cent, with an average of 0.30 per cent. Three others of the same series contained 0.10 per cent or less, while the 17th carried 0.76 per cent BaO. The SrO

TABLE 24A

Analyses of Specimens Taken from the Same Rock Mass at Different Dates

	Earlier Analysis	Later Analysis *		Earlier Analysis	Later Analysis *
SiO_2	54.42	53.70	Li_2O	Trace	Trace
TiO_2	.....	1.92	H_2O below 110°	.....	0.80
Al_2O_3	13.37	11.16	H_2O above 110°	2.76 ‡	2.61
Cr_2O_3	.....	0.04	CO_2	1.82	
Fe_2O_3	0.61 †	3.10	P_2O_5	.....	1.75
FeO	3.52 †	1.21	SO_3	.....	0.06
MnO	.....	0.04	F	.....	0.44
CaO	4.38	3.46	Cl	.....	0.03
SrO	.....	0.19			
BaO	.....	0.62		99.58	100.40
MgO	6.37	6.44	Less O for F	.....	0.19
K_2O	10.73	11.16			
Na_2O	1.60	1.67			100.21

* A still more recent analysis of another of the series of rocks of which this is an example has shown that this "later analysis" is itself probably incomplete and incorrect in part—incomplete because of the probable presence of 0.2 per cent or more of ZrO_2, incorrect because of the error in Al_2O_3, resulting from the ZrO_2 being counted as Al_2O_3, and from the fact that titanium is not fully precipitable in the presence of zirconium by Gooch's method (the one employed). This latter error involves both the TiO_2 and the Al_2O_3 (see p. 887).

† From the fact that repeated determinations of the iron oxides in this and related rocks from the same region show always a great preponderance of ferric oxide, it is not improbable that the figures given for the two oxides in the first analysis were accidentally transposed.

‡ In the published analysis, it does not appear whether this is total water or, as seems probable, only that remaining above 100°.

TABLE 24B

Analyses of Specimens Taken from the Same Rock Mass at Different Dates

	Earlier Analysis	Later Analysis		Earlier Analysis	Later Analysis
SiO_2	44.31	44.65	Na_2O	4.45	5.67
TiO_2	Not est.	0.95	Li_2O	.....	Trace
Al_2O_3	17.20	13.87	H_2O below 110°	0.77	0.95
Fe_2O_3	4.64	6.06	H_2O above 110°	.....	2.10
FeO	3.73	2.94	H_2O by ignition	3.30	
MnO	0.10	0.17	CO_2	.....	0.11
CaO	10.40	9.57	P_2O_5	.....	1.50
SrO	.....	0.37 *	Cl	.....	Trace
BaO	.....	0.76	SO_3	.....	0.61
MgO	6.57	5.15			
K_2O	3.64	4.49		99.11	99.92

* Not entirely free from CaO.

ranged from 0.37 per cent in the 17th rock to an average of 0.06 for the other 16. Certain peculiar rocks from Wyoming carry from 0.62 to 1.25 per cent BaO and from 0.02 to 0.33 per cent SrO. Surely this concentration of certain chemical elements in certain geographic zones has a significance which future geologists will be able to interpret, if those of today are not.

Again, vanadium is an element that few chemists ever thought of looking for in igneous rocks, though it had long been known to occur in magnetites and other iron ores. A. A. Hayes, in 1875, reported its occurrence in a great variety of rocks and ores. To quote from Thorpe's *Dictionary of Chemistry:* "It is said to be diffused with titanium through all primitive granite rocks [Dieulafait] and has been found by Deville in bauxite, rutile, and many other minerals and by Bechi and others in the ashes of plants and in argillaceous limestone, schists, and sands." It is further reported to comprise, as the pentoxide, up to 0.1 per cent of many French and Australian[3] clays, 0.02 to 0.03 per cent of some basalts, 0.24 per cent of a coal of unknown origin, and 0.45 per cent of a coal from Peru. Still later examinations in the Survey laboratory of about 100 rocks, chiefly igneous, covering nearly the whole continental territory of the United States, show, not only its general qualitative and quantitative distribution, but also that it predominates in the less siliceous igneous rocks and is absent, or nearly so, in those high in silica. In some of the more basic rocks it occurs in sufficient amount to affect seriously the figures for the oxides of iron unless separately estimated and allowed for, a matter of considerable importance, because the petrographer lays great stress on accuracy in their determinations.

The same investigation also threw some light on the distribution of molybdenum, which seems to be confined to the more siliceous rocks and to occur in quantities far below those commonly found for vanadium.

Finally, had it not been the practice to look for sulfur in rocks, even when no sulfides were visible to the eye, its almost invariable presence in the form of sulfide and consequent connection with the long mystifying lack of agreement between results for ferrous iron obtained by the Mitscherlich and the hydrofluoric acid methods might not have been suspected (see b, p. 909).

Although strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from our intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But

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[3] J. C. H. Mingaye confirmed its wide distribution in Australian rocks, coals, etc. [*Records Geol. Survey N. S. Wales,* 7 [3], 213 (1903)].

we maintain that, in general, the constituents which are likely to be present in sufficient amount to admit of determination in the weight of a sample usually taken for analysis—say, 1 g for SiO_2, Al_2O_3, etc., to 2 g for certain other constituents—should be sought for, qualitatively at least, in the ordinary course of quantitative work, and their presence or absence noted among the results. If present in little more than traces, that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0.02 or 0.06 per cent. In the tabulation of analyses, a special note should be made, in case of intentional or accidental neglect, to look for substances that it is known are likely to be present. Failure to do this may subject the analyst to unfavorable criticism when, at some future time, his work is reviewed and the omissions are discovered by new analyses.

Finally, whenever possible, a spectroscopic and a thorough microscopic examination of the rock in thin section should precede the chemical analysis. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents or of more than customary amounts of certain constituents, whereby, possibly, necessary modifications in the analytical procedure may be employed without waste of time or labor.[4] It is better, for both the geologist and the chemist, to turn out a moderate amount of thorough work than a great deal of what may ultimately prove to be of more than doubtful utility.

2. The Constituents Occurring in Silicate Rocks

It is to the decomposition of the original igneous rocks or their magmas and their derivatives that nearly all ore bodies in the United States owe their origin by one or another process of concentration. A certain class of concentrates probably separated from magmas in the fluid state before solidification. Hence, it is the natural and inevitable inference that sufficiently careful examination of these rocks would show them to contain all or nearly all the known elements, not necessarily all in a given rock, but many more than were formerly found.[5] Mechanical and analytical diffi-

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[4] See also H. S. Washington, *Manual of the Chemical Analysis of Rocks,* 6–7 (1919). The foregoing tables and accompanying remarks, including several sentences preceding the tables, were taken largely from a paper entitled A Plea for Greater Completeness in Chemical Rock Analysis, *J. Am. Chem. Soc.,* 16, 90–93 (1894); *Chem. News,* **69,** 1163 (1894). See also Distribution and Quantitative Occurrence of Vanadium and Molybdenum in Rocks of the United States, *Am. J. Sci.,* [4] **6,** 209 (1898); *Chem. News,* **78,** 216 (1898); and *U. S. Geol. Survey Bull.* **167,** 49 (1900).

[5] F. Sandberger's researches showed to what extent this is true of a large number of those elements contributing to the filling of metalliferous veins, and L. Dieulafait by his elaborate qualitative researches showed how universal was the distribution of copper, zinc, barium, strontium, etc., in the primordial rocks.

TABLE 25

Minor Elements of Certain Rocks *

Element	Rock Sample 1	2	3	4	5
Cr	0.23	0.013	0.003	—	—
Ni	0.015	0.0081	—	—	—
Co	0.0017	0.0025	0.0003	—	—
Sc	0.0019	0.0055	0.0002	—	0.0005
V	0.013	0.022	0.0026	—	0.0062
Cu	0.0023	0.0089	0.0015	0.0003	—
Mn	0.099	0.13	0.014	0.054	0.13
Sr	0.044	0.014	0.012	0.0034	0.019
Ba	0.074	0.038	0.13	0.013	0.0086
Pb	—	—	0.0022	0.0005	0.0016
Zr	0.013	0.0096	0.027	0.028	0.069
Ga	0.0013	0.0012	0.0018	0.0024	0.0022
Y	—	......	0.0025	0.011	0.010
La	—	......	0.017	0.0094	0.033
Mo	—	......	0.0007	—	0.0012
Be	—	......	0.0002	0.0004	0.0003
B	—	0.001	—	—	—
Nb	—	—	—	0.0045	0.017

A dash in the table means element was below the limit of spectrographic detection by the method used.

1. Basaltic andesite (49-687SC), lava from Parícutin volcano, Mexico.
2. Diabase (W-1), Centerville, Virginia.
3. Granite (G-1), Westerley, Rhode Island.
4. Rhyolite (50-511SC), Jemez Mountain, New Mexico.
5. Nepheline syenite (49-93SC), Pulaski County, Arkansas.

* Information furnished through the courtesy of K. J. Murata and Joseph J. Fahey of the U. S. Geological Survey (1951).

culties have thus far stood in the way of experimental proof that this is so, owing to the great scarcity of many of the elements. In exceptional cases, it may be desirable to subject a given material to very exhaustive analysis, as, for instance, when searching for the origin of ore deposits. Ordinarily, however, the demands of the petrographer and geologist are satisfied with a knowledge of the quantitative relations of those constituents that can be determined in a limited amount of the sample—say, from 0.5 g to 2 or occasionally 5 g. In general the discussion relating to silicate analysis in this volume will be confined to such separations as may be required in the analysis of an igneous, metamorphic, or sedimentary rock of complex mineralogical composition, in which the majority and possibly all of the ingredients in the list given below may occur in weighable or readily discoverable quantities:

SiO_2, TiO_2, ZrO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, V_2O_3, FeO, MnO, NiO, CoO, MgO, CaO, SrO, BaO, ZnO, CuO, K_2O, Na_2O, Li_2O, H_2O, P_2O_5, S,[6] SO_3, C,[7] CO_2, F, Cl, N.

To the above list might be added certain others, as the group of so-called rare earths, besides tin, platinum, tantalum, columbium, boron, beryllium, helium. Some of these occur at times in determinable amounts and may very well have been overlooked by reason of the absence of distinctive tests for identification. Thorium, cerium, and other rare earths are probably more common as constituents of silicate rocks than has been generally supposed. Their presence and amount can be so readily and certainly detected by the methods given in their proper place that the reason for neglecting to look for them is no longer so strong as it used to be, especially when there is microscopic or other evidence of the presence of minerals likely to contain them.

That still other elements might be added is indicated by the elements found by W. N. Hartley and H. Ramage[8] by spectrographic tests of certain minerals and by a systematic study of minor elements in rocks by members of the U. S. Geological Survey as shown in Table 25.

3. Preliminary Qualitative Analysis

A complete qualitative analysis of a rock preceding the quantitative examination is in most cases a sheer waste of time. A few constituents may now and then be specially looked for, but, in general, time is saved by assuming the presence of most of them and proceeding on that assumption in the quantitative analysis.

This statement must not be misinterpreted so as to convey the impression that qualitative analysis should receive little consideration. For ores, mineral species, waters, etc., it is indispensable, as also in the testing of precipitates and filtrates during the course of quantitative analysis.

The student of qualitative analysis will find in papers by A. A. Noyes, W. C. Bray, and E. B. Spear[9] a vast fund of information relating not only to the making of separations but also, and this is often of greater importance, to the completeness of these separations and to the possible limits of detection. The scope of these papers is less restricted than their titles might be thought to imply, for such elements as beryllium, uranium, vanadium, titanium, zirconium, and thorium are included.

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[6] Usually as pyrite, occasionally as lazurite, not infrequently as pyrrhotite.

[7] As graphite or coaly matter.

[8] *Trans. Chem. Soc.*, 79, 61 (1901).

[9] *J. Am. Chem. Soc.*, 28, 137 (1907); 30, 481 (1908); *Chem. News*, **95**, 89, etc. (1907); **98**, 6, etc. (1908). See also A. A. Noyes and W. C. Bray, *A System of Qualitative Analysis for the Rare Elements*, Macmillan Co. (1927).

4. Summation of Analytical Results and Limits of Allowable Error

As is well known, a complete silicate-rock analysis which foots up less than 100 per cent is generally less satisfactory than one that shows a summation somewhat in excess of 100. This is due to several causes. Nearly all reagents, however carefully purified, still contain or extract from the vessels used traces of impurities, which are eventually weighed in part with the constituents of the rock. The dust entering an analysis from first to last may be considerable, washings of precipitates may be incomplete, and, if large filters are used for small precipitates, the former may easily be insufficiently washed.

Given the purest obtainable reagents, an ample supply of platinum, facilities for working, and a reasonably clean laboratory, there is usually little excuse for failure on the part of a competent chemist to reach a summation within the limits 99.75 and 100.50. Summations obtained by analysts working with one of us (L.) are shown in Table 26. Failure to attain 100 per cent in several of a series of analyses of similar nature should be the strongest evidence that something has been overlooked. Excess above 100.5 per cent should be good ground for repeating portions of the analysis in order to ascertain where the error lies, for it is not proper to assume that the excess is distributed over all determined constituents. It is quite as likely—in fact, more than likely—to affect a single determination and one that may be of importance in a critical study of the rock from the petrographic side.

Washington would extend the allowable limits above given to 99.50 and 100.75. If the analysis has to be made in other vessels that those of platinum and careful blank determinations are not carried along, a higher limit than 100.50 is certainly called for, but it is extremely doubtful if a lower one than 99.75 should be accepted, for, as has been said, there is a tendency toward too high results in any case, and a summation of less than 99.75 with vessels other than platinum would be indicative of rather gross error on the part of the analyst.

As for the allowable variation in duplicate determinations of the same constitutent no rigid rules can be laid down. Washington[10] proposed the following, with which the experimental values of Dittrich[11] made substantial agreement: For SiO_2 and others that amount to 30 per cent and over, 0.2 to 0.3 per cent; for Al_2O_3 and others that amount to 10 to 30 per cent, 0.1 to 0.2 per cent; for constitutents that amount to 1 to 10 per cent, 0.05 to 0.1 per cent. These percentages are in terms of the whole rock. The agreement that can be obtained in very careful determinations of certain constituents is illustrated by the results shown in Table 27. Analyses of a granite and a diabase rock by 34 chemists, working in 25 world-wide

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[10] *Manual of the Chemical Analysis of Rocks*, p. 127 (1919).

[11] *Neues Jahrb.*, 2, 69 (1903).

TABLE 26

Summations That Can Be Expected in Careful Analyses

Constituent	Dolomite *	Feldspar		Bauxite †	Refractories			Glasses	
		*	†		†	†	†	Soda-Lime *	Lead-Barium *
SiO_2	0.311	66.68	66.63	6.32	54.68	32.49	20.78	74.09	65.36
Al_2O_3	0.069	18.01	18.04	55.00	37.63	59.30	69.86	0.32	0.181
Fe_2O_3	0.086	0.031	0.031	5.63	2.35	0.86	0.73	0.064	0.048
MgO	21.54	0.02	0.006	0.015	0.59	0.43	0.52	3.23	0.029
CaO	30.48	0.052	0.085	0.047	0.25	0.27	0.32	4.65	0.21
Na_2O	0.08	2.37	2.38	0.18	0.36	0.89	0.54	16.63	5.73
K_2O	0.03	12.58	12.58	0.05	1.43	2.10	2.90	0.04	8.38
TiO_2	0.004	0.002	0.002	3.04	2.23	2.97	3.34	0.02	0.011
ZrO_2				0.068	0.074	0.095	0.12	0.003	0.003
P_2O_5	0.002	0.009	0.014	0.116	0.07	0.45	0.61		0.22
SO_3	0.069			0.063				0.41	0.031
MnO	0.009	0.001	0.001	0.55				0.003	0.089
	0.01 SrO	0.033 BaO	0.035 BaO	0.031 Cr_2O_3	0.02 V_2O_5	0.029 V_2O_5	0.038 V_2O_5	0.031 As_2O_3	17.50 PbO
	0.013 S			0.03 CuO				0.068 As_2O_5	1.41 BaO
	47.25 CO_2			0.025 V_2O_5				0.047 Cl	0.031 As_2O_3
	0.08 C								0.39 As_2O_5
	0.008 H								0.051 Cl
Loss on ignition	47.52	0.21	0.23	28.81	0.26	0.23	0.27	0.30	0.30
Total	100.04	99.99	100.03	99.99	99.91	100.10	99.97	99.92	99.98

* Analyst: H. B. Knowles.
† Analyst: J. I. Hoffman.

TABLE 27

Precision That Is Possible in Careful Analyses

Results in parentheses were obtained by the use of a different method.

Constituent	Dolomite	Feldspar	Bauxite	Refractories			Soda-Lime Glass	Lead-Barium Glass
SiO_2	0.311 0.311 0.310	66.53, 66.76, 66.66 66.65, 66.55, 66.65 66.65, 66.63, 66.62	6.34 6.33 6.30	54.56 54.68 54.80	32.40 32.58	20.74 20.82	74.07 74.17 74.03 74.10	65.35, 65.36, 65.35 (65.38, 65.38, 65.36)
Al_2O_3	0.069 0.068 0.070	18.05, 18.07, 17.93 18.16, 18.11, 18.14 (18.01, 17.99, 17.96) (18.00, 17.99)	54.95 55.01 (54.94) (55.09)	37.62 37.76 (37.56)	59.40 59.30 (59.32) (59.18)	69.80 70.00 (69.78) (69.84)	0.325 0.313 0.321 0.313	0.180 0.182
Fe_2O_3	0.086 0.086 0.085	0.032, 0.030, 0.030, 0.028 (0.032, 0.031)	5.57 5.63 5.65 5.65	2.33 2.39 2.31 2.36	0.82 0.89	0.76 0.70	0.064 0.062 0.066 0.064	0.048, 0.048, 0.048, 0.050
MgO	21.54 21.56 21.53	0.024, 0.019 (0.005, 0.007)	0.015 0.014	0.59 0.58	0.41 0.44	0.51 0.52	3.22 3.22 3.23 3.24 3.25 3.22 3.23 3.23	0.029 0.028 0.028 0.0296
CaO	30.47 30.47 30.51	0.051, 0.050, 0.053 0.053, 0.051 (0.088, 0.082)	0.044 0.050	0.25 0.25	0.26 0.27	0.32 0.32	4.71 4.67 4.61 4.63	0.211 0.210 0.210 0.208
Na_2O	0.08 0.06 0.10	2.35, 2.39, 2.41 2.35		0.36 0.35	0.91 0.87	0.52 0.56	16.64 16.62	5.72 5.76 5.70
K_2O	0.04 0.03 0.03	12.56, 12.58, 12.60 12.58, 12.58		1.40 1.47	2.10 2.10	2.87 2.92	0.04 0.04 0.04 0.03	8.38 8.39 8.38
TiO_2	0.004 0.004	0.002, 0.002, 0.003 0.003	3.06 3.03 3.04	2.19 2.20 2.26 2.25	2.93 2.95 3.01 2.99	3.37 3.32 3.32 3.35	0.03 0.02 0.02 0.02	0.0136 0.0102 0.0102 0.0085
ZrO_2			0.069 0.065 0.069	0.075 0.071 0.076 0.072	0.099 0.090 0.093 0.097	0.12 0.12 0.13 0.11	0.0027 0.0027 0.0027 0.0018	
P_2O_5	0.002 0.002	0.009, 0.009, 0.010 0.013 (0.015, 0.016, 0.014)	0.114 0.120 0.115	0.07 0.06 0.07	0.44 0.47 0.44	0.64 0.61 0.59		0.22 0.22
SO_3	0.069 0.069 0.070		0.064 0.062				0.404 0.402 0.404 0.413 0.419 0.416 0.422	0.033 0.029
MnO	0.0086 0.0088	0.001, 0.001, 0.001, 0.001	0.545 0.559 0.547				0.003 0.003	0.091 0.086
	47.24, 47.25 47.20, 47.27 47.28, 47.23 CO_2	0.035 0.033 0.037 BaO	0.031 0.030 Cr_2O_3				0.047 0.047 Cl	0.051 0.051 Cl
	0.013 0.013 S		0.025 0.025 V_2O_3	0.02 0.02 V_2O_5	0.027 0.030 V_2O_5	0.038 0.038 V_2O_5		1.408 1.409 1.412 1.411 BaO
	0.01 0.01 SrO							17.48 17.48 17.50 17.52 PbO
	0.081 0.083 0.078 0.078 C						0.030 0.032 0.029 As_2O_3	0.031 0.031 As_2O_3
	0.0084 0.0080 0.0080 0.0087 0.0078 H						0.068 0.068 0.070 As_2O_5	0.39 0.39 As_2O_5
Loss on ignition	47.55 47.52 47.49	0.22, 0.21, 0.20 0.19, 0.25, 0.25	28.78 28.82 28.83 28.84 28.78	0.25 0.27	0.22 0.24	0.27 0.26	0.27 0.28 0.33 0.32	0.30 0.30 0.29

rock-analysis laboratories, have been reported by W. G. Schlecht and R. E. Stevens.[12] The precision and range of the values for approximately 15 constituents are somewhat discouraging. These data indicate the continuing need for improvement in both the art and the science of rock analysis.

Although it is desirable sometimes, and for the beginner imperative, to make duplicate determinations, agreement is not to be taken as proof that the results are correct unless they have been arrived at by different methods.

Too great stress cannot be laid upon the importance, especially for the analyst of limited experience, of consistently testing most of his final precipitates and filtrates as carefully as possible in order to be sure, on the one hand, that the substances reported by a given name are wholly such and, on the other, that all is reported. In no other way can an analyst so soon acquire the needed confidence in himself and his methods. Likewise methods should be checked with standard samples of like material whenever possible.

5. Statement of Analyses

For many years it was the practice in the laboratory of the U. S. Geological Survey to tabulate the constituents of a rock somewhat in the order of their determination, beginning with SiO_2 as the chief constituent and grouping together all chemically related oxides, as shown, for instance, on page 797.

From a strictly scientific point of view, a chemical classification, founded on a separation into basic and acidic atoms or radicals, would be more satisfactory, but, until we learn to find out what silicic radicals are present and in what relative amounts, and also how much free silica there may be, it is useless to think of employing the arrangement used in stating water analyses.

Petrographers now demand, with considerable reason, an arrangement "which shall bring the essential chemical features—both the percentage figures and the molecular ratios—prominently and compactly before the eye, so that the general chemical character and the relations of the various constituents may be seen at a glance." [13]

In accordance with this demand, it is now the practice to follow pretty closely the arrangement proposed by Pirsson and later strongly advocated by Washington, namely:

SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O (above 105 to 110°), H_2O (below 105 to 110°), CO_2, TiO_2, ZrO_2, P_2O_5, SO_3, Cl, F, S (FeS_2), Cr_2O_3, V_2O_3, NiO, CoO, CuO, MnO, SrO, BaO, Li_2O, C, NH_3.

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[12] A Cooperative Investigation of Precision and Accuracy in Chemical, Spectrochemical, and Modal Analysis of Silicate Rocks, *U. S. Geol. Survey Bull.* 980, 7 (1951); see also, W. G. Schlecht, *Anal. Chem.*, 23, p. 1568 (1951).

[13] H. S. Washington, The Statement of Rock Analyses, *Am. J. Sci.*, [4] 10, 61 (1900).

By this arrangement the nine constituents which in the great majority of cases determine the character of the rock are placed at the head of the list, thus facilitating greatly the comparison of different analyses similarly arranged, especially when, as Washington recommends, the molecular ratios are calculated for these leading constituents and placed immediately after the corresponding oxides. The order of the remaining members is determined somewhat by the following considerations: CO_2 is placed next after H_2O, for these two are generally a measure of the alteration the rock may have undergone. TiO_2 and ZrO_2 naturally follow CO_2 on chemical grounds, and SO_3 and Cl, being common constituents of the sodalite group, are conveniently placed together.

It may be said with regard to the use of the word "trace" that the amount of a constituent thus indicated is supposed to be below the limit of quantitative determination in the amount of the sample taken for analysis. In general, for analyses laying claim to completeness and accuracy, it should be supposed to indicate less than 0.01 per cent.

6. Time Needed for Making an Analysis

The question has often been put, "How long does it take to complete an analysis of this kind?" This will depend, of course, on the mineral complexity of the sample and on the personal factor of the individual worker. If there is a competent assistant to do the grinding, and specific-gravity determinations are not required, it is quite possible after long experience for a quick worker to learn so to economize every moment of time in a working day, with an abundance of platinum utensils and continuous use of air and water or steam baths through the night, as to finish every three days, after the completion of the first analysis, barring accidents and delays, one of a series of rocks of generally similar character, each containing 18 to 20 quantitatively determinable constituents, excluding, for instance, fluorine, carbon as such, nitrogen, metals of the hydrogen sulfide group, and cobalt. But such an output of work implies an unusual freedom from those occasional setbacks to which every chemist is exposed.

II. METHODS APPLICABLE TO SILICATE ROCKS

1. Introductory Remarks

The order hereinafter followed in describing the various chemical separations has little relation to the affinities of the constituents of the rock, but those are grouped together that can be determined conveniently in the same portion of rock powder. Thus, in the main portion, it is usual to determine SiO_2, TiO_2, MnO, NiO, CaO, SrO, MgO, total iron, and the combined weight of all the following: Al_2O_3, TiO_2, P_2O_5, ZrO_2, all iron as Fe_2O_3, and nearly if not quite all vanadium as V_2O_5, also perhaps rare earths if present. In a separate portion is estimated FeO, and also the total iron, as well as BaO, if these last are desired as checks. The alkalies need a portion for themselves. In another it is convenient to determine ZrO_2, BaO, rare earths, and total sulfur. For V_2O_3 and Cr_2O_3 still another and usually much larger portion is to be used. Determinations of CO_2, C, H_2O, F, and Cl are all made best in separate portions of substance, though various combinations are possible, as CO_2 and H_2O, C and H_2O, or H_2O, F, and Cl. In fact, by a judicious selection and combination of methods, a very satisfactory analysis can sometimes be made on 4 g of material without omission of anything of importance, though the time consumed will be greater than if ample material is available.

As an illustration of the advantage to be gained by a little judgment in the combination of methods, the case of sulfur, barium, zirconium, and rare earths may serve. Many chemists never look for any but the first of these, but, by following the procedure given under 9, A (p. 889), not much more labor is expended in confirming their presence or absence than that of sulfur alone.

With only occasional exceptions, nearly all the constituents mentioned on page 801 can be determined, if present, in portions of powder not exceeding 1 g each in weight.

This is a convenient weight to take for the main portion, in which silica, alumina, etc., the alkaline earths, and magnesia are to be sought; but it should, in general, be a maximum, because, if a larger quantity is taken, the precipitate of alumina, etc., is apt to be unwieldy. It cannot often be much reduced with safety if satisfactory determinations of manganese, nickel, and strontium are to be expected. For the alkali portion, ½ g is a very convenient weight. In general, it may be made a rule not to use more than 2 g for any portion that has to be fused with an alkali carbonate, as for sulfur, fluorine, and chlorine. For carbon dioxide, the weight may rise to 5 g, or even more, if the amount of this constituent is very small, without expenditure of any more time than is required by 1 g and with correspondingly greater approach to correctness in the result. For vanadium also usually a larger weight than 2 g is demanded.

For the attainment of accurate results, such as are needed for the close classification of a rock in the system devised by Cross, Iddings, Pirsson, and Washington,[14] too great stress cannot be laid on the exercise of the utmost care throughout the analysis. This applies not only to routine manipulations, but even more in the matter of double precipitations, where these are called for, and in the testing of filtrates and precipitates to insure complete

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[14] *Quantitative Classification of Igneous Rocks,* 286 pp., University of Chicago Press (1903).

recovery of the desired substances, on the one hand, and freedom of them when obtained from matter that should not be there, on the other. These cautions are especially applicable to analysts who have little experience. It must always be remembered that analysis can at best afford but approximate results, which will be more serviceable the greater the care bestowed in obtaining them.[15]

2. Preparation of Sample for Analysis

A. QUANTITY OF ROCK TO BE CRUSHED

The amount of material that must be used in preparing the analysis sample varies. Most rocks are well represented by a few chips from a hand specimen, but, if a rock in which porphyritic structure is strongly developed is to be analyzed a large sample should be provided, gaged according to the size of the crystals, and the whole of this should be crushed and quartered down for the final sample. Unless this is done, it is manifest that the analysis may represent anything but the true average composition of the rock. The geologist should see that a fairly representative sample is provided; else the chemist's work, however careful, may count for little.

B. CRUSHING

For accurate analyses, the use of steel power crushers and mortars is out of the question because of the danger of contamination by particles of metal and the impossibility of cleansing the roughened surfaces after they have been in use a short time. Extraction, by the aid of a magnet, of steel particles thus introduced into the powder is quite inadmissible, for the rocks themselves, almost without exception, contain magnetic minerals.

a. *Methods Used at the U. S. Geological Survey.* For breaking large pieces of rock to small sizes a thick steel plate with specially hardened surface and a similarly hardened pounder, such as street pavers use, will probably render the best service, but the hardening must be done with extreme care.

Satisfactory crushing on a small scale can be done in a mortar devised by C. W. H. Ellis, mechanician in the geophysical laboratory of the Carnegie Institution, which entirely obviates loss of material by flying fragments. The method of operating is apparent from Fig. 37. The block, cylinder, and pestle are of the best chilled tool steel, surface-hardened to the utmost limit. The cylinder fits snugly into a depression in the block, after the manner of an ordinary "diamond" mortar, but the pestle has a diameter less than the inner diameter of the cylinder. The crushing is done by the pestle, without the aid of a hammer, and may be carried so far, if

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[15] For applications of microanalytical methods in the analysis of silicate rocks, consult F. Hecht, *Mikrochim. Acta,* 2, 120, 188 (1937).

necessary (see 2, C, p. 811), as to furnish by the aid of a fine sieve, preferably of the best silk bolting cloth, a powder that is fit for analysis without needing further pulverization in an agate mortar. For very many rocks and minerals, a material that passes a sieve of 30 meshes to the linear centimeter can be used directly for the analysis. Much the greater part of this will consist of grains of a diameter less than that of the mesh of the sieve, even when the intervals between successive applications of the pestle and siftings are very short.

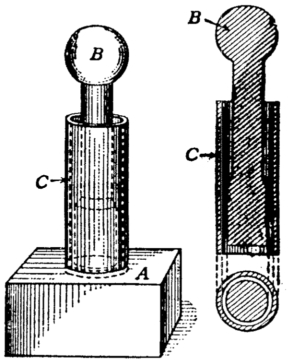

Fig. 37. Ellis's mortar for crushing coarse materials. All parts of best chilled and surface-hardenel tool steel. *A*, Block, 12½ by 12½ by 6 cm, with depression in center 0.6 cm deep; *B*, pestle, 20 cm high, 3.5 cm in diameter at base; *C*, cylinder, 12½ cm high, 5 cm outside diameter, 4.4 cm inside diameter, fitting accurately the depression in the block.

Metal sieves must on no account be used if search is to be made for elements identical with those of which the sieves are made.

An imperative precaution, when using this method, however, is to refrain absolutely from the least grinding or rubbing motion with the pestle. Even quartz can be broken down by vertical blows to a size fit for the agate mortar without showing any darkening in color, whereas, if a rubbing motion has been employed to even a slight extent, the powder will, by contrast, be perceptibly dark after grinding in the mortar. The hardest steel is very susceptible to abrasion by minerals less hard than quartz.[16] The crushing must be carried to such a degree of fineness that, after the grains are transferred to the mortar, the grinding motion of its pestle will not occasion further loss of flying particles because the portions lost will not have the same composition as those retained unless the material is glassy or very fine-grained.

If grinding is not to follow crushing, the sieve should be chosen of a mesh that will afford a powder susceptible of complete or nearly complete decomposition within 20 minutes by boiling with dilute hydrofluoric acid (see C, below, and 15, A, p. 907). In order to obtain the minimum of "flour," it is important to sift at very frequent intervals.

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[16] When the crushing has been done with proper care, the amount of steel contaminating the sample is so small as to cause no important error. This steel is for the most part apparently not in splinters but as thin films on the mineral grains. Its presence can be shown readily by grinding the crushed sample to a very fine powder in presence of water. The films thus become separated from the grains and still further flattened, and, as the grinding progresses, they rise as a visible scum to the surface of the water, whence they can be removed by careful handling of a magnet. This behavior of the films might perhaps afford a means of testing for native iron in rocks, provided the use of steel for crushing could be avoided altogether.

Some flour is, however, essential to the production of a homogeneous sample when flaky minerals, like the micas, are present. If the flour is first separated from a micaceous powder, no amount of mixing of the coarser material will afford a sample in which the mica does not show in streaks instead of being uniformly distributed. The sample finally obtained is to be very thoroughly mixed on glazed paper or by gentle shaking in a clean bottle.

b. *Washington's Method.* The rock is first reduced, as by the methods described in a, to lumps that will fit into a "diamond" steel mortar of Plattner's form, the bottom of the cavity being hemispherical and matched in shape by the end of the pestle. The lumps are crushed, one by one, in the mortar by a dozen blows of a half-pound hammer (billet of wood, Dittrich), and the contents of the mortar are emptied into a cylindrical glass box about 3.5 cm deep and 7.5 cm in internal diameter, with walls about 2 mm thick. When the whole sample, or a quartered portion if it is large, has been thus crushed, a piece of best silk bolting cloth with about 25 meshes to the linear centimeter is stretched over the open side of the box and clamped fast by a brass ring 1 cm in height. The box is now inverted and the finest powder gently sifted onto a sheet of glazed paper. The material left on the cloth is recrushed in the mortar and resifted, these operations being repeated until nearly all has passed the sieve. The final small oversize portion is ground in an agate mortar. It will, of course, not do to reject any portion, for thereby the composition of the mass will be affected.

Washington found that in this way there is no danger of serious contamination by metallic iron (see preceding footnote) and that any error resulting from the introduction of cloth fiber is negligible. This last will hardly be true of the method practiced in parts of Europe (the German *beuteln*), which, at least as it was carried out in Bunsen's laboratory, differs in essential points from the gentle sifting recommended by Washington.

C. GRINDING

Ordinarily an extremely fine state of division of the analysis sample is unnecessary, except for those portions in which alkalies and ferrous iron are to be determined or where soluble constituents are to be removed by acids, etc., and for such portions the final grinding can be done at the balance table on a small quantity of the crushed sample.

Not only is fine grinding for most purposes needless, but also it may be positively harmful, allowing escape of contained gases, and, as R. Mauzelius showed,[17] it is absolutely imperative for the correct determination of ferrous iron to use the coarsest powder that can be decomposed completely

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[17] *The Determination of Ferrous Iron in Rock Analysis; Sveriges geol. Undersökn.*, Arsbok 1, no. 3 (1907).

by the method of attack employed. W. F. Hillebrand showed[18] that this is true for the water that is not given off at 100 to 110°. Mauzelius discovered that, the finer the material (containing ferrous iron) is ground, the less ferrous iron is found. In all his experiments on rocks and on iron-bearing minerals separated from rocks, the oxidation was marked and in the most extreme case amounted to about 40 per cent of the total ferrous iron (3.13% FeO found in the finest powder against 5.13% in the coarsest). This totally unexpected behavior has been confirmed (see 15, A, p. 908). The necessity for an entire reversal of the hitherto prevalent practice of preparing a very fine powder for the ferrous-iron determination is obvious.

The preparation of two samples, one coarse for the ferrous iron and another much finer for the other constituents, though perhaps unavoidable at times, is objectionable for several reasons. (1) The finer the powder, the more loosely held (hygroscopic) water it contains, easily 5 to 20 times as much as unground grains, and also the more water that is not given off at 100°. If two samples are used, the water given off both below and above 100° must be determined in each and a correction applied to the other constituent or constituents that may be determined in the finely ground sample. (2) The composition of the unground sample will differ in another respect from that of the ground material by the amount of silica derived from the mortar. This may easily reach or exceed one half of 1 per cent of the weight of the mineral powder (see p. 813), depending on the hardness of the minerals and on the length of grinding.

In order to obviate the need for two samples, experiments have been made with a view to securing fine grinding and at the same time avoiding oxidation. These experiments need to be multiplied before positive conclusions can be reached and precise directions formulated. So far as they go, however, they show that grinding in a nonoxidizing medium, such as absolute alcohol, is fairly satisfactory. Water is somewhat less satisfactory, notwithstanding the lower solubility in it of oxygen.[19] Alcohol does not seem to exercise a reducing effect on ferric minerals when they are ground in it. These experiments have served to show at the same time that the oxidation of the iron is not due merely to the greater exposure of surface, but

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[18] The Influence of Fine Grinding on the Water and Ferrous Iron Content of Minerals and Rocks, *J. Am. Chem. Soc.*, 30, 1120 (1908); *Chem. News*, 98, 205–215 (1908). J. W. Mallet [*Phil. Trans.*, 171, 1017 (1880)] seems to have been the first to notice that mechanical crushing could expel water from hydrous minerals (alum). He ascribed the effect to heat developed by the crushing, a view with which we are in accord. M. Carey Lea [*Phil. Mag.*, 34, 36 (1892); 37, 31 (1894)], however, regarded mechanical stress, especially shearing stress, as the effective factor.

[19] W. F. Hillebrand, *J. Am. Chem. Soc.*, 30, 1120 (1908); *Chem. News*, 98, 205–15 (1908).

that it is probably aided by intense local heat from friction and fracture of the grains under the pestle. Probably grinding in an inert gas would be more satisfactory, but, although this might be arranged with a mechanical grinder, it would be impossible when the grinding has to be done by hand, and in any case it would involve much inconvenience and trouble. When alcohol is used, it should be in small quantities at a time, enough to wet the powder thoroughly and to give a very liquid mass. A second and third application of alcohol are sometimes needed, because of the rather rapid evaporation. When the grinding is finished, the alcohol is allowed to evaporate spontaneously under a cover placed a few centimeters above the mortar and pestle, so as to exclude falling dust and yet allow free circulation of air. When thoroughly free from alcohol, the powder is removed gently from mortar and pestle with a flexible knife blade and then bottled.

Formerly all rock samples in the laboratory of the U. S. Geological Survey were, after crushing, reduced to powder by hand grinding, with expenditure of much time and labor. Since then, except in special cases, the work has been done by mechanical grinders run by a small electric motor. It will be evident from the foregoing statements, however, that care must be exercised in their use.

D. ABRASION OF MORTAR AND PESTLE

The abrasion of crushing apparatus has been touched on in B.

The abrasion of pestle and mortar becomes more manifest with mechanical grinders than with hand grinding, notwithstanding the fact that each has its motion simulating as far as possible that of the hands. There is undoubtedly a very considerable introduction of silica into the sample from these sources, but, in comparison with the amount invariably present in an igneous rock, the quantity abraded is hardly of moment. Rocks normally free from silica, or nearly so, like many iron ores, are as a rule softer than igneous rocks and consequently cause less abrasion of the grinding implements.

E. T. Allen, in order to get an idea of the amount of silica introduced into an ordinary rock sample through the abrasion of the grinding implements, caused 200 g of quartz sand to be ground in portions at a time until all passed a sieve of 150 meshes to the linear inch (60 to the centimeter), the time required being 19.5 hours. The mortar (635 g) lost 0.189 g in weight, and the pestle (268 g) lost 0.102 g, a total of 0.291 g, or 0.145 per cent of the weight of the sand. The powder obtained in this case was less fine than that ordinarily sought at that time by rock analysts, but, on the other hand, the material was all quartz, a mineral much harder than most of those constituting the average rock.

W. Hempel[20] tested experimentally the effect of grinding in mortars of agate, glass, iron, and hardened steel and found that, for hard bodies, like glass, hardened steel is far superior to agate, and that even mortars and pestles of green bottle glass showed much less abrasion than agate. In grinding 10 g of glass to very fine powder, the agate mortar and pestle, weighing 416 g, lost 0.052 g in weight (or 5 mg per g of glass), against a tenth of that loss with a hardened steel mortar and pestle of the same weight that had been some time in use.

Notwithstanding these observations in favor of steel, the use of metal in rock analysis is, as said above, forbidden by the conditions of the case. Still more so is that of glass because of its complex composition. If impurity cannot be avoided, it is far better that it should be of one kind only, and that one productive of less disturbance than any other.

E. WEIGHT OF SAMPLE

The sample when crushed or ground should weigh not less than 10 g, and preferably 20, in case it should be necessary to repeat or be advisable to employ unusually large portions for certain determinations, notably carbonic acid. Rock analysis has in this respect an advantage over mineral analysis, as rock material is almost always available in ample quantity, and any desired number of separate portions may be used, whereas, with a mineral, the analyst is frequently compelled to determine many or all constituents in a single, perhaps very small, portion of the powder. This course often involves delay and the employment of more complicated methods of separation than are usually necessary in rock analysis.

3. Water—General Considerations

A. THE ROLE OF HYDROGEN IN MINERALS[21]

As the purpose of this chapter is primarily the instruction and guidance of the analyst, it has been thought best to curtail the discussion of the role of hydrogen in minerals to such data as are likely to be of direct aid in the interpretation of the analytical results. Fuller discussions of certain more general aspects of the subject will be found in the works listed in the footnote,[22] although it should be noted that the changes in viewpoint concerning crystal structure, solid solution, etc., since then render many of the conclusions of the earlier writers of doubtful validity.

a. *Conditions in Which Hydrogen May Occur.* The outline that follows presents a classification of the ways in which hydrogen (especially that given off as water) may occur in minerals. In using this outline, it should be borne in mind that the subdivisions are not, in general, sharply delimited, but that a certain amount of gradation between them exists; that a given mineral may contain hydrogen in several different forms; and that some of the hydrogen originally present in one form may pass into another on grinding or on heating.

Classification of the Condition of Hydrogen in Minerals, Mineral Aggregates, and Mineral Powders

A. Essential hydrogen—present in regular atomic arrangement in molecular or crystal structure.
  I. Present in definite, stoichiometric proportions.
    a. As hydrogen—called acidic by analogy to behavior in solutions.
    b. As hydroxyl—the hydrogen called basic, again by analogy.
    c. As water—especially water of crystallization.
  II. Not present in stoichiometric proportions with reference to the substance as a whole, but present, in one of the above forms, in one or more of the constituents of mixed crystals, including isomorphous mixtures.
B. Nonessential hydrogen—its presence not necessary for characterization of the mineral (considered as water or other compounds).
  I. In liquid solution, specially in deliquescent powders, also in amorphous material, including undercooled liquids.
  II. Held by surface forces.
    a. Adsorbed on surfaces in films of molecular thickness.
      1. On walls of cavities within grains of aggregates.
      2. On exteriors of grains.
    b. Held by capillarity, in liquid form.
      1. In colloids with mesh structure.
      2. Indefinite openings within grains of aggregates.
      3. In spaces between separate grains.
  III. Included.
    a. As liquid droplets in cavities.
    b. As included grains of minerals belonging to one of the above listed classes.

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[20] Z. *angew. Chem.*, 14, 843 (1901).

[21] This chapter appeared in Analysis of Silicate and Carbonate Rocks, *U. S. Geol. Survey Bull.* **700** and was prepared by Edgar T. Wherry, H. E. Merwin, and Elliot Q. Adams, on the basis of the matter on this subject in the older *U. S. Geol. Survey Bull.* **422.**

[22] H. Le Chatelier, Z. *physik. Chem.*, **1**, 396 (1887); *Compt. rend.*, 104, 1443–1517 (1887); *Bull. soc. franç. minéral.*, **10**, 204 (1887).

A. Hamberg, *Geol. Fören. i Stockholm Förh.*, **12**, 591 (1890).

G. Tammann, Z. *physik. Chem.*, **10**, 255 (1892); **27**, 323 (1898); Z. *anorg. Chem.*, **15**, 319 (1897).

J. M. Van Bemmelen, *ibid.*, 13, 233 (1897), and subsequent volumes.

G. Tschermak, Z. *physik. Chem.*, **53**, 349 (1905); Z. *anorg. Chem.*, **63**, 169 (1909).

U. Panichi, *Pubbl. inst. studi pract., Sez. di. sci. fis. e nat.*, 1 (1908). Lengthy abstract in *Neues Jahrb. Mineral.*, Band 2, p. 2 of Referate (1910).

F. Zambonini, *Mem. accad. sci. fis. mat. Napoli*, **14** [2], no. 1, 127 (1908).

E. Löwenstein, Z. *anorg. Chem.*, **63**, 69 (1909).

S. J. Thugutt, *Centr. Mineral.*, 677 (1909).

A. Beutell and K. Blaschke, *ibid.*, **4**, 195 (1915).

I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).

The following notes will help to interpret the table.

A. I. Investigations by X-rays and infrared radiation indicate that groups, such as OH and H_2O, may have identity within crystals, and so the separation of essential, stoichiometric, hydrogen into three classes, a, b, and c, is believed to be justified.[23]

A. II. This class is intended to include such minerals as topaz, which is believed to consist of an isomorphous mixture of two end members, one hydrous and the other anhydrous, $Al_2(OH)_2SiO_4$ and $Al_2F_2SiO_4$. As the proportion of these members may vary widely, the hydrogen content may vary also; but, even though the hydrogen is not present in stoichiometric proportions with reference to the mineral as a whole, it does bear definite relations to one of the constituent members and is therefore properly considered essential. It is not necessary, however, that the members entering the substance be isomorphous in the strictest sense—that is, of homologous formula type; for instance, the mineral turgite is believed to be made up of two components, Fe_2O_3 (hematite) and FeO(OH) (goethite), in variable proportions, forming mixed crystals.[24]

B. I. The liquid surrounding deliquescing crystals belongs here. A part of the water in opal may be dissolved, but probably most of it falls in B, II, b, 1, where the water of most hydrous "amorphous minerals" is thought to belong. Such substances as liquid hydrocarbons and volcanic glass, though not strictly minerals, may be mentioned here.

B. II. a. Adsorption of water in molecular films upon surfaces is believed to be a general property of solids, and, if the surface exposed is large in proportion to the amount of material involved, the quantity of water thus held may be analytically significant. The increase in water content shown by many minerals upon fine grinding represents, thus, chiefly an increase in class B, II, a, 2. A few instances are known where water of class B, II, a, 1 is present in appreciable amount, one being the fibrous form of goethite, which is generally known as limonite.[25]

B. II. b. 1. With reference to this class, it may be pointed out that studies of colloids, among which are to be included many "amorphous minerals," have shown that they often possess a submicroscopic mesh structure, water (or other liquid phase) being held in the interstices of this structure. It is possible that certain crystalline substances, and in particular certain of the zeolite minerals, may contain water in this form also, but this has not been convincingly demonstrated. Classes 2 and 3 under this heading are of special significance in connection with finely fibrous minerals, such as the above-mentioned goethite which often contains considerable amounts of capillary water.

B. III. Liquid inclusions of either water or hydrocarbons and solid inclusions of hydrous minerals may be the source of a considerable content of hydrogen.

b. *Bearing of the Classification on Analytical Procedure.* α. *Behavior of hydrogen on grinding the mineral.* The fine grinding of minerals may lead to either an increase or a decrease in total hydrogen content (see B, p. 819). An increase is the result of the subdivision of grains and the consequent development of a greater surface upon which water can be adsorbed and otherwise held. A decrease is for the most part due to decomposition caused by local heating—by pressure or by mere change in grain size.

As in general (though by no means invariably) the decomposition temperatures of minerals containing water of crystallization are lower than those of minerals belonging to other classes, a marked loss of hydrogen on grinding may be regarded as pointing to the probable existence of the hydrogen in this form (A, I, c). Members of other classes, however, show low decomposition temperatures with sufficient frequency to render it unsafe to depend too much on this criterion. A decrease may of course also be due to the evaporation of water or other hydrogen-bearing liquids originally included as droplets (class B, III, a) when the grinding exposes them. It is to be inferred from the foregoing discussion that, in order to be representative of the mineral, the sample to be used for determination of water should be ground as little as possible; still the material must be fairly well subdivided in order that the water shall be liberated within reasonable limits of time and temperature. The effect of grinding on the water content may have at least confirmatory value in the final conclusion as to the role of hydrogen in the substance.

β. *Behavior of hydrogen on desiccation at constant temperature.* On exposure of a mineral containing essential hydrogen which is given off as water to an atmosphere in which the partial pressure of water vapor is being continuously diminished, water is likely to be lost discontinuously. Hydrogen of class A, II may, however, behave differently; this class requires further investigation.

The behavior of nonessential hydrogen is likely to vary with the class concerned. If it is included (class B, III, a and b), no loss is to be expected. If it is held by capillarity (B, II, b), the mode of loss will depend on the size and shape of the capillary openings. Water adsorbed on the surfaces of grains probably will be lost continuously—that is, it will be given off gradually as the water-vapor pressure diminishes, and dehydration will not be complete at any definite pressure. Hydrogen dissolved in "amorphous" material (B, I) would be expected to behave likewise.

The change here described is often reversible, water that has been lost by decreasing the aqueous vapor pressure being taken up again when this pressure is increased. Such rehydration may often be more readily followed than the original loss of water, and the continuity or discontinuity of the effect be more certainly determined thereby. In any thorough study of the role of hydrogen in a mineral, both dehydration and rehydration data should be obtained and preferably represented graphically, for conclusions as to the relations existing are often best drawn from the examination of curves.

γ. *Behavior of hydrogen (expelled as water) on heating.*[26] The behavior of hydrogen which is expelled as water on heating a mineral substance may be considered under three heads.

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[23] W. W. Coblentz, *Carnegie Inst. Wash. Pub.* **65** (1906); *Bull. Bur. Standards,* **2,** 457 (1906); C. Schaefer and Martha Schubert, *Ann. Physik,* 50, 339 (1916); A. Johnsen, *Physik. Z.,* **5,** 712 (1914).

[24] E. Posnjak and H. E. Merwin, *Am. J. Sci.,* [4] **47,** 325–37 (1919).

[25] *Ibid.,* 311–48.

[26] Thermal dehydration may give some other hydrogen compound, HCl from $MgCl_2 \cdot 6H_2O$, or from $AlCl_3 \cdot 6H_2O$, for example.

1. Heating to approximately constant weight at each step of a series of increasing temperatures in an atmosphere of uniform or regularly changing and usually small water-vapor pressure.

Minerals containing essential hydrogen are likely to lose it discontinuously —that is, at one or more rather definite temperatures. The temperatures at which dehydration occurs in dry air depend chiefly on the element or elements with which the hydrogen, hydroxyl, or water is associated. But, aside from this, in class A, I, a, "acidic" hydrogen, the dehydration temperature is likely to be relatively high; in A, I, b, "basic" hydrogen, somewhat lower; and in A, I, c, water of crystallization, relatively low, especially for the first water given off from a series of hydrates. In this case the water from two or more states of hydration may come off at one temperature unless the surrounding atmosphere has a carefully controlled and rather high water content.

The escape of water from mixed crystals is likely to be gradual as temperature increases, but experimental results are lacking.

Nonessential hydrogen is most likely to be given off continuously, but there are exceptions. For example, included water may escape discontinuously as the cavities containing it are burst open (decrepitation of the mineral); and even capillary water may escape more or less discontinuously if the heating changes the size of the pore spaces.

2. Heating with continuously increasing temperature, the water-vapor pressure being largely determined by the dehydrating substance.

The rate of loss of water as determined by frequent weighings[27] or by Le Chatelier's method of heat absorptions is either discontinuous or continuous, about as stated in the preceding section, except that the temperatures at which discontinuities occur are much influenced by such factors as rate of heating, state of subdivision of the material, and method of agitating the material during heating; the discontinuities themselves, however, tend to be more marked, especially in case of a series of hydrates.

3. Determination of vapor-pressure curves in cases of reversible changes in water content.

This determination gives very definite information concerning the state of hydration of a substance, but it is not commonly made as an analytical procedure.

c. *Effect of Dehydration on Physical Properties.* In general the crystallographic, optical, and other properties are likely to be profoundly changed by dehydration when the hydrogen is essential, and but slightly changed when it is nonessential. There are here, however, as in most other phenomena, important exceptions to the rule. In particular, some of the

zeolite minerals, in which the water is presumably in part essential, may show only minor changes in their properties when they are partly or even completely dehydrated. In minerals of class A, II, also, the change in properties incident to loss of water may be but slight. On the other hand, when minerals contain considerable quantities of nonessential water, marked changes in properties may result upon its removal.[28]

d. *Conclusion.* From the foregoing discussion, it is evident that, although determination of the condition of hydrogen in minerals is by no means a simple matter, considerable information upon it may be obtained by appropriate analytical procedure. No conclusions should be drawn from single observations, but, when the results of several methods of study show converging indications, it is quite possible to decide, for the majority of minerals, the condition in which their hydrogen is present.

B. WATER TAKEN UP OR LOST ON GRINDING

Before considering methods of determining water, attention must again be called to the effect of fine grinding of mineral powders on their ability to take up from the air and retain at temperatures far above 100° very appreciable amounts of water, even in excess of 1 per cent (see p. 811). Table 28 contains typical data on this subject. For fuller details see the paper already cited.[18]

TABLE 28

Water Content of Powders of Varying Fineness, Ground in Air

Material	Number	Condition	Water, %	
			Below 100°	Above 100°
Diabasic norite or gabbro	1a	<60 meshes to 1 cm	0.03	0.66
	1b	Ground 30 min	0.10	0.66
	1c	Ground 120 min	0.74	1.00
Altered basaltic greenstone	2a	<40 meshes to 1 cm	0.22	3.13
	2b	Ground 120 min	1.70	4.19
Andesite	3a	<60 meshes to 1 cm	1.01	3.40
	3b	Ground 30 min	1.18	3.54
Quartz	4a	<60 meshes to 1 cm	None	0.06
	4b	Ground 120 min	0.35	0.45
Meerschaum	5a	Coarse	5.76	6.79
	5b	Ground 600 min	6.33	9.81
Unglazed Berlin porcelain	6a	Coarse	None	None
	6b	Ground (?) min	0.62	0.18

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[27] W. F. Hillebrand, H. E. Merwin, and F. E. Wright, *Proc. Am. Phil. Soc.*, **53**, **45** (1914); *Z. Kryst.*, **54**, 221 (1915).

[28] E. S. Larsen and E. T. Wherry, *J. Wash. Acad. Sci.*, 7, 178–208 (1917).

On the other hand, water of crystallization may be expelled from minerals by long-continued grinding. Thus the content in water of a specimen of gypsum was reduced from over 20 to about 5 per cent.[18] The inference is obvious that water of crystallization should be determined on unground material, if possible.

The following excerpt from the work of Day and Allen[29] on the feldspars, already cited, has direct relation to the above:

> There is another error to which accurate specific-gravity determinations upon powdered minerals will be subject unless suitable precaution is taken. The exposure to the air during the period of grinding the samples gives opportunity for the condensation of sufficient atmospheric moisture upon the grains to affect the weight in air. The amount varies measurably with the size of the grains, as may be seen from Table 29 and probably with the degree of saturation of the atmosphere and the time of exposure.
>
> In the last two groups in Table 29, note that the moisture in graded portions of the same sample varies with the fineness.

TABLE 29

Determination of Moisture in 1 G of Powdered Mineral upon Exposure to the Air

< = finer than. > = coarser than.

Mineral	Fineness (Meshes to the linear inch)	Moisture, g
Orthoclase (natural glass)	<150	0.0006
Ab_1An_5 (artificial glass)	Selected, coarse	0.0001
Ab_1An_5 (artificial crystal)	<100>120	0.0010
Ab_1An_1 (artificial glass)	<100>120	0.0007
Ab_1An_1 (artificial crystal)	<100>120	0.0010
Ab (natural crystal)	Coarse	0.0006
	<150	0.0069
Orthoclase (natural crystal)	<120>150	0.0011
Orthoclase (same sample)	<150	0.0031
	Still finer	0.0059
Orthoclase (artificial glass)	Everything>100	0.0065
Orthoclase (portion of same)	>150	0.0022

> We also verified the conclusion of Bunsen[30] that this absorbed moisture is not altogether removed at temperatures only slightly above 100° but requires 600° to 800°—equivalent to low red heat. Several samples for which the moisture had been determined were laid away in corked test tubes for a number of weeks, after which redetermination gave exactly the former value.
>
> It is worth noting in this connection that these measured quantities of absorbed water are of the same order of magnitude as those usually obtained for the water content in feldspar analyses, where, again, of course, the finer the sample is ground for the analysis, the greater the possible error from this cause. It may be that a part and occasionally all of the moisture usually found in these analyses is absorbed and the significance of its presence there mistaken.

C. IMPORTANCE OF EMPLOYING AIR-DRY POWDER FOR ANALYSIS

The time-honored custom of drying a powdered specimen before bottling and weighing has no sound basis in reason. Its object is plain, namely, that of securing a uniform hygroscopic condition as a basis for convenient comparison of analytical results, because some rock powders contain more hygroscopic moisture than others and the amount is dependent further on the degree of fineness of the powder. Nothing, however, is more certain than that, by the time the dried substance is weighed, it has reabsorbed a certain amount of moisture, small, indeed, in most cases, but very appreciable in others; and, further, that, with every opening of the container tube, moisture-laden air enters and is enclosed with the remainder of the dry powder. Therefore it may very well happen that a powder that has been dried will, after several openings of the tube, especially at considerable intervals, be nearly as moist as it was at first. Dittrich has expressed views similar to the above. Of course, it is understood that no deliquescent substance is present.

It is preferable to weigh the air-dry powder and to make a special determination of moisture. If all the portions necessary for an analysis are weighed one after another, or even at different times on the same day, the error due to difference of hygroscopicity in dry and moist weather, which for most of the separate portions is an entirely negligible quantity, is eliminated. Only in the main portion, in which silica and the majority of the bases are to be estimated, can it ever be an appreciable factor. Especially is this true if a rather coarse powder is employed, such, for instance, as passes a sieve of 30 to 60 meshes to the linear centimeter. In many powders of this grade, the moisture will fall below 0.1 per cent, whereas, in those that have been ground for 1 to 2 hours, it may easily exceed 1 per cent.

D. ARGUMENT IN FAVOR OF INCLUDING HYGROSCOPIC WATER IN THE SUMMATION

The question has been asked: "If the so-called hygroscopic water is not always such, but not infrequently includes essential water, why are not its separate determination and entry in the analysis unnecessary? Why make a distinction which after all may not be a true one?" The question involves the further consideration of the need in any event of including the loss at 100 or 110°.

It would seem to be a reasonable desire on the part of petrographers to have all analyses referred to a moisture-free basis in order that they shall be

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[29] *Carnegie Inst. Wash. Pub.* 31, 56–67; *Am. J. Sci.* [4th ser.], 19, 93 (1905). Consult also R. Mauzelius, *loc. cit.*; W. F. Hillebrand, *loc. cit.*

[30] *Wied. Ann.*, **24**, 327 (1885).

strictly comparable. This involves the omission of the "hygroscopic" water from the list of constituents, which would be eminently proper were it always possible to be sure that the loss at 100 to 110° truly represents such water. As it very often represents more, and the determination of whether or not it does in each case is not always possible and would add to the time required for the analysis, it seems necessary to include this water. What errors may arise from its exclusion, the following rather extreme case well illustrates: Certain rocks of Wyoming in powder form lost 1 to 2 per cent of moisture at 110°. That not even an appreciable fraction of this was truly hygroscopic is fully demonstrated by the fact that the uncrushed rocks lost the same amount; yet the rule followed by many chemists and petrographers would have involved the removal of all this water as a preliminary to beginning the analysis, and not only would a most important characteristic have passed unnoticed, but also the analyst would have reported an incorrect analysis, inviting false conclusions and possibly serious confusion. (See examples cited on p. 825.)

Hence it may be said that the estimation of the loss at 100 or 110° and its separate entry in the analysis are advisable as affording to the lithologist an indication of the mineral character of one or more of the rock constituents, thus perhaps confirming the microscopic evidence or suggesting further examination in that line. A marked loss in weight at 100° by a coarse powder other than that of certain igneous glasses may be taken as almost positive proof of the presence of zeolites or other minerals which characteristically contain loosely held water. It has been objected that the hygroscopic moisture varies with the degree of comminution of the sample and with the condition of the air at the time of weighing, and that therefore it should not be incorporated in the analysis, but this variation is ordinarily not at all great if the powder is coarse.

4. WATER—METHODS OF DETERMINATION

With the coarse powders that are needed to afford a true value for the hydrogen content of rocks and minerals, one or another of the methods described in this section will be found more or less unsatisfactory, especially with those materials that lose their hydrogen at very high temperatures or that are difficult to decompose with fluxes. Unfortunately at present no directions can be given to cover all such cases. The analyst must exercise judgment in the selection of a method. In any event duplicate determinations should be made until he has acquired the experience that will permit him sometimes to make exceptions. M. Dittrich[31] compared different ignition methods.

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[31] *Z. anorg. Chem.*, **78**, 191 (1912).

A. INDIRECT METHODS

a. *General Considerations.* The means employed for the indirect determination of water differ according to whether fractional or total amounts are needed. For the latter, simple ignition is adopted; for the former, exposure to the effects of dehydrating reagents or different temperatures. These methods, as ordinarily carried out, although exceedingly simple, are affected in most cases by serious errors, which will be considered in turn in their proper places. The methods should not be employed, therefore, when accuracy is essential, unless it is known that the errors are too slight to be significant or unless modifications are introduced to guard against them. A complication, sometimes serious, is added by the fact that with coarse powders the time required for expulsion of the water may be much greater than when a fine powder is used.

b. *Methods Involving the Use of Dehydrating Agents.* Calcium chloride, sulfuric acid, and phosphorus pentoxide are the chemical dehydrants commonly employed in mineral analysis. Magnesium perchlorate and magnesium perchlorate trihydrate should also be kept in mind (see Reagents, p. 48). Of these, sulfuric acid finds most extended use, generally in a condition of high concentration, but in varying degrees of known concentration if detailed study of the behavior of a mineral during dehydration is in progress. The importance of employing in desiccators only sulfuric acid of maximum dehydrating power when the full effect of the acid is desired has been shown.[32] Acid that has stood long in desiccators that are in constant use is by no means so effective as fresh strong acid. Furthermore, the acid becomes dark from access of organic matter from dust or from the lubricant of the vessel, and this gives rise to the formation of appreciable amounts of sulfur dioxide.

A mineral that loses much water over a strong dehydrant may need an exposure of several days or even weeks for its complete extraction. If the weighings are made from day to day, the apparent limit may be reached long before all water really removable has been taken up by the acid. Whenever the crucible, after weighing, is replaced in the desiccator, it is no longer in a dry but a more or less moist atmosphere, and its contents, even when covered, sometimes absorb a part of this moisture and retain it so persistently that the acid is unable to bring the powder beyond its previous state of dryness in the next 24 hours. In fact, it may be unable even to reach it unless greater time is allowed. An experiment on tyrolite (Table 30), made and published many years ago, illustrates this point in part:

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[32] *Am. Chem. J.*, **14**, 6–7 (1892).

TABLE 30

Experiment of Drying 1 G of Tyrolite over Strong Sulfuric Acid

Time Exposed, hr	Loss, g	Time Exposed, hr	Loss, g
18	0.0231	24	0.0002
26	0.0083	24	0.0003
23	0.0029	48	0.0006
24	0.0012	24	0.0002
23	0.0008	—	———
24	0.0001	283	0.0380
25	0.0003		

The experiment might reasonably have been considered ended after the 138th hour, when a loss of but 0.1 mg was shown during 24 hours; but nevertheless a nearly steady loss of 0.3 mg per day took place for six days more, and might have been observed longer but for the interruption of the experiment.[83] The sample was in fine powder. Had it been coarse, the rate of dehydration would have been much slower. The time can of course be greatly reduced if the operation is performed in a vacuum.

The indirect method can be made more accurate by heating the mineral or rock in a weighed tube, through which a current of air or other gas can be passed, either dry or of definite moisture content, according to the object in view, and then determining the loss in weight of the tube and its contents. If the drying agent for the gas is phosphorus pentoxide, it is well to cause the gas to pass first over or through calcium chloride or sulfuric acid, for the effectiveness of the pentoxide rapidly lessens as it becomes glazed with metaphosphoric acid.

c. *Methods Involving the Application of Heat.* α. *Fractional determinations.* As to the temperature to be adopted for drying in order to determine so-called hygroscopic moisture,[84] the practice has varied at different times and with different workers, ranging from 100 to 110°. For the great majority of rock specimens, it is quite immaterial which of these temperatures is adopted, for no greater loss is experienced at the higher than at the lower temperature, given a sufficient time for the latter. It has been the practice in the Survey laboratory to employ a toluene bath giving a temperature of about 105°. Should the results show a very unusually high loss, the powder is reheated at, say, 125°, in order to learn if the loss is progressive with increased temperature, as this knowledge is important for the interpretation of results. To insure accuracy, this experiment should never be made in crucibles or dishes which must be cooled in a desiccator. One instance will suffice: A gram of a mineral mixture containing about 17 per cent of water, of which about 3 per cent was driven off at 100° and 8 or 9 per cent at 280°, was placed in a desiccator over sulfuric acid, after several hours' heating at the latter temperature, weighed as soon as cold, and then replaced and again weighed the next day. It had regained 1½ per cent of its original weight, although the desiccator was tightly closed and the crucible covered.

A specimen of tyrolite was found on one occasion to lose 10.34 per cent at 280°, and on another occasion 14.33 per cent. In the latter case the drying and heating at progressive temperatures had continued during a period of 528 hours, the weighings being made usually from day to day; whereas in the former the duration of the experiments was much shorter and the intervals between weighings were but a few hours each.

An important research of G. Friedel[35] well showed what errors are possible in the determination of this easily removable water, as he found that certain zeolites which had been largely dehydrated but not heated to the point of rupture of the molecular net, could then absorb, instead of water, various dry gases in which they might be placed, as carbon dioxide, ammonia, carbon disulfide, and others, even air in large quantities, and certain liquids. In the light of this observation, the cause of the great increase of 1½ per cent in weight of the partly dehydrated mineral mentioned above may very possibly be attributed to air from the desiccator instead of moisture, as was at the time supposed. At any rate, as Friedel said, the danger of accepting a loss in weight as an index of the amount of water lost is clearly shown, and thus that method of determining water is for many cases fully discredited. Just what method to adopt must be left largely to the judgment of the operator, who will often be guided by the mineral composition of the rock as revealed by the unaided eye or the microscope.

Friedel indicated a means for determining the true weight of water lost by minerals behaving like the zeolites, even without collecting the water lost, namely, by driving out of the dehydrated and weighed mineral, under proper precautions, any air it may have absorbed in the process of drying and cooling, and collecting and measuring this air and thus finding its weight, which, added to the apparent loss, gives the true content of water.

But, aside from the above reasons for avoiding the use of indirect methods of water determination, there is another very important one. They never give correct results where air baths are used in the ordinary way, for the reason that the drying is performed in an atmosphere far from dry, and

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[83] Consult J. W. Mallet, *Phil. Trans.*, **171,** 1006 (1880), for an example of slow loss of water from alum in air in an experiment lasting six months.

[84] For an exhaustive and most important discussion of the determination of moisture, with special reference to coals, see the Report of the International Committee on Analysis, *8th Intern. Congr. Applied Chem.*, 77–131 (1912).

[35] *Bull. soc. mineral.*, **19.** 14–94 (1896); *Compt. rend.*, **122.** 1006 (1896).

therefore the substance cannot lose all its moisture. As examples, if the indirect method shows 0.12 and 0.75 per cent in two samples, the direct method may afford 0.17 and 1.00 per cent, respectively. Similar observations have been repeated many times and admit of no dispute. They apply as well to rocks as to minerals. Therefore, if the moisture content is more than an insignificant factor, the indirect method must be avoided or so arranged as to insure a constantly changing dry atmosphere.

To effect this the powder should be heated in a weighed tube, through which a current of dry air can be passed, and allowed to cool therein, after which a second weighing gives the loss of moisture. The degree of drying will depend on the nature of the reagent used for drying the air, sulfuric acid being more effective than calcium chloride, and phosphorus pentoxide most effective of all. When using the last, it is well to cause the air first to pass over or through one of the first-named dehydrants, for its effectiveness rapidly lessens as it becomes glazed with metaphosphoric acid. For experiments carried out at room temperature no bath is required, but for artificial temperatures the tube should pass through a suitable thermostat.

β. *"Loss on ignition" method for total water.* In a few cases, the loss on ignition of a rock will give the total water with accuracy, but, in the great majority, there are so many possible sources of error that this old-time method can seldom be used with safety.[36] Only when the rock is free from fluorine, chlorine, sulfur, carbon, carbon dioxide, and fixed oxidizable (FeO) or reducible (MnO_2) constituents, can the loss be accepted as the true index of the amount of water present, and it is seldom that a rock is encountered that fulfills these conditions, especially as to the absence of ferrous iron. Ignition at 1100 to 1200° C, in the presence of carbon dioxide alone of the above list, may give a correct result, after separate estimation of the carbon dioxide, provided this emanates from carbonates of the earths and not from those of iron or manganese. Another source of error lies in

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[36] For example the following results were obtained by crushing a sample of ferberite, $FeWO_4$, and then sieving and heating as indicated:

	48–65 Mesh Portion, %	Finer than 100 Mesh Portion, %
3 hours at 110° C, loss	0.005	0.130
3 hours * at 110° C, loss	0.015	0.050
2 hours at 150° C, loss	0.050	0.010
1 hour at 200° C, loss	0.090	0.040
2 hours * at 200° C, loss	0.020	0.010
1 hour at 600° C, loss	2.410	1.930
1 hour * at 600° C, gain	0.060	0.070
1 hour * at 600° C, gain	0.040	0.090

* Additional.

the fact that from some minerals the hydrogen is not all driven out, even at the highest temperature obtainable by a blast lamp. Such heat may, on the other hand, drive out other difficultly volatile constituents, as the alkalies. This happens particularly when mixtures of alkaliferous silicates and alkaline earth carbonates are concerned, such as argillaceous limestones.

The long-maintained idea that in presence of ferrous iron a sufficiently correct result is obtainable by adding to the observed loss an amount needed for oxidizing all ferrous iron is not justifiable. There can be no certainty that the oxidation has been complete, especially in the case of readily fusible rocks, and, at the high temperature of the blast, a partial reduction of higher oxides is not only possible but sometimes certain.[37] If the quantity was in any degree large, it is sometimes decidedly magnetic, presumably from presence of magnetic oxide, which no amount of heating wholly oxidizes, especially in the larger grains. Neither is evaporation with nitric acid and reignition sufficient to destroy the magnetic property of the oxide, as has been asserted.

P. G. W. Bayly,[38] in a paper on methods of rock analysis, gave the following method for determining water. The total ignition loss is corrected for carbon dioxide when this is present, and for ferrous oxide by determining the ferrous iron both before and after ignition. Deduction of the separately determined moisture gives finally the more firmly held water. It need hardly be said that this method presupposes very exact determinations of both moisture and ferrous oxide.

B. DIRECT METHODS WITHOUT ABSORPTION TUBES—PENFIELD'S METHODS

a. *For Minerals Easily Deprived of Their Water.* If no other volatile constituents than water are present, the beautifully simple method first used by G. J. Brush and extended by S. L. Penfield[39] leaves nothing to be desired for accuracy, provided that the expulsion of water can be effected at relatively low temperatures. It consists simply in heating the powder in a narrow tube of hard glass, enlarged at the closed end and provided with one or two further enlargements in the middle to hold the water and prevent its running back and cracking the hot glass. A capillary glass stopper fitted in with rubber tubing prevents loss of water by circulating air currents. The tube being held horizontally, the bulb is heated to any required degree by the Bunsen or blast flame. Moistened filter paper or cloth wound about the cooler parts of the tube insures condensation of all

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[37] H. Warth [*Chem. News*, **84**, 305 (1901)] also mentioned this and drew attention to the effect of alumina, not only in decolorizing ferric oxide when the two are heated together, but also in restraining the reduction of the latter to the magnetic oxide.

[38] Australasian Association for the Advancement of Science, Adelaide meeting (1907).

[39] *Am. J. Sci.* [3d ser.], **48**, 31 (1894); *Z. anorg. Chem.*, **7**, 22 (1894).

water. The heated end being finally pulled off, the tube is weighed after cooling and external cleansing, and again after the water has been removed by aspiration. For most rocks, as they contain little water, central enlargements of the tube are hardly needed.

Various forms of tubes used by Penfield are shown in Fig. 38.

Before being used, even if apparently dry, "these tubes must be thoroughly dried inside, which is best accomplished by heating and aspirating a current of air through them by means of a glass tube reaching to the bottom."

How this simple tube is made to afford entirely satisfactory results with minerals, even when carbonates are present, is fully set forth in the paper cited.

Comparatively few rocks are altogether free from other volatile constituents. Hence, for refined work the application of this apparatus in the simple manner above set forth is limited. However, it may be used with the addition of a retainer for fluorine, sulfur, etc., such as the oxide of calcium, of lead, or of bismuth. It gives, of course, the total water.

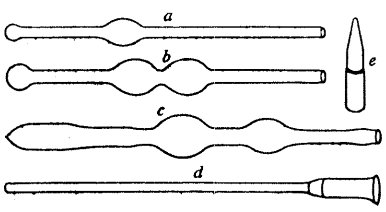

FIG. 38. Penfield's tubes for water determination in minerals. *a*, *b*, *c*, different forms of tubes; *d*, thistle tube for introducing the powder; *e*, capillary-tipped stopper.

b. *For Minerals not Easily Deprived of Their Water.* When minerals are present that do not give up their water wholly, even over the blast, as talc, topaz, chondrodite, staurolite, Penfield recommended the use of a simple combination of firebrick and charcoal oven, either with or without a retainer in the tube for fluorine, as circumstances demand. The part of the tube in the fire is to be protected by a cylinder of platinum foil tightly sprung about its end, and the part outside by asbestos board, as well as by wet cloth or paper. A piece of charcoal is likewise laid on the tube, as well as beneath and behind, and the blast flame is given a horizontal direction, so as to play upon the side of the apparatus. In this way a most intense temperature can be reached, but the platinum foil does not last long.

M. Dittrich[80] condemned the above method as giving variable results, after comparative trial of different methods, but it would seem that he did not use a retainer for fluorine or sulfur.

In whichever way the apparatus may be used the water found is the total water, from which that found separately at 105° may be deducted if desired.

C. DIRECT METHODS WITH ABSORPTION TUBES

a. *General Considerations.* In general it is preferable to collect and weigh the water in suitable absorption tubes after its expulsion from the rock or mineral. The method is especially suited for the determination of total water or of that escaping above 105°. It is less suited for those fractional determinations where the escape of water is very slow at the different temperatures, for the absorption tube in such cases may gain weight, other than that of water from the mineral, sufficient to introduce appreciable error. This may sometimes be corrected to a certain extent by running a parallel blank test.

Absorption, following ignition without a flux, is not suited for rocks or minerals which yield other volatile substances than water and carbon dioxide, unless some substance is employed to retain these before they pass into the absorption tube. Even so, at extreme temperatures the results are likely to be in error, so that, for materials which yield their water only at very high temperatures, fusion with a flux is imperative.

A precaution too often overlooked is to see that the drying agent used for the air current (always forced, not drawn) is the same as that in the absorption tube in which the water from the sample is collected—not only the same in kind, but as near as may be in strength also, especially with calcium chloride. Therefore the contents of drying and absorption apparatus should be changed often, and, when the apparatus is refilled, the reagents should be taken from the same stock. Fresh calcium chloride in absorption tubes should be exposed to a current of carbon dioxide and the excess removed by air before use. Furthermore, all connections should be as nearly as possible glass against glass, with the least possible inside exposure of rubber. With long rubber connections, the error may be a very sensible plus one. Again, the direction of the air current through the absorption tube should always be the same as long as a filling lasts. Care must also be taken that the conditions at the several times of weighing of the tubes are nearly alike in temperature and hygrometric state of the atmosphere, for the afternoon weight of a tube may be appreciably different from the weight on the following morning. It is well, therefore, to avoid error from this cause by approximately counterpoising the absorption tube by another of about the same volume and weight. Finally, the electrifying effect of wiping a tube before placing it on the balance must not be overlooked. In our experience this has often amounted to as much as 1 to 2 cg in a balance resting on glass (always an increase in weight) after wiping with a clean linen handkerchief. The charge can be removed by repeated application of the hand, but disappears slowly without such aid. A strongly electrified condition makes itself apparent by marked irregularities in the swing of the needle. Although more pronounced in cold weather, the phenomenon is not peculiar to winter.[40]

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[40] With regard to electrification, consult also Ernst Bornemann, *Chem. Ztg.*, 125, 220 (1908).

The absorption tubes should not weigh in general over 30 g each when filled. Sulfuric acid as an absorbent has no apparent advantage over calcium chloride if the drying apparatus for the air contains also calcium chloride of the same absorptive power as that in the collecting tube.

b. *Heating the Sample.* The heating of the sample is carried out most satisfactorily in tubes heated in electrically heated ovens or muffles that are equipped with means for regulating and for indicating the temperature.[41]

Of more elaborate apparatus, designed to be used with fluxes, the tubulated platinum crucible invented by F. A. Gooch [42] is capable of affording most excellent service.

Figure 39, which hardly needs detailed description, shows it in a modified form, which differs from the original forms of Gooch in that the tubes for connecting with both the drying and absorption vessels are constructed wholly of platinum instead of lead glass. With inlet and exit tubes of the lengths shown in the figure, there is absolutely no danger of the ends becoming hot enough by conduction to scorch or soften the rubber connection.

As an adjunct to its convenient use, there is needed an ordinary upright iron ring stand, with two small sliding rings, and a sliding ring burner provided with entering ducts for gas and air blast. Across the uppermost ring there is an arrangement of stout platinum wire *S* (Fig. 40), forming at the center of the ring a secure seat for the upturned flange of the crucible proper. Both rings and burner can be clamped firmly at any height.

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[41] For an apparatus devised by George Steiger in which the sample is heated at temperatures up to 110° C in a tube immersed in a toluene bath, consult *U. S. Geol. Survey Bull.* 700, 81, and, for a description of a gas-heated oven for use at temperatures up to 300° C, see T. M. Chatard, *Am. Chem. J.*, 13, 110 (1891). For heating at 1000 to 1050° C, M. Dittrich and W. Eitel [*Z. anorg. Chem.*, **75**, 373 (1912)] recommended a tube of fused quartz of 45 cm length, 22 mm diameter and 0.5 mm wall thickness drawn out at the exit end and provided with a stopper and inlet tube of the same material in one piece. The stopper and end of the large tube are grounded to fit and rubbed with a little graphite to insure tightness. Further security against loosening is provided by two pairs of quartz hooks on both stopper and tube, over which wire springs can be stretched. For holding the sample, mixed with 5 to 6 g of dry sodium carbonate, a boat of platinum-iridium (10 per cent iridium), 12 cm long, is used, having a cover of the same alloy. To protect against injury to the tube by spilling of the contents of the boat, a cylindrical shield of the same alloy is used. Fusion is brought about by heating in an electric furnace or by the heat of a row of burners, increased toward the end of the operation by that of a large blast lamp. For the determination of water and carbon dioxide simultaneously at approximately 1400° C and without flux, the same authors (*ibid.*) described the use of a platinum-iridium tube of smaller bore and containing a spiral of silver at the exit end.

[42] *Am. Chem. J.*, **2**, 247 (1880); *Chem. News*, **42**, 326 (1880).

The rock powder, having been placed in the cylindrical crucible (*C*, Fig. 39), is there mixed with not more than 3 or 4 g of fully dehydrated sodium carbonate,[43] or more of lead chromate if carbon is to be likewise determined. The crucible is sunk in its seat *S* (Fig. 40), in the upper ring *R′*, and the tubulated cap *T* (Fig. 39) is fitted on and attached to the calcium-chloride drying towers—preceded by one containing potassium hydroxide if carbon dioxide is likewise to be estimated—on the one side, and to a sulfuric acid bulb tube *B* (Fig. 41), on the other. Powdered sodium tungstate [44]—free from arsenic, which would soon ruin the crucible

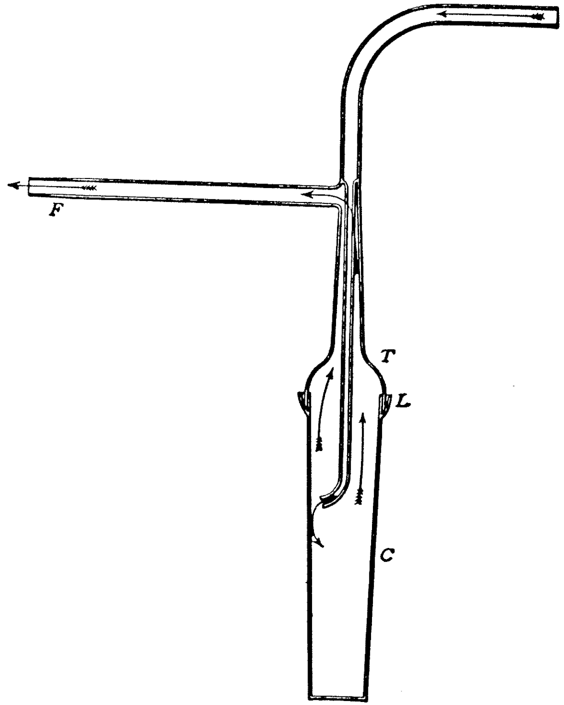

FIG. 39. Modified form of Gooch tubulated platinum crucible for the determination of water, one-half natural size. Weighs about 75 g.

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[43] This has been heated for a length of time to near its fusing point over a free flame or in an air bath, to decompose the bicarbonate it usually contains, and then placed in a desiccator. Thus heated, it is not very hygroscopic. Penfield found that 2.5 g of it, spread out on a watch glass, gained only 0.0002 g in 15 minutes. Potassium carbonate and potassium-sodium carbonate are too hygroscopic by far to be available.

[44] Private advice from E. W. Morley conveys the information that sodium carbonate is perfectly satisfactory as a substitute for the tungstate. If so, its use is preferable when the contents of the crucible are to be used for other determinations.

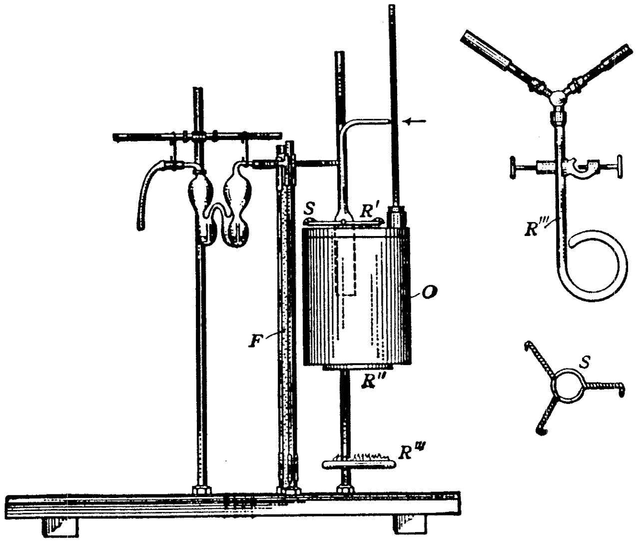

Fig. 40. Arrangement, during drying, of Gooch apparatus for determining water. *S*, seat of stout platinum wire resting on ring *R'* and serving as a support for the crucible; *R'''*, blast-fed ring burner; *R''*, support for air or toluene bath, *O*; *F*, asbestos-board shield.

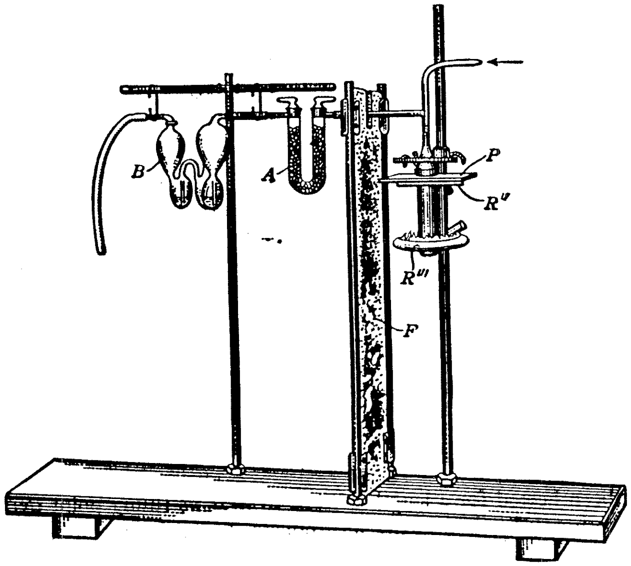

Fig. 41. Arrangement, during fusion, of Gooch apparatus for determining water. *R'''*, blast-fed ring burner; *P*, protective asbestos shield resting on ring *R''*; *F*, asbestos-board shield; *A*, calcium-chloride tube; *B*, sulfuric acid bulbs serving to show the rate of gas flow through the absorption tube and at the same time to prevent back entry of moisture from the air into *A*.

lips—is now poured into the flanged lip *L* (Fig. 39), in which the cap rests, and a metal vessel of cold water having been raised by the lower ring *R''* (Figs. 40 and 41), until the platinum crucible is immersed sufficiently, the flame of an ordinary blast lamp is turned on to melt the tungstate. As soon as this is fused, the flame is removed, and the salt solidifies and makes an air-tight joint, the test of which is the permanence of the column of sulfuric acid in the bulb tubes caused by the contraction of the air in the platinum apparatus as it cools.

After drying by a current of air at 105° for 2 hours, more or less, by means of an air or toluene bath, as shown in Fig. 40, the absorption tube *A* (Fig. 41) is interposed between the sulfuric acid bulbs and the apparatus, and, while a slow current of air continues to pass, the gradual heating and subsequent fusion of the flux are brought about by the blast-fed sliding ring burner *R'''* (Figs. 40 and 41). The sodium-tungstate joint is shielded from the flame by small pieces of asbestos board *P* (Fig. 41), cut out so as to fit the crucible. It is well to begin fusing at the top of the mixture in the crucible and to lower the blast gradually till the bottom is reached. In this way may be avoided all danger of the outlet tube becoming stopped by flux carried up by the escaping carbon dioxide. When fusion is complete, as shown in the case of sodium-carbonate flux by the decided slackening of the gas current through the safety bulbs attached to the drying tube, the flame is extinguished, and a current of air is allowed to continue until the apparatus is cold.

This apparatus suffers from the drawback of being slightly permeable to combustion gases at high temperatures. The defect can be overcome by causing the flame to play upon an outer ordinary platinum crucible, kept permanently filled with sodium-potassium carbonate. This protective crucible, however, is soon ruined for other purposes, being distorted by the alternate expansion and contraction of the carbonate, unless this is poured out before it solidifies after each fusion.

It has been found that, if the operation is carried out expeditiously and the final full heat applied for but a few minutes, the error due to penetrating water gases is inappreciable. This hastening may be rendered safer by using rather finely powdered calcium chloride or magnesium perchlorate trihydrate (p. 48), in the central section of the U-shaped absorption tube to avoid large air channels. Through this or any other apparatus based on similar principles, the air current should always be forced, not drawn. A warm air blast directed upon the exit tube near its entrance into the absorption tube greatly shortens the time required and is to be recommended.

In this apparatus only the water expelled above 100 to 110° should be determined as a rule. The reason why it is unsafe to attempt to determine "hygroscopic" moisture in this apparatus is that the luting of the two parts must be done by direct application of a flame to the tungstate, and considerable water vapor may enter the apparatus and be retained in part by the dried sodium carbonate.

For the determination of water in those hydrous sulfates that are apt to lose some of their acid radical when heated, S. B. Kuzirian[45] developed a method which may find application for hydrous salts other than sulfates. An ignition tube, which may be of hard glass, is used for heating the mineral. The sample is mixed in a boat of porcelain or platinum with six times its weight of sodium paratungstate[46] and inserted into the tube, which has been dried thoroughly by passing through it a rapid current of dry air. The ignition is started gently while dry air passes over the boat at a rate of 3 bubbles a second for 15 minutes. Then the temperature is increased gradually until the mixture forms a clear melt. The usual precautions for drying the air and absorbing the water evolved from the mineral are to be observed.

Kuzirian's experiments were carried out on sulfates of copper, aluminum, and nickel and the potassium alums of chromium and aluminum. They gave good results, the sulfate radical being retained quantitatively by the paratungstate.

The Gooch and the Dittrich-Eitel methods permit the determination of other constituents besides water in the same portion if necessary, and, by the use of lead chromate instead of sodium carbonate, graphite or the carbon of organic matter can be simultaneously determined with the water. If carbonates are present, together with graphite or organic matter, the total carbon is obtained.

To one accustomed to its use, and with a drying and suspension attachment permanently set up, the Gooch apparatus, considering its limitations above set forth, offers a handy and convenient means for the determination of water in rocks. Its high first cost, in comparison with the glass or quartz tube, is made up in time by its durability.

The apparatus shown in Fig. 42 has been recommended by C. O. Harvey[47] for the determination of water in rocks that are substantially free from volatile constituents other than water or carbon dioxide. After the apparatus has been assembled, the rounded end of tube *A* is heated at the temperature to be used, and then allowed to cool. To determine the correction for the "blank," the weighing bottle is removed, quickly stoppered, weighed, and replaced in the apparatus. The heat is then increased during

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[45] *Am. J. Sci.*, [4] 36, 401 (1913); *Chem. News*, 109, 173 (1914); *Z. anorg. Chem.*, 85, 127 (1914).

[46] In order to purify the commercial paratungstate, which ordinarily contains sodium carbonate, it is fused in a large platinum dish over the blast, and pure tungsten trioxide is added until carbon dioxide ceases to bubble out.

[47] *Bull. Geol. Survey Grt. Brit.*, 1, 8 (1939).

a period of 30 minutes, and maintained for 90 minutes. The apparatus is next allowed to cool for 30 minutes, after which the weighing bottle is again removed, stoppered, and weighed. The determination is made by placing 2 g of the sample in the platinum boat and proceeding in the same manner. The weighing bottle should always be left on the balance for 15 minutes before weighing, the tube *A* being closed meanwhile by a similar but empty weighing bottle. With rocks that evolve carbon dioxide, the bottle is moved rapidly in an upward direction four times before stoppering, in which case the bottle is treated similarly during the determination of the blank.[48]

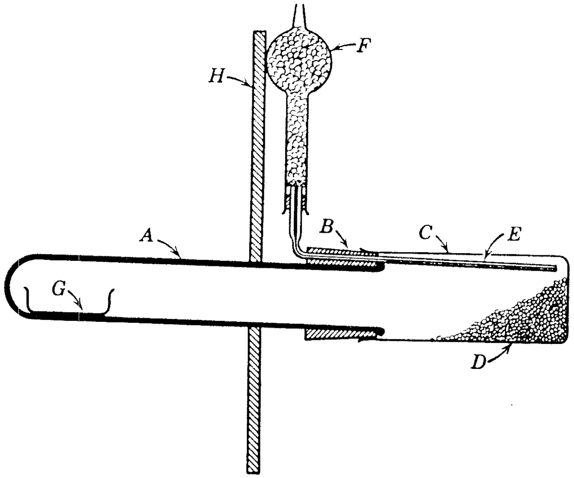

Fig. 42. Modified Penfield method. *A*, silica test tube supported at *B* in a position slightly inclined from the horizontal, and carrying a rubber stopper; *C*, snugly fitting weighing bottle; *D*, 4 to 5 g of $CaCl_2$; *E*, capillary tube leading to *F* which also contains $CaCl_2$; *G*, platinum boat for sample; *H*, asbestos screen. Circulation within the system is based on unrestricted convection.

5. Methods of Decomposing Rocks

The almost universal practice in silicate analysis is to determine silica, titania, and most of the basic elements in one and the same portion of the sample after fusion with sodium carbonate. For the determination of other constituents, other methods of decomposition may be required. These, as well as suggested substitutes for the sodium carbonate fusion, are described in the following section.

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[48] The determination of water by micro methods is discussed by F. Hecht, *Mikrochim. Acta*, 1, 127 (1937).

A. DECOMPOSITION BY THE USE OF FLUXES

a. *General Considerations.* In this chapter are considered those fluxes that find application in mineral analysis for the treatment of different classes or types of minerals and often with different objects in view—either simple breaking up or oxidation of one or more components or both. Fluxes or semifluxes which find but a single application, like the mixture of calcium carbonate and ammonium chloride used for the alkali determination in silicates, will be discussed in connection with the specific use.

With the exception of boric oxide, the common fluxes are compounds of the alkali metals: hydroxides, peroxides, carbonates, and borates on the alkaline side; bisulfates, pyrosulfates, and acid fluorides on the acid side. The sulfates and fluorides are sometimes used jointly for the purpose of generating hydrofluoric acid and so increasing the disintegrating action. At the fusion temperatures the alkaline peroxides are powerful oxidizers as well as disintegrators, too powerful for use in vessels of platinum unless diluted.

Fusion with the carbonates too effects oxidation of many elements in minerals, mainly by bringing them into more intimate contact with the air than is possible by simple ignition without a flux. In order to expedite this effect, an alkali nitrate, chlorate, or peroxide is sometimes mixed with the carbonate, but, given time, the oxidation will usually go to completion without the added agent. This is exemplified in the case of the mineral chromite by the complete oxidation of its trivalent to sexivalent chromium, whether or not a special oxidant is used. The action of the sulfates is also frequently oxidizing but markedly less so than that of the hydroxides and carbonates. Thus they oxidize bivalent to trivalent iron with comparative ease but do not oxidize bivalent manganese or trivalent chromium.

In addition to the more common fluxes, others such as lead oxide and carbonate and basic bismuth nitrate are occasionally used, especially for silicates. One of the advantages these have in common with boric oxide over the alkali carbonates is their removability after serving their purpose, thus allowing the various operations to be made without the annoying interference of several grams of foreign fixed salts, which are most troublesome in that part of the analysis which is devoted to the separation of silicon, aluminum, iron, calcium, and magnesium. Another of their advantages is that with them it is possible to determine in one portion of sample the alkalies in addition to a number of other bases and silicon. Where the material is limited, as so often it is in mineral analysis, this is a most important advantage, sufficient to outweigh all possible objections; but in rock analysis, where the supply of material is usually ample, it is seldom worth considering. A further point in their favor is that it is probably easier to obtain them free from fixed impurities than an alkali carbonate.

Of the three compounds named, lead carbonate precipitated by ammonium carbonate and basic bismuth nitrate, both of which upon heating yield oxide as the fluxing agent, are to be preferred to lead oxide because they are more readily obtainable pure. In the absence of reducing substances and with the exclusion of flame gases, the fusions can be made safely in a platinum crucible of even small size under a good draught hood.

There are, however, objections to some of these less commonly used fluxes. For some of them an extraordinary amount of time must be devoted to grinding the mineral to an impalpable powder with the result of introducing appreciable material from the grinding implements (Grinding, p. 813) and of oxidizing some ferrous iron (Iron, p. 907). The flux too may need considerable hand pulverization (B_2O_3).

In mineral analysis these objections are entitled to far less weight than in rock analysis, for the object sought—usually the deduction of a formula—warrants the expenditure of much time and painstaking care. Finally it has been found that one or more of these fluxes are not available for altogether general use because certain minerals do not succumb fully to their attack under simple conditions.

It seems unnecessary to describe the simple fusion procedures used with these unusual fluxes. Those interested can consult the original papers.[49]

b. *The Commoner Fluxes.* α. *Sodium carbonate.* By far the most frequently used flux is anhydrous normal sodium carbonate. Except in special cases, as when chlorine or fluorine is to be determined, there is no advantage in using the more fusible double carbonate of sodium and potassium or the equimolecular mixture of the normal carbonates, for the temperatures used for most mineral fusions are much above those at which the mixed carbonates melt, and, as is well known, potassium salts are more prone to pass into precipitates than sodium salts.

The fact that the so-called dry sodium carbonate almost always contains some bicarbonate and hence yields water on ignition in no wise detracts from its usefulness; in fact C. Holthof[50] recommended the bicarbonate itself, which is more easily obtainable of fair purity. Holthof said further that with it there is less spattering onto the lid of the crucible than with the normal salt. However, as he uses 12 to 15 parts of it to 1 of mineral instead of the customary 4 to 8 parts of the normal salt, the advantage of possibly greater purity is in considerable measure lost.

Fusions with sodium carbonate should be made ordinarily only in vessels of platinum or its alloys.

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[49] G. Bong, *Bull. soc. chim. France*, 29, 50 (1878); W. Hempel, *Z. anal. Chem.*, 20, 496 (1881). P. Jannasch and J. Locke, *Z. anorg. Chem.*, 6, 321 (1894); P. Jannasch, *ibid.*, 12, 219 (1896).

[50] *Z. anal. Chem.*, 23, 499 (1884).

β. Potassium carbonate. The hygroscopic character of potassium carbonate makes it less suited for mineral fusions than the sodium salts; yet it finds application now and then, mainly because with certain elements the products of fusion are more soluble than the corresponding sodium salts. Its chief use by itself is in certain procedures for analyzing tantalates and columbates, and in admixture with sodium carbonate to furnish a flux of lower melting point than either carbonate alone has. Naturally the salt must be dehydrated immediately before use.

γ. Alkali hydroxides. Sodium and potassium hydroxides are powerful fluxes, but are seldom used by themselves for complete analyses, because the purity of even the best commercial articles is inferior to that of the best sodium carbonate or bicarbonate, and because fusions must be made in crucibles of silver or gold instead of platinum. With these a much lower temperature is called for than is permissible with platinum, and, although they are less attacked, an appreciable amount of the metal is dissolved and must be subsequently removed.

As the hydroxides, particularly the potassium compound, give off water more or less copiously when fused, accompanied by frothing or spitting, it is not good practice to mix mineral and flux until the latter has been brought into quiescent fusion by itself. Then, if it is known that the action will not be violent, the mineral powder may be poured upon the liquid flux in portions at a time; otherwise the liquid should be allowed to solidify and the powder then placed in its entirety on the cool melt before heat is again applied.[51]

δ. Sodium peroxide. Sodium peroxide, although a powerful disintegrator, is not so much used in making complete analyses as in industrial assaying when it is desired to bring a certain element to a required state of oxidation and perhaps to separate it from others that might interfere with its determination—chromium from iron for instance and sulfur in many sulfides. When so used, its entire freedom from foreign matter is unessential so long as the element to be determined is absent. Here, as with the alkali hydroxides, the use of platinum is not generally permissible, but crucibles of iron[52] or nickel are required instead. These are, however, strongly attacked in the usual procedure and hence have a short life. With both metals, most of the elements alloyed with them dissolve and therefore limit the possibilities in a subsequent analysis. In some analyses, the crucibles can be weighed before and after fusion and corrections applied as based on the composition of the crucible. Platinum may be used if the inside of the crucible is well coated with fused sodium carbonate and then with a thin fused layer of sodium peroxide, and the fusion is made at the lowest possible temperature and is not unduly prolonged.

In peroxide fusions, the sample should be well mixed with 5 to 15 g of dry sodium peroxide, the charge covered with 1 to 2 g of peroxide, and the crucible well covered and heated in an electric muffle at 600 to 700° C or over a free flame. In the former case, gradually insert the crucible, and, when the contents are molten, gently rotate to stir up any unattacked particles and heat for 5 minutes longer. In the latter case, first heat the crucible and contents on a hot plate for 5 to 10 minutes to expel any water in the peroxide, and then carefully fuse the charge by holding the crucible with a pair of tongs and slowly revolving it around the outer edge of the flame until the charge has melted down quietly, taking care not to raise the temperature so rapidly as to cause spattering. When the contents are in quiet fusion, give the crucible a slight rotary motion to stir up any unattacked particles on the bottom or sides. While still rotating the crucible, continue the heating at about 600° C for about 5 minutes, and finally heat for 1 minute at about 700° C. Let the melt solidify, and then loosen it in a solid cake by tapping the bottom of the crucible, while still warm, several times on an iron plate.

A simple procedure for sodium peroxide fusions and one that results in little or no attack on nickel crucibles is that recommended by Muehlberg.[53] In this method, the sample is mixed with sugar carbon and sodium peroxide and ignited, the crucible being immersed in water during the ignition and subsequent cooling. The melt shrinks from the crucible when cool or at most requires but a slight tap to loosen it entirely. A small unfused residue usually remains. This, however, settles quickly when the melt is dissolved in acid and can easily be caught on a filter and again fused with peroxide as before or with sodium carbonate in a platinum crucible. Although the danger of violent explosion is very slight, it is well to wear goggles when the mixture is ignited.

PROCEDURE. Transfer 0.5 to 1 g of the finely ground sample and 0.5 to 0.7 g of sugar carbon (prepared by igniting granulated sugar in a covered porcelain crucible) to a nickel crucible about 52 mm high and 44 mm in diameter and having a capacity of about 60 ml. Transfer 15 g of fresh, dry, yellow sodium peroxide to the crucible, mix well by turning the crucible with the left hand against a spatula held at an angle, and finally brush adhering particles of the charge into the crucible. The crucible and con-

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[51] According to C. J. van Nieuwenburg and H. H. Dingemans [*Chem. Weekblad*, 25, 266 (1928)], the decomposition of a number of technical silicates can be satisfactorily carried out by molten KOH or NaOH at about 400° C in a nickel crucible; and the attack on the crucible is very slight if it is protected from direct contact with the flame. See also E. W. Koenig, *Ind. Eng. Chem. Anal. Ed.*, 11, 532 (1939).

[52] Very satisfactory iron crucibles are those stamped from no. 20 gage (0.032″ thick) 1′ x 12′ sheets of ingot iron, which is manufactured by the American Rolling Mill Company, Middletown, Ohio. This iron contains approximately 99.9 per cent of iron and but traces of silicon, chromium, and copper.

[53] W. F. Muehlberg, *Ind. Eng. Chem.*, 17, 690 (1925).

tents should be perfectly dry. Tamp the charge firmly, cover the crucible with a cover having a small hole 5 to 6 mm in diameter in the center, and immerse it for two thirds of its height in water. If many fusions are made, the crucibles are best supported in a suitable tray. Immediately grip about 10 cm of cotton string in the end of a crucible tongs, light the end of the string, and insert it through the hole in the cover. When cool, tap the crucible sharply against the table if the melt has not already loosened, and transfer the contents to a dry, covered 600-ml beaker. Fill the crucible with water, empty the solution into the beaker as the cover glass is drawn to one side, and then immediately recover. When the action has moderated, wash any particles from the crucible and cover into the beaker, and dilute the solution to 300 ml. Add a distinct excess of hydrochloric acid while stirring vigorously, being careful to add the acid very slowly as the neutral point is neared, to prevent excessive foaming. If a residue is left, allow to settle, filter, wash moderately and ignite in platinum. Fuse with as little carbonate as possible, cool, dissolve the melt in dilute acid, and add to the main solution.[54]

ε. Borax. Borax is a powerful disintegrator and is used with advantage in the analysis of some refractory minerals like chromite and zircon. Unfortunately its use involves almost always complete removal of the boron after a fusion is made before the usual analytical operations can be carried out (see e, 848, and also Silicon, p. 672). It is best to prepare a stock of the fused salt if it is to be used frequently. For occasional use, a suitable amount of crystallized borax can be dehydrated and then fused in a platinum crucible and the mineral powder placed upon the solidified and cooled melt. As the molten salt is very viscous, it is well to place and keep in the crucible during the fusion a short stout rod of platinum with which to stir the mass from time to time.

ζ. Boric oxide. Like borax, boric acid is a powerful nonoxidizing flux which labors under the same disadvantage as borax in that the boron must be removed as a rule after the fusion operation before the analysis can proceed. Practically, it has been used only for silicate rocks and acid-resisting minerals with a view to determining their alkali content.[55]

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[54] G. G. Marvin and W. C. Schumb [*J. Am. Chem. Soc.*, 52, 574 (1930)], after a quantitative study of the method, state that (1) 15 g of a mixture of 150 g of sodium peroxide and 10.0 g of sugar carbon (100 mesh) are best for general purposes, (2) very refractory materials such as corundum should be ground to pass 100 mesh, (3) the unfused residue from a 0.5- to 1-g sample need not exceed 2 mg and consists of unattacked particles (chiefly thrown on the lid), (4) the temperature of the fusion is probably higher than 1450° C, and (5) no loss in weight of the nickel crucible can be detected after repeated use.

[55] P. Jannasch and O. Heidenreich, *Z. anorg. Chem.*, 12, 208 (1896). This method of decomposing rocks with a view to the determination of their contained alkali originated with Sir Humphry Davy [*Phil. Trans.*, 231 (1805) and elsewhere]. Original with Jannasch and Heidenreich is the manner of getting rid of the introduced boric oxide.

The flux gains added interest from an observation made by Jannasch and Weber,[56] but never followed up by them: namely, that it seems to afford complete expulsion of fluorine without loss of silicon. This provisional claim appears to be supported by some work of A. Travers[57] who used boric oxide successfully in analyzing cryolite, and later for expelling fluorine from artificial fluophosphates and fluovanadates in order to facilitate the determination of phosphorus and vanadium. However, the claim was not substantiated by J. I. Hoffman and G. E. F. Lundell.[58]

The boric oxide method demands, if the alkalies are to be determined in the same portion of sample as silica, etc., an absolutely alkali-free boric oxide, which can be prepared by two or three recrystallizations of a good commercial article. To dehydrate the purified crystals, fuse in a large platinum crucible. Cool suddenly to cause the anhydride to crack into pieces of a size convenient for powdering. Keep these in a tight glass vessel, and powder them only as needed, as the anhydrous oxide is hygroscopic. To this flux nearly all silicates readily succumb if very finely powdered. The authors recommend the expenditure of one-half to one hour's time for grinding one-half to one gram of powder.

η. Bisulfates and pyrosulfates. The sulfate fluxes are the bisulfates and pyrosulfates of sodium and potassium. Formerly the use of bisulfates was always prescribed, but, inasmuch as these become really effective only when converted by the heat of fusion to pyrosulfates and these last are commercial articles, it is better to use them and not bisulfates. An additional reason—one that has militated against a wide use of bisulfates—is that the fusion must be watched closely in its initial stages in order to prevent overflow, for much water is given off accompanied by frothing, and substance is spattered onto the crucible lid. With pyrosulfates, the fusion is much more tranquil. If pyrosulfates are not available and bisulfates are, these can be easily converted into the former by melting them in a platinum dish and keeping them in fusion till spattering ceases and white fumes begin to come off freely. In this way a considerable stock can be prepared in one operation. If the melt is poured into other dishes, it solidifies in thin sheets or cakes which can be readily broken up and bottled for future use. If a good article cannot be purchased, it is only necessary to mix and melt together equivalent weights of sulfuric acid and the normal sulfate until the water of the acid has been mostly expelled and the conversion to pyrosulfate accomplished.

The recommendation of J. Lawrence Smith[59] to use the sodium instead of the potassium salt can be followed in many cases with satisfaction. This

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[56] *Ber.*, 32, 1670 (1899).

[57] *Bull. soc. chim. France*, 31, 293 (1922); 33, 297 (1923).

[58] *Bur. Standards J. Research*, 3, 581 (1929).

[59] *Am. J. Sci.*, 40, 248 (1865).

salt melts more quickly and forms more soluble double salts with aluminum and some other metals. It has the slight disadvantage that the progress of decomposition of the mineral powder is not so readily followed because of the greater tendency of the sodium salt to crust over.

For a mineral fusion, a platinum crucible [60] is used, and the heat applied should be no more than is required to maintain liquidity until the last of the powder has been dissolved. This point is not always evident because the liquid is apt to become opaque even when not crusted over, but if the crucible is removed to a good light and allowed to cool, at a particular point the liquid becomes transparent and allows the bottom of the crucible and any undecomposed residue to be seen. This is truer of the potassium than of the sodium salt. More attention should be paid to proportions of powder and pyrosulfate and the temperature of fusion than usually is.[61]

In very prolonged fusions, it may be necessary to let the melt solidify, to add then a drop or more of concentrated sulfuric acid, and to heat cautiously to restore the flux to its original effective state, after which the operation is continued. This addition of acid may also be advisable at the end of a fusion if the decomposition of the flux has proceeded far toward the formation of neutral sulfate, the reason being that salts of one or more of the mineral constituents may have been deposited that are difficult to dissolve in the next succeeding operation. This holds particularly in the cases of titanium and zirconium, not to mention tantalum and columbium.

The platinum crucible is always more or less attacked in pyrosulfate fusions, the more the longer the operation, and it should be borne in mind that the dissolved platinum [62] usually must be removed at some subsequent stage of the analysis.

θ. Acid fluorides. Acid fluorides, usually the potassium salt KHF_2, are used for opening up certain refractory minerals such as some tantalates and columbates and zircon, and then more often for an assay than for a complete analysis. Silicates are of course not amenable to this treatment if silicon is to be determined, but, even with siliceous materials, the method may be very useful for the other constituents, especially as in the fusion operation the silicon is gotten out of the way.

Platinum is the only material in which the attack may be made and none of it goes into solution. The temperature required for the fusion is very low, and the operation is usually completed in a much shorter time than with other fluxes. No special directions are needed for carrying out the operation except that the fact must be borne in mind that fluorides of a number of metals are more or less volatile and that therefore the temperature of fusion and the time should be reduced to the lowest possible limit, especially when tantalum, columbium, titanium, and zirconium minerals are under treatment.

c. *Choice of a Flux.* The composition of the mineral substance and the purpose of the analysis will determine which flux to employ when one has to be used. If only an assay is contemplated, a flux may be suitable that will not serve when several constituents are to be determined in the same portion of sample.

For most of the vast list of silicates and other oxidized minerals not soluble in acids, sodium carbonate alone is best. For many of them that are soluble in acids the statement is also true concerning certain of their constituents, for instance the fluophosphates of calcium and indeed phosphates in general. For many such, the object is not only to obtain a water solution of the anion in which it can be precipitated or otherwise determined, but also to remove the anion so as to render possible the determination of other elements in the part of the melt that is not soluble in water.

It is impossible and unnecessary to indicate at this point all the cases in which it may be necessary or advisable to use one of the composite fluxes referred to on page 847 or the single fluxes. A few observations will suffice; additional ones will be found in the chapters on individual elements or mineral classes. Those discussed on page 847 are used for sulfides and arsenides chiefly, sodium peroxide and potassium chlorate without dilution being too powerful in their action on such materials. The purpose in using them is to oxidize sulfur to sulfate and arsenic and antimony to arsenate and antimonate, respectively. It is true that most of these minerals can be thoroughly oxidized by liquid reagents, but an alkali fusion has the advantage, as already said, that aqueous extraction of the anions separates them from a number of elements that might interfere subsequently or else makes possible their immediate determination without having to go through a preliminary precipitation, as for instance of arsenic by hydrogen sulfide.

Potassium carbonate is used seldom and then usually because some of the products of fusion are more soluble than the corresponding sodium compounds.

Borax and boric oxide are used only for oxidized substances that are not volatile at the temperatures required. In either case, the boron must as a rule be expelled before the analysis can be completed. Boric oxide has the advantage over borax that no fixed solid is introduced.

Potassium chlorate is never used alone on account of the attendant danger.

Sodium peroxide may be used alone, but care must be exercised with unoxidized substances.

The sulfates are used only for oxidized substances or when it is desired to expel fluorine at the start from those that are free from silicon. Not-

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[60] For some work a quartz crucible can be substituted.

[61] G. W. Sears and L. Quill, *J. Am. Chem. Soc.*, **47**, 922 (1925); G. W. Sears, *ibid.*, **48**, 343 (1926); **51**, 122 (1929). See Titanium (p. 577) and the Earth Acids (p. 594).

[62] This averages about 3 mg in an ordinary fusion.

withstanding their powerful disintegrating action even upon some silicates (zircon), there are many silicates that yield very slowly or incompletely to them (the feldspars for instance). Their most common use as initial attacking agents is with tantalates and columbates, but they are extensively used in the subsequent course of analysis for dissolving ignited precipitate mixtures with a view to the determination of their components.

The acid fluorides are used but seldom and then only for a few refractory minerals free from silica or in which the silica is to be determined after some other mode of attack. The volatility of some metallic fluorides during fusion militates somewhat against more frequent use of the acid fluoride fluxes.

d. *Procedures for Sodium Carbonate Fusions.* α. *Procedure for oxidized minerals in absence of appreciable chlorine, fluorine, or sulfide sulfur.* It is assumed that any small amount of sulfur that may be present will be determined in a separate portion of sample. Mix thoroughly 4 to 6 g of flux with 1 g of rock or mineral powder in a platinum crucible of 20- to 30-ml capacity.[63] It is inadvisable to use the much larger amount of flux recommended by some writers except as it may be shown to be needed in isolated cases, for they introduce more impurity and necessitate longer washing of precipitates.[64] Place the crucible, covered at first, over a moderately low flame, increase this gradually to a maximum (approximately 1000° C), and maintain it there till the mass is quiescent. There should be no violent action. The contents of the crucible will then appear in the case of highly siliceous materials as a viscous liquid, occasionally almost clear, though generally more or less turbid, and, when it is placed over the blast flame (approximately 1200° C) little or no further effervescence occurs. Melts of this character disintegrate very readily in water. With less siliceous matter, the fusion is less pronounced, though this does not necessarily imply incomplete decomposition. It is generally advisable and often necessary to heat these less fusible mixtures at approximately 1200° C, when a further and very marked escape of carbon dioxide often takes place and the crucible cover should be lifted cautiously at intervals to avoid loss by boiling over. This boiling is due not merely to further action of the carbonate on the mineral substance but sometimes more to the decomposition of alkaline earth carbonates, whose bases then enter into combination with other constituents of the flux and mineral or rock to form compound silicates, and probably aluminates if silicon or aluminum or both are present. It is a mistake to regard, as many have done, the alkaline earth metals, magnesium, iron, and manganese as present in the form of carbonates after fusion at 1200° C. They are seldom in that state even when the fusion has been carried out at 900 to 1000° C. Certain very refractory minerals (chromite and zircon for instance) may need heating at 1200° C for 1 or 2 hours, or even longer.

As a general rule, the blast flame during fusion should not be directed vertically against the bottom of the crucible but at an angle against side and bottom, nor should the flame be allowed to envelop the whole crucible. These precautions apply in all ignitions of reducible substances and yet they are too often neglected. In neither case, if they are neglected, will there be the necessary oxidizing atmosphere within the crucible; on the contrary, reduction may occur fraught with serious consequences. This is especially true if the sample (silicate rock for example) contains more than traces of pyrite or other sulfide, when, after cleansing and igniting the crucible, there may appear on its interior a darkening due to oxidation of reduced iron which had alloyed with the platinum. In exceptional cases, this may amount to several milligrams in weight and can be removed only by repeated ignitions in air, followed each time by scouring or by treatment with hydrochloric acid or an alkali bisulfate.

In order to avoid this trouble and also the use of niter with pyritiferous and carbonaceous rocks, it is well first to roast gently the weighed powder in the crucible in which the fusion is to be made, turning the crucible around a few times to expose all of the powder to the air. With rocks exceptionally high in pyrite, the roasting must be done in a porcelain crucible. In such case, transfer the roasted powder to the platinum crucible, and, if brushing with a camel's hair brush does not remove the last of any adhering dust, scour it off with a little of the sodium carbonate flux.[65]

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[63] With materials, such as soda-lime glass, that are easily decomposed, fusions can be made in a platinum dish, as of the Payne type, in which the solution of the melt and the evaporation for silica can be made directly without any transfer.

[64] In fact, for many materials it may be advantageous to use less than the customary proportion of flux. A. N. Finn and J. F. Klekotka [*Bur. Standards J. Research*, 4, 813 (1930)] recommend the following procedure for decomposing aluminous silicates: Thoroughly mix 0.5 g of the powdered sample and 0.6 g of powdered anhydrous sodium carbonate in a platinum crucible by stirring with a platinum rod for at least 5 minutes. Cover the crucible, and heat at 875° C for 2 hours. Cool, add 1 or 2 ml of water, digest for about 10 minutes, and then stir, or grind if necessary, to break up all particles as completely as possible. Wash the contents of the crucible into a beaker or casserole, using not more than 50 ml of water. Heat to boiling, and, while stirring constantly, rapidly add about 20 ml of concentrated hydrochloric acid. Crush as well as possible any gritty particles that remain, evaporate to dryness, and proceed as usual with the determination of silica. See also James I. Hoffman, Decomposition of Rocks and Ceramic Materials with a Small Amount of Sodium Carbonate, *J. Research NBS*, 25, 379 (1940).

[65] Duparc [*Bull. soc. franç. minéral.*, 42, 156 (1919)] attributed the alloying with iron to the reducing effect of flame gases that diffuse through the platinum, and claimed to avoid it by fusing in a muffle. In this, however, another serious error is incurred: namely, strong attack of the crucible around its rim by the molten alkali and consequent introduction of platinum into the analysis. Tests made by E. Wichers at the Bureau

When sulfate is to be determined in the melt, the heating should be done in a muffle if sulfur-bearing flame gases cannot be rigidly excluded otherwise.[66]

It happens sometimes that the cooled melt indicates absence of manganese when it is really present in amount to give normally a strong coloration. Two fusions of a rock powder made side by side or successively under apparently like conditions may in one case show little or no manganese, in the other considerable. Therefore the absence of a bluish-green color in the cooled melt is not to be taken as proof of the absence of manganese if but little is present. This difference of behavior we can ascribe to no other cause than that of a neutral or nonoxidizing atmosphere in one of the crucibles and an oxidizing one in the other. It is of course not to be expected that the green color will show until all other oxidizable components of the mineral substance such as sulfides, ferrous iron, and organic matter have been fully oxidized, which, however, is soon the case if air has access to the surface of the melt.

The melt may be yellow from sodium chromate if chromium is present and not enough manganese to obscure the effect. An aqueous extract will be green in the case of manganese and yellow in the case of chromate without manganese. If both are present, the yellow of chromate can be made to show by warming the solution with a few drops of alcohol and, if need be, filtering from the precipitated manganese compound.[67]

If the melt is swirled gently just as it is cooling and then cooled thoroughly, it can usually be detached by sharply tapping the inverted crucible on the bottom of the dish in which the melt is to be dissolved. In extreme cases, separation is aided by gentle pressure insufficient to deform the crucible. Another simple way of loosening the melt consists in letting it cool slowly, then heating the crucible quickly to 300 to 400° C, and immediately plunging it for two thirds of its depth into cold water. Still another procedure consists in letting the melt solidify as above, half filling the well-cooled crucible with water and then, after a minute, gently heating (but not boiling) at the edges of the melt by means of a small flame. When the melt has been loosened at the edges, the bottom is gently heated, whereupon the whole melt generally detaches itself. If time is no object, the bent end of a stout platinum wire can be placed in the melt before it solidifies, and most of the melt lifted out by again heating to melt a thin layer next to the crucible.[68]

β. Procedure for oxidized minerals in presence of appreciable chlorine or fluorine and absence of appreciable sulfide sulfur. With a chlorine-containing mineral which it is permissible to subject to carbonate fusion (the silver halides for instance are not) or one containing enough fluorine to determine or to cause appreciable loss of silicon or incomplete precipitation of aluminum in the subsequent treatment (pp. 860–869), the flux should be an equimolecular mixture of sodium and potassium carbonates, and the blast flame should not be used if a lower heat will serve. In order to lessen the danger of loss of alkali chloride or fluoride by volatilization, it may be advisable to utilize a J. L. Smith crucible (Fig. 44, p. 926).

Although not strictly germane at this point, it may be remarked that certain fluorides (fluorite or CaF_2) and certain phosphates [apatite or $Ca_3(PO_4)_2$] are not completely decomposed so as to permit aqueous extraction of the anion unless silica is incorporated with the flux and mineral powder before the fusion is made. These cases will be considered in the chapters on fluorine and phosphorus.

γ. Procedure for sulfides and arsenides. If sulfide or arsenide minerals are to be fused with sodium carbonate, this is done with admixture of an alkali nitrate, chlorate, or peroxide, all free from sulfur or arsenic, the addition being made for oxidizing and not for fluxing. An important precaution to be observed is that the proportion of oxidizer shall not be so great as to injure the crucible if platinum is used, or to cause too sudden and violent reaction with consequent loss of substance by projection or volatilization. The latter source of loss is particularly to be feared with arsenides, when the heat of reaction may expel some of the element before it has become oxidized, a condition that reveals itself usually by the characteristic odor. A too violent reaction is also guarded against by very gentle heating at the start and, if need be, instant temporary removal of the crucible from the external source of heat. In general, it is well to limit the oxidizer to an amount little greater than is needed to oxidize fully all the oxidizable components of the sample.

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of Standards showed this attack in a muffle and not over the blast flame. The explanation therefore probably is that over the flame the creeping alkali is kept carbonated but in the muffle becomes causticized. This appears to explain the conflicting statements that have been made regarding the effect on platinum of molten sodium carbonate.

[66] It should not be assumed that the use of a muffle furnace is a sure guarantee against contamination by sulfur, for it has been our experience that alkaline melts may absorb compounds of sulfur from the atmosphere within the muffle if the furnace was previously used for ignition of sulfides or other volatile sulfur compounds.

[67] It cannot be taken for granted that extractions of sodium carbonate melts with water, followed by filtration and washing of the residue with water, will yield sharp separations of elements, such as silicon, aluminum, or tin, that might be expected to form soluble compounds, from elements, such as lead, that might be expected to form insoluble compounds. Moreover, the distribution of the elements between residue and filtrate is often affected by accompanying elements.

[68] To facilitate the solution of sodium carbonate melts, R. S. Young [*Ind. Eng. Chem. Anal. Ed.*, 16, 590 (1944)] recommends that the melts be cast as flat buttons by pouring into depressions in a Monel metal "pouring plate."

1. *Sodium carbonate with potassium nitrate.* Intimately mix in a crucible 1 part of mineral[69] (usually 0.5 to 1 g, depending on the sulfur content) with 10 parts of a mixture of sodium carbonate and potassium nitrate, and cover with a layer of the flux. Potassium nitrate is preferable to the sodium salt chiefly because it is not hygroscopic. The proportion of nitrate to carbonate usually recommended is 1 to 2, but some writers advise as low as 1 to 4. It may be even much less if the oxidizable content of the sample is low. The lower the proportion is, the less is the crucible likely to suffer, which is of importance if the metal is platinum. If only sulfur or arsenic is to be determined, nickel may be used. Special care must be taken to exclude flame gases from the interior of the crucible, either by use of a sulfur-free fuel or the device shown in Fig. 6. Heat at first gently, then more strongly until the contents are melted and for 15 to 20 minutes afterwards. If the melt or its solution is to be heated with hydrochloric acid, this should not be done in contact with platinum.

2. *Sodium carbonate with peroxide.* For other than a sulfur or chromium content, sodium peroxide is not often used in mineral analysis for oxidizing fusions with sodium carbonate, because it introduces more impurity than a nitrate; otherwise it is quite as effective if not more so, and the time required is less. The caution given under α about the exclusion of flame gases applies here too.

Fuse 1 part of mineral with say 10 parts of peroxide and 8 parts of carbonate in a nickel crucible, with the protecting device as in α, for 10 minutes and then for 20 minutes with a full burner flame. By taking the precaution first to coat the whole inside of the crucible with molten sodium carbonate, one may be warranted in using a crucible of platinum, provided the fusion is made at the lowest possible temperature and is not unduly prolonged.

3. *Sodium carbonate with potassium chlorate.* Fuse one part of mineral with 5 parts of carbonate and 1 of chlorate, at first gently, and then more strongly until no more oxygen is given off. With this mixture a platinum crucible may be used and more components determined than is possible when a nickel or iron crucible is used.

e. *Procedure with Boric Oxide.* α. *Fusion of easily decomposable silicates.* Mix with 1 part of finely powdered mineral 3 to 8 parts of flux, according to the nature of the silicate, in a platinum crucible of 40 to 65 ml capacity. Apply heat from a burner turned low for 5 to 10 minutes until water is expelled, and then increasingly till the gas is fully turned on. Prevent bubbling and rising in the crucible as much as possible by using a short platinum rod which does not rise above the rim of the crucible and is not removed during the fusion operation. When the mass has been in quiet fusion for a time in the covered crucible, apply a blast flame for 20 to 30 minutes or as long as necessary.

β. *Fusion of refractory silicates.* For those minerals that like andalusite, cyanite, and topaz are not fully decomposable by the heat of the ordinary blast flame, use a flame fed by oxygen instead of air. The blast lamp, of 2½ mm opening, is supplied with ample gas (the authors of the method used 5 or 6 ordinary gas cocks), and the flame is made broad and free from luminosity. To the mineral having been first heated as described under α, but with a much larger proportion of flux—as high as 30 to 1—add a few grams more of boric oxide, and apply the oxygen blast flame until, in 10 to 15 minutes, the fusion is as transparent as glass.

γ. *Treatment after fusion.* From this point the further treatment is the same in both cases, and as modified by Jannasch and Weber[56] is as follows:

Cool the hot crucible (covered to avoid loss of flying fragments of the melt) in water, and turn the contents into a very large porcelain or platinum dish, to which, after covering with a glass, add a saturated solution of hydrochloric acid gas in methyl alcohol.[70]

The cover being removed, heat the liquid to boiling, over an asbestos board, by an inch-high flame, with constant stirring, or leave it without attention over a lower flame or on a water bath heated short of boiling. Cleanse the crucible in a similar manner, and add its contents to the dish. In 10 to 15 minutes, with occasional addition of the methyl chloride, solution is complete. Then boil the liquid down to a small volume, and evaporate to dryness on the bath. Digest the residue, on the bath, at 80 to 85° three or four times in succession with the ester solution in order to remove the last traces of boron as boric ester. Take care each time to wash down from the sides of the dish, with methyl chloride solution, the boric acid that formed and deposited thereon during the evaporation. For the subsequent treatment of a silicate, see Silicon (p. 860).

δ. *Drawbacks of the method.* (1) The boric ester, driven off in such quantities, at once decomposes in contact with moisture, and boric acid settles over all objects with which it comes in contact. Hence a special hood for these operations seems to be called for; otherwise boric oxide may at any time fall into other vessels and cause untold trouble. (2) A second objection attaches to the use of the oxygen flame when alkalies are to be estimated in the melt—and the ability to do this is one of the chief claims in favor of the method—for it cannot be doubted that, at the high temperature of this flame, alkalies are volatilized. Sodium borate can be volatilized slowly but wholly over an ordinary blast flame; hence there is

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[69] The recommendation to use very finely ground mineral substance should not be adhered to too closely for fear of loss by oxidation. Pyrite, for instance, yields some sulfur dioxide on grinding (see p. 712).

[70] Made by passing dry hydrochloric acid gas into cooled methyl alcohol for 1 to 2 hours.

great reason to fear sufficient loss at this much higher temperature to give rise to serious error. (3) Incomplete expulsion of the boric oxide gives rise to errors later in the analysis.

When alkalies are not to be determined, boric oxide is almost certainly a much less suitable flux than fused borax, for it is almost certainly less energetic.

B. DECOMPOSITION BY THE USE OF ACIDS

The practice of separating alumina, etc., by the usual methods after first attacking the rock powder by hydrofluoric and sulfuric acids—silica being estimated in a separate portion—although attractive in principle, was long ago abandoned by one of us (W. F. H.) after fair trial, owing to the disturbance sometimes occasioned by incomplete expulsion of fluorine and to a less degree by the presence of sulfates instead of chlorides. The elimination of all fluorine can be made more certain if, after the solution has been heated to fumes of sulfuric acid, it is cooled, the inside of the dish is washed down with a little water, and the solution is again heated to fumes after the addition of a moderate excess of pure powdered silica,[71] preferably chemically prepared. In this case the final solution must be filtered; the residual silica ignited, treated with sulfuric and hydrofluoric acid, evaporated to complete expulsion of hydrofluoric acid; and the small recovery added to the main solution.

In some cases, especially when alkaline earths are present, decomposition by the use of hydrofluoric and perchloric acids possesses an advantage in that the attack yields soluble perchlorates which cause no difficulties in succeeding operations. As a rule, the expulsion of hydrofluoric acid is more difficult when perchloric acid is used, and the heating should be carried on until a dry residue is obtained if circumstances will permit. As in the case of sulfuric acid, the addition of a little silica may be needed in the last stages.

Jannasch[72] poured upon the finely ground rock powder contained in a platinum tube of about 26 ml capacity a somewhat diluted hydrochloric acid (4 acid to 1 water), placed over the open end a cap which did not hermetically close the tube, inserted the latter in a larger tube of potash glass, likewise partly filled with the diluted acid, sealed the glass tube, placed it in turn in an inclined position in a steel Mannesmann tube containing ether or benzine to equalize the pressure, and heated to any desired temperature up to 400°.

The chief drawback seems to be a somewhat incomplete decomposition, doubtless due to the necessarily inclined position of the tube, which causes the powder to collect at the lower end, and thus renders decomposition less complete than if the material were spread evenly throughout the length of the tube. Further, the acid attacks the platinum strongly unless the air in both the platinum and the glass tubes is replaced by carbon dioxide. Even when this is done, several milligrams of platinum are found in the silicate solution.

Nevertheless, to those possessing the necessary platinum and steel tubes, the method can render efficient service in special cases when economy of material is imperative.

Many silicates, ceramic materials, refractory oxides, and refractory platiniferous materials can be decomposed without contamination with alkali salts by heating at elevated temperatures with acids in sealed glass tubes in which the internal pressure is compensated for by external pressure of carbon dioxide within a steel container.[73]

Kaolin, which is only slowly attacked by dilute hydrochloric acid, can be quickly decomposed if it is roasted at about 700° C for 15 minutes before treatment with the acid. Practically all the silica remains insoluble.[74]

6. SILICON

A. SPECIAL CASES

Before taking up the more general subject of silicate analysis, two special and simpler cases will be disposed of.

a. *Quartz and Very Highly Siliceous Minerals.* Occasion may arise for determining the elements other than silicon that happen to be present in quartz, chalcedony, or other highly siliceous materials. In such cases it may be convenient, if the impurities make up but a very small percentage of the mineral, to determine the silicon first, but indirectly, by volatilizing it with hydrofluoric and sulfuric acids, instead of by the much more lengthy procedure that is ordinarily followed. In that case, the volatilization has to be preceded by a determination of the loss in weight on ignition, and this carries with it the limitation that the composition of the nonvolatile material after this ignition must not undergo change when the residue that is left after the volatilization is again subjected to the same degree of heat as in the first ignition. Thus, minute amounts of sulfides, if present, would probably be converted to oxides in the first heating, which would remain as such after the second and therefore not interfere; but substances that yield nondecomposable sulfates (alkali and alkaline earth metals) would interfere.

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[71] A. A. Noyes, *Technol. Quart.*, **16** [2], 101 (1903).

[72] *Ber.*, **24**, 273 (1891); *Z. anorg. Chem.*, **6**, 72 (1894).

[73] E. Wichers, W. G. Schlecht, and C. L. Gordon, *J. Research NBS*, 33, 363, 451, 457 (1944); see also C. L. Gordon, *ibid.*, 30, 107 (1943).

[74] James I. Hoffman, R. T. Leslie, H. J. Caul, L. J. Clark, and J. D. Hoffman, *J. Research NBS*, 37, 409 (1946).

Having determined the ignition loss in a platinum crucible, moisten the powder, pour upon it concentrated hydrofluoric acid entirely free from nonvolatile impurities, and evaporate slowly upon the steam bath or over a radiator. Repeat the operation with fresh acid until no unattacked mineral remains. To effect this, a number of repetitions may be necessary, for the ordinary crystallized form of silica yields very slowly to the action of hydrofluoric acid in comparison with most silicate minerals and still more with precipitated silica. The end of the operation can usually be recognized by the final disappearance of all gritty particles as determined by gentle stirring with a rod of platinum or Bakelite. After the final evaporation to dryness, add a drop of strong sulfuric acid, fume this off, and heat the residue to decompose completely sulfates such as those of iron or aluminum. This last is important if it is desired, as assumed, to determine the percentage of silica and not merely that of the foreign matter. A second weighing gives the weight of silica volatilized and of the impurities as oxides if the sulfates were completely decomposed. The nature and amounts of these can be determined by the usual methods if desired. Should any of their compounds have been silicates originally, their silicon content will have been volatilized with the free silica.

b. *So-called Soluble Silica.* Very often in treatment of minerals by acids, silica is separated in granular or gelatinous form mixed with unattacked substance, and it may become necessary to remove or estimate this silica, or perhaps to discriminate between soluble and insoluble silica existing together. Usually a boiling solution of sodium carbonate has been employed for this purpose, though the caustic alkalies have found advocates. G. Lunge and C. Millberg[75] showed conclusively: (1) that quartz is not nearly so insoluble in solutions of the caustic alkalies as was supposed, but that, given a sufficient degree of subdivision, it can be brought wholly into solution; (2) that it is impossible to obtain correct separation of quartz and opaline silica by the use of either caustic or carbonated alkalies; and (3) that digestion on the steam bath for 15 minutes with a 5 per cent solution of sodium carbonate is the only way to insure a good separation of unignited precipitated silica from quartz, and then only when the finest flour has been removed by levigation. The authors said:

> If, however, no more of such flour is present than is produced in the ordinary operations of powdering and sifting through cloth of the finest mesh, the error arising from the above-mentioned treatment is so slight that it can generally be neglected; it reaches 0.1 to, at the most, 0.2 per cent of the total silica, by which amount the quartz will appear too low, the amorphous silica too high.

Lunge and Millberg also said, however, that the solvent action of the caustic alkalies on quartz becomes very apparent only when the material has been reduced to such an utterly impalpable degree of fineness as is practically never reached in the preparation of samples for mineral analysis. For this reason, there need be no hesitation in employing a dilute solution of sodium hydroxide when the silica separated by acid from one of several constituents of a rock is to be estimated. Even when the dilution is considerable, solution is almost immediate, and, as soon as this is accomplished—the point being known by the change in appearance of the residue—the solution should be diluted with cold water and filtered at once. The difficulty met with in filtration may often be overcome by acidifying faintly, which has the added advantage of at once arresting any further action of the alkali. If the dilution is sufficient, no separation of silica results from so doing. Very dilute acid should be used for washing. Lunge, when using sodium carbonate, washed with hot carbonate solution to which alcohol was added, thus obtaining clear filtrates.

c. *Quartz in the Presence of Silicates.* α. The following method, proposed by Line and Aradine,[76] is based on treatment with fluoboric acid, which dissolves a variety of silicates, but attacks quartz so slowly that a correction factor can be applied. Quantitative decomposition in 2 to 8 days can be obtained with wollastonite, biotite, orthoclase, albite, muscovite, pyroxene, andalusite, cordierite, talc, amphibole, and zoisite. Decomposition is incomplete with forsterite, garnet, dumortierite, sillimanite, beryl, and zircon.

Under favorable conditions determinations should be accurate to approximately 1 per cent of the amount of quartz present.

PROCEDURE. 1. *Decomposition of silicate.* Grind the sample to pass a 100-mesh sieve, and transfer 0.15 to 0.2 g to a platinum crucible. Add 5 ml of fluoboric acid,[77] 1 ml of phosphoric acid (sp. gr. 1.39), and 2 ml of 2 *M* ferric chloride. Heat at 50° C for 48 hours, adding more ferric chloride if the yellow color of the solution fades. Transfer the residue to an ashless filter, and wash four times with *N* hydrochloric acid and five times with hot water. Unless the residue is negligible at this point, place paper and residue in the crucible, and destroy the paper by heating only

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[75] Z. *angew. Chem.*, 393, 425 (1897).

[76] W. R. Line and P. W. Aradine, *Ind. Eng. Chem. Anal. Ed.*, 9, 60 (1937). The authors assert that fluoboric acid is superior to fluosilicic acid, which has been recommended for the same purpose by A. Knopf [*U. S. Pub. Health Repts.*, 48, 183 (1933)], in that it dissolves a greater number of silicates, solution is more rapid, and the correction factor is 0.34 per cent for a 24-hour attack at 50° C, compared with 0.7 per cent per 24-hour attack at room temperature. See also H. Jung, *Naturwissenschaften*, 30, 266 (1942), and F. H. Goldman, *Ind. Eng. Chem. Anal. Ed.*, 13, 789 (1941).

[77] Prepared as follows: Pour 75 ml of pure 48 per cent hydrofluoric acid into a 125-ml platinum dish, cool in an ice bath, and add 32 g of purified boric acid in small amounts, allowing each portion to dissolve before more is added. To dissolve the last portions, heat on a steam bath, and then concentrate the solution to about 50 ml. Cool to 0 to 5° C, and filter. The resulting acid should have a specific gravity of about 1.45 and give no test for fluoride. It must be stored in wax or rubber bottles, but filtration can be done in glass.

to dull redness. Repeat this treatment for 48 hours longer. Filter, wash, and determine the weight of the residue. Unless solution has been complete, repeat this treatment for 48-hour periods until a loss of only 1 to 2 mg is found. This indicates complete solution of the silicate. Some siliceous materials may be dissolved in less than 48 hours, in which case treatment with the fluoboric acid should be stopped as soon as complete decomposition is apparent. In other cases, even 12 days may not effect complete decomposition.

2. *Determination of free silica.* Treat the residue insoluble in fluoboric acid with 2 to 3 ml of 48 per cent hydrofluoric acid, evaporate, ignite, weigh, and repeat until constant weight is obtained after ignition. The loss in weight corresponds to the free silica content of the residue, provided undecomposed silicates are absent. This value must be corrected for the amount of free silica dissolved during the time required to decompose the silicate. This correction factor is 0.34 per cent of the free silica present for each day's treatment.[78] Results for quartz will, of course, be too high if undecomposed silicates remain and are attacked by the hydrofluoric acid.

β. Trostel and Wynne [79] point out that petrographic methods for determining quartz in refractory clays are capable of only fair accuracy, and that chemical methods based on attack with fluosilicic or fluoboric acids are slow and uncertain. They recommend a method in which the quartz remains as a residue after the clay has been fused with pyrosulfate and the silicic acid liberated from the clay minerals has been dissolved in a hot solution of sodium hydroxide. Alleged advantages are that simple reagents are used, determinations can be made in 8 hours or less, and net errors should not exceed 0.15 per cent. The accuracy is dependent on a minus error caused by solution of the quartz, and a plus error due to contamination of the quartz by unattacked mineral matter. The net error ranges from a minus error of about 0.15 per cent with clays containing 50 per cent quartz, to a plus error of about 0.13 per cent with clays containing 10 per cent or less of quartz, plus and minus errors being practically balanced with a clay containing 25 per cent.

PROCEDURE. Weigh a 0.5-g sample of the dried clay, ground to pass 150 mesh, in a vitreous silica crucible, and add 10 to 15 g of potassium pyrosulfate. Fuse thoroughly, at first by gradual heating to prevent loss of sulfur trioxide, and finally at 900 to 1000° C. Do not continue heating to a point where salts begin to freeze on top of the melt and on the sides of the crucible. Dissolve the cooled melt in 150 to 200 ml of hot water in a

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[78] E. Kaplan and W. T. Fales [*Ind. Eng. Chem. Anal. Ed.*, 10, 388 (1938)] recommend that the computation of the correction be made by applying a form of the compound-interest law.

[79] L. J. Trostel and D. J. Wynne, *J. Am. Ceram. Soc.*, 23, 18 (1940).

400-ml beaker, and then add about 12 g of sodium hydroxide pellets, one or two at a time, to dissolve the precipitated silicic acid. Digest on the hot plate for 30 minutes, maintaining the temperature at 85 to 90° C.

Filter quickly through a paper of close texture, and scrub and wash the beaker thoroughly with hot water to insure complete transfer of the quartz. Finally wash the paper and residue 10 times with hot water, 5 to 10 times with hot dilute hydrochloric acid (1 + 1) to dissolve iron and other contaminants of the quartz, and then 5 times with hot water. Transfer the paper and residue to a tared platinum crucible, ignite, cool in a desiccator, and weigh to obtain the weight of free quartz.

Occasionally, the quartz is contaminated by compounds not decomposed during fusion or dissolved in the subsequent treatments. The quartz residue should therefore be examined under the microscope, and then treated with 2 drops of dilute sulfuric acid (1 + 1) and 10 ml of hydrofluoric acid, evaporated to dryness, ignited, and weighed. If the weight of the residue exceeds 0.001 g, the results should be discarded and the determination repeated.

γ. Other methods for the determination of free silica that should be mentioned are (1) a modified petrographic immersion method,[80] (2) a grain-count method for the rapid estimation of free quartz in feldspars to be used in preparing enamels,[81] and (3) an X-ray powder diffraction method for the determination of quartz in industrial dusts.[82]

B. SILICATE ANALYSIS

After bringing silicate minerals or siliceous mineral products into appropriate solution, the determination of silicon is the starting point in a succession of operations that lead to the determination, in one and the same portion of sample, of other elements, the number of which varies with the nature or complexity of the substance to be analyzed and is often very considerable. These may be, after first separating the silicon as silica, first, elements precipitable by hydrogen sulfide, then others precipitable by ammonium hydroxide or ammonium sulfide, next calcium and strontium, and finally magnesium. The General Procedure usually followed is given in outline form by G. E. F. Lundell and J. I. Hoffman in *Outlines of Methods of Chemical Analysis*, John Wiley & Sons, pages 30–78 (1938). One or another of the indicated operations may be unnecessary, or variations in the general procedure may be called for in special cases. It should be emphasized that not all of the elements in a group are necessarily determined in the group precipitate. Some of them may require special portions of the sample, but

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[80] H. L. Ross and F. W. Sehl, *Ind. Eng. Chem. Anal. Ed.*, 7, 30 (1935).

[81] G. H. McIntyre and M. Bozsin, *ibid.*, 12, 326 (1940).

[82] J. W. Ballard, H. I. Oshry, and H. H. Schrenk, *U. S. Bur. Mines Repts. Invest.* 3520 (1940).

they must as a rule be separated from solution in this portion and even weighed as part of a composite precipitate. This is particularly true of the group that is ordinarily precipitated by ammonium hydroxide and that is sometimes of great complexity.

In illustration may be cited the familiar instance of the ammonia precipitate in rock analysis. Besides aluminum, iron, titanium, and a little silicon as almost invariable components, this contains also the phosphorus, chromium, zirconium, and the like that may be present in the rock, more or less of the vanadium, and, if desired, the manganese. The weight of the aggregate having been found, it is customary to determine one or all but aluminum in it or in separate portions, to subtract the several amounts from the sum, and to regard the remainder as aluminum for lack of an exact method for determining that element in such a mixture.

Most silicate rocks are amenable to well-worked-out analytical procedures, which as to the main constituents are the same for all rocks, for, although in general more complex than any one mineral species, the constituents that are apt to occur in them in amounts determinable in 1- to 5-g portions of substance seldom exceed 25 and are in many rocks no more than 15.[88] Silicate minerals, on the other hand, offer a much greater diversity of composition with respect to the major constituents and demand a correspondingly greater variety of methods for their analysis. Even to them, however, many of the methods applicable to rocks apply also, at least in their main features. With the precipitate formed by ammonium hydroxide are encountered as a rule the greatest possibilities of choice or necessity for variations in procedure.

As the analysis of a complex silicate-rock covers many of the operations and separations that have to be made in analyzing very many minerals, a full outline of such an analysis will be given immediately after the detailed procedure for silicon itself. This is done in order the better to indicate the precautions and corrections that are necessary in work that lays claims to accuracy, for a correct determination of silicon is not an operation that can be done at one stroke as it were, but as a rule is bound up with other operations which involve corrections for impurities in the crude silica and recovery of residual silica from other precipitates. The actual methods used for determining the several components other than silica will not be considered in that outline except by cross references to the chapters where descriptions are given in detail. Certain special cases where silica occurs as a minor constituent or mere accessory associate of a mineral can be treated more conveniently in other chapters, as for instance in that devoted to the columbates and tantalates.

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[88] This statement in nowise conflicts with the belief that in igneous rocks as a whole every element may exist.

a. *Opening up of Silicates.* α. *By acids.* 1. *When silicon is to be determined.* When a silicate mineral is decomposable by an acid, the one chosen for the portion in which silica is to be determined is almost always hydrochloric acid. It is preferred to nitric acid chiefly because, when the solution is evaporated to render the silica insoluble, there is usually less tendency for difficultly soluble salts to form; and to sulfuric acid because the latter produces more or less insoluble lead and alkaline-earth sulfates to contaminate the silica. Naturally, for lead silicates, nitric or perchloric acid will usually be employed, and other circumstances may sometimes dictate their use. With some silicotitanates sulfuric or perchloric acid may perhaps be used advantageously instead of hydrochloric because, with a sufficient excess, the titanium can be held in solution while the silica is being rendered insoluble.

No fixed rule can be given for the strength of the solvent acid. If a dilute acid will effect the purpose, it should in general be used in preference to concentrated acid because there is less tendency for silica to separate prematurely and so protect the remaining powder from attack, and for chlorides ($BaCl_2$, $PbCl_2$) to precipitate that are insoluble in the strong acid.

Neither can a definite temperature be prescribed. Some silicates dissolve without warming; others require heat, frequently for a long time. A few silicates contain carbon dioxide, in which case the vessel should be kept covered as long as gas is given off. A cover should also be used if the acid has to be boiled, particularly if it is strong hydrochloric acid.

The end of decomposition, if not patent to the eye, can generally be recognized by the disappearance of all grit as revealed by gentle pressure with a glass rod.

For the rapid determination of silica in siliceous materials, such as cements, which can be decomposed by hydrochloric acid, E. E. Maczkowske[84] recommends that the sample be mixed with ammonium chloride, treated with hydrochloric acid, digested on the steam bath for 30 minutes, filtered, and the siliceous residue washed with hot water.

Here a warning is in order against what might at first thought seem to be an acceptable procedure for a pure homogeneous mineral that is attackable only with difficulty under atmospheric pressure by an acid such as hydrochloric or sulfuric. The procedure is to subject a weighed portion of the mineral to a prolonged attack by the acid, to filter, and to analyze the filtrate, taking into account any silica that may have been set free in the insoluble state by the action of the acid. The insoluble matter separated from this freed silica is weighed in order to get the weight of the dissolved matter. The assumption here made is that the percentage relations of the constituents of the decomposed part of the mineral are the

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[84] *J. Research NBS,* **16,** 549 (1936).

same as those of the part that was not attacked. That the assumption is unwarranted has been amply shown.[85]

For the opening up of refractory minerals that require long treatment, platinum or porcelain vessels should be used instead of glass because silica and other constituents are sure to be dissolved from glass and even from porcelain. Platinum, however, should not be used for substances that yield chlorine with the acid nor for ferric minerals that have to be heated with hydrochloric acid for a long time. Neither should a stirring rod, especially one of platinum, be allowed to scrape the sides or bottom of a platinum dish, because the dish suffers and a measurable amount of metallic platinum may become detached and be reported later as a part of something else.

Having decomposed the mineral, evaporate the solution to dryness, and treat the residue according to b (p. 860).

2. *When silicon is not to be determined.* Before the J. Lawrence Smith procedure for decomposing silicates preliminary to determining alkalies came into general use, it was customary to break up a rock, or a mineral that was resistant to hydrochloric, nitric, or sulfuric acid, by the use of hydrofluoric acid to which sulfuric acid was added so as to obtain the bases as sulfates.[86] This procedure enabled the analyst to determine other bases as well as the alkalies in the same portion of sample, but of course precluded determining silicon in it. The method, sometimes with the substitution of perchloric for sulfuric acid, still finds occasional use but is subject to the drawback that, unless the last trace of fluorine is expelled, it is impossible to precipitate aluminum completely by ammonium hydroxide.[87] According to E. Selch,[88] complete expulsion of fluorine can be effected by bringing the residue of salts, left after a first evaporation, into clear solution with dilute sulfuric acid and then evaporating a second time till fumes escape copiously. With perchloric acid the evaporation had better be carried to dryness.

β. By fluxes. No silicate rocks yield wholly to hydrochloric acid; hence for them and practically all the insoluble silicates, fusion methods are employed, a statement that holds of necessity also for soluble silicates that carry fluorine insofar as concerns the silicon determination itself. The

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[85] Consult in particular L. Duparc, *Bull. soc. franç. minéral.*, 42, 138 (1919). An observation of interest made by Duparc is that, with silicates which are for the most part quickly decomposable by acids, it happens frequently that a small residue is left which is very resistant to the acid attack. The bearing of this is obvious.

[86] Cold treatment with hydrofluoric acid overnight before evaporation with the acid favors completeness of decomposition.

[87] Consult also F. P. Veitch, *J. Am. Chem. Soc.*, 22, 246 (1900); F. W. Hinrichsen, *Ber.*, 40, 1407 (1907), and *Z. anorg. Chem.*, 58, 83 (1908); H. Cavaignac, *Compt. rend.*, 158, 948 (1914). See also p. 738.

[88] *Z. anal. Chem.*, 54, 395 (1915).

flux almost universally used is dry normal sodium carbonate, though various other reagents have been recommended and to some extent used, such as lead and boric oxides, lead carbonate, borax, and boric oxide. Consult the section on Decomposition by the use of Fluxes (p. 836).

1. *Fusion with sodium carbonate.* Although strict accuracy requires that all fluoriferous silicates should be treated according to *b*, below, it is not necessary to resort to that tedious procedure when the fluorine content is very small, as it is in practically all silicate rocks. The reason is that the fluorine could not cause a loss of much more than three fourths of its own weight of silica if it were all to volatilize as silicon tetrafluoride when the sodium carbonate fusion is evaporated with hydrochloric acid. The loss is, however, less, as silicon fluoride is unstable in presence of moisture. Some of the fluorine escapes perhaps as hydrofluoric acid, and more is fixed in fluosilicates. These last, if eventually ignited with the silica, would undergo at least partial decomposition, and, on treatment of the ignited silica with hydrofluoric and sulfuric acids, their metal (presumably sodium) would be weighed eventually as sulfate if not volatilized by the heat of ignition. In any event the error is of comparatively slight importance, for it attaches always to the constituent that is present in greatest amount.

a. Procedure in absence of appreciable fluorine. See Fluxes (p. 844).

b. Procedure in presence of appreciable fluorine. With a rock or mineral containing sufficient fluorine to determine, or to cause appreciable loss of silica by the procedure just given, or incomplete precipitation of aluminum, proceed as directed under Fluorine (p. 943).

According to Travers,[89] silicon can be satisfactorily determined in silicate rocks containing fluorine by fusing with potassium hydroxide, extracting with water, precipitating with potassium fluoride and an excess of potassium chloride in the acidified extract, and titrating the precipitated potassium fluosilicate with a standard solution of potassium hydroxide. The method fails in the presence of titanium and zirconium and requires modification when applied to silicates containing aluminum.

2. *Fusion with boric oxide.*[90] See Fluxes (p. 840), and (p. 848).

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[89] *Compt. rend.*, 173, 714 (1921).

[90] Silica that separates in the presence of boric acid always contains boron, and high results, through volatilization as BF_3, ensue if the boron is not removed. The interference can be avoided by treating the melt with methyl alcohol and hydrochloric acid as described on page 849, or, less satisfactorily, by digesting the moist contaminated silica with the same mixture. The extent of the error caused by the presence of boron is indicated by the following results obtained by M. O. Lamar, chief chemist, Norton Company (private communication): Samples of the Bureau of Standards glass indicated 74.63 and 74.52 per cent as against the true content of 74.1 per cent of silica when 0.5-g samples were fused with 3 g of sodium carbonate and 1 g of boric oxide and the silica then determined by solution of the melt in hydrochloric acid and the usual double evaporation with intervening filtration. Similarly, two analyses of the Bureau's standard

b. *Separation and Determination of Silica.* α. *Dehydration.* The following procedures are adapted for silicate minerals free from fluorine and for rocks carrying no more than 0.3 per cent of fluorine.

1. *By hydrochloric acid.* Place the contents of the crucible in a rather tall beaker with some water. A green color imparted to the water indicates manganese, a yellow one chromium. Cover the beaker, and add gradually under the lid in some excess dilute hydrochloric acid (1 + 1). If an evanescent pink color appears, manganese is present, and its depth indicates roughly whether much or very little. Place the beaker on the steam bath, and assist disintegration of the cake by gentle pressure with a blunted glass rod. When all has dissolved except perhaps some flocculent silica, transfer the contents of the vessel to a large dish, and evaporate on the bath. It is permissible to dispense with the beaker and to perform the whole operation of solution in the dish. Ordinarily this should be of platinum, but one of porcelain is required if the mineral held manganese, chromium, or vanadium in amount greater than is usually found in rocks, because they are oxidized to manganate, chromate, and vanadate, respectively, by the fusion, and these compounds yield chlorine with hydrochloric acid. Porcelain is also indicated for highly ferruginous substances because ferric chloride in contact with platinum is slowly reduced with corresponding solution of platinum as chloride.

From this point the general treatment will be the same whether the silicate was opened up by fusion with sodium carbonate, by solution in hydrochloric acid, or by fusion with boric oxide followed by expulsion of the boron. If by either of the second or third of these, the separation of the silica should be more perfect than by the first because of the absence of a mass of sodium chloride.

The dish containing the dissolved carbonate melt or mineral should be capacious enough to permit considerable surface distribution of the residue that will be left after evaporation. A dish of one-liter capacity is ample when fusions have been made and a smaller one in other cases. Steam bath temperature suffices—is indeed demanded—for the evaporation to approximate dryness. If the analysis is begun in the morning, the first filtration can be made in the afternoon. Nothing is gained by continuing the evaporation beyond apparent dryness this first time, for a slight reduction in the soluble silica gained by so doing is offset by a large loss of time; nor is there much advantage in crushing to powder the residue obtained from fusions, whereby moreover the dish is easily scratched. The amount of silica passing into the filtrate will generally vary from 1 to 3 per cent of the amount present and is little less after 20 hours' drying than after one tenth of that time.

Cover the dish, add cautiously to the dry and cool mass 10 ml of hydrochloric acid, and then, after 1 or 2 minutes, 100 ml of hot water. With residues from solutions of melts it is well to have the dish covered, for sudden addition of acid is apt to cause expulsion of dustlike particles. Allow to stand on the bath for 5 to 10 minutes, and stir the solution occasionally. Filter, first by decantation, leaving nearly all the silica at the bottom of the dish. If the silica is in a coarse condition, crush it finer with a pestle. If much iron is present, it may be advisable at this stage to add hydrochloric acid of half strength and heat. Then bring the silica upon the filter. Should a film of it remain adhering to the dish beyond the power of a stiff feather to dislodge, this need not be removed, for in the subsequent evaporation it will disappear. If only a single evaporation is contemplated, warm the film with ammonium hydroxide, evaporate this, then evaporate with a little hydrochloric, and so recover the silica. Wash the main lot of silica with hot dilute hydrochloric acid (5 + 95) until the color of the paper of the filter indicates removal of most of the iron. Hot water may be used with advantage for the last washings and the filter should be sucked dry at the pump. Reserve the paper and residue.

Evaporate the filtrate and washings to dryness in the same dish. Usually this state will be reached by the following morning if the bath is allowed to run overnight. When dry, place the dish in an air bath, and heat for 1 hour at 110° C. It is probable that a higher temperature would have no bad effect in most cases except to increase the amount of insoluble matter other than silica, especially with highly titaniferous and ferruginous materials. Cover, take up the residue with 5 ml of hydrochloric acid, add 50 ml of hot water, and heat on the bath for 5 to 10 minutes. Filter immediately on a new and smaller paper, and wash with cool dilute hydrochloric acid (1 + 99) and finally with hot water. Reserve the paper and residue and also the filtrate and washings. The silica in the second filtrate should not amount to much more than 2 or 3 mg in the usual case. A third evaporation is usually a waste of time if the preceding evaporations have been properly carried out, for equilibrium has been reached. The silica still in solution can be recovered later if an ammonia precipitation is made and a fair-sized precipitate is obtained. The second filtration with its attendant operations consumes less time than the first. The second silica is, especially with rocks, more colored than the first, and, if the mineral or rock is even moderately titaniferous, is by no means pure.

With minerals like zeolites, or artificial products like Portland cements, which are directly soluble in hydrochloric acid, the first dehydration may be much hastened by placing the covered dish, after approximately drying

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sample of bauxite, which contains 6.30 per cent of silica, gave 6.49 and 6.44 per cent when the sample was fused with carbonate and boric oxide, dissolved in sulfuric acid and then evaporated twice to fumes of the acid, with intervening filtration.

on the bath, on a sand bath or on a triangle which itself rests on a hot plate. The temperature may rise in the dish to 200°; in fact, according to Blount, it should not be lower. After an hour's exposure to this temperature, less silica (in the absence of magnesium) will perhaps pass into the filtrate than after prolonged drying at steam-bath temperature, but this is usually at the expense of greater contamination of the filtered silica. As this contamination is very large (p. 865) with highly titaniferous and ferruginous rocks and minerals, the operator should use discretion in his choice of a high drying temperature.

As already intimated, the silica obtained does not represent quite all that the mineral or rock held, nor is it ever perfectly pure. A further small but appreciable portion is to be found and determined in the precipitate produced by ammonium hydroxide as in 7, B (p. 874), if one is so obtained. If there are no metals precipitable by ammonium hydroxide, the recovery of the remainder of the silica is best accomplished by adding 0.1 g of iron or aluminum as chloride, precipitating with ammonium hydroxide, and recovering the silicon in the precipitate as described in 7, B (p. 874).

2. *By perchloric acid.* H. H. Willard and W. E. Cake[91] recommended perchloric acid as a dehydrating agent for silica on the ground that the silica obtained is purer than when hydrochloric acid is used, the time required is much less, and the salts formed are all wholly and quickly soluble. The acid—60 to 70 per cent as sold—can be used directly if the material contains no organic matter and is soluble in it, or added after its solution in another acid, or after opening up by an alkali-carbonate fusion. The test results upon silicates, cements, irons, steels, and other metals compare most favorably with those obtained by the usual method.[92] No statement appears concerning the effect upon the subsequent course of analysis (Section 7, p. 867), which as herein set forth assumes dehydration of the silica by hydrochloric acid. The procedure for mineral analysis is as follows for 1 g of substance:

Dissolve soluble minerals in a mixture of 10 ml of perchloric acid and twice as much water, or use a hydrochloric or nitric acid solution, and add the requisite amount of perchloric acid. If the silica content is very high, use more perchloric acid. Fuse refractory minerals with sodium

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[91] *J. Am. Chem. Soc.*, 42, 2208 (1920).

[92] In the analysis of 0.5-g portions of a lead-barium glass containing 17.5 per cent PbO and 1.41 per cent BaO, H. B. Knowles obtained 65.38, 65.38, and 65.36 per cent SiO_2 by the perchloric acid method, as against 65.35, 65.35, and 65.36 per cent by the hydrochloric acid method. In both methods, double dehydrations were made, and silica was recovered in the ammonia precipitate. The silica obtained in the second dehydration ran from 3 to 6 mg in the hydrochloric and 0.6 to 0.9 mg in the perchloric acid method, whereas that obtained from the ammonia precipitate ran from 0.3 to 0.6 mg in the former and 0.4 to 1.1 mg in the latter.

carbonate, treat the melt with water until disintegrated, and dissolve it in sufficient perchloric acid. Evaporate till copious fumes of perchloric acid come off, and then boil gently for 10 to 15 minutes. Use a beaker or deep dish to avoid undue loss of the acid. Do not allow the contents of the vessel to become solid, or the separation of the silica will be incomplete. If there is a tendency for much insoluble perchlorate to separate, either the heating was not properly regulated or insufficient acid is present. However, if much aluminum is present, some insoluble perchlorate always separates in the hot solution. As the solution cools, it usually becomes solid. Dilute with 4 to 5 times its volume of water, heat to boiling, filter, and wash the silica with dilute hydrochloric acid (1 + 99) and finally with water. Ignite and weigh as in the succeeding section. The correction for impurity is usually very small. If potassium carbonate was used in the fusion mixture or if potassium salts were introduced during the course of analysis, there may be some separation of potassium perchlorate; perchlorates must be completely washed out of silica and filter before ignition.

β. *Ignition of silica.* Place the combined papers containing the silica in a platinum crucible, moisten with a few drops of dilute sulfuric acid (1 + 4), and carefully heat so that the silica is slowly dried and the paper charred without inflaming. Partly cover the crucible, slowly increase the heat until the carbon has been burned, then cover the crucible, and heat at approximately 1200° C for 10 to 30 minutes.[93] Cool over a good desiccant, weigh while still covered, and repeat the ignition until constant weight is obtained. Tightly fitting crucible lids must be used to avoid loss of silica by drafts; if a blast lamp is used, the crucible should be sunk two thirds of its depth in a hole in an asbestos shield.

γ. *Correction for impurities in the silica.* The weight of the crude silica should always be corrected for impurities, which in rock analysis certainly are never absent, by evaporating with hydrofluoric and sulfuric acids (both free from nonvolatile impurities), heating for a minute or two, and again weighing. Blast flame ignition is here hardly ever called for because of the small masses involved. It is a mistake to neglect another weighing at this point, even if the residue appears to be insignificant. In rock analysis it is never unweighable, and furthermore the error due to loss in weight of the crucible itself during the heating of the silica is eliminated if the weighing is made. Before adding the hydrofluoric acid, moisten the silica in the crucible with water, though with strongly ignited silica the action

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[93] The duty of every analyst to test the efficiency of his burner or muffle cannot be emphasized too strongly. The discordance of many statements and results on a variety of subjects is to be attributed to a difference in the ignition temperature employed by different writers. A really good blast will readily melt a few centigrams of orthoclase powder in the bottom of a small platinum crucible, showing a temperature of about 1200° C.

of the acid is not so violent as with that which has not been heated over the blast flame. One treatment with a few milliliters of hydrofluoric acid is sufficient to remove all the silica. With quartz the case would be different, for it is attacked much less readily than precipitated silica. With rocks containing 60 to 80 per cent of silica, one or two drops of dilute sulfuric acid (1 + 1) suffice, but, with less siliceous rocks, the amount ought to be increased, not only in order surely to afford enough acid for the conversion of all the contaminating bases to sulfates but also to prevent loss of titanium (if present) by volatilization as fluoride.[94] With rocks the percentage of this element in the residue is likely to be larger, the more basic their character.

In routine analyses, the subsequent precipitate of alumina, etc., is usually ignited in the crucible containing the residue from the silica. In accurate analyses, the residue must be fused with a pinch of sodium carbonate, dissolved, and added to the filtrate from the silica. For silicotitanate minerals, a different procedure is probably to be preferred, because of the large amount of titanium that would be rendered insoluble along with the silica. In such cases it might be better to rinse the several portions of impure silica as far as possible from the filters into a dish, to ignite the papers and burn them at as low a temperature as possible, to add the joint residue to the contents of the dish, to evaporate the water, to add strong sulfuric acid and fume this in order to bring the titanium into solution, to dilute with water somewhat, digest on the bath for a short time, filter, wash with water acidified with sulfuric acid, and then ignite and weigh the silica. It is possible that the silica treated in this way would still not be entirely free from titanium, but the amount would be so small as to cause no trouble when the usual test with hydrofluoric and sulfuric acids is made. The filtrate would

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[94] Hydrofluoric acid alone suffices when iron or aluminum oxides are involved. With zirconia or titania, sulfuric acid had better also be used, although volatilization losses in well-covered crucibles are not so great as are commonly believed. This is shown by the following data obtained by J. I. Hoffman:

	Weight after Igniting, Treating with HF–H_2SO_4, and Reigniting	Weight after Treating with HF Alone and Reigniting	Weight after Treating with HF–HNO_3 and Reigniting
1	0.0159 g TiO_2	0.0155 *	....
2	0.0158 g TiO_2	....	0.0155 *
3	0.0591 g ZrO_2	0.0591 †	....
4	0.0591 g ZrO_2	....	0.0591 †
5	0.1176 g Fe_2O_3	0.1176 ‡	
6	0.1177 g Fe_2O_3	0.1179 ‡	
7	0.1056 g Al_2O_3	0.1056 ‡	

* White film on inside of crucible and cover and a little on outside.
† Very faint coating on crucible cover.
‡ No sign of volatilization.

then be treated substantially like the main one, but separately from it although the corresponding precipitates would be united and treated as one.

δ. *Accuracy of the silica determination.* By observing the foregoing rules—use of platinum, repeated evaporations and filtrations, proper ignitions, and correction for foreign matter—the determination of silica, from being one subject to grave error, has become one of high accuracy, provided care is also taken to recover as hereinafter described (7, B, p. 874) the small portion that has passed inevitably into the filtrates. With careful work, variations of 0.1 per cent are the exception in duplicate rock analyses.[95]

ε. *Composition of the residue obtained from the silica.* 1. *From rocks.* The qualitative composition of the residue obtained from the silica varies with different rocks less than the quantity. The residue will contain alumina and ferric, titanic, and phosphoric oxides invariably if the rock contains them. If it is low in the last three, particularly the last two, the residue should be slight, occasionally less than 1 mg. Usually it is much greater, and it may amount to 2 or even 3 per cent with basic rocks rich in titanium and phosphorus. It may contain as much as one third of the total amount of the titanium. Conceivably it may contain also zirconium or thorium when these are present, especially if there is much phosphorus, and it would also carry columbium and tantalum.

It might be supposed that the residue would contain most of the barium of those rocks which carry that element together with sulfides or sulfates, but this is not so because barium sulfate is appreciably soluble in hot hydrochloric acid, and the metal is a very minor constituent of most rocks. Should some of it be present in the residue, its removal and estimation at this stage are not necessary as it can be recovered more conveniently later, together with the silica accompanying the precipitate of alumina, etc. (7, B, p. 874). Quite as rarely is calcium a component of the residue if the decomposition of the rock powder was complete at the outset. When the analysis has been properly done, the residue, after resolution, is quantitatively precipitable by ammonium hydroxide in presence of an ammonium salt. This fact and special tests made by one of us (W. F. H.) controvert certain statements that the residue is likely to contain calcium, magnesium, and alkalies. Occasionally magnesium was found but not in excess of 0.3 mg MgO. A statement that sodium chloride is one cause of persistent small losses of weight when the silica is ignited is opposed to our observations and to those of Lenher and Truog.[96] The contrary experience of Bloor[97] and of Aurousseau[98] is perhaps to be attributed to incomplete decomposition of the rock by the alkali carbonate fusion.

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[95] See footnote 92, p. 862, and Table 27, p. 804.
[96] *J. Am. Chem. Soc.*, 38, 1050 (1916).
[97] *Ibid.*, 29, 1063 (1907).
[98] *J. Wash. Acad. Sci.*, 13, 330 (1923).

2. *From minerals.* Nothing so definite can be said as to the contaminants of the silica that is obtained in analyzing silicate minerals as distinct from silicate rocks. They will of course vary with the composition of the mineral and be sometimes small or even absent; at other times large, especially with minerals containing titanium, zirconium, tin, tungsten, antimony, columbium, or tantalum. With the latter, special procedures for separating silicon before its final determination are to be preferred, as for example by dehydrating with sulfuric acid when antimony is present.

7. Analysis after Separation of Silica

Section 6 deals with the determination of all but a small residuum of the silicon in silicates, with special reference to rocks. This section continues the analysis, but for the most part more in outline. Much of this is not restricted to silicates but finds equal application to many other minerals if interfering elements are absent. It is, however, written as a sequel to Section 6, with special reference to rocks, because their analysis constitutes a large part of the work of many mineral analysts.

After silica has been separated as completely as possible, the analyst is confronted with the question as to whether treatment with hydrogen sulfide is necessary or desirable. In rock analysis, the treatment is usually unnecessary and a waste of time, for the only member of the hydrogen sulfide group that is likely to be present in determinable amount in a 1-g sample is the platinum derived from the crucibles and dishes, and this causes no difficulties if it is left in solution. In the analysis of minerals or material of unknown composition, the treatment should not be omitted, for it is simple, and may lead to the separation and detection of elements that should not be missed and that would cause errors if left in solution.

Before proceeding with the analysis after the separation of silica, or the precipitation of the hydrogen sulfide group if this was deemed desirable, the next concern is to make sure that all of the iron is in the trivalent state. Bivalent iron is to be expected if hydrogen sulfide was used, and may be present in small amount if evaporations for silica were made with hydrochloric acid in platinum dishes. The oxidation of the iron can be done by treating with bromine in excess and boiling until the excess is expelled, or by boiling with nitric acid, after prior expulsion of hydrogen sulfide if this was used.

The analysis can now follow any one of several courses, depending on the end in view. In the usual case, iron, aluminum, and the like are precipitated by carefully neutralizing with ammonium hydroxide. There is little danger of coprecipitation of manganese if the *p*H value is kept under 7 and the solution is filtered quickly after the neutralization. The necessity

of employing the basic acetate method whenever appreciable amounts of manganese are present is not so great now as when less attention was paid to the proper conditions for precipitating with ammonium hydroxide, or from homogeneous solutions (p. 497). In the older methods, the separation of manganese was far from perfect, and the error was allowed to distribute itself among aluminum, calcium, and magnesium, when the total amount of manganese did not exceed a few tenths of 1 per cent. The errors caused by such a procedure are illustrated by the data given in footnote 117, page 879. With large amounts of manganese, the basic acetate method was usually recommended.

Either treatment leaves manganese in solution associated with elements such as nickel, zinc, calcium, and magnesium. In rock analysis, the next step therefore usually consists in separating the manganese, zinc and nickel by precipitating with ammonium sulfide, after which the calcium is thrown down as the oxalate and then the magnesium as the phosphate. In such procedures, strontium accompanies the calcium, and barium is found with magnesium.

For some purposes it is desirable to gather all of the manganese in the ammonia precipitate, and this is done by using bromine or persulfate in conjunction with the ammonium hydroxide. Such a course leaves elements such as nickel and zinc still to be separated if they were present in the original material.

The stumbling block to the use of a greater diversity of methods after the separation of silica and the hydrogen sulfide group is the incomplete separation of the silica at the start of the analysis. If the silica still left in solution can be ignored, a number of variations may be employed. For example, the hydrogen sulfide filtrate can be treated with tartaric acid and then made ammoniacal for the separation of iron, zinc, nickel, cobalt, and more or less of the manganese as the sulfides. The filtrate can then be acidified and treated with cupferron for the determination of columbium, tantalum, zirconium, titanium, and vanadium. If desired, one half of the oxidized filtrate from the silica or the hydrogen sulfide treatment can be precipitated with ammonium hydroxide as usual and the other half with cupferron. The first gives such oxides as Al_2O_3, P_2O_5, Fe_2O_3, TiO_2, ZrO_2, and V_2O_5, while the second gives the last four and leads to a more accurate determination of alumina by difference. Still another method that is useful in the absence of magnesium and nickel is the treatment of the oxidized filtrate from the silica or hydrogen sulfide precipitation with sodium hydroxide in slight excess, whereby iron, titanium, zirconium, and the like are separated from aluminum, vanadium, and phosphorus (see Precipitation by Sodium Hydroxide, p. 84).

A. METALS PRECIPITABLE BY HYDROGEN SULFIDE

Appreciable amounts of elements precipitable by hydrogen sulfide are of very infrequent occurrence in most rocks, and their removal is therefore seldom called for. It is of course different with many minerals, and in general the procedure to follow is that given under Precipitation with Hydrogen Sulfide (p. 60).

Little attention has been paid to the determination or even detection in rocks of minute amounts of the hydrogen sulfide elements. For some references see Minute Traces of Certain Constituents (p. 953).

The sample should never be passed through copper or brass sieves when copper or copper and zinc are to be determined.

The filtrate from the silica almost always contains notable amounts of platinum. This is derived in very small degree if at all from the action of the alkali carbonate on the crucible unless fusion was made in a muffle instead of over the flame (footnote 65, p. 845) or unless in special cases niter was used as an oxidant in too large amount;[99] to a larger degree indirectly from the action of the hydrochloric acid on the manganate, chromate, and vanadate of sodium formed during the fusion; and finally, if much iron is present, in no small degree from the reduction of ferric to ferrous chloride by the platinum of the evaporating dish. The second and third sources of contamination are eliminated by using a porcelain dish, and this should always be done if other elements of the hydrogen sulfide group are present and are to be determined in this portion of the sample. The presence of platinum alone causes no inconvenience, however, in rock analysis, as it can be removed easily at a later stage instead of by the action of hydrogen sulfide. In the descriptions that follow, it is assumed that platinum is absent, or, if present, does not need to be eliminated at this stage, or that, if other metals precipitable by hydrogen sulfide were present, they together with platinum have been removed.

It should be borne in mind that, if much titanium is present, a little of it may be thrown down with the sulfides.

B. JOINT PRECIPITATION OF ALUMINUM, IRON, TITANIUM, ZIRCONIUM, CHROMIUM, RARE EARTHS, PHOSPHORUS, AND VANADIUM WITH AND WITHOUT MANGANESE

The difficulties are considerable in the way of successfully producing and handling the sometimes very complex precipitate which is obtained in the next stage of the analysis of silicates. It should or may contain aluminum, iron, titanium, phosphorus, and the remainder of the silicon besides chromium, vanadium, zirconium, and rare earth metals, not to mention beryllium, gallium, and indium as possible components, though in rock analysis these last are seldom if ever reported. It is not necessary nor indeed is it readily possible to determine all of them in the one precipitate. For some at least, separate portions of sample have to be used, but their joint weight must be found.

If a precipitation by hydrogen sulfide was not necessary, treat the filtrate from the silica directly; otherwise boil out the hydrogen sulfide, reoxidize the iron by bromine water,[100] and boil out the excess of bromine. Then the procedure to follow depends on whether it is desired to precipitate the manganese or not to do so at this stage.

a. *Precipitation without Manganese.* α. *Precipitation by ammonium hydroxide.* Two precipitations by ammonium hydroxide at boiling heat usually suffice to separate ferric iron, aluminum,[101] titanium, phosphorus, vanadium, trivalent chromium, rare earth metals, zirconium (beryllium, gallium, and indium) if all should happen to be present, from manganese, nickel, the alkaline earth metals, and magnesium in the relative proportions in which these elements ordinarily occur in rocks, provided an ammonium salt—usually the chloride—is present in sufficient quantity. This last point is of special importance as regards magnesium, and failure to observe it is doubtless the reason why many old analyses show utterly improbable percentages of alumina, especially as analysts were formerly satisfied with a single precipitation. The necessary ammonium chloride is obtained better by the use of purified ammonia water and hydrochloric acid than by adding the solid salt, which may not be pure enough. The analyst should always satisfy himself as to the amounts of ammonium salt that are needed to hold in ammoniacal solution the maximum percentage of magnesium that the rock or mineral he is analyzing may contain. With an extremely high magnesium content, a third precipitation is generally requisite.

For the complete precipitation of aluminum and a sharp separation of manganese, an excess of ammonium hydroxide must be carefully avoided (see Aluminum, p. 501, and Precipitation by Ammonium Hydroxide, p. 77). Desirable conditions are as follows: To the solution containing at least 5 g of ammonium chloride per 200 ml of solution, or an equivalent amount of hydrochloric acid, and no oxidizing agent such as nitric acid that would destroy the indicator, add a few drops of methyl red, and heat just to boiling. Carefully add dilute ammonium hydroxide (1 + 1), drop by drop

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[99] Needless to say, if niter was used, the subsequent evaporation should be made in porcelain.

[100] If much iron is present and evaporations for silica have been made with hydrochloric acid in platinum, oxidation is desirable, even though hydrogen sulfide was not used, for some of the iron may have been reduced.

[101] It is well to bear in mind that, in the presence of fluorine, aluminum is precipitated very incompletely by ammonium hydroxide.

until the color of the solution changes to a distinct yellow. Boil the solution for 1 to 2 minutes, adding more ammonium hydroxide if the color of the solution changes to orange or red, and filter at once. For the complete precipitation of rare earth elements, see page 548. Wash the precipitate thoroughly with a hot 2 per cent solution of the ammonium chloride. Reserve the filtrate and washings. Dissolve the precipitate in warm dilute hydrochloric acid, wash with hot water, and reserve the paper. Reprecipitate the aluminum, filter, and wash as before. The final precipitation may be made with advantage in the presence of macerated filter paper (p. 98), and the precipitate should be well drained.

Combine the ammoniacal filtrates and washings for treatment as described on page 872, and ignite the precipitate as described in d.

β. *Precipitation by the basic acetate method.* In the presence of moderate amounts of manganese, nickel, and iron, the ammonia method of precipitation as just specified is preferable by far to the basic acetate method (Precipitation by Regulation of the Hydrogen Ion Concentration, p. 75) once greatly in vogue. Nevertheless the latter method gives good service in the presence of much iron together with zinc or cobalt, or in the presence of large amounts of manganese or nickel, especially for the first precipitation. The chief objection to the method, aside from its poor serviceability for precipitating aluminum unmixed with much iron, was that the last traces of manganese were often incapable of removal even by more than one repetition of the process. The precipitate produced in the basic acetate method contains essentially the same elements as when ammonium hydroxide is used. Perhaps the most marked difference is that some of the rare earth metals are not precipitated in the basic acetate process. If then later, on rendering the combined filtrate ammoniacal, an unexpectedly large precipitate appears, this should be carefully examined as to its nature. In an analysis of piedmontite from Maryland, over 2 units per cent of rare earths, including cerium and others not identified, were quantitatively separated from iron, aluminum, etc. On the other hand, Pope [102] said that quinquevalent vanadium is completely precipitated, which is a very desirable effect.

After making the precipitation, dissolve the precipitate in hydrochloric acid, and reprecipitate by ammonium hydroxide as in α. Treat the filtrates separately as described on page 872.

b. *Precipitation Together with Manganese.* α. *By ammonium hydroxide and ammonium persulfate.* Precipitation by ammonium hydroxide and ammonium persulfate has for its object the coprecipitation of manganese with a view to simplifying subsequent operations. It is, however, defective in case the rock carries appreciable amounts of barium or strontium by reason

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[102] *Trans. AIME,* 29, 372 (1899).

of the certain partial precipitation of some of one or both as sulfates. Calcium can be held completely in the filtrates by two precipitations in any case.[103] If strontium is not present in sufficient amount to be retained by the precipitate, there is no vital objection to the method on this score, for barium can be recovered as described on page 876.

The applicability of the method as above limited being assured, it may be carried out as follows:

PROCEDURE. To the filtrate from the silica, held in a platinum dish, add enough hydrochloric acid to prevent precipitation of magnesium when made ammoniacal (p. 869), then methyl red indicator, and finally ammonium hydroxide until the indicator turns yellow. Add about 1 g of ammonium persulfate free from all interfering impurities,[104] and heat to boiling. When the liquid begins to boil, add dilute ammonium hydroxide carefully until in *slight* excess as shown by the odor, and continue boiling for several minutes.[105] Let the precipitate settle, filter quickly, wash three or four times with a 2 per cent solution of ammonium chloride, and suck the precipitate dry. Dissolve it in a small amount of hot hydrochloric acid containing a few drops of sulfur dioxide, add macerated filter paper, and reprecipitate, wash, and filter as before. Combine the filtrates for treatment as on page 873, and ignite the precipitate as described in d. Manganese is weighed as Mn_3O_4. Any chromium would be in the filtrate wholly oxidized by the persulfate, but it will be recovered with the precipitated traces of aluminum

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[103] A. W. Epperson, *Ind. Eng. Chem.,* 17, 744 (1925).

[104] The reagent as bought should always be tested for strength as well as for aluminum and other impurities (see Reagents, p. 37). Jannasch [*Prakt. Leitfaden Gewichtsanalyse* [2], 179 (1904)] purified it as follows: To a warm saturated solution (not over 95°) add ammonium hydroxide until its odor persists (more will have to be added at intervals, for the continual decomposition of persulfate sets free sulfuric acid). When the precipitate of alumina, etc., has settled, filter as rapidly as possible (through asbestos in a porcelain funnel, because the strong solution attacks both paper and glass markedly. When cooled to about 30°, pour the filtrate into twice its volume of alcohol, and cool it further by ice applied externally. After half an hour, filter, wash with alcohol and then with ether, and dry in the air. The alcohol must be removed thoroughly.

A commercial article purified thus was found to contain no interfering impurities though not free from alkali, and it held, moreover, much ammonium sulfate. Because of the decomposition and consequent loss that results when Jannasch's method of purification is employed, it is preferable to use a weighed amount of a reasonably pure reagent in the analysis and to correct for the impurities as shown in the blank determination.

It has not been determined if such a very dilute solution of the persulfate as would be handled in the analysis has any appreciable effect on glass, but apparently not, so far as our limited experience shows.

[105] There is need of adding more ammonium hydroxide because of the acid that is liberated when the persulfate decomposes. Methyl red cannot be used as indicator because it is too rapidly destroyed.

as detailed on page 873 and should be added to the main precipitate. It is not best to determine it colorimetrically in the filtrate.

β. *By ammonium hydroxide and ammonium sulfide.* Although the old method of precipitation by ammonium hydroxide and ammonium sulfide can be employed in special cases, it is not well adapted generally to silicate rocks and will not be discussed in this connection. It is often very useful with minerals, although the precipitation of aluminum is, as a rule, incomplete.

c. *Recovery of Unprecipitated Aluminum and Iron from the Filtrates.* α. *After an ammonium hydroxide precipitation.* Aluminum, iron, and the like will ordinarily be completely precipitated by ammonium hydroxide in the procedure described on page 869. In case of doubt, and especially if it is desired to destroy ammonium salts before the precipitation of manganese or calcium, transfer the combined ammoniacal filtrates to a beaker, acidify with hydrochloric acid, and evaporate to small volume. Cover the beaker, and heat with nitric acid as described under the Removal of Ammonium Salts (p. 133). When these are destroyed and evolution of gas has ceased, remove and wash the cover, dilute not more than necessary to hold salts in solution, and heat to boiling. Render faintly ammoniacal as described on page 869, boil for 2 minutes, and filter at once through a small paper if a precipitate appears. Wash with a hot 2 per cent solution of ammonium chloride, ignite, and add the weight of the residue to that of the main precipitate. Reserve the filtrate and washings for treatment according to C, b, or D.

β. *After a basic acetate precipitation.* Evaporate the first filtrate to or nearly to dryness. Take up the residue with only enough hot water to keep it in solution, and replace the dish on the bath for a short time. Collect the precipitate, which will generally be appreciably larger than any ever obtained in α, on a small filter and the filtrate in a flask of 150 to 200 ml capacity. While the acetic acid-acetate filtrate is being evaporated, evaporate the second or ammoniacal filtrate separately, and treat with ammonium hydroxide as described in α. This solution serves as first wash water for the other dish and for the precipitate on the filter. Finally rinse both dishes and the filter with 2 per cent ammonium chloride solution. The ammoniacal filtrate contains enough ammonium nitrate to prevent precipitation of magnesium in the first filtrate when the two come together.

If manganese peroxide has deposited on the surface of the dish, remove it by hydrochloric acid and a drop or two of sulfur dioxide, pass the hot mixture through the filter, and catch the filtrate in a small beaker. Reprecipitate then by ammonium hydroxide, and collect the precipitate again on the same filter, and the filtrate in the flask that contains the previous filtrate.

If much manganese is present, a second precipitation by ammonium hydroxide of the small precipitate may be required. In these cases, where the original amount of manganese is small, there is no difficulty in getting all of it into the filtrate. Treat the final precipitate and the filtrate or combined filtrates as in the foregoing section.

γ. *After precipitation by ammonium hydroxide and ammonium persulfate.* Acidify the combined filtrates, reduce chromates if present by the addition of a drop or two of hydrogen peroxide, and evaporate as in α to destroy ammonium salts. Dilute the solution to 100 ml, precipitate by ammonium hydroxide in *slight* excess, and place on the steam bath till the small precipitate has coagulated. Collect the precipitate on a 7-cm filter, and reserve the filtrate. Dissolve the precipitate in hydrochloric acid, reprecipitate in a small bulk of solution by ammonium hydroxide, and finally add it to the main portion obtained on page 870. Add the ammoniacal filtrate to that already reserved, and treat according to C, b or D.

d. *Ignition of the Joint Precipitate of Aluminum, Iron, etc.* Ignite the combined precipitates of aluminum, etc., obtained in a, b, or c, without preliminary drying in a platinum crucible weighed with a well-fitting cover. A precipitate formed in the presence of thoroughly macerated paper, as recommended by Dittrich, yields on ignition a powder, and the fine state of division makes reoxidation of any reduced iron easy, besides wonderfully shortening the time required for subsequent resolution.

O. Hackl[106] warned against using paper pulp with ferric or aluminum hydroxide for any but the last of two or more contemplated precipitations. M. F. Connor,[107] instead of using macerated paper, moistened the washed and dried precipitate, separated from the filter, with an alcoholic solution of ammonium nitrate, dried again, and ignited, the paper being ignited separately.

Alumina in the quantities usually found in rocks and in many minerals cannot be dehydrated completely by the full heat of the ordinary Bunsen burner (see Aluminum, p. 502). It must be heated with a blast flame (1200° C or its equivalent) until constant weight is obtained. If iron is present in large amount, this heating must be so conducted as to insure access of air to the crucible. The crucible and contents must be cooled over a good desiccant and weighed while covered with a well-fitting cover.

For ignitions of this kind, which involve very prolonged heating, an electric furnace is well adapted by reason of its nonreducing atmosphere, provided the temperature is not high enough (over 1200° C) to cause by temperature alone reduction of ferric to magnetic oxide of iron or, by contact

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[106] *Chem. Ztg.*, 43, 70 (1919). Consult also E. Wilke-Dörfurt and E. Locher, *Z. anal. Chem.*, 64, 436 (1924).

[107] *Congr. Geol. Intern. 12e Sess. Canada*, 885 (1913).

with the platinum formation of an iron alloy accompanied by liberation of oxygen (see Iron, p. 390).

The crucible itself may have changed in weight since the silica was ignited in it. Its correct weight is found after treatment of its contents as explained in the next section.

e. *Determination of Residual Silicon and Possibly Barium in the Joint Precipitate.* Because of the extreme difficulty of its determination in a mixture of the kind under consideration, it is customary to determine alumina by difference after deducting, from the precipitate produced by ammonium hydroxide, by sodium acetate, or by ammonium hydroxide and ammonium persulfate, the sum of all other oxides this precipitate may contain. Of these, only ferric oxide (representing the total iron of the rock or mineral), titanic oxide, and the small amount of residual silica that is not recovered by the procedure detailed in 6, B (p. 860), and in rare instances perhaps a little barium are determined in this portion. The oxides of phosphorus, vanadium, chromium, rare earth metals, zirconium, titanium if desired, and sometimes manganese are usually best determined in other portions of the sample, sometimes in larger portions than are usually treated for the major constituents. (Consult the chapters on the respective elements.) The same would hold for beryllium, uranium, gallium, and indium, should these happen to be present. Because of their rarity and the very small amounts in which they would probably occur, it is customary to disregard these last in rock analysis, although there is no doubt that they could be found in certain rocks, especially of the highly siliceous granitic type. This throws on the alumina all errors that are involved in the separate determination of the other components of the oxide mixture, but these errors may balance. In any event the probable error can hardly be as high as that involved in the direct determination of the alumina itself, considering the difficulty of effecting a satisfactory separation of it from the other components of the mixtures, an operation which would moreover extend immoderately the time required for each analysis.

Phosphorus cannot be determined in the ignited oxides after these have been fused with pyrosulfate (α below) for the reason that the treatment is likely to volatilize some of it.[108]

α. *Residual silicon.* The first step in the analysis of the joint precipitate is to obtain the ignited oxides in a suitable solution. Some early writers recommended dissolving the oxides in hydrochloric acid, but this is a most ineffective mode of attack. Perfect solution is effected in the manner detailed in the next paragraph.

Transfer the weighed precipitate as far as possible from the original crucible to another of 25 to 30 ml capacity if a smaller one was used for the ignition,[109] or if it is desired to ascertain the loss of weight of the crucible. Bring the small adhering residue into solution by fusion with a small amount of sodium or potassium pyrosulfate. This fusion takes but a few minutes and must not be continued beyond the time actually needed; otherwise it will be impossible, after cleaning and igniting, to get the correct weight the crucible possessed after the ignition of the alumina, etc.[110] Pour the hot liquid onto the main mass of the precipitate in the other crucible, add more pyrosulfate (up to 7 g in all),[111] and renew and continue the fusion with the crucible covered and at as low a temperature as will keep the contents molten until the whole has been dissolved. In the case of the potassium salt, this is always easily ascertained, even when the liquid is dark red and opaque, by removing the crucible from the flame to a good light and allowing the vessel to cool. At one point during the cooling, the liquid becomes transparent and so permits the bottom of the crucible to be seen. This is less true of the sodium salt.

When all is dissolved, pour the melted mass into a large *dry* platinum dish, remove with dilute sulfuric acid (1 + 9) what adheres to the two crucibles, and pour the solution and rinsings into the dish. Add enough of the dilute acid to bring the volume to 100 ml, and heat the dish until the solid is dissolved. Evaporate the solution as far as can be done on the steam bath, and then gradually higher until fumes come off copiously. During this heating, the mass is apt to darken from reduction and separation of platinum dissolved from the crucible. The acid must be used in

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[108] W. F. Hillebrand and G. E. F. Lundell, *J. Am. Chem. Soc.*, 42, 2607 (1920).

[109] This crucible may be of gold, as that metal is less attacked by the subsequent treatment than platinum. If gold is used, the remarks in the text concerning the recovery of dissolved platinum apply to the dissolved gold.

[110] Long blast or furnace ignition may have reduced the weight of the crucible by an appreciable amount; hence the need for getting its weight empty at this point.

[111] The total weight of pyrosulfate should be known approximately in order to correct later for the effect of the salt in the colorimetric determination of titanium (Titanium, p. 582), unless a precipitation with ammonium hydroxide is to be made in order to eliminate the alkalies and so obviate the precaution.

The recommendation of J. Lawrence Smith [*Am. J. Sci.*, 40, 248 (1865)] to use the sodium instead of the potassium salt is excellent. This salt acts more quickly and forms a more soluble double salt with aluminum, but has the slight disadvantage that the progress of decomposition of the ignited mass is not so readily followed because of the greater tendency of the sodium salt to crust over. Fused pyrosulfate dissolves platinum from the crucible. To avoid this Deussen [*Z. anorg. Chem.*, 44, 423 (1925)] fused the ignited oxides with about 1 g of acid potassium fluoride. The mass melts over a low flame and then solidifies. He evaporated its solution with sulfuric acid to expel most of the fluorine and determined iron by titration. The use of the fluoride is however incompatible with accurate work in silicate analysis because the silica in the ignited oxides cannot be determined. Moreover the oxides must be finely powdered, and consequently an aliquot part only can be taken for the fusion. The expulsion of the fluorine by sulfuric acid must be thorough if titanium is to be determined in the solution.

such quantity that, after cooling, the mass is pasty and not solid, for it then dissolves readily, on heating, in the water which is now to be added, the sodium salt dissolving much more readily than the potassium salt.

Place the dish on the bath and as soon as the silica can be seen in coagulated form at the bottom, collect it on a small filter, wash well with hot water, burn, and weigh in a platinum crucible. As it is seldom pure, correct it by a few drops of hydrofluoric and a single drop of sulfuric acid, evaporate, ignite, and reweigh the crucible. Bring the slight residue that may remain in the crucible into solution by pyrosulfate, and add it to the main portion, for the treatment of which see f after filtering from barium sulfate if any of this shows itself (see β below).

The amount of silica so recovered (see Table 20, under Silicon, p. 677) ranges usually between 0.5 to 5 mg after two filtrations of the main silica and is of course to be added to this. Only in this way is the full amount of silica in the ignited oxides to be recovered.[112] Formerly it was customary to regard that remaining undissolved when the pyrosulfate melt was taken up with water or dilute acid as the total amount present. It is however but a small part of what the alumina, etc., held, the greater part having formed alkali silicate during the fusion and remaining in solution afterward, unless set free and rendered insoluble by the treatment above given.

The silica thus recovered may not, however, represent quite all of that which originally escaped separation by evaporation with hydrochloric acid. A small part, depending on the amount that escaped separation by evaporation with hydrochloric acid and the size of the ammonia precipitate, sometimes escapes recovery altogether. The amount may be several milligrams if but a single separation of silica was made. It is therefore apparent why a thorough separation of silica at the start is so urgently called for.

In case the recovery of the residual silica is not required, the procedure of Trautmann [113] for removing it from alumina is serviceable, especially for small amounts of ignited oxides. He recommends the evaporation of hydrofluoric and sulfuric acids in the crucible containing the ignited alumina, after which the alumina is to be again ignited and weighed. In following this procedure it is wise not to hasten the expulsion of the sulfuric acid unduly for fear of incomplete conversion of the fluorides to sulfates and consequent loss by volatilization of the anhydrous fluoride. Selch [88] maintained that there is no danger of a sensible loss of aluminum by volatilization as fluoride when this procedure is followed, and this has been our experience.

β. *Barium.* Should by any chance the alumina precipitate have held barium sulfate, something that has not happened in our experience with rocks, unless ammonium persulfate was used as described on page 870, it

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[112] For proof see *J. Am. Chem. Soc.*, **24**, 368–70 (1902).

[113] *Z. angew. Chem.*, **26**, 702 (1913).

will be found as a contaminant of the silica recovered after the pyrosulfate fusion. If the weighed residue remaining after expulsion of this silica by hydrofluoric acid is dissolved by a little pyrosulfate and the cooled melt taken up with dilute sulfuric acid, any barium will be left in the form of sulfate. Now and then a few particles of metallic platinum may be observed with it. If so, a sufficiently satisfactory separation of the two can be effected by levigation.

f. *Determination of Iron in the Joint Precipitate.* α. *Volumetrically without regard to vanadium.* Treat the cooled filtrate obtained in e by method δ or ε under Iron (p. 393) if titanium is present, or by β if absent, then titrate the resulting ferrous iron with permanganate as described on page 395, and follow IV, A, under Titanium (p. 581), for a titanium content. Or, if titanium is absent or not to be determined in this solution, the iron can be titrated in the ferric state by a titanous salt (Iron, p. 398).

β. *Volumetrically having regard to vanadium.* The procedures that follow assume that vanadium is present only in very small amount, as in silicate rocks, clays, and siliceous limestones. In such cases the value found for total iron by permanganate titration will be in error whatever the reducing agent (see Iron, p. 390). In view of what has been said, it seems advisable when a little vanadium is present to use the method of reduction by sulfur dioxide (Iron, p. 393) even when titanium is absent. When the amount of vanadium is known, a correction can be applied on the assumption that all of it is collected in the precipitate now under consideration, a point that needs further investigation. Various writers have asserted its precipitability with aluminum and iron by ammonium hydroxide and by ammonium acetate, though Carnot [114] said that repeated precipitation by ammonium hydroxide, ammonium carbonate, or ammonium sulfydrate separates it from iron. Ridsdale [115] determined its precipitability with various metals and gave numerous figures which show an approximation to 90 per cent when thus thrown down under the conditions prevailing in analysis of iron slags, the remainder passing into the filtrates and appearing in small part with the calcium and to a greater extent with the magnesium. For all practical purposes it is probably safe to assume that the small amounts of vanadium met with in rocks are wholly in the alumina-iron oxide precipitate.

If the amount of vanadium is not known and great accuracy is necessary, caution requires the determination of the total iron to be made either in a separate portion after vanadium is removed or to precipitate in the sulfate solution (p. 876), by ammonium hydroxide the iron, aluminum, titanium, vanadium, etc., and then to separate the iron from the vanadium by igniting and fusing the oxides with sodium carbonate, extracting with water, filter-

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[114] *Compt. rend.*, **104**, 1803 (1887).

[115] *J. Soc. Chem. Ind.*, **7**, 73 (1868).

ing, bringing the insoluble residue into sulfuric acid solution, reducing, and titrating as in absence of vanadium. But, unless a certain precaution is here observed, an error greater than that which it is designed to avoid will be committed. Contrary to general belief, the aqueous extract from the sodium carbonate fusion carries a small but appreciable fraction of 1 per cent of iron. This iron is thrown out with the aluminum (and silica, if present) by the usual methods of neutralizing the alkaline solution, and can be brought to light when the precipitate thus formed is treated with a fixed caustic alkali or again fused with sodium carbonate and the melt leached with water, when it remains wholly or in part undissolved. Hence it is necessary to collect this iron and add it to the main portion before titrating.

The differential method of Edgar[116] for determining iron and vanadium in the presence of each other is not well suited to rocks because of the very small amounts of vanadium held by them.

γ. *Gravimetrically after separating as sulfide.* In view of the errors involved in the titrimetric determination of the iron, it is desirable in accurate analyses to determine it gravimetrically by precipitating with ammonium hydroxide after first precipitating it as the sulfide from a solution containing ammonium tartrate (Precipitation by Ammonium Sulfide, p. 65), the function of which is to hold in solution most of the other elements.

δ. ***True value for ferric oxide in a rock or mineral.*** In order to ascertain the percentage of ferric oxide in a rock or mineral containing also ferrous oxide, it is customary to deduct from the total iron oxide the ferric equivalent of the ferrous oxide separately determined. If the content of ferric oxide were as surely determinable as that of the ferrous oxide, the latter could be found by deducting the ascertained ferric oxide from the total oxide and calculating the remainder to ferrous oxide. Assuming precise work, the result in either case is satisfactory if interfering elements are absent. This is, however, often not quite the case, particularly with rocks and clays. In rocks, small amounts of sulfides are common—almost always pyrite. The oxide content that is found by difference will then be in error unless the proper amount of pyritic iron calculated as ferric oxide is known and deducted from the total oxide. It is possible to determine this amount from the sulfur content if this is wholly pyritic, a fact that can usually be ascertained with considerable certainty. If, however, the sulfide is soluble in sulfuric or hydrofluoric acid, the hydrogen sulfide liberated in dissolving the sample for the ferrous or ferric oxide determination will probably reduce a little ferric salt and so increase the ferrous and decrease the ferric oxide. This effect is indeterminable. Finally the small amounts of vanadium present in most rocks and clays are disturbing. Hence it is evident that the final result which passes for ferric oxide may be only an approximation.

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[116] *Am. J. Sci.*, 26, 9 (1908).

g. *Determination of other constituents in the joint precipitate.* It is unnecessary to consider here the procedure that can be used to determine the other possible components of the joint precipitate, of which a list is given on page 868. Suffice it to refer to the chapters on the different elements and to the chapter on Separations in the Ammonia Precipitate (p. 86).

C. MANGANESE, NICKEL, COBALT, COPPER, AND ZINC

a. *Difficulties in the Way of a Correct Gravimetric Determination of Manganese.* The gravimetric determination of manganese in small amounts seems to be more of a stumbling block to the average chemist than that of almost any other of the frequently occurring elements met with in mineral analysis. This is due almost always to incomplete prior separation of elements which later suffer coprecipitation with the manganese. The error is therefore generally a plus one, and often amounts to many times the weight of the manganese actually present. The importance of thorough separation of the constituents treated of in the foregoing pages is therefore manifest, particularly since, to the inexperienced analyst, very small amounts of manganese precipitated in the form of a higher hydroxide may easily mask a good deal of alumina or other colorless precipitates.[117]

If the directions already given have been carefully followed, however, there will be little chance of error due to foreign contamination, by either alumina or magnesia, a sufficiency of ammonium salts being a guaranty against the latter. Consideration must be given, however, to the rather remote possibility of the presence of rare earths which were not thrown out by the basic acetate precipitation (see p. 870), for they will appear at this stage.

b. *Precipitation of the Group and Separation of Its Constituents.* α. *The ammonium-sulfide method.* 1. *Its advantages and disadvantages.* The usual methods of separation of manganese from the alkaline earths and magnesia by bromine or ammonium sulfide are imperfect, in part because of incompleteness and in part because of coprecipitation of small amounts of these metals. The former error, though absolutely slight, is probably of more consequence in rock analysis than the latter. In completeness of precipitation, bromine offers no advantage over ammonium sulfide, and the latter has the advantage that, by a single operation, nickel, cobalt, copper, and

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[117] It was for these reasons that Washington deemed it better for the novice in rock analysis to make no attempt to determine the manganese, but to allow the error from this neglect to distribute itself over the alumina, lime, and magnesia. The relative order of this distribution was determined by George Steiger in the Survey laboratory while analyzing a series of carbonate rocks, some of them highly siliceous. The results are

zinc, if present, are likewise separated from the earth metals and alkalies. There need be no fear of overlooking nickel or copper, for, under the conditions of the precipitation they are not retained in solution. It is for this reason chiefly that the ammonium-sulfide method is to be preferred. Most of the small amount of manganese that escapes precipitation is weighed later with the magnesium as pyrophosphate and can be corrected for readily by the colorimetric method described on page 641.

The precipitation of manganese in alkaline solution by hydrogen peroxide, as proposed by P. Jannasch and E. v. Cloedt,[118] a method that appeared to

instructive. Double precipitations were the rule, and iron and aluminum were thrown out by ammonia in slight excess, according to the procedure then followed.

If the addition of ammonium hydroxide is stopped when the *p*H value reaches 7, and the solution is filtered after 1 to 3 minutes, very little if any manganese is found in the ammonia precipitate.

Tests Showing Distribution of Manganese in Gravimetric Separations

No.	Partial Composition of Rock			MnO by Colorimetry			
	Al_2O_3, Fe_2O_3	CaO	MgO	Total	With		
					Al_2O_3, Fe_2O_3 (by difference)	CaO	$Mg_2P_2O_7$
957	2.03	10.60	6.30	0.193	0.085	0.011	0.097
973	9.35	11.84	2.81	0.311	0.036	0.023	0.252
974	4.80	50.51	1.04	0.700	0.301	0.087	0.312
975	12.71	11.98	4.30	0.442	0.088	0.016	0.338
1126	0.58	30.54	20.41	0.281	0.030	0.030	0.221
1128	0.98	29.69	19.07	0.245	0.019	0.055	0.171
1130	3.49	3.99	0.92	0.016	0.016	None	None
1131	1.00	28.04	19.11	0.574	0.032	0.101	0.441

Steiger's practice followed to a degree that of Washington, assuming a method of precipitating aluminum, etc., that does not also precipitate manganese. The procedure is to determine total manganese by colorimetry in a separate portion of the sample and to correct the magnesium pyrophosphate for its manganese content by another colorimetric determination. This correction is the more permissible because, as the table above shows, the major part of the manganese remains in solution until precipitated as phosphate with the magnesium, and the error thus thrown upon the alumina and lime is slight. Indication of contamination of ignited calcium oxalate by even very little manganese is revealed usually by a brownish discoloration, sometimes by the green color of calcium manganate.

[118] *Z. anorg. Chem.*, **10**, 405 (1895).

be simple and accurate, besides affording a separation from zinc, was shown by C. Friedheim and E. Brühl[119] to be valueless.

2. *Precipitation by ammonium sulfide and separation of manganese and zinc from nickel, cobalt, and copper.* Two or three milliliters of ammonia are added to the flask containing manganese, the earth metals, etc. (p. 872), and hydrogen sulfide gas is introduced to saturation, whereby manganese, nickel, cobalt, copper, zinc, and a small part of the platinum from the dish are precipitated. A second like amount of ammonia is now added. The flask, filled to the neck and corked, is set aside for at least 12 hours, and preferably 24, or even longer. The precipitate, collected and washed on a small filter with water containing ammonium chloride and sulfide, is extracted by hydrogen sulfide water acidified with one-fifth its volume of hydrochloric acid (sp. gr. 1.11), manganese and zinc, if present, going into solution.

(For treatment of the ammonium sulfide filtrate see D, p. 883.)

β. *Manganese and zinc.* The hydrochloric acid filtrate is evaporated to dryness, ammonium salts are destroyed by evaporation with a few drops of sodium carbonate solution, hydrochloric acid and a drop of sulfurous acid are added to decompose excess of carbonate and to dissolve precipitated manganese, and the latter is precipitated at boiling heat by sodium carbonate after evaporation of the hydrochloric acid. If zinc is present, it can be separated from the manganese after weighing. For the small quantities of managnese usually found the sodium carbonate method of precipitation is to be preferred to that by bromine or sodium phosphate, as equally accurate and a time saver. For the amounts of manganese found in rocks, the error caused by retention of alkali is negligible.

The manganese is weighed as Mn_3O_4 and calculated to MnO, or, if present in some quantity, it may preferably be weighed as the sulfate,[120] or, finally, it may be determined colorimetrically with much greater certainty, as in C, below, when the amount is within the usual limits for rocks. In the last case, in the absence of zinc, the hydrochloric acid solution of the sulfide may be used for the colorimetric test, after the hydrochloric acid is first evaporated off with nitric or sulfuric acid.

γ. *Nickel, cobalt, and copper.* The paper containing nickel, cobalt, and copper is incinerated in porcelain, and the ash is dissolved in a few drops of aqua regia, and the solution evaporated with hydrochloric acid; the copper and platinum are thrown out warm by hydrogen sulfide, and, in the filtrate made ammoniacal nickel and cobalt are thrown down by hydrogen sulfide. This liquid is then rendered faintly acid by acetic acid and allowed to stand. The sulfide precipitate, after filtering, is burned and

[119] *Z. anal. Chem.*, 38, 681 (1899).

[120] J. Volhard, *Ann. Chem.*, **198**, 329 (1879); F. A. Gooch and Martha Austin, *Am. J. Sci.*, [4] **5**, 209 (1898); *Z. anorg. Chem.*, **17**, 264 (1898).

weighed as oxide—its weight being always very small, hardly ever over 0.3 or 0.4 mg—which is then tested for cobalt in the borax bead. The color of the last drop or two of the hydrochloric acid solution, after the aqua regia is decomposed, is a good indication of the presence or absence of nickel and cobalt. It is always well at this point to separate by ammonia any traces of iron that may be present, and then to acidify and treat with hydrogen sulfide as above.[121]

It is somewhat unsafe to consider traces of copper found at this stage to belong to the rock if the evaporations have been conducted, as is usually the case, on a copper water or steam bath, or if water has been used which has been boiled in a copper kettle, even if the kettle is tinned inside. Therefore, and because of its contamination by a little platinum, it is better to determine copper in a separate portion if its presence is indicated with certainty (see p. 868). This warning is particularly to be heeded if copper or brass sieves were used in preparing the sample.

c. *Colorimetric Determination of Manganese.* As has been shown above (p. 879), the gravimetric determination of manganese is subject to grave error, even when great care is used. This is due to a variety of reasons, such as incompleteness of separation from aluminum and iron, incomplete precipitation by ammonium sulfide, and contamination by other bodies. Because of the small amounts in question, these errors may be relatively enormous, and they cannot be depended on to balance each other. Therefore, it would be an advance if the total manganese could be determined in a separate portion of the sample, and in the main portion only that part which is weighed with the magnesium pyrophosphate, and this only as a correction to the magnesia. This course is readily feasible with carbonate rocks, which can usually be brought into a fit state in a few minutes without a fusion or the separation of silica. With silicate rocks, more labor is involved, but the determination itself is very accurately performed by colorimetry, as in the case of carbonates.

The preliminary treatment consists in decomposing a gram or half a gram of the rock powder in a small platinum dish or capacious crucible (placed in the radiator shown in Fig. 5, p. 24), with hydrofluoric and sulfuric acids till all is disintegrated. The hydrofluoric acid is then to be driven off by repeated evaporations with small portions of sulfuric acid, after which either sulfuric or nitric acid free from chlorine is added, together with water, and as much of the residue is brought into solution as possible. What remains insoluble is usually barium and calcium sulfates. This is filtered off on a small filter, the filtrate is caught in a small beaker or flask, and the manganese determined as under Manganese (p. 451).

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[121] Consult O. Hackl, *Chem. Ztg.*, **46**, 385 (1922), regarding the determination of small amounts of nickel and cobalt in rocks.

D. CALCIUM, STRONTIUM (BARIUM)

Sections I, III, and IV under The Alkaline Earths (p. 611) should be read carefully before the next steps are undertaken.

The platinum derived from the dish during the silica evaporation is now wholly in the filtrate from the manganese sulfide obtained in C (p. 880), except for the small portion that may have been precipitated with the manganese. Its special separation is unnecessary, nor is removal of ammonium chloride usually demanded, for, as a rule, there is no undue amount present, particularly if the first precipitation of iron and aluminum was effected by the basic acetate method. Therefore, without destroying the ammonium sulfide, the calcium and strontium can be thrown out by ammonium oxalate, the solution filtered, and the precipitate washed with a 0.1 per cent solution of ammonium oxalate in accordance with the directions given under The Alkaline Earths (p. 622). The filtrate is reserved and combined with that obtained after reprecipitation. There is needed here only the additional observation that the precipitate is often dark from deposited platinum sulfide. The platinum so held can be removed by filtration after solution of the oxalate or after ignition of it and resolution of the oxide in water and hydrochloric acid. In any case, the calcium must be reprecipitated as the oxalate, washed, ignited, and weighed as directed under The Alkaline Earths (p. 624), while the filtrate is combined with that already reserved for the determination of magnesium as in E.

Transfer the final weighed precipitate to a small flask of 20-ml capacity, slake carefully, dissolve in dilute nitric acid, and evaporate the solution to dryness. Heat at 130 to 160° C and separate strontium from calcium by extraction of the latter with ether-alcohol as described under The Alkaline Earths (p. 615).

Although the foregoing procedure for the precipitation of calcium is applicable to almost all silicate rocks, when an extremely accurate determination of very little calcium in the presence of much magnesium is desired, recourse must be had to successive precipitation of the calcium, first as sulfate, then as oxalate (Alkaline Earths, p. 615).

E. MAGNESIUM

Sections III and IV under Magnesium (p. 632) should be carefully read before the determination of magnesium is attempted.

The preliminary precipitation of magnesium can be done directly in the combined filtrates from the calcium determination if the solution does not contain excessive amounts of ammonium salts, particularly ammonium oxalate, and the volume does not exceed 600 ml. If, by chance, the volume is greater than this, the solution should be acidified and its volume reduced by boiling. If excessive amounts of ammonium salts are present, particularly when the amount of magnesium is small, acidify the solution, evaporate, and destroy the ammonium salts by careful ignition or by treatment with nitric acid as described under the Removal of Ammonium Salts (p. 133).

An excess of approximately 2 g of diammonium phosphate, $(NH_4)_2HPO_4$, should be added per 100 ml of solution which should finally contain approximately 10 per cent by volume of ammonium hydroxide and be allowed to stand 12 hours before filtering. In this filtration the solution should be decanted through a rapid filter, the precipitate and beaker washed three or four times with small portions of dilute ammonium hydroxide (5 + 95), and the filtrate and washings stirred and set aside to determine whether any further precipitation takes place. In analyses in which a platinum dish has been used in separating silica, and ammonium sulfide for separating manganese, the first magnesium ammonium phosphate precipitate may be contaminated by platinum sulfide, but this matters not, as it remains on the filter when the phosphate is dissolved in hydrochloric acid prefatory to the second precipitation. In this operation the precipitate clinging to the walls and bottom of the beaker should be dissolved in hot dilute hydrochloric acid (1 + 9), the solution poured through the paper, and the filtrate caught in a 200-ml beaker. Complete solution of all of the precipitate must be assured; the beaker, paper, and funnel thoroughly rinsed with water; and the second precipitation and final ignition of the phosphate carried out as described under Magnesium (p. 639), not omitting the addition of a small amount of the precipitant and the corrections there cited.

8. TITANIUM

A. GENERAL CONSIDERATIONS

In recent years the analytical study of titanium has received great attention, not so much from rock analysts as from industrial chemists, with respect to both the ores and the metals and alloys derived from them. The same is true to a degree of zirconium. As zirconium is a very common though minor constituent of rocks and in many of its chemical characteristics patterns after titanium, no presentation of methods of precipitation and separation of the latter can be made without frequent reference to the former, particularly when gravimetric methods are considered.

When titanium and zirconium are unaccompanied by other elements that would be precipitated, it is best to throw them out by ammonium hydroxide. Otherwise, under favorable conditions the colorimetric method for titanium (p. 581) gives results that are probably fully equal to those attainable by the best gravimetric method and in much less time, for such percentages as are found in rocks, clays, and soils (usually under 1 per cent, but occasionally rising to 2 or even 3 per cent or more). Normally the error should not exceed 2 per cent over a wide range of concentrations.[122]

The favorable conditions referred to are absence of large amounts of iron and phosphorus, alkali salts, vanadium, and even traces of fluorine. The use of the colorimetric method when one or more of these are present in disturbing amount introduces so many complications that it is advisable to employ this method, whenever possible, only after the titanium has been separated from all interfering elements by one or another of the procedures given in the references listed under 7, g (p. 879). Under certain conditions, as in the absence of zirconium, it may suffice to weigh the titanium, so separated, but generally the determination by color or by titration will be necessary. Which course to pursue the analyst will soon learn to decide when he has familiarized himself with the limitations and advantages of all the methods.

Of gravimetric methods, the cupferron method, being much simpler than that of Gooch, has superseded it to a large extent. The interference of zirconium, if present in more than traces, also limits the usefulness of the Gooch method. The older method of precipitation by long boiling of a nearly neutral sulfuric acid solution need not be considered.

The volumetric methods have the great advantage of being applicable in the presence of aluminum and zirconium and therefore find most extended use in assaying ores and technical products.

In general it will be advisable to employ either the colorimetric (p. 581) or a volumetric method (p. 584) as the final test after separating interfering elements. The choice of a procedure will also be influenced by the purpose in view. If only the percentage of titanium is sought, a method may be acceptable that could not be introduced in a scheme for complete analysis.

The above remarks are predicated upon the assumption that it is titanium without regard to its state of oxidation that is to be determined. In almost all titaniferous minerals the element is beyond doubt in the quadrivalent state, corresponding to the oxide TiO_2. There is some reason to believe, however, that it may here and there be in the trivalent state, corresponding to the oxide Ti_2O_3. The proof is fraught with almost unsurmountable difficulty at present, mainly because of the general occurrence of iron. J. Jakob (*Chemische Analyse der Gesteine und Silikatische Mineralien*, 1952 ed., p. 73, Verlag Birkhauser A. C. Basel) gives analyses of two phlogopites and one biotite showing that in these particular minerals the titanium is almost equally distributed between the tri- and quadrivalent states.

B. COLORIMETRIC DETERMINATION WITH HYDROGEN PEROXIDE

For detailed directions, see under Titanium (p. 581).

If the colorimetric method is to be followed, a rough estimate of the amount of titanium can be had by treating the sulfuric acid solution of the

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[122] R. C. Wells, *J. Am. Chem. Soc.*, 33, 501 (1911); *Z. anorg. Chem.*, 70, 399 (1911).

pyrosulfate melt of the ammonia precipitate with hydrogen peroxide before evaporating for its silica content (p. 875). It can be determined conveniently as a rule, in the solution that has served for the titration of total iron (p. 877). The direct use of this solution involves, however, for accurate work, provision for its iron and alkali sulfate contents, and sometimes for vanadium. Interference by iron can be avoided by adding a solution of ferric sulfate to the solution of the standard until the colors match before peroxide is added. The effect of the alkali salt can be overcome by a prior precipitation with ammonium hydroxide, moderate washing of the precipitate, and solution of the precipitate in 5 per cent sulfuric acid. The interference of vanadium can be avoided by precipitating with sodium hydroxide instead of ammonium hydroxide (p. 581), or by fusing the ignited ammonia precipitate with sodium carbonate, extracting the vanadium with water, and bringing the residue into sulfuric acid solution.

The error arising from the use of alkali sulfates can also be avoided by making the determination on some other portion of the rock powder than that indicated in the foregoing paragraph. It can be combined with the determination of barium, by decomposing the powder by sulfuric and hydrofluoric acids,[123] expelling the latter by repeated evaporations with sulfuric acid, taking up with dilute sulfuric acid,[124] filtering from barium sulfate, etc., and estimating the titanium colorimetrically in the filtrate. The expulsion of fluorine must be thorough, or else the titanium result will be low, as already stated (p. 581), and it is not always easy to effect this complete removal, though the time required to do so seems to be in no slight degree dependent on the nature of the fluorides to be decomposed. Long after every trace of fluorine seems to be gone, the formation of a crust on the evaporating solution sometimes allows an accumulation of enough hydrofluoric acid gas to become plainly manifest to the smell when the crust is broken.[125]

Both the iron and alkali effects are excluded if the determination is made on the precipitate of TiO_2 and ZrO_2 obtained by one of the methods given in the references listed under 7, B (p. 879).

[123] It is to be borne in mind that evaporation, followed by ignition with hydrofluoric acid alone, results in loss of titanium by volatilization, but that there is no loss if excess of sulfuric acid is also present.

[124] With acid rocks, solution is very complete, and it can be made nearly so with the most basic by transference to a small beaker and gentle boiling. The residue thus obtained may contain, besides barium sulfate, a little calcium sulfate, zircon, andalusite, topaz, and possibly a trace of titanium in some form. It is therefore to be fused thoroughly with sodium carbonate, leached with water, fused with potassium pyrosulfate, dissolved in dilute sulfuric acid, and filtered, and the filtrate added to the main one. The insoluble matter will now be chiefly barium sulfate, for the further treatment of which see 9, A (p. 889).

[125] See p. 741 for a procedure to facilitate the removal of fluorine.

The residue from an alkali-carbonate fusion of rock powder, which has been obtained as in 9, A (p. 889), can be used conveniently, either before or after separation of zirconium (10, A, p. 891).

The conditions are such as to involve in the titanium determination, a correction for the iron of the rock, whether zirconium is first removed or not. If it is removed first, a further correction may have to be made for the alkali sulfate that results from the addition of the sodium phosphate used to precipitate the zirconium and also, possibly, for the phosphoric acid in the rock and that added. However, in most cases the amounts of sodium phosphate needed for two precipitations of the zirconium should not produce a sensible error in the value found for the titanium. The precaution should never be omitted, when determining the titanium here, to combine the two filtrates from the zirconium phosphate in order to find all the titanium.

The needs of the case or the convenience or preference of the analyst after he has acquired experience will determine which of the courses to pursue in determining titanium by colorimetry. Naturally, a procedure is to be preferred that will obviate the need for corrections, but, in order to secure final conditions that satisfy this aim, it is folly to run the risk of incurring other errors of uncertain and varying magnitude when it is possible, though perhaps troublesome, to apply corrections.

Even if no corrections are applied in rock analysis, the error in the titanium value found is so small as to be of rather slight importance, especially if it is known to be always in one direction. Of course, any error incurred involves an equal and opposite one in the value found indirectly for alumina.

C. GRAVIMETRIC METHODS

When titanium is present in excess of 4 or 5 per cent, and whenever for any reason it is desired to employ a gravimetric method, either the cupferron (p. 116) or the Gooch (p. 586) method can be employed. In the former, fewer operations are required and zirconium is precipitated quantitatively with the titanium. In the latter, zirconium prevents complete precipitation of titanium, especially when but little of the latter is present.[126] Gooch's method is applicable to any solution of the rock that is free from silicon, iron, zirconium, and elements such as columbium and tantalum that are easily hydrolyzed. The cupferron method is applicable to any solution of the rock that is free from silicon, the hydrogen sulfide group, and appreciable amounts of phosphorus. It usually serves for the separation of tita-

[126] For example 0.2 per cent of ZrO_2 prevented precipitation of 0.3 per cent of TiO_2 in a certain series of rocks, and the titanium that came down in excess of this amount did not settle out in flocculent condition, as happens when zirconium is not present, and it was difficult to filter.

nium along with zirconium, iron, vanadium, etc. (p. 119), from aluminum, chromium, and also phosphorus, except when the latter is present in appreciable amount and accompanied by zirconium, thorium, or titanium. With phosphatic materials, the phosphorus is first leached out with water after a carbonate fusion, and the cupferron method then applied to a sulfuric acid solution of the insoluble residue, after fusion with pyrosulfate if need be. The water extraction also removes vanadium. Metals of the hydrogen sulfide group can be removed from the sulfuric acid solution by treating with hydrogen sulfide (p. 60), and then iron by adding tartaric acid and ammonium sulfide (p. 65). These treatments serve to remove all ordinary interfering elements save zirconium, which is usually weighed with titanium after precipitation by cupferron in the acidified filtrate from the iron. Titanium is then found by difference after fusion of the mixed oxides with pyrosulfate, solution of the melt in sulfuric acid, and the determination of zirconium as the pyrophosphate (p. 569).

D. VOLUMETRIC METHODS

Of the volumetric methods, that calling for reduction in a Jones reductor (p. 108), collection of the reduced solution under an excess of ferric sulfate, and final titration with permanganate (p. 584) is to be preferred for accurate work. This method is subject to interference by substances such as iron, vanadium, chromium, and nitric acid which are also reduced. It must therefore be applied after the separation of these substances from titanium if the result cannot be corrected for their effect.

9. Barium (Zirconium, Rare Earths, Total Sulfur, Chromium)

The five constituents barium, zirconium, rare earths, total sulfur, and chromium can be determined with great economy of time and labor in the same portion of rock powder, of which a 2-g portion should be used, though, if vanadium is to be looked for it will be best to determine it and chromium in a different portion (14, C, p. 902). It has been said (Alkaline Earths, p. 614) that only in very exceptional cases will barium be found with the calcium and strontium after two or possibly three precipitations of the latter as oxalate, since it passes into the filtrates with the magnesium, whence it may be obtained as sulfate after removal of ammonium salts. Addition of some alcohol insures also the simultaneous recovery of traces of strontium if the rocks are very rich in it; but it is unsafe to regard the amount of barium thus separated from the magnesium as representing the total amount in the rock. It will almost always be found lower than the truth, probably for the reason that there are opportunities during the analysis for slight losses.

A. THE GENERAL METHOD

Decomposition is effected by fusing the 2-g portion with sulfur-free sodium carbonate and an amount of niter insufficient to injure the crucible (0.5 to 1 g), first over the Bunsen flame, and then over the inclined blast, the crucible being fitted snugly into a hole in a disk of platinum foil or asbestos board (Fig. 6, p. 25) to prevent access of sulfur from the gas flame. If sulfur is not to be regarded, the niter and disk are omitted. After thorough disintegration of the melt in water, to which a drop or two of methyl or ethyl alcohol has been added for the purpose of reducing manganate, the solution is filtered and the residue washed with a very dilute solution of sodium carbonate free from bicarbonate. This is to prevent turbid washings. A yellow color in the filtrate indicates chromium.

After reduction of the manganate by alcohol, the filtrate contains silica, alumina, and all the other acid constituents except titanium, and also a very little iron, but the separation of these from the remaining constituents is not always quantitative, never so as to silica and alumina. The proportions of these two that go into the aqueous extract vary greatly, according to their relative proportions in the original material and the amounts and character of the bases other than alumina. For instance, with alkali feldspars, much of each dissolves, but, with pure kaolinite, very little of either. With most rocks, both filtrate and residue contain large amounts of both.

(For the further treatment of the filtrate see Sulfur, 20, B, p. 949, and Chromium, 13, B, p. 899.)

The residue is washed from the paper into a small beaker without the filter being removed from the funnel and is digested with little more than enough warm dilute sulfuric acid to effect solution of all soluble constituents (stronger acid may be used and in larger amount if barium only is sought). If zirconium is to be determined, the amount of acid used at this stage and later should be measured, so as to permit control of the concentration given under 10, A (p. 892). A few drops of sulfurous acid are added at the same time to effect solution of the brown hydroxide of manganese. There will remain undissolved more or less residue. Care must be taken not to digest so long with acid as to cause gelatinization of the dissolved silica. The liquid is passed through the original filter and collected in an Erlenmeyer flask of 100 to 150 ml capacity. The paper with its contents after washing is ignited, evaporated with hydrofluoric and sulfuric acids together, and the final residue taken up with a little hot dilute sulfuric acid. All the barium will remain undissolved, besides some of the strontium and perhaps a good deal of calcium. This is collected on a small filter and the filtrate added to the former one, which now contains all the zirconium and rare earths. (For its further treatment see 10, A, p. 891, and 11, A, p. 894.)

The residue last obtained is ignited and fused with sodium carbonate, and leached with water, and the residue dissolved off the filter by a few drops of hydrochloric acid, from which solution the barium is thrown out by sulfuric acid. A single solution of the ignited barium sulfate in concentrated sulfuric acid and reprecipitation by water suffice to remove traces of calcium which might contaminate it if the rock was one rich in calcium, and even strontium is seldom retained by it in quantity sufficient to give concern. Should this be the case, however, which will occur when the SrO and BaO are together in the rock in, roughly speaking, 0.2 and 0.4 per cent, respectively, the only satisfactory way is to convert the sulfates into chlorides and to apply to the mixture the ammonium-chromate method of separation (Alkaline Earths, p. 618).

Barium and strontium sulfates can be brought into a condition for testing spectroscopically by reducing for a very few moments the whole or part of the precipitate on a platinum wire in the luminous tip of a Bunsen burner, then moistening with hydrochloric acid, and testing in the usual manner. This test should not be omitted.

The procedure outlined in the foregoing paragraphs for the determination of barium in silicate rocks and its separation from calcium and strontium is the one that long experience has shown to be best adapted for securing the most satisfactory results with a minimum expenditure of time.[127] Even where no attempt is made to separate contaminating traces of strontium and barium from each other, the error is usually of no great consequence, for an absolute error of even 25 per cent in a substance constituting only 0.1 or 0.2 per cent of a rock is ordinarily of small moment compared with the ability to certify to its presence with approximate correctness.

With such small amounts of barium as are usually found in rocks, it is doubtful if Mar's method [128] for the separation of barium from calcium and magnesium by the solvent action of concentrated hydrochloric acid mixed with 10 per cent of ether on the chlorides could be conveniently applied here, although, for larger amounts, the method would seem to be accurate and easily executed. Moreover, it would probably not entirely remove contaminating strontium, and hence offers no advantage.

B. THE METHOD WITHOUT REGARD TO ZIRCONIUM AND SULFUR

If zirconium and sulfur are not to be looked for, the simplest procedure is to decompose the powder by sulfuric and hydrofluoric acids (see 8, B, p. 886 under Titanium) and to complete the purification of the barium sulfate thus obtained in the manner described in the fourth paragraph of A, above.

10. Zirconium

Zirconium is one of the most constant rock constituents, usually in the form of zircon, in which occurrence its amount can be approximately judged and a chemical test rendered almost unnecessary; but sometimes it occurs in other minerals, and is then unrecognizable under the microscope. In most exceptional cases, it may be present up to a few per cent of the rock, rarely reaches 0.2 per cent, and is usually much less than 0.1 per cent.

A. HILLEBRAND'S METHOD

a. *Preliminary Remarks.* For its detection and estimation in such cases, or whenever a search for it seems called for, the following procedure, resulting from an attempt to use a method of G. H. Bailey,[129] has been devised, which serves, when carried out with care, to detect with certainty the merest trace—0.02 per cent, for instance—in 1 g. The precipitant is a soluble orthophosphate.

The preliminary treatment of the rock powder has been fully given under Barium (9, A, p. 889), where the separation from barium has been described and also the concentration of the zirconia in a small amount of dilute sulfuric acid solution.

At first the statement was made that the precipitation should be made in a solution containing only a small amount of sulfuric acid, probably not more than 1 per cent. George Steiger [130] showed, however, that precipitation is complete in the presence of as much as 3 per cent of the acid, and more recently P. Nicolardot and A. Reglade [131] found that it is complete with even 20 per cent of acid (by weight). This higher acidity has the advantage of preventing contamination of the precipitate by titanium, iron, and chromium. According to Nicolardot and Reglade, separation from aluminum is complete with 10 per cent of acid.

At the National Bureau of Standards, it was found that the composition of the precipitate is affected by the amount of precipitant used and by the manner of washing. With not less than 10 times the theoretical amount of precipitant, the composition is uniformly such, after washing with ammonium nitrate solution, that on ignition it yields ZrP_2O_7, containing 46.5 per cent of ZrO_2. With less precipitant, the composition is variable, although precipitation is complete if twice the theoretical amount is used. It

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[127] For details, consult W. F. Hillebrand, *J. Am. Chem. Soc.*, 16, 83 (1894); *Chem. News*, 69, 147 (1894).

[128] *Am. J. Sci.*, 3d ser., 43, 521 (1892).

[129] *J. Chem. Soc.*, 49, 149, 481 (1886).

[130] *J. Wash. Acad. Sci.*, 8, 637 (1918).

[131] *Compt. rend.*, 168, 348 (1919).

was also found that washing with pure water extracts phosphorus. Nicolardot and Reglade used in their tests 1 g of ammonium phosphate, which they prefer to sodium phosphate, although the latter precipitates zirconium completely.

PROCEDURE. To the solution, which should be in a small flask or beaker and contain about 10 per cent by volume of sulfuric acid, is added hydrogen peroxide to oxidize the titanium and then at least ten times the theoretical amount of a soluble alkali orthophosphate in water solution. The ammonium salt is preferred. Ordinarily 1 g of the precipitant may be used. The solution is then kept at 40 to 50° C for 2 hours. If the solution bleaches after a time, more hydrogen peroxide should be added. Under these circumstances the zirconium is thrown out as phosphate and collects as a flocculent precipitate. If it can be assumed to be free from titanium and iron, the precipitate may be filtered, washed thoroughly with water containing ammonium nitrate (5 per cent), ignited, and weighed as ZrP_2O_7 (46.5 per cent ZrO_2). For the amounts of zirconium found in rocks, the phosphate may be ignited without special precautions, but, if the amount is large, such as is obtained with ores of zirconium, marked decrepitation occurs, which makes it necessary to ignite up to a certain point in a tightly covered crucible. Even then, slight loss may be suffered. (For the treatment of the filtrate see Rare Earth Metals, p. 894.)

If there is reason to think that the precipitate is not pure, it is collected on a filter, ignited, fused with sodium carbonate, and leached with water. The insoluble matter collected on a filter is washed, ignited, and fused with potassium or sodium pyrosulfate. The melt is dissolved in dilute sulfuric acid $(1 + 9)$, a little hydrogen peroxide is added, and the precipitation with alkali phosphate is repeated. Naturally the volume of the solution should be gaged by the amount of the zirconium. For most rocks it need not exceed 20 ml. Titanium is now almost never present, and the zirconium soon appears as a colorless flocculent precipitate in a fit condition to be collected and weighed as phosphate.

If there is doubt of the precipitate having the normal composition, especially if large, or if the qualitative identification of zirconium is desired, the following procedure is in order. Fuse with sodium carbonate, leach, ignite, fuse with pyrosulfate, reprecipitate by ammonia, and weigh as ZrO_2. Certainty as to its identity can be had by again bringing it into solution, precipitating by ammonia, dissolving in hydrochloric acid, evaporating to a drop or two, and testing with turmeric paper or by a microchemical reaction. With the very smallest amounts no color can be obtained by this turmeric-paper test, which, however, responds readily to as little as 1 mg of dioxide and with proper care for as small an amount as 0.3 mg (H. N. Stokes). No elements other than hafnium, thorium, columbium, or tantalum are ever likely to contaminate the zirconium thus precipitated.

The above-described method is applicable to the separation of zirconium, if present, in the mixture of it and titanium obtained by the cupferron method (8, C, p. 887).

In Bailey's experiments the precipitation was not made by addition of a phosphate but is said to be due solely to the hydrogen peroxide, the precipitate being a hydrated peroxide, Zr_2O_5 or ZrO_3.[132] Our efforts as well as those of others to secure a precipitate in acid solutions of zirconium sulfate by hydrogen peroxide alone have been unsuccessful, except in very concentrated solutions and with 30 per cent peroxide. The ability to obtain the zirconium free from phosphoric acid would certainly be a great improvement on the method described above.

B. OTHER METHODS

G. Streit and B. Franz[133] claimed to secure complete separation of titanium from iron and zirconium by boiling the neutralized solutions of the sulfates with a large excess (50 per cent) of acetic acid. The method has been recommended from time to time, but without any data showing its value. The single separation made by Streit and Franz was far from perfect.

I. T. Davis[134] separated zirconium sharply from aluminum, though not from iron, by precipitation as an oxyiodate in a boiling neutralized solution of chlorides, but the method has not been studied further.

C. Baskerville[135] proposed a method for the separation of zirconium from iron and aluminum similar to his method for the separation of titanium from those elements. It is based on the precipitability of zirconium by boiling the neutralized chloride solution for 2 minutes in presence of sulfurous acid and seems to be excellent. As titanium is always present and is quantitatively thrown down also, the two would have to be separated by hydrogen peroxide and a soluble phosphate. No tests on the availability of the method for separating the small amounts encountered in rock analysis have been made, but M. Dittrich and S. Freund used it successfully in slight modification for larger amounts and also devised a method for the direct separation of zirconium from titanium by precipitation with ammonium salicylate.[136]

The "cupferron" method as given under Titanium (p. 887) can be used also for the precipitation of zirconium alone or in company with titanium.

[132] *Chem. News,* 60, 6 (1889).

[133] *J. prakt. Chemie,* 108, 65 (1869).

[134] *Am. Chem. J.,* 11, 27 (1889).

[135] *J. Am. Chem. Soc.,* 16, 475 (1894); *Chem. News,* 70, 57 (1894).

[136] *Z. anorg. Chem.,* 56, 344 (1907).

11. Rare Earth Metals

If it is necessary to look for rare earths, the following procedures will prove satisfactory and not at all difficult.[137]

A. USUAL METHOD

The filtrate from the zirconium phosphate (10, A, p. 891) or, if zirconium is not to be determined, the earlier solution (9, A, p. 889) is treated with excess of potassium hydroxide to precipitate the rare earths and ferric and titanic oxides, while retaining the silica and alumina in solution. After settling, the liquid is decanted, and the precipitate is washed once or twice by decantation and slightly on the filter. The precipitate is washed from the paper into a small platinum dish and treated with hydrofluoric acid, and the liquid evaporated nearly to dryness. A little water with a few drops of hydrofluoric acid is added and the insoluble rare earth fluorides (crude) are collected on a small filter held by a perforated platinum or rubber cone and washed with water acidified with the same acid. The precipitate is washed into a small platinum dish and evaporated to dryness with sulfuric acid, the paper being burned and added before expulsion of the acid. The sulfates are dissolved in dilute hydrochloric acid, the rare earth hydroxides precipitated by ammonia added in moderate excess (see p. 548) and redissolved in hydrochloric acid, the solution evaporated to dryness, and the residue heated with a few drops of a solution of oxalic acid. Anything that may be present except the rare earths dissolves readily, these remaining as insoluble oxalates. If there is a doubt about the complete separation of the alkaline earths, the ignited oxalates may be dissolved in hydrochloric or nitric acid, precipitated by ammonia, and redissolved in whichever one of the acids may have been used, the solution evaporated to dryness, the oxalates reprecipitated and ignited, and the resulting oxides weighed.

In rocks, the amounts are too small to permit separation into further groups, but the presence of cerium can be readily shown if a strong yellow color develops when the ignited oxides are heated with strong sulfuric acid.

B. ALTERNATIVE METHOD

The rock powder is thoroughly decomposed by several partial evaporations with hydrofluoric acid, and the transparent precipitate of silicofluorides and of the fluorides of all earth metals except zirconium is collected on a platinum cone, washed with water acidulated by hydrofluoric acid, washed back into the dish or crucible, and evaporated with enough sulfuric acid to expel all fluorine. The filter is burned and the ash added. By careful heating, the excess of sulfuric acid is removed and the sulfates are taken up by dilute hydrochloric acid. The rare earths, with perhaps some alumina, are then precipitated by ammonia, washed, redissolved in hydrochloric acid, and evaporated to dryness, then taken up with water and a drop of hydrochloric acid, and only enough ammonium acetate to neutralize the latter added, followed by oxalic acid (not ammonium oxalate, which would fail to precipitate thorium). In this way as little as 0.03 per cent of rare earths has been found in working on not more than 2 g of material.

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[137] M. Dittrich [*Ber. deut. chem. Ges.*, **41**, 4373 (1908)] called attention to the fact that ferric, aluminum, and chromic, as well as uranic compounds prevent precipitation of cerium and presumably other rare earth metals as oxalate, unless a very large excess of the precipitant is used, but that, with such excess, precipitation is complete. Salts of these metals even dissolve cerium oxalate, but excess of oxalic acid or ammonium oxalate throws it out again. This behavior need hardly be considered in the procedures here given.

12. Phosphorus

A. PRELIMINARY REMARKS

It is sometimes possible to extract all phosphorus from a rock by simple digestion with nitric acid, but not always; hence the necessity for resorting to one of the longer methods of extraction detailed below. Whatever method is used great care is required in order to obtain accurate results.

Unless the utmost economy of material is called for, it is inadvisable to determine the phosphorus in the mixture of oxides obtained as described in Section 7, B (p. 868), but an independent portion of the rock sample should be used. Furthermore, phosphorus should never be determined in any solution that has been obtained from a fusion with alkali bisulfate or pyrosulfate, or after fuming with sulfuric acid, because these operations cause a loss of P_2O_5 (see 7, B, p. 874), either by volatilization (as metaphosphoric acid) or by reversion to metaphosphoric acid without volatilizing. In the latter event, the subsequent treatment of the solution may not effect its complete retransformation to the orthophosphate state, in which alone is the ordinary precipitation by magnesia mixture applicable.

B. PROCEDURE WHEN MATERIAL IS AMPLE

a. *Washington's Method of Preliminary Treatment.* Decompose about 1 g of rock powder in a platinum dish or capacious crucible with dilute nitric and hydrofluoric acids. When all gritty particles have disappeared, evaporate the solution to dryness, and re-evaporate with nitric acid two or three times to decompose fluorides and silicofluorides to a considerable extent.[138] Treat the residue on the bath with dilute nitric acid, and eventu-

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[138] The method as originally described in Washington's *Manual of the Chemical Analysis of Rocks* was modified by Washington and by one of us (W. F. H.) independently to the extent of doing away with the filtration of the precipitate of silicofluorides and fluorides before proceeding with the evaporation.

ally filter from any undissolved matter. This last should be for precaution's sake always ignited, fused with a little sodium carbonate, and extracted with water, and the extract acidified with nitric acid and added to the main solution. (For further treatment see c, below.)

b. *Alternative Method of Preliminary Treatment.* Fuse with sodium carbonate, separate silica by a single evaporation with nitric acid, treat the ignited silica with hydrofluoric and nitric acids, evaporate to expel hydrofluoric acid, repeat the evaporation with nitric acid alone two or three times, bring the small residue into solution by boiling with nitric acid, and add it to the main portion.

c. *Subsequent Treatment.* Add, to the solution obtained in a or b, 5 g of ammonium nitrate, 1 to 2 g of boric acid, and then molybdate solution as prescribed under Phosphorus (p. 699). Allow to stand at a temperature of not over 40° for 12 hours, or until it is certain that precipitation is complete.

Filter on paper, and wash the precipitate with water containing 5 per cent ammonium nitrate and 1 per cent nitric acid, after which transfer it by a jet of water to a small beaker, which is then placed under the funnel containing the filter paper. Wash the paper with dilute ammonia water and two or three times with pure water. If the ammonia is insufficient to dissolve the whole of the yellow precipitate in the beaker, add more, and, if a clear solution does not result, pass the liquid through the same filter in order to collect the insoluble matter.

The turbidity often observed on dissolving the precipitated and washed phosphomolybdate in ammonia is due to a compound of phosphorus. If the addition of a small fragment of a crystal of citric or tartaric acid fails to dissolve it, this should always be fused with sodium carbonate and extracted with water, and the filtrate otherwise treated as above, in order to obtain the phosphorus in it.

Treat the ammoniacal solution with magnesia mixture, and proceed to the final weighing of the phosphorus as $Mg_2P_2O_7$ as described under Phosphorus (p. 702). A second precipitation of magnesium phosphate is not required when the precipitate is very small, as is usually the case in rock analysis.

Vanadium, if present, is not only partially precipitated with phosphorus by the molybdate reagent, but it also retards and may even render the precipitation of the phosphorus incomplete. Further, the mixed precipitate is affected differently by wash solutions from the pure phosphomolybdate. An orange color of the phosphomolybdate betrays the presence of vanadium. However, in rocks the vanadium content is so low that ordinarily its effect may be disregarded. If the unexpected case should present itself, precipitation must be made in a cold, reduced solution as described under Phosphorus (p. 702).

C. PROCEDURE WHEN MATERIAL IS SCANTY

The following procedure admits of determining in the same portion not only phosphorus but also barium, iron, vanadium, chromium, and titanium, the last two either colorimetrically or gravimetrically, and is in part extracted from a paper by T. M. Chatard.[139]

Silica is removed by hydrofluoric and sulfuric acids, excess of fluorine expelled [140] (6, B, p. 858), the residue brought into solution as far as possible with dilute warm sulfuric acid (1 + 10) and filtered, the residue ignited, fused with sodium carbonate, dissolved in hydrochloric acid, and reduced if chromates are indicated, and the solution, after precipitation of barium, added to the main one, which is now precipitated by ammonium hydroxide to get rid of the magnesium salts usually present, and thus insure a cleaner subsequent fusion with sodium carbonate.

The precipitated Al_2O_3, P_2O_5, V_2O_5, Cr_2O_3, Fe_2O_3, ZrO_2, and TiO_2 are dissolved in hot hydrochloric acid and filtered into a large platinum crucible, the filter is burned and added, the solution evaporated to pastiness, a little water added to dissolve the salts, and dry sodium carbonate added in portions and stirred in thoroughly to prevent lumpiness in the fusion to follow, which is continued for half an hour. Addition of sodium nitrate is not necessary.

The fused mass is boiled out with water and filtered, and the insoluble matter is washed with a 1 per cent solution of sodium carbonate. In the residue, iron, titanium, and zirconium can be determined by the methods already described.[141] In the filtrate, chromium can be determined colorimetrically if present in sufficient amount to give a pronounced color (see 13, B, p. 899). Afterward, or immediately if the chromium is not to be thus estimated, enough ammonium nitrate is added to react with all the carbonate, and the solution is digested on the bath till most of the ammonium carbonate is gone. Nearly if not quite all alumina is thus thrown out, carrying with it the phosphorus and some of any vanadium present. The precipitate is washed with a dilute solution of ammonium nitrate till the yellow color of the chromate wholly disappears, after which it is dissolved in nitric acid and the phosphorus is thrown out by molybdate solution. The filtrate from the aluminum and phosphorus, containing chromium as the chromate and more or less of the vanadium, can be treated as detailed in the following sections.

[139] *Am. Chem. J.*, 13, 106 (1891); *U. S. Geol. Survey Bull.* 78, 87 (1891); *Chem. News*, 63, 267 (1891).

[140] The expulsion of fluorine should be made without excessive volatilization of sulfuric acid, so as to avoid loss of P_2O_5 (see p. 874).

[141] See 7, B, p. 877, concerning recovery of a small amount of iron that may have passed into the alkaline filtrate.

13. Chromium

If vanadium is absent, or nearly so, as it is likely to be in those highly magnesian rocks (peridotites) which usually carry a good deal of chromium, the following separation and gravimetric method for chromium gives good and concordant results, but in the presence of vanadium, and it is best generally to assume its presence, the colorimetric method should always be adopted.

A. GRAVIMETRIC METHODS

a. *Hillebrand's Method.* Having obtained chromium in solution as chromate and free from all else but a little alumina, as at the conclusion of the preceding section on phosphorus, proceed as follows:

Concentrate if necessary and add fresh ammonium sulfide, or introduce hydrogen sulfide. The chromium is reduced and appears as a precipitate of sesquioxide mixed with the rest of the alumina. This precipitate is now treated, according to H. Baubigny,[142] by dissolving in nitric acid, evaporating nearly to dryness, heating with strong nitric acid and potassium chlorate, and finally evaporating to dryness to get rid of the acid. Oxidation is complete and very speedy. On dilution with cold water, sodium bicarbonate is added in slight excess, and, after 2 or 3 hours, the precipitated alumina is filtered off. From the filtrate the chromium is then thrown out by fresh ammonium sulfide, redissolved, reprecipitated to free from alkali, and weighed. The results will be a trifle high because of partial oxidation of the oxide during ignition (p. 531), but this is of no moment with the small amounts of chromium in question.

b. *Jakob's Method.* W. Jakob[143] recommended the following method for the precipitation of aluminum (and evidently of ferric iron, titanium, zirconium, and manganese) and its separation from chromium. To the hydrochloric acid solution containing the equivalent of 0.1 to 0.2 g of Al_2O_3 and 20 to 100 ml in volume, in an Erlenmeyer flask of 100 to 300 ml capacity, is added, drop by drop, a freshly prepared solution of sodium hydroxide (about 5% strength) until the aluminum hydroxide formed redissolves. Avoid an excess. The solution is then boiled, and saturated bromine water is added, drop by drop at first in order not to lower the temperature of the solution too much and so produce a slimy precipitate. Toward the end, the bromine may be added faster until the solution remains red. The excess bromine is then boiled out, the liquid is filtered, and the precipitate is washed with hot water. Precipitate adhering to the glass is loosened by

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[142] *Bull. soc. chim.* [New Ser.], 42, 291 (1884); *Chem. News,* 50, 18 (1885).

[143] *Z. anal. Chem.,* 52, 651 (1913).

a little nitric acid and reprecipitated by ammonia. Some chromium is carried down with the aluminum but can be removed, after decanting, by boiling for a few minutes with water containing ammonium nitrate and ammonia. It is possible that a little aluminum may be redissolved by this treatment. The combined precipitates are ignited and weighed.

The chromium can be determined in the filtrate by applying the treatment given under a, above.

Magnesium and zinc, if present, are partly precipitated with the aluminum. Jakob maintained that small amounts of these can be removed by the treatment with ammonium nitrate and ammonia. In the presence of sulfates and borates, the method is unsatisfactory.

B. COLORIMETRIC METHOD

For the chromate colorimetric method, which is very accurate and by far the quickest method of determining chromium in rocks and ores[144] where the amount does not exceed a few per cent, there is needed the aqueous extract of a sodium carbonate fusion of the rock (as obtained, for instance, in the manner explained under Phosphorus, p. 897, or under A, above) in order to compare its color with that of a standard solution.

a. *Preparation and Strength of Standard Solution.* This standard solution is made by dissolving 0.1935 g or double that amount of pure potassium dichromate (for example, NBS standard sample no. 136) in 1 liter of water made alkaline by a little sodium carbonate. Each milliliter then corresponds to 0.1 or 0.2 mg of chromic oxide (Cr_2O_3), in which condition chromium is usually reported in rocks and ores. It is probably inadmissible to increase the strength of the standard much above the higher of the figures given.

b. *Preparation of the Test Solution.* Before filtering the aqueous extract of the sodium carbonate fusion, a few drops of alcohol (ethyl or methyl) are added to destroy the color of sodium manganate. If the yellow color of the filtrate is very faint, concentration by evaporation will strengthen it, and less than 2 mg of chromic oxide in 1 g of rock can then be determined exactly. For smaller amounts, it is best to employ 3 to 5 g of powder and then to concentrate the chromium by precipitation by mercurous nitrate, as detailed in the next section under Vanadium (p. 902); otherwise it may be difficult or impossible, because of the large amount of alkali carbonate

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[144] W. F. Hillebrand, *J. Am. Chem. Soc.,* 20, 454 (1898); *Chem. News,* 78, 227, 239 (1898); *U. S. Geol. Survey Bull.* 167, 37 (1900). First applied by L. de Koningh [*Nederland Tijdschr. Pharm. Chem. Tox.* (1889)] for the estimation of chromium in foodstuffs.

For the application of the diphenylcarbazide method to the determination of chromium in rocks, consult references cited in footnotes 13 and 14, p. 531.

present, to obtain a filtrate of sufficiently small bulk to show a decided color.

If niter has been used in the fusion and the crucible has been at all attacked by it, a yellow coloration of the filtrate may be due to dissolved platinum, but neither the proportion of niter nor the temperature of the blast should ever be high enough to permit the crucible to be attacked. A passing yellowish coloration of the filtrate, due to this or some other cause,[145] is not to be ascribed to chromium.

If it is desired to use the solution obtained as in either A, a or A, b above, there will be no need to add alcohol, for manganese is absent.

c. *Comparison of Colors.* The final solution is transferred to a graduated flask, which is then filled to the mark with water. The flask should be of such size that the color of the oxidized solution shall be weaker than that of the standard chromium solution. Definite amounts of the latter are then diluted with water from a burette until of the same strength as the test solution. For very minute amounts, it may be necessary to use Nessler tubes, as in ammonia estimations, instead of the glasses and apparatus there described and depicted.

As with colorimetric methods in general, better results are obtained with small than with large percentages of chromium; yet the method can be applied in the latter cases with satisfactory results by making a larger number of consecutive comparisons with the same solution.[146]

C. COMPARATIVE DATA

A few comparisons between colorimetric and gravimetric determinations of chromium made by one of us (W. F. H.) are given in Table 31 to show the order of agreement, the former having been made several months and even years after the latter.

TABLE 31

PERCENTAGE DETERMINATIONS OF CHROMIUM (Cr_2O_3)

Gravimetric	Colorimetric
Trace	0.018
0.05	0.051
0.14	0.12
0.08	0.083
Trace	0.013
None	0.0086
None	0.0067

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[145] Consult R. S. McBride and J. A. Scherrer, *J. Am. Chem. Soc.*, **39**, 928 (1917).

[146] D. W. Horn studied the "Variable sensitiveness in the colorimetry of chromium." See *Am. Chem. J.*, **35**, 253 (1906); **36**, 196 (1906).

The outcome was somewhat surprising, for it was hardly to be expected that the long and laborious quantitative separations should have resulted so well. It should be mentioned that, for the gravimetric tests, but 1 or 2 g at most were used, which accounts for the reported absence of chromium in two instances, this report being based on the lack of color in the aqueous extract of the alkali fusion after removal of manganese.

14. VANADIUM (CHROMIUM) AND MOLYBDENUM

A. DISTRIBUTION OF VANADIUM AND MOLYBDENUM

The wide distribution of vanadium throughout the earth's crust has been clearly established (see Vanadium, p. 452), not only in ores and in coals, but also in clays, limestones, sandstones, and igneous rocks.[147] It has been shown by one of us (W. F. H.) that vanadium occurs in appreciable amounts in the more basic igneous and metamorphic rocks up to 0.08 per cent or more of V_2O_3, but that it seems to be absent or nearly so from the highly siliceous rocks. Some of their ferric aluminous silicate constituents carry still higher percentages—up to 0.13 per cent V_2O_3 in a biotite separated from a pyroxenic gneiss. Molybdenum, on the other hand, appears to be confined in quantities susceptible of detection to the more siliceous rocks, and, except perhaps in rare instances, is not present in them in quantitatively determinable amount when operating on 5 g of material. Hence the quantitative search for vanadium will usually be limited to rocks with less than 60 per cent of silica. The search for it even then will perhaps not often warrant the necessary expenditure of time, but in this connection it is to be remembered that neglect to determine it introduces an error in the figures for both ferrous and ferric oxides, which in extreme cases may be of considerable moment (see 7, B, p. 877, and 15, A, p. 917).

B. CONDITION OF VANADIUM IN ROCKS

The connection below and elsewhere mentioned of vanadium with the ferric aluminous silicates of rocks, taken in connection with the existence of the mineral roscoelite, classed as a vanadium mica, indicates that the vanadium corresponds in condition to aluminum and ferric iron, and that it is to be regarded as replacing one or both of these elements. Hence it should be reported as V_2O_3 and not as V_2O_5.

What its condition may be in matter of secondary origin, like clays, limestones, sandstones, coals, and ores of iron, is yet open to discussion. It was the opinion of one of us (W. F. H.) at one time that it should be regarded as in the pentavalent state (V_2O_5), but work on certain remarkable vana-

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[147] W. F. Hillebrand, Distribution and Quantitative Occurrence of Vanadium and Molybdenum in Rocks of the United States, *Am. J. Sci.*, [4] **6**, 209 (1898); *Chem. News*, **78**, 216 (1898); *U. S. Geol. Survey Bull.* **167**, 49 (1900).

diferous sandstones[148] of western Colorado, in which it unquestionably occurs as trivalent vanadium (V_2O_3), has led to a decided unsettling of this view. It is proper to recall that C. Czudnowicz,[149] because of the extreme difficulty in completely extracting it from iron ores by an alkali carbonate fusion and because of the easy reducibility of vanadic acid by ferrous salts, under the conditions in which brown iron ores are supposed to form, considered the vanadium in such ores to be in a lower condition of oxidation (V_2O_3). O. Lindemann's contrary conclusion[150] about certain iron ores, because the vanadium was extracted as V_2O_5 by sodium carbonate fusion without niter, is not valid, since this would probably be the case even if it existed in the ore as V_2O_3.

C. HILLEBRAND'S METHOD

a. *Description of the Method.* In the following method, there is nothing absolutely novel except that chromium and vanadium, when together, need not be separated, but are determined, the former colorimetrically, as already described (13, B, p. 899), the latter volumetrically, in the same solution.[151]

Five grams weight of the rock is thoroughly fused over the blast with 20 of sodium carbonate and 3 of sodium nitrate. After extracting with water and reducing manganese with alcohol, it is probably quite unnecessary, if the fusion has been thorough, to remelt the residue as above, though, for some magnetites and other ores containing larger amounts of vanadium than the generality of rocks, this may be necessary, as Edo Claassen showed.[152] The aqueous extract is next nearly neutralized by nitric acid, the amount to be used having been ascertained conveniently by a blank test with exactly 20 g of sodium carbonate, etc., and the solution is evaporated to approximate dryness. Care should be taken to avoid overrunning neutrality, because of the reducing action of the nitrous acid set free from the nitrite produced during fusion. Chromium and occasionally vanadium will be retained by the precipitated silica and alumina. The use of ammonium nitrate, instead of nitric acid, for converting the sodium carbonate into nitrate does not seem to lessen the amount of chromium retained by the silica and alumina.

As a precautionary measure, therefore, and always when chromium is to be determined also, the silica and alumina precipitate should be evaporated with hydrofluoric and sulfuric acids, the residue fused with a little

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[148] W. F. Hillebrand and F. L. Ransome, *Am. J. Sci.*, [4] **10**, 120 (1900); *U. S. Geol. Survey Bull.* **262**, 9 (1905).

[149] *Pogg. Ann.*, **120**, 20 (1863).

[150] Dissertation, Jena (1878), through *Z. anal. Chem.*, **18**, 99 (1879).

[151] W. F. Hillebrand, *J. Am. Chem. Soc.*, **20**, 461 (1898); *Chem. News*, **78**, 295 (1898); *U. S. Geol. Survey Bull.* **167**, 44 (1900).

[152] *Am. Chem. J.*, **8**, 437 (1886).

sodium carbonate, and the aqueous extract again nearly neutralized with nitric acid and boiled for a few moments, the filtrate being added to the main one.

Mercurous nitrate is now added to the cold alkaline solution in some quantity, so as to obtain a precipitate of considerable bulk, containing, besides mercurous carbonate, chromium, vanadium, molybdenum, tungsten, phosphorus, and arsenic, should all happen to be in the rock. The mercurous carbonate serves to counteract any acidity resulting from the decomposition of the mercurous nitrate. Precipitating in a slightly alkaline instead of a neutral solution renders the addition of precipitated mercuric oxide unnecessary for correcting this acidity. If the alkalinity, as shown by the formation of an unduly large precipitate, should have been too great, it may be reduced by careful addition of nitric acid until an added drop of mercurous nitrate no longer produces a cloud.

After heating and filtering, the precipitate is ignited at not over 500° C in a platinum crucible after drying and removing from the paper to obviate any chance of loss of molybdenum and of injury to the crucible by reduction of arsenic. The ignited precipitate is fused with a very little sodium carbonate and leached with water, and the solution, if colored yellow, is filtered into a graduated flask of 25 ml or more capacity. The chromuim is then determined accurately in a few minutes by comparing with a standard alkaline solution of potassium dichromate (13, B, p. 899). Then, or earlier in absence of chromium, sulfuric acid is added in slight excess, and molybdenum and arsenic, together with occasional traces of platinum, are precipitated by hydrogen sulfide.[153] If the color of the precipitate indicates absence of arsenic, the filter with its contents is ignited carefully in a weighed porcelain crucible at not over 500° C and weighed, and the delicate sulfuric acid test for molybdenum is applied as follows: The residue is heated with a single drop of strong sulfuric acid until the acid is nearly volatilized. On cooling, the appearance of a beautiful blue color is proof of the presence of molybdenum. If arsenic is present, molybdenum can be determined colorimetrically after solution of the mixed oxides as directed under Molybdenum (p. 314). Arsenic should be determined in a separate portion of rock, after distillation from hydrochloric acid solution as described under Arsenic (p. 260).

The filtrate in bulk from 25 to 100 ml is boiled to expel hydrogen sulfide and titrated at a temperature of 70 to 80° with a very dilute solution of permanganate, representing about 1 mg of V_2O_5 per ml, as calculated from the iron strength of the permanganate, one molecule of V_2O_5 being indicated for each one of Fe_2O_3. One or two checks are always to be made by reducing again by means of a current of sulfur dioxide gas, boiling this

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[153] From a sulfuric solution the separation of platinum and molybdenum by hydrogen sulfide is much more rapid and satisfactory than from a hydrochloric solution.

out again,[154] and repeating the titration. The latter results are usually a very little lower than the first and are to be taken as the correct ones.

The high results in the first titration are caused by the formation of polythionic compounds as vanadium is reduced by hydrogen sulfide[155] and by extraction of oxidizable matter from the filter paper. The former is not easily avoided; the latter effect can be eliminated almost wholly by first passing as little as 25 ml of water through the paper and completely with a larger amount or by the use of an asbestos or platinum-felted perforated crucible (p. 101).

b. *Confirmatory Qualitative Tests.* In case the volume of permanganate used is so small as to make doubtful the presence of vanadium, it is necessary to apply a qualitative test, which is best made as follows: The solution is evaporated and heated to expel excess of sulfuric acid, the residue is taken up with 2 to 3 ml of water and a few drops of dilute nitric acid, and a couple of drops of hydrogen peroxide are added. A characteristic brownish tint indicates vanadium. Unless the greater part of the free sulfuric acid has been removed, the appearance of this color is sometimes not immediate and pronounced; hence the above precaution. It is also necessary that the nitric acid shall be in considerable excess, since, in a neutral or only faintly acid solution, the color does not appear strongly.

The above is a surer test to apply than the following: Reduce the bulk to about 10 ml, add ammonia in excess, and introduce hydrogen sulfide to saturation. The beautiful cherry-red color of vanadium in ammonium sulfide solution is much more intense than that caused by hydrogen peroxide in acid solution, but the action of ammonia is to precipitate part or all of the vanadium with the chromium or aluminum that may be present or with the manganese used in titrating, and ammonium sulfide is unable to extract the vanadium wholly from these combinations. Usually, however, the solution will show some coloration, and addition of an acid to the filtered solution precipitates brown vanadium sulfide, which can be collected, ignited, and further tested if desired.

c. *Application of the Method in Presence of Relatively Much Chromium.* The application of the method in its foregoing simplest form is subject to one limitation—the chromium must not be present above a certain moderate amount. This limitation is due to the considerable amount of permanganate then required to produce a clear transition tint when titrating in a hot solution, as is advisable with vanadium (p. 459). In a cold solution of chromic sulfate, much less permanganate is needed to produce the peculiar blackish tint without a shade of green, which affords a sure indication of excess of permanganate, but, in a hot and especially a boiling solution, the oxidation of the chromium itself takes place so rapidly that a very large excess of the reagent may be added before a pronounced end reaction is obtained. Nevertheless, fairly satisfactory determinations of as little as 1 or 2 mg of vanadium pentoxide can be made in the presence of as much as 30 mg of chromic oxide. To accomplish this it is only necessary to apply a simple correction obtained by adding permanganate to a like bulk of equally hot chromic sulfate solution containing approximately the same amount of chromium.

Tables 32 and 33 contain the results of a considerable number of tests, those in Table 33 being tabulated separately, in order to show the degree of accuracy attainable with a large excess of chromium by applying the correction mentioned above and also the amount of this correction.

In spite of the fact that the correction in most of the trials of this last table represents a large proportion of the permanganate used, the results must be considered satisfactory in view of the small amount of vanadium present, and they show that the method in competent hands after a little experience affords trustworthy figures.

The method of T. Fischer[156]—digestion of the precipitated lead salts with a strong solution of potassium carbonate—appears to offer the long-needed satisfactory quantitative separation of arsenic, phosphorus, chromium, tungsten, and molybdenum from vanadium, the normal lead metavanadate remaining quite unattacked, according to Fischer, while the other lead salts are wholly decomposed, but the applicability of this method to the separation of the minute amounts often found in rocks and ores has not been tested. The object has been in the present case to reach satisfactory results with the greatest expedition, and, when chromium is not present in considerable amount, this is accomplished.

Fortunately chromium is almost never a prominent constituent of clays, coals, iron ores, and those rocks in which vanadium has thus far been reported.[157]

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[154] The direct use of a solution of sulfur dioxide or of an alkali sulfite is inadmissible unless these have been freshly prepared, for, after a lapse of time, they contain other oxidizable bodies than sulfurous acid or a sulfite. The sulfur dioxide is best obtained as wanted by heating a flask containing a solution of sulfur dioxide, or of a sulfite to which sulfuric acid has been added.

The expulsion of the last trace of sulfur dioxide is accomplished more effectively by boiling with simultaneous passage of a rapid current of carbon dioxide for a few minutes at the last than by boiling alone. Because of the small amount of air carried with it, long passage of the gas is said to result in slight oxidation of the vanadium [O. Manasse, *Ann. Chem. u. Pharm.*, 240, 23 (1887); *Z. anal. Chem.*, 32, 225 (1893)].

[155] G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, **43**, 1560 (1921).

[156] Inaugural dissertation, Rostock (1894).

[157] For colorimetric methods for the determination of as little as 0.001 per cent of vanadium or chromium and 0.0001 per cent of molybdenum following a sodium carbonate fusion of a 1-g sample of silicate rock, see E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, **8**, 336 (1936).

TABLE 32

Tests for Vanadium in the Presence of Chromium

No.	Chromic Oxide, mg	Vanadium Pentoxide, mg	Vanadium Pentoxide Found, mg	Error, mg	No.	Chromic Oxide, mg	Vanadium Pentoxide, mg	Vanadium Pentoxide Found, mg	Error, mg
1	1	9.37	9.22	−0.15	7	3.5	18.74	18.97	+0.23
2	1	0.94	1.04	+0.10	8	6	5.6	6.1	+0.50
			0.98	+0.04	9	6	4.68	4.78	+0.10
3	1.5	5.25	5.49	+0.24	10	6	5.62	5.58	−0.04
			5.43	+0.19	11	10	5.62	5.58	−0.04
4	2	5.62	5.5	−0.12	12	10	23.52	23.81	+0.29
			5.5	−0.12				23.71	+0.19
5	3	4.68	4.78	+0.10	13	10	46.85	46.98	+0.13
			4.78	+0.10				47.20	+0.35
			4.83	+0.15	14	25	23.52	23.65	+0.13
6	3	5.62	5.58	−0.04				23.75	+0.23
			5.58	−0.04	15	87.5	23.52	23.71	+0.19
7	3.5	18.74	18.89	+0.15					

TABLE 33

Application of Correction for Larger Amounts of Chromium, Obtained by Adding Potassium Permanganate to an Equal Bulk of Solution Containing a Like Amount of Chromic Sulfate

No.	Chromic Oxide, mg	Vanadium Pentoxide, mg	Vanadium Pentoxide Found, mg		Error, mg	Volume of Solution, ml
			Uncorrected	Corrected		
16	20	0.94	1.59	0.99	+0.05	50 to 100
17	20	1.87	2.69	2.09	+0.22	50 to 100
			2.39	1.79	−0.08	
			2.59	1.99	+0.12	
18	20	18.74	19.4	18.73	−0.01	50 to 100
			19.3	18.63	−0.11	
			19.3	18.63	−0.11	
19	30	1.87	2.99	2.14	+0.27	About 100
			2.79	1.94	+0.07	
			2.79	1.94	+0.07	
			2.69	1.84	−0.03	
			2.69	1.84	−0.03	
20	30	1.87	2.69	1.79	−0.08	200
			2.89	2.09	+0.22	
			2.89	2.09	+0.22	
			2.79	1.99	+0.12	
21	62	46.85	48.90	47.60	+0.75	200

15. Iron

A. FERROUS IRON

A correct determination of the ferrous iron content of minerals is beset as a rule with great difficulties, which begin with the preparation of the sample, and it is desirable to discuss these at some length. The effect of grinding in air is to lower the FeO and increase the Fe_2O_3 in a mineral that contains FeO.[158] Of the latter, 20 to 30 per cent or more may be caused to disappear by grinding steadily for 2 hours. Attempts to prevent this chemical change by grinding under water, alcohol, and carbon tetrachloride have been partly successful, but not enough to permit the substitution in general practice of one of these media for air. Grinding in a wholly inert atmosphere, such as nitrogen (not carbon dioxide, which seems to form carbonates), might be successful in preventing oxidation in large part if not wholly, but is quite impracticable for general work. That it would not prevent taking up both loosely and firmly held water on subsequent contact with the air is certain as a result of the increased surface exposure. From the fact that oxidation is greatly lessened by grinding under one of the above-named liquids, even though the powder be then exposed to the air, it follows that increased surface is not the dominant factor in promoting oxidation, but probably local heating as the grains are fractured and rubbed under the pestle. The effect seems to be influenced also by the hardness of the iron minerals and those associated with them in mixtures, and perhaps still more by the chemical nature of the iron-bearing molecules themselves. Typical data are given in the article by one of us last cited.[158]

The experiments made, mainly upon silicates, show several things: (1) Although comparatively brief grinding (15 to 30 minutes) in air and long grinding under alcohol do not, as a rule, yield powders that are markedly oxidized (sometimes almost no oxidation seems to have taken place), this is not always so; hence grinding under one or the other of these media cannot be recommended as a practice to follow at all times. (2) Alcohol, in spite of its greater solvent power for oxygen, seems to be a little more effective in preventing oxidation than water. It has the further advantage that it can be removed more quickly afterward. (3) Of the organic media employed, alcohol seems to be more efficacious than carbon tetrachloride. (4) The effect of the presence of refractory iron-bearing minerals (garnet and others) in mixtures is indicated by rather wide variations in duplicate determinations when the material is not in a fine state of division. (5) The agreement that can be expected in duplicate determinations by either the Pratt or the Cooke method is excellent with fine powders or with coarse

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[158] R. Mauzelius, *Sveriges Geol. Undersökning*, Arsbok 1, no. 3 (1907); W. F. Hillebrand, *J. Am. Chem. Soc.*, 30, 1120 (1908).

powders that yield readily to attack by hydrofluoric acid. (6) Inasmuch as powders so fine as to pass sieves of 30 and even 60 meshes to the linear centimeter often show much less than 0.1 per cent of moisture, if hydrous alteration products are absent, it is reasonable to conclude that, in their preparation, there has been occasioned relatively as little oxidation of ferrous iron as absorption of moisture, on the assumption that the small amount of water found results from the increased surface exposure due to crushing and is not inherent. Therefore if the powder is completely decomposed by hydrofluoric acid, it is safe to assume that a determination of ferrous iron in it carried out with proper precautions will give a result close to the truth when other disturbing factors are not in evidence. (7) With different minerals, very different degrees of oxidation are brought about under like conditions—from a few per cent up to about 45 per cent of the FeO after several hours' grinding—and it is not always the mineral that might a priori be regarded as most oxidizable that shows most oxidation. Further, a soft or tough mineral undergoes greater oxidation if ground with a hard one than by itself alone.

It is plain that nearly all mineral analyses that were made before the effect of fine grinding was considered are affected by more or less serious errors, in respect not only to the oxides of iron but also to water, the error being greater, the further the comminution of the sample was carried. Very many analyses show ferric iron in minerals that should apparently contain none and small amounts of water for which there seems to be no place in any probable formula. These are discordances for which a simple and in most cases probable explanation is now offered. A revision of much past analytical work, particularly that relating to iron minerals, is called for, but, before it can be properly done, adequate provision must be made to avoid the old errors. In the paragraphs following are set forth the procedures that seem best adapted to attain this end in the light of present experience. Much routine and experimental work, however, must yet be done before rules to fit all cases can be formulated. It is perhaps advisable to add here, in order to prevent misconception, that the errors in past work are not as a rule to be assumed equal to those cited in the table referred to, for these resulted from grinding for 2 hours or more, although few if any analysts have made it a rule to grind for such a length of time.

a. *Preparation of Sample.* The mineral powder that has been prepared by crushing without grinding (2, B, p. 809) serves as the starting point. If trial shows that gentle boiling of it for 20 minutes with hydrofluoric acid leaves no residue or but little, use this sample directly for the ferrous iron determination. If the residue is considerable, grind a weighed portion (0.5 to 1.0 g) of the sample with absolute alcohol in a large agate mortar only long enough to yield a powder that will leave little or no residue. Allow the alcohol to evaporate spontaneously, and, when the last trace has disappeared, transfer the powder by aid of a fine jet of water to a platinum crucible of 20 to 100 ml capacity, not neglecting that which may adhere to the mortar and pestle. The subsequent operations are given under the respective methods (c, below), which are those involving decomposition by hydrofluoric acid. The Mitscherlich method (p. 911) requires in almost every case a very fine powder. For this and other reasons, that method finds little application. For the same reason, the modifications of the hydrofluoric acid method that require a powder of considerable fineness will be less applied than the one that permits the use of a relatively coarse powder. If a very fine powder must be employed, there seems to be no way known at present of correcting for whatever oxidation may have taken place during grinding. It will be preferable in such cases to grind under alcohol a small weighed portion of the coarse sample, instead of grinding a large portion and taking from this an aliquot part, the reason being that, in the latter case, separate determinations of both loosely and firmly held water must be made in order to be able to correct the FeO found for the considerable weight of water taken up during grinding (3, B, p. 819).

b. *Comparison of Sealed-Tube and Hydrofluoric Acid (Cooke) Methods.* No point in rock analysis has been the cause of greater solicitude to the chemist, and especially to the mineralogist and petrographer, than the determination of iron in ferrous condition. The sealed-tube or Mitscherlich method with sulfuric acid under pressure, for a long time the only available one for opening up the mineral, is in theory perfect, as complete exclusion of oxygen is easily attainable. Its earliest recognized defect lies in the inability to secure always complete decomposition of the iron-bearing minerals, and even to ascertain, oftentimes, whether or not the decomposition has been complete. The addition of hydrofluoric acid to the sulfuric in the tube, in order to insure this breaking up, is of very doubtful utility in most cases, as the glass may be so strongly attacked as to add an appreciable amount of iron to the solution, and the hydrofluoric acid may have exhausted itself in attacking the glass before the more refractory minerals succumb. Nevertheless, if decomposition can be effected by sulfuric acid alone, the results obtained are sharp and concordant; but they are in rock analysis usually higher than when made by any of the modifications of the hydrofluoric acid method. This difference is not very marked with rocks containing but 1 or 2 per cent of ferrous iron, but it increases with rising percentage to such an extent that, where the sealed-tube method will show 12 per cent ferrous oxide, the other may indicate no more than 10 per cent. Experiments with soluble iron salts of known composition, like ferrous sulfate and ferrous-ammonium sulfate, throw no light on the subject, for both methods give with them the same sharp and accurate results.

The key to the problem was discovered by L. L. de Koninck[159] in 1882 but remained unknown to the chemical world until rediscovered by H. N. Stokes in 1901 during an investigation on the action of ferric salts on pyrite and other sulfides.[160] That oxidation of the sulfide and reduction of the ferric salt hereby takes place had been recognized a little earlier by J. H. L. Vogt[161] but not the ease with which the change takes place and the completeness of the oxidation of the pyrite, not only of its iron but of the greater part of the sulfur as well. Pure pyrite itself is attacked with extreme slowness by boiling dilute sulfuric and hydrofluoric acids, either alone or mixed, but, the moment a ferric salt is introduced, the case is altogether different.

The complete solution to the problem was afforded by the observation made by one of us (W. F. H.) that rocks with hardly an exception and many minerals carry pyrite or pyrrhotite, or both, often in considerable amount, often in traces only. Sulfur can almost always be detected in 2 g of rock powder.

Experiment has shown (p. 916) that, with the amounts of sulfides usually found in igneous rocks, their effect on the estimation of ferrous iron by the hydrofluoric acid method at atmospheric pressure and boiling heat is negligible, though, if the amount of sulfide is increased, the effect becomes more and more apparent, because of the greater surface of pyrite exposed to the action of the ferric iron of the rock.

Under the conditions of the sealed-tube method, on the other hand—a temperature of 150 to 200° and even higher, high pressure, much longer time of action, and impossibility of escape of any hydrogen sulfide that may be formed—the sulfur of the sulfides becomes nearly if not fully oxidized to sulfuric acid at the expense of the ferric iron in the rock or mineral, with the production of an equivalent amount of ferrous iron in addition to that resulting from the sulfide itself.

Let us now see what the effect of these traces of sulfides amounts to when fully oxidized. One atom of sulfur (32) requires for its complete conversion to trioxide the oxygen of three molecules of ferric oxide (480), which then become six molecules of ferrous oxide (432). In other words, 0.01 per cent of sulfur may cause the ferrous oxide to appear too high by 0.135 per cent, and 0.10 per cent of sulfur may bring about an error of 1.35 per cent in ferrous oxide. The case is still worse if the sulfur is set free as hydrogen sulfide from a soluble sulfide, for then the above percentages of sulfur produce errors of 0.18 and 1.8 per cent, respectively, in the ferrous oxide determination.

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[159] *Ann. soc. géol. Belg.*, **10**, 101 (1882–3).

[160] *U. S. Geol. Survey Bull.* 186 (1901); *Am. J. Sci.*, [4] **12**, 414 (1901).

[161] *Z. prakt. Geol.*, 250–51 (1899).

The error caused by sulfides tends to become greater the more there is present of either or both sulfide and ferric salt. Now, the highly ferruginous rocks usually carry more ferric iron than the less ferruginous ones, and they are often relatively high in pyrite and pyrrhotite; hence the increasing discrepancy between the results by the two methods as the iron contents of the rocks rise is fully in accord with the above explanation.[162]

Of course carbonaceous matter will, under the conditions of the Mitscherlich method, likewise reduce sulfuric acid and cause the determination of ferrous iron to be faulty.

Notwithstanding the fact that the sealed-tube method has thus been discredited in its general applicability to rocks and minerals, it is still probably the best with those that are totally free from sulfides and wholly decomposable. Hence the conditions under which success can best be achieved by it are set forth in the following paragraphs:

c. *Description of Methods.* α. *The sealed-tube method.* 1. *Filling, sealing, and heating of the tube.* The sealed-tube or Mitscherlich method in its original and usual application calls for a mixture of 3 parts of sulfuric acid and 1 of water by weight, or about 3 to 2 by volume, though a still stronger acid is sometimes used. In some cases, however, perhaps in most, much better decomposition of the silicates is effected by reversing the proportions of water and acid, or at any rate by diluting considerably beyond the above proportions. Hereby the separation of salts difficultly soluble in the stronger acid is avoided, and the actual solvent effect on the minerals seems to be in no wise diminished.

The very finely powdered mineral having been introduced into a tube of resistant glass free from ferrous iron, draw out the open end in such a way as to leave a funnel for introduction of the acid. Pour in very little water, and carefully heat to boiling for a moment to expel all air from the powder. Next introduce the diluted acid—which has just been boiled down from a state of greater dilution in order to have it free from air—until the tube is about three fourths filled. Pass in carbon dioxide free from hydrogen sulfide from a generator which has been in active operation for some time, through a narrow glass tube drawn out of the same kind of glass as that of which the decomposing tube consists. In a few moments the air is expelled. Finally seal the small tube into the large one over the blast lamp without interrupting the gas current until the very last instant, when to prolong it would perhaps cause a blowing out of the softened glass. The interruption of the current at the proper moment is easily effected by

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[162] For details of experiments, see W. F. Hillebrand and H. N. Stokes, *J. Am. Chem. Soc.*, 22, 625 (1900) and *Z. anorg. Chem.*, **25**, 326 (1900).

the pressure of the thumb and finger holding the small tube at the point where it enters the rubber tube leading from the gas generator. No breakage in the next operation ever occurs as a consequence of thus fusing one tube into the other.[163]

Heat the tube, inserted horizontally, in a bomb oven at any desired temperature up to, say, 200° C until decomposition is complete or has progressed as far as can be hoped for. This is determined by withdrawing the tube at intervals and examining its contents with a low-power lens. By enclosing the tube in an outer one of strong steel, properly capped and containing a little ether, benzine or solid CO_2 to equalize the pressure on both sides of the glass, the temperature can be raised far beyond what is otherwise permissible, and the decomposition will then doubtless be more complete with refractory minerals.

2. *Titration of the iron.* File a scratch around the upper end of the tube well above the liquid, break off that end, rinse it and the contents of the rest of the tube into a beaker or dish, and titrate the cold solution with permanganate as directed under Iron (p. 395). Duplicate determinations should agree almost exactly.

If other reducible compounds are absent, the total iron can then be determined volumetrically by reduction with titanous chloride as described under Iron (p. 398) as a check upon the result obtained in some other stage of the analysis.

β. Hydrofluoric or Cooke method. The hydrofluoric method, devised by J. P. Cooke,[164] consists simply in decomposing the mineral powder in the absence of air and at atmospheric pressure by means of hydrofluoric acid in presence of sulfuric acid and titrating the ferrous iron in the resulting solution by permanganate. The method as ordinarily carried out is subject to two errors of opposite sign but unequal value, the second and greater of which long remained unsuspected.[165]

It is possible to titrate ferrous iron in the presence of sulfuric acid and as much as 5 to 7 ml of 40 per cent hydrofluoric acid in a total volume of 200 to 400 ml almost if not quite as exactly as in sulfuric acid alone, provided the iron solution is diluted with air-free water and the titration is made immediately after adding the hydrofluoric acid and with all possible dispatch. This condition cannot be fulfilled in practice, because the mineral must be in contact with the acid for a long time in the apparatus commonly employed, and it seems to be almost impossible to prevent some oxidation during this period. It is not known whether, after titrating the ferrous iron in hydrofluoric acid solution, the total iron can be satisfactorily titrated with titanous chloride (p. 398), as it can be when the sealed-tube method of attacking the sample is employed.

1. *Defects of the method. a. Oxidizability of bivalent manganese by permanganate in the presence of hydrofluoric acid.*—Manganic fluoride in dilute solutions is hardly at all dissociated, wherein it differs from manganic sulfate. The entering of the manganic ion as fast as formed into the undissociated state or into a complex ion[166] explains the fact that, in the presence of hydrofluoric acid, bivalent manganese is oxidized readily by permanganate, whereby a sharp end reaction is rendered unattainable in the presence of much hydrofluoric acid, say, over 7 ml of 40 per cent acid. It is easy to obtain a transitory pink color throughout the liquid, but this disappears rapidly, the more rapidly the greater the amount of hydrofluoric acid or of manganous salt present. The oxidant can be added by the milliliter to solutions already containing manganous sulfate in the presence of hydrofluoric acid without producing a more than passing pink color. The solution, however, takes on in ever-increasing intensity the red-brown color characteristic of manganic salts. Hence the decolorization due to this cause is much more pronounced in rocks high in ferrous iron than that of those low in this constituent, because of the greater amount of manganous salt resulting from reduction of a correspondingly larger amount of permanganate, and is also greater with increasing hydrofluoric acid. In the presence of but little ferrous iron, up to, say, 2 cg, and 5 to 7 ml of hydrofluoric acid, the color produced by a drop of permanganate lasts some time, but is very evanescent as the ferrous iron, and consequently the manganous salt formed, increases.

Numerous tests were made by one of us (W. F. H.) to ascertain the error due to oxidation of the manganese under conditions similar, in respect to the amounts of iron involved, to those encountered in rock analysis. Increasing amounts of hydrofluoric acid were added to fixed amounts of ferrous sulfate and sulfuric acid, and the titration was made with the least possible expenditure of time. With not more than 7 ml of 40 per cent hydrofluoric acid, a very slight tendency was observed toward high results, but, in most cases, the results were identical with those obtained in the presence of sulfuric acid alone. As the amount of hydrofluoric acid was increased to 10

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[163] The usual practice has been to expel air before sealing the tube by introducing a few crystals or lumps of an alkali carbonate, the gas set free from their contact with the acid being supposed to displace the air effectively. That this is not accomplished has been fully shown [W. F. Hillebrand, *U. S. Geol. Survey Bull.* 78, 50 (1891); *Chem. News*, 64, 232 (1891)], the error often being large.

[164] *Am. J. Sci.*, [2] 44, 347 (1867).

[165] It is not clear what if any bearing certain observations of E. Deussen [*Monatsh.*, 28, 163 (1907)] may have on the method. He asserted that solution of ferric oxide in hydrofluoric acid involves partial reduction of the iron with formation of both ferrous iron and hydrogen peroxide: $2Fe_2O_3 + 8HF = Fe_3F_8 + FeO + 3H_2O + H_2O_2$. If this is true, it would seem that the two must neutralize each other with respect to consumption of permanganate.

[166] E. Müller and P. Koppe, *Z. anorg. Chem.*, 68, 160 (1910).

ml, a perceptible increase was noticed, which became markedly greater with 15 ml of the acid, amounting in this case to about 0.2 ml in the average on a normal consumption of 20 ml of permanganate of 0.0032 FeO titer.

Hence, after the mineral is decomposed, removal of the excess of hydrofluoric acid is called for if the best results are to be expected, or else its effect must be counteracted.

A distinct contribution to the subject was made when O. L. Barnebey [167] investigated the effect of a large number of proposed preventives and found that boric acid is the most effective of all. When added, either as solid or in solution, it renders the fluorine inactive by formation of fluoboric acid (HBF_4), "which does not dissociate appreciably to yield hydrofluoric acid in the presence of boric acid."

b. *Extreme oxidizability of bivalent iron by free oxygen in the presence of hydrofluoric acid or a fluoride.* In comparing two series of results obtained with the Cooke apparatus, using a solution of ferrous sulfate in sulfuric acid alone in the one and in sulfuric acid with hydrofluoric acid in the other, a minus error was observed in all cases when the latter acid was present. An observation made by R. Peters,[168] but not applied by him to the present case, explains this. Ferric fluoride, like the corresponding manganic salt, is almost undissociated in solution, whereas the sulfate undergoes considerable dissociation and in this state counteracts, to a great extent, the tendency of any ferrous iron present to become oxidized by free oxygen. Hence the slow oxidation of bivalent iron by air in sulfuric acid solution and its very rapid oxidation in the presence of hydrofluoric acid. Although a sulfuric solution of ferrous sulfate exposed to the air in an open dish will hardly change in strength during an hour, a similar solution to which hydrofluoric acid has been added will suffer a large measure of oxidation in a quarter of the time. The change in titer becomes pronounced after a few minutes.[169]

In the experiments with the Cooke apparatus referred to, the minus error should amount to not more than 0.1 to 0.2 ml of permanganate on a normal consumption of 20 ml or 0.5 to 1 per cent of the iron, but it may be considerably greater if the utmost care is not taken to employ carbon dioxide as free as possible from air and to exclude most carefully the entrance otherwise of air into the apparatus. It will also be greater, the higher the concentration, within certain limits, of the solution during titration.

With a view to lessening the error, if possible, the mode of operating was varied by doing away with carbon dioxide, except at the start, shutting it

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[167] O. L. Barnebey, *J. Am. Chem. Soc.*, **37**, 1481 (1915).

[168] *Z. physik. Chem.*, **26**, 193 (1898).

[169] The oxidation of ferrous sulfate in acid solution is also greatly accelerated by the presence of copper sulfate [E. Posnjak, American Institute of Mining and Metallurgical Engineers (1927)].

off as soon as the bath was in active ebullition, and transferring the crucible direct from the hot bath to the titration vessel. The results were, if anything, a trifle better. As the employment of either the Cooke, Barnebey, or Treadwell apparatus involves long contact of the mineral with the acids, and as the experiments last mentioned were favorable in their results, it seemed as if the simple method of J. H. Pratt [170] might be modified in the same sense. He avoided the use of all apparatus other than a capacious platinum crucible fitted with a perforated cover for the introduction of carbon dioxide, in which he boiled the mineral powder with sulfuric and hydrofluoric acids, the decomposition being greatly hastened by the active movement and higher temperature and usually completed in 5 to 10 minutes. The modification consists in doing away altogether with carbon dioxide, except at the start, and depending on the steam of the boiling iron solution to exclude air, a modification which Pratt himself tried with rather considerable minus errors, resulting perhaps from his having a smaller crucible at command than the method really demands. With a crucible of 100 ml capacity, the results with ferrous sulfate given in Table 34 show what are the possibilities of the method.

TABLE 34

Ferrous Iron Determinations by the Modified Pratt Method

Strength of Permanganate 0.0032 g FeO per ml

Time of Boiling, min	Permanganate Used, ml	Normal Consumption of Permanganate, ml	Time of Boiling, min	Permanganate Used, ml	Normal Consumption of Permanganate, ml
10	4.9	4.8	10	19.4	19.2
10	4.8	4.8	10	19.3	19.2
10	5.0	4.8	15	19.25	19.2
10	4.9	4.8	15	19.1	19.2
10	9.6	9.6	15	19.3	19.2
10	9.6	9.6	20	19.2	19.2
10	9.6	9.6	20	19.3	19.2
10	19.2	19.2			

These results leave little, if anything, to be desired. They show either normal values or a slight plus error instead of the invariable negative one of all previous determinations. The procedure was tested during two years in comparison with that of Cooke with favorable results. It is the method preferred not only because of its simplicity and quickness, but also because with it a coarser powder can be decomposed than with the Cooke, the Barnebey, or the Treadwell procedure. However, as the exigencies of the

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[170] *Am. J. Sci.*, [3] **48**, 149 (1894).

FeO determination are now known to demand a powder as coarse as possible, a longer treatment has to be given than was called for by the fine powders used by Pratt.[171]

2. *Influence of sulfides, vanadium, and carbonaceous matter on the determination of ferrous iron by the hydrofluoric acid method.* A dark color of the insoluble fluorides and silicofluorides may be due to pyrite, graphite, or carbonaceous matter. The first of these affects the result but little, and the second probably not at all, and they can be distinguished by their behavior toward nitric acid. Organic matter, of course, renders impossible the determination of ferrous iron. These contaminants are seldom encountered with minerals as distinguished from rocks.

a. Sulfides. Pyrite, in the quantities usually met with in igneous rocks, is probably without serious effect on the ferrous iron determination by any of the hydrofluoric acid methods. This sulfide is very resistant toward attack in the absence of oxygen, as is shown by the fact that, if present in any quantity, it can be recognized readily in the residue after titration. In any case it is impossible to allow for an error introduced by its possible decomposition, and the result of titration must count as ferrous iron. In the case of soluble sulfides two sources of error are introduced—that of reduction of ferric iron by hydrogen sulfide evolved, and that due to the ferrous iron which the sulfides themselves may contain, especially if pyrrhotite is present. The first of these is perhaps negligible, for most of the hydrogen sulfide would probably be expelled without reducing iron. The second is approximately measurable if it is known that pyrrhotite is the only soluble sulfide present, and its amount has been ascertained by determining the hydrogen sulfide set free on boiling with hydrochloric acid in a current of carbon dioxide. In this case a correction is to be applied to the result of titration for total ferrous iron (see also p. 950 under Sulfur).

In order to obtain quantitative data regarding the effect of pyrite on the ferrous iron determination by the hydrofluoric acid method, the following tests were made: Part of a fine crystal of pyrite was powdered rather finely and boiled with dilute sulfuric acid, which extracted considerable ferrous iron, derived presumably from admixed or intergrown pyrrhotite, as a second boiling with fresh acid gave a negative test for ferrous iron. After washing by decantation with water, followed by alcohol and ether, the powder was dried and further pulverized. A quarter of a gram of it, when treated with hydrofluoric and sulfuric acids in a large crucible by the Cooke method for ferrous iron and then rapidly filtered through a very

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[171] M. Dittrich [*Ber.*, 44, 990 (1911)] facilitated the attack of refractory minerals by adding half a gram of not too finely ground quartz (not precipitated silica). The effect was to separate the mineral grains and prevent caking on the bottom of the crucible, thus exposing them to more effective action of the acid.

large perforated platinum cone fitted with filter paper, required but 2 drops of a permanganate solution representing only 0.0032 g of FeO to the milliliter.

However, as H. N. Stokes found[172] that the oxidizing effect of ferric salts on pyrite and other sulfides is vastly greater than seems to have been suspected (see pp. 910–911), the following tests were made, in order to ascertain the probable error due to this action under the conditions prevailing in rock analysis: Successive portions of 1 g each of a hornblende schist, free from sulfur and carrying 10.09 per cent FeO as the mean of several determinations and 4.00 per cent Fe_2O_3, were mixed in a large 100-ml platinum crucible with 0.02, 0.025, and 0.10 g, respectively, of the above purified pyrite powder, and treated with hydrofluoric and sulfuric acids by the Cooke method, the water bath being at boiling heat for 1 hour. The cooled contents of the crucible were poured into a platinum dish containing water and titrated rapidly nearly to an end. Then, in order to get rid of the pyrite, which would obscure the end reaction by its reducing effect on the permanganate, the solution was filtered as above, and in the clear filtrate the titration was carried to completion. The results were 10.02, 10.16, and 10.70. Inasmuch as the smallest of these three charges of pyrite was several times greater than what may be considered an unusually high amount for an igneous rock, it is very evident that, for all practical purposes, the influence of pyrite on the ferrous determination by the Cooke method is negligible. At the same time it is to be borne in mind that, with increased content in ferric iron, an increased amount of pyrite will be attacked, and that the extent of this attack is influenced by the degree of fineness of the pyrite powder, which itself undergoes oxidation during grinding.

b. Vanadium. If vanadium, when present, exists in the trivalent condition, it affects with an error varying with its amount the result of titration for ferrous ion. If the amount of the trivalent vanadium is known, a correction can be applied.

c. Carbonaceous matter. As said before (p. 916), matter of organic origin other than graphitic carbon renders the results of the ferrous iron determination altogether unreliable.

3. *The method in its various modifications. a. According to Pratt (modified).* Place ½ to 1 g of the coarsest powder[173] that can be used successfully in a platinum crucible of 80 to 100 ml capacity and provided with a tightly fitting cover. Moisten with 1 to 2 ml of air-free water, and add 10 ml of dilute sulfuric acid (1 + 3). If the powder contains carbonates, there will

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[172] *U. S. Geol. Survey Bull.* 186 (1901); *Am. J. Sci.*, 4th series, No. 12, p. 414 (1901).

[173] The fineness of grinding will depend on the nature of the rock. Most granite rocks require but moderately fine grinding; those high in ferruginous and refractory minerals generally, as tourmaline, need to be very fine.

be effervescence; hence the acid must be added cautiously and the cover placed on until the action is over. There need be no fear of oxidation of ferrous iron at this stage, should any go into solution. Now add air-free hot water till the crucible is at least half full; cover the crucible, and place on a triangle well down over a lamp turned low and protected from drafts. Displace the air in the crucible rapidly by carbon dioxide entering through a small glass tube inserted beneath the lid slightly raised on one side. Heat to boiling rapidly, and, as soon as steam issues from the crucible, *slightly* move the crucible cover aside, and at one stroke add 7 ml of hydrofluoric acid from a small platinum crucible. A second of time suffices.[174] As soon as the solution again boils remove the tube carrying the carbon dioxide, cover the crucible completely, and boil gently for 12 to 15 minutes. At the conclusion of the boiling, *quickly* transfer the crucible, cover, and contents to a titration vessel (which may be of glass) containing 300 ml of a standard air-free solution of boric acid[167] containing an excess of the solid acid, 10 ml of dilute sulfuric acid (1 + 3), and all except 1 to 2 ml of the standard solution of potassium permanganate that will be required to oxidize the iron. Complete the titration in the customary manner.[175]

Even without boric acid and with little iron, the color will last some time, but, with increasing amounts of iron, as also with increasing amounts of hydrofluoric acid, it fades with ever greater rapidity. In making a duplicate determination, it is well to run in a little less than the calculated amount of permanganate before introducing the contents of the crucible.

The method should be tested first by the novice with ferrous sulfate solution that has been standardized without hydrofluoric acid. It is important

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[174] Hydrofluoric acid sometimes contains particles of the material of which the container is made. These, as well as dissolved organic matter, must be avoided.

[175] L. A. Sarver [*J. Am. Chem. Soc.*, **49**; 1472 (1927)] pointed out that dichromate reacts much less readily on organic matter than permanganate, and recommended its use, together with diphenylamine as an internal indicator. For the determination of ferrous iron in silicates, he proceeded as follows: Provide an ordinary platinum crucible with a snugly fitting cover of transparent Bakelite having a Bakelite tube for the introduction of carbon dioxide and a small Bakelite funnel for the addition of acid and the escape of vapors and steam. Transfer 0.5 g of coarsely powdered sample, moisten with water, and treat with 10 ml of 12 *N* hydrochloric or 18 ml of 18 *N* sulfuric acid. Drop in a small coil of platinum wire to prevent bumping, fit the cover tightly, and pass carbon dioxide through for at least 10 minutes as the mixture is gradually brought to boiling. Stop the stream of gas as soon as steam escapes, immediately add 7 ml of 48 per cent hydrofluoric acid through the funnel and gently boil for 10 to 15 minutes. When decomposition is complete, as seen through the cover, again start the stream of gas, and cool to room temperature. Add a measured excess of standard dichromate solution through the funnel, remove and rinse the cover, and pour the solution onto solid boric acid in a ceresin-lined porcelain crucible. Titrate at once with an equivalent solution of ferrous sulfate, using diphenylamine as indicator. See also C. J. Schollenberger, *J. Am. Chem. Soc.*, 53, 88 (1931).

not to prolong the boiling unduly, for salts not easily soluble will separate, and, as the temperature rises, the oxidizing action of the concentrating sulfuric acid comes into play.

If an unattacked residue shows after titrating, allow it to settle completely, and then free it from the liquid by a decantation with water, once repeated. Now transfer it by a jet of water to a small agate mortar, allow to settle again, free from most of the water by decantation, grind for a few minutes under the water that remains, and wash back into the large crucible. Repeat the treatment with hydrofluoric and sulfuric acids, in smaller amounts and for a shorter time than at first. The succeeding titration can be made in the crucible itself after quickly filling this nearly full of cold air-free water. Usually decomposition will now be complete; if not, repeat the various operations. In the very short time required for grinding the residues under water, no appreciable oxidation of ferrous iron need be feared.

The directions given by Pratt[176] for the treatment of a possible undissolved residue of very refractory minerals must be understood as applying only to homogeneous minerals and not to rocks, where the relations of ferrous and ferric iron in the undecomposed portion are certainly different from those in the part dissolved.

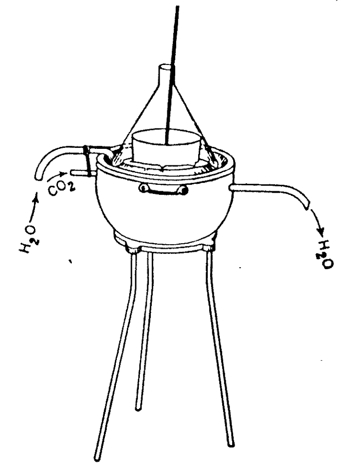

FIG. 43. Cooke's apparatus for ferrous iron determination.

b. According to Cooke.[164] The apparatus, as shown in Fig. 43, consists of a small water bath of a single opening and covered with a glass funnel, the stem of which has been cut off near the flare, resting in a troughlike depression of the specially made cover. Into this trough water constantly drops from a tubulated bottle, thus securing a perfect water joint and serving to keep the bath full by overflowing on the inside. For the more perfect exclusion of air, it is best to use water that has been freshly boiled. Through a small metal pipe, carbon dioxide gas flows into the bath under the cover, but above the surface of the water, and, rising through notches in the edge of the opening of the cover, fills the funnel and crucible.[177]

Treat ½ to 1 g of the powder exactly as in *a* until any carbonates that may be present cease to effervesce. Rinse the cover of the crucible if need be, and place the open crucible at once in the opening of the bath, put the

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[176] *Am. J. Sci.*, [3] **48**, 150 (1894).

[177] The gas generated from every new lot of even white marble must be tested carefully for hydrogen sulfide. It should be washed by passing it through a large U tube containing glass beads and a solution of copper sulfate.

funnel in place, start the gas current, as also the flow of water from the reservoir, and light the lamp under the bath already full of water. As soon as it can be safely assumed that the air in both funnel and crucible has been displaced, pour a measured volume of strong hydrofluoric acid (5 to 7 ml) into the crucible through a funnel of platinum, rubber, or Bakelite, and insert a platinum stirring rod through the stem of the glass funnel into the crucible. In the absence of a suitable funnel for the acid, the glass may be momentarily raised for the introduction of the acid, but not before the crucible has become filled with carbon dioxide.

When steam issues strongly from the funnel, stop the gas current from the generator, and leave the apparatus to itself for an hour, except for occasional stirring of the powder. When gritty matter can no longer be felt or when experience tells that decomposition must be complete, again turn on the gas current, extinguish the lamp, and increase the water flow to the capacity of the outlet tube from the bath. In 15 minutes the crucible and contents should be cool. Remove the rod, place it in the titration vessel, and make the titration as in *a*. Until the operator has become experienced a duplicate determination should invariably be made. It is to be noted that the crucible is always much fuller at the end of the heating than when first placed on the bath, because of condensation of steam.

Instead of the crucible being allowed to cool in a current of carbon dioxide, it may be transferred at once to the titration dish and permanganate run in as above directed. If carefully done, the experiments already referred to seem to show that the results by this variation of the method may be a trifle better than those obtained after cooling.

Those inexperienced with the method in either variation should not fail to test it first with a solution of ferrous sulfate that has been standardized without hydrofluoric acid, and in practice duplicate determinations should be made if possible.

c. According to Barnebey. O. L. Barnebey[178] described a simplified form of the Cooke apparatus. In an 8-inch porcelain dish are placed some glass beads and a 5-inch porcelain desiccator plate having under supports. On the plate is a suitable support of glass or porcelain to hold in place the platinum dish in which the decomposition of the sample is effected. Over the plate is placed a 6-inch funnel like that for the Cooke apparatus. This extends far enough down to form a trap when a suitable liquid is poured into the outer dish. For the determination of ferrous iron, Barnebey used as the liquid a solution of phosphoric acid (1 + 2). This serves not only as a trap but also to furnish steam for expelling and excluding air from the funnel and inner dish. The bath is heated by a direct flame or by a hot plate. If needed, air-free water can be added to replace that which evaporates, by the aid of a platinum rod. Reference to the description of the Cooke apparatus renders further explanation unnecessary.

Of course, the absence of provision for introducing carbon dioxide makes it necessary to transfer the hot solution of the sample to the titration vessel, and the need of a fine powder is a serious objection, as with the Cooke apparatus. The latter has the advantage over Barnebey's modification that the introduced carbon dioxide effects more rapid expulsion of the air in the decomposition vessel than is possible by the aid of steam alone.

d. According to Treadwell. F. P. Treadwell[179] used a paraffin bath in which was supported a lead box having a lead cover provided with two openings, one at the side for introducing carbon dioxide, the other in the center for the escape of steam and the insertion of a stirring rod. In the box the small dish containing the sample rested on a support, under the central opening.

Although the chief object of this device was, by raising the temperature to 120° at the end of the experiment, to remove the excess of hydrofluoric acid and thus avoid one source of error in the titration, it may be said, so far as our limited experience with it goes, that the expulsion of the acid is by no means perfect and that the long duration of the experiment (about 2 hours) renders it likely that lower results will be obtained than with the procedures already described, especially the procedure given under *α*.

e. According to Soule. B. A. Soule[180] recommended that the sample be dissolved in a Pyrex or, preferably, quartz flask because the completeness of the reaction can be readily observed and the solution need not be transferred. A correction factor per gram of glass dissolved must be applied, and is determined by weighing the flask, treating a weighed portion of pure ferrous ammonium sulfate as in the method, titrating, again weighing the empty flask, and dividing the difference between the volume of permanganate consumed and the volume required in the direct titration of a similar portion by the weight of glass that was dissolved. The procedure is as follows: Clean the flask, weigh against another used as a counterpoise, fill with carbon dioxide, and introduce the sample for analysis. Add 15 ml of water, 10 ml of dilute sulfuric acid (1 + 3), and 5 to 8 ml of hydrofluoric acid (40%). Place on a hot plate, and boil gently under a slow stream of carbon dioxide. When no undecomposed particles are observed upon swirling the solution, remove the flask, and immediately add 100 ml of a freshly prepared cold solution containing 6 g of boric acid and 5 ml of dilute sulfuric acid (1 + 1). Cool to approximately 15° C, and titrate with 0.05 *N* potassium permanganate. Clean and dry the flask, again weigh, and correct the volume of permanganate on the basis of the dissolved glass.

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[178] *J. Am. Chem. Soc.*, 38, 374 (1916).

[179] *Kurzes Lehrbuch analytischen Chem.*, [6] 2, 425 (1913).

[180] *J. Am. Chem. Soc.*, 50, 1691 (1928).

In a later article,[181] Soule stated that ferrous iron can be determined quickly and accurately in magnetites and materials of higher silicate content by potentiometric titration with a 0.05 *N* solution of ceric sulfate (p. 190). In such case, the sample (0.3 to 0.4 g) is decomposed by treating with a mixture of 10 ml of hydrochloric and 3 ml of hydrofluoric acids in a Pyrex flask filled with carbon dioxide, and heating at 40 to 50° C for 3 to 5 minutes. The solution is then treated with 100 ml of water containing 5 g of boric acid and 5 ml of dilute sulfuric acid (1 + 6) and titrated with the aid of a bimetallic (Pt-Ag) electrode system. Arsenic, the chief reducing agent derived from the glass, is without effect.[182]

A procedure for the determination of ferrous iron in silicate materials that are soluble in cold hydrochloric acid or hydrochloric-hydrofluoric acids containing iodine monochloride (ICl), by titrating the liberated iodine with potassium iodate, is described by M. H. Hey.[183]

For the determination of ferrous iron in silicate minerals that are insoluble in acids, H. P. Rowledge found that sodium metafluoborate[184] $(NaF)_2B_2O_3$ was the most suitable flux. A. W. Groves[185] has modified the Rowledge method by making the fusion at 950° C in an atmosphere of carbon dioxide in a silica tube and using either the boric acid-permanganate titration or the iodine monochloride (ICl) procedure.

f. Uncertainties of the ferrous iron determination. From the foregoing, it is apparent that, despite the utmost care in practical manipulation, the exact determination of ferrous iron in rocks is one fraught with extraordinary difficulties and uncertainties. Only in the absence of decomposable sulfides and carbonaceous matter and when the amount and condition of vanadium are known and relatively coarse powders can be used, is it permissible to regard the result as fairly above suspicion.

B. FERRIC IRON

a. *Direct Determination in Presence of Ferrous Iron.* The applicability of the titanous chloride method (see Iron, p. 398) to the direct determination in minerals of ferric iron when accompanied by ferrous iron has not been studied. If suitable for minerals that are readily soluble in sulfuric or hydrochloric acid, it might not be so for rocks and the minerals that have to be attacked by hydrofluoric acid with exclusion of air, the resulting conditions being then quite different from those under which the authors of the method worked.

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[181] B. A. Soule, *ibid.*, **51**, 2117 (1929).

[182] H. H. Willard and P. Young, *ibid.*, **50**, 1335 (1928).

[183] *Mineralog. Mag.*, **26**, 116 (1941).

[184] *J. Royal Soc. W. Australia*, **20**, 165 (1934).

[185] A. W. Groves, *Silicate Analysis*, 2d ed., p. 184, G. Allen and Unwin, London (1951).

In any event, the solution of the mineral and titration of the iron would have to be hedged about with all the precautions that are described under ferrous iron, and the result would be subject to errors similar but of opposite sign.

b. *True Value for Ferric Iron in a Rock or Mineral.* If, in the substance undergoing analysis, iron is present in both the ferric and ferrous states and the amount corresponding to only one of these (usually ferrous) has been determined in addition to the total iron in terms of ferric oxide, it remains only to deduct from this last the ferric oxide equivalent of the first in order to obtain the value for the ferric oxide. This is the most favorable case. With minerals and rocks that are contaminated with sulfides—whether iron-bearing or not—two errors result. One of these arises from an iron content of the sulfides; another from the indeterminable reducing effect upon ferric iron of hydrogen sulfide that may be liberated in the ferrous iron determination (p. 916). To these sources of error should be added that due to vanadium (p. 917). Hence in all such cases the final value deduced for ferric iron as well as for ferrous iron is subject to some uncertainty.

16. ALKALIES

A. GENERAL CONSIDERATIONS

It is seldom that any one of the metals of the alkali group occurs quite unaccompanied by one or more of its fellows. Ordinarily one has to deal only with sodium and potassium, in occasional company with appreciable lithium in a few minerals. In rocks, lithium occurs widely distributed but practically never in more than spectroscopic traces. Rubidium and cesium are found in only a very few rare minerals, local concentrations of which in depth have no doubt given rise to the rubidium and cesium content for which a few natural mineral waters are noted. The first step in determining alkalies in minerals is to collect and weigh the metals as chlorides. Lithium and potassium (rubidium and cesium) are then determined separately. Sodium is usually found by difference.

The methods most commonly used for the determination of the group require that all other metals be first removed, as well as all nonmetals except chlorine or, occasionally, the sulfate radical. In the very exceptional case that but one of the alkali metals is present, it is permissible to weigh it as sulfate. However, that there is no second or third member of the group present is not always and perhaps but seldom known in advance; hence it is necessary to have a solution better suited for making the required separations, and this is a chloride solution.

Soluble sulfates are converted to chlorides by treatment with barium chloride; in general, other salts are converted by repeated evaporation with hydrochloric acid, for which methyl alcohol saturated with the acid named is substituted when soluble borates are to be converted.[186] Bromides and iodides are best converted to chloride by evaporation (not in platinum) with hydrochloric acid containing hydrogen peroxide. [See G. E. F. Lundell and James I. Hoffman, *Outlines of Methods of Chemical Analysis*, p. 76, John Wiley & Sons (1938).]

There are but two well-known and generally applicable procedures for obtaining the metals in the form of chlorides when the mineral is not soluble in hydrochloric acid. One of these is old, having been devised by Berzelius;[187] the other is more recent and is due to J. Lawrence Smith.[188] Both find their commonest application in silicate analysis. The first begins with attack by hydrofluoric and sulfuric acids and expulsion of silicon and excess fluorine, followed by removal of all metals except the alkalies and conversion of the remaining sulfates to chlorides. In the Smith method, decomposition of the mineral is effected by heating the powder with a mixture of ammonium chloride and calcium carbonate, whereby complete decomposition is expected and the alkali metals are converted to chlorides which can be extracted by water. In the ordinary case nothing else except much calcium, and the sulfate radical, if present, dissolves. Both of these are easily removable, so that one has finally a solution of the alkali chlorides only. In the analysis of unusual compounds such as borosilicates or complex glasses, other compounds such as borates may dissolve and require special treatments for their removal.

Other methods less used are those in which boric, lead, or bismuth oxide is used as the decomposing agent. The first of these methods and the subsequent procedure are described under Silicate Analysis (p. 848); the others need no specific description. They involve the separation of large amounts of boron, lead, or bismuth from the resulting solutions, but are very useful when paucity of material requires that other metals as well as those of the alkali group be determined in one and the same portion of sample, or when a given mineral will yield to attack by one of them but not by the others. Which to select in a given case may be more a matter of preference than of necessity, or the choice may be determinable by trial. No rule can be laid down.[189]

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[186] The extent of error caused by boron in determinations of alkalies is illustrated by the results 5.01 and 4.73 per cent of Na_2O, as compared with the most probable content 4.15, which were obtained when boron was ignored in a J. Lawrence Smith determination of the alkalies in a glass containing 12.7 per cent of B_2O_3. The data were as follows:

Weight of "Chlorides" When Boron Was Ignored, g	Weight after Treating "Chlorides" with CH_3OH-HCl, g	Weight of Chlorides Probably Present,* g	Most Probable Na_2O Content,* %	Na_2O Content Indicated When Boron Was Ignored, %
0.0486	0.0403	0.0404	4.15	5.01
0.0458	0.0401	0.0403	4.15	4.73

* As found by careful determinations in which all of the known precautions were taken. Errors caused by boron would probably fall entirely on sodium.

[187] J. J. Berzelius, *Pogg. Ann.*, 1, 169 (1824).

[188] *Am. J. Sci.*, [2] 50, 269 (1871); *Am. Chemist*, 1 (1871); *Annal. Chem. u. Pharm.*, 159, 82 (1871).

The method of Berzelius was long the only one in use, but it has now been largely superseded by that of Smith. The Smith method has certain great advantages, of which the most important is that no magnesium accompanies the alkalies into the water solution, and the troublesome and error-inviting separation of that metal and all other metals except calcium is obviated. Most of the boron also remains insoluble as calcium borate. Further, in the Smith method, the precipitation of the large amounts of barium sulfate with the attendant danger of occlusion of alkali salts is not called for. Lastly, the operations, after the mixed sample is ready, are simpler than those of the Berzelius procedure. Hence, the Smith method is now preferred by all who have used both methods, and it is even recommended for silicates that are soluble in hydrochloric acid, especially for those that carry magnesium.

B. THE J. LAWRENCE SMITH METHOD OF ATTACK FOR INSOLUBLE SILICATES AND COLLECTION OF THE ALKALIES AS CHLORIDES

a. *Reagents.* Decomposition of the sample is effected by heating it with its own weight of ammonium chloride and eight times as much precipitated calcium carbonate. The ammonium chloride is best made by slowly subliming the commercial article, dissolving the crusts in water in a platinum dish, filtering if need be, evaporating on the steam bath (not heated by a gas flame), and stirring as the crystals form, in order to keep them small and easy to grind. Pour off the hot liquid, throw the crystals onto a porous filter, and let them dry in the air. Keep the stock in a well-stoppered small bottle.

If calcium carbonate of sufficient purity is not obtainable it is best prepared from pure calcite, by dissolving the calcite in hydrochloric acid, precipitating with pure ammonium carbonate and ammonium hydroxide, and washing thoroughly with hot water. When dried, it should be kept in a

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[189] For the determination of potassium in soils by the cobaltinitrite method, J. E. Gieseking and H. J. Snider [*Ind. Eng. Chem. Anal. Ed.*, 9, 232 (1927)] recommended pretreatment of the soil, followed by the use of a flux containing two parts of sodium carbonate and one part of lithium carbonate, and a fusion temperature between 500 and 600° C.

well-stoppered bottle by itself, not mixed with the ammonium chloride. However obtained, the carbonate is perhaps never free from alkali chlorides, which must be estimated once for all in a blank test in order that a correction may be applied. Eight grams of the carbonate will yield usually 0.0012 to 0.0016 g of alkali chlorides, almost entirely the sodium salt, when platinum vessels are used throughout the test, but the amount has been brought down to half this by very long washing of the precipitated carbonate.

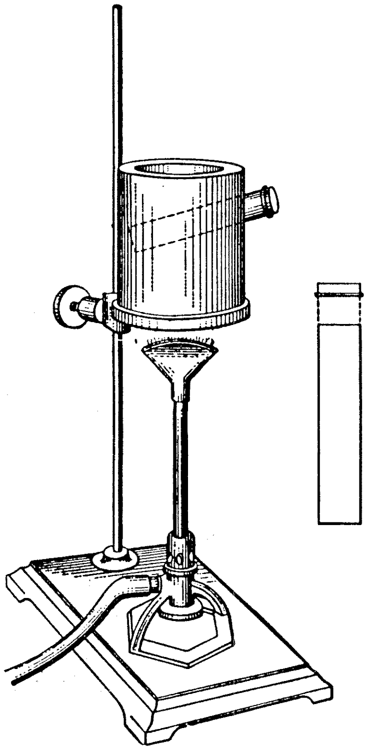

Fig. 44. The J. Lawrence Smith crucible for alkali determinations. For dimensions see text.

This correction is admittedly a defect, but it is one easily applied with safety if the blank was run with care. It is probable that not all the alkali found in the blank test comes from the carbonate, for much hot water is used, and a hot-water bottle, even of the best glass, will afford weighable amounts of alkali to the water it holds.

M. O. Lamar, W. M. Hazel, and W. J. O'Leary [190] point out that better disintegration of the sample is obtained, and less fuming occurs, if a "ball-milled" mixture of calcium carbonate and ammonium chloride is used. This is prepared by adding one part of resublimed ammonium chloride to eight parts of precipitated and washed calcium carbonate, and ball-milling in a porcelain mill with flint balls for 5 hours. Such a mixture is just as effective and has the same blank after storage for 12 months.[191]

b. *Apparatus.* For decomposing the mineral powder the elongated platinum crucible with cap, like that shown in Fig. 44, is the most satisfactory because it permits the use of a higher temperature than any other form of vessel, and hence of obtaining more thorough decomposition of the powder without the need for such very fine grinding of it as may otherwise be required. A crucible of suitable size for treating one-half gram of mineral is 8 cm long, 1.8 cm wide at the mouth, and 1.5 cm at the bottom. For double the amount the dimensions may be 8 cm, 2.5 cm, and 2.2 cm. The weights are 25 and 40 g. Crucibles of nickel having the same shape are now obtainable and are entirely satisfactory, provided the covers fit snugly.[192]

The ignition may, however, be made in a covered crucible of the ordinary shape and of 20 to 30 ml capacity, and this was the practice of the senior author when he first used the Smith method, as indeed it was of Smith himself. In order to utilize a high temperature without loss of alkali chloride by volatilization when using an ordinary crucible, it is necessary to insert it in a hole in a clean asbestos-board shield so that about one fourth projects below the shield.[193] As a further precaution, the cover can be replaced by a closely fitting small platinum dish filled with water.[194]

c. *Treatment of the Mineral Powder.* In a large smooth agate mortar, grind half a gram of the powdered sample (see Preparation of Sample, p. 809) to an impalpable powder,[195] add half a gram of the ammonium chloride reagent, and incorporate the two most intimately by further grinding. Then add in several portions nearly all of 4 g of the calcium carbonate reagent, and mix the whole most thoroughly in the mortar. Line the bottom of the crucible with a little of the carbonate so as to prevent adhesions of the mass to the crucible upon ignition. Transfer the mixture to the crucible by the aid of a somewhat flexible and not too broad-bladed spatula. Use the rest of the carbonate for rinsing mortar and pestle, and transfer the rinsings also. All this should be done over a sheet of glazed paper, preferably black.

If the sample is high in iron, the proportion of carbonate should be increased so as to prevent formation of a too strongly sintered or even melted cake, which is hard to slake. As an aid in producing a well-sintered button, W. P. Echdahl [196] recommends that 1 g of quartz sand be ground in with the sample. The button is then leached, the residue transferred and ground in an agate mortar, and the slurry washed back into the original solution for further slaking.

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[190] *Ind. Eng. Chem. Anal. Ed.*, **7**, 429 (1935).

[191] Mixtures of CaO and $CaCl_2$ are recommended by S. R. Scholes and J. E. Wessels [*Chemist-Analyst*, **25**, 38 (1936); W. Pukall, *Sprechsaal*, **66**, 23 (1933); and D. Japhe, *Sklarske Rozhl*, **14**, 123 (1937)]. E. Makinen [*Z. anorg. Chem.*, 74, 74 (1912)] recommended the use of calcium chloride (melted, crushed, and kept in a well-stoppered bottle) instead of the mixture of ammonium chloride and calcium carbonate, and claimed to get with it a slightly more perfect attack, in consequence of the complete fusion that attends its use. For minerals containing sulfates, R. E. Stevens [*Ind. Eng. Chem. Anal. Ed.*, **12**, 413 (1940)] recommends a mixture of $BaCl_2$ and $CaCO_3$.

[192] A. W. Epperson and R. B. Rudy, *Ind. Eng. Chem.*, **17**, 35 (1925).

[193] Th. Döring, *Z. anal. Chem.*, **49**, 158 (1910); E. Wilke-Dörfurt, *ibid.*, **51**, 755 (1912).

[194] E. W. Morley (private communication).

[195] M. O. Lamar (*loc. cit.*) states that "an impalpable feel" is not a good criterion and points out (1) that comparable disintegrations can be obtained only when samples have been ground to a comparable controlled size and (2) that highly aluminous samples of low silica content (such as fused alumina) must be ground so that *all* of the sample passes a 200-mesh sieve.

[196] *Chemist-Analyst*, 28, 47 (1939).

Cap the long crucible, tap it gently to cause the powder to settle, and place it in an inclined position in a clay cylinder provided with a suitable hole to receive the crucible (Fig. 44) or through a hole in a piece of stout asbestos board clamped at a slight angle. Heat the part within the cylinder or projecting through the board by a fish-tail flame placed considerably beneath and untroubled by drafts, for about 15 minutes or until the odor of ammonia is no longer perceptible. The heat should not be strong enough to cause escape of vapors of ammonium chloride. Replace the fish-tail flame by a burner of the Meker type, raise the temperature to 1000 to 1100° C in the course of 20 to 30 minutes, and then continue the heating for 90 minutes. The sintered or semifused cake usually detaches readily from the crucible or can be made to do so by gentle pressure with a rod. If it does, transfer it to a 5-inch porcelain dish, pour hot water into the crucible, and digest until all remaining matter can be washed out into the dish or until it is thoroughly extracted. Slake the cake in the dish with 1 or 2 ml of water for 10 to 15 minutes, then add 50 ml more, and digest on the steam bath until thoroughly disintegrated. If the cake should not detach from the crucible, the slaking must be done without removing it. When the cake has disintegrated and the solution is saturated with calcium hydroxide, filter by decantation upon a 9-cm filter, and let the filtrate run into a capacious dish, preferably of platinum. Keep as much as possible of the residue in the dish. Add 50 ml more of water, break up any lumps by gentle pressure with a pestle, let settle, and, when the solution is saturated with calcium hydroxide, again decant. Repeat the extraction three or more times, depending on the alkali content of the material. If little or no magnesium is present, wash the residue in the paper and dish with 50 to 100 ml of hot water, otherwise with a saturated solution of calcium hydroxide.

The final residue should dissolve completely in hydrochloric acid without leaving any traces of unattacked mineral, though sometimes a few black particles of iron or other ores, if originally present, will dissolve but slowly. In careful work it is rare indeed that the residue still contains alkalies, in spite of the assertion of some chemists that 1 to 3 mg of alkali are not recovered.[197] The unfavorable results reported may have been due to an insufficient temperature or coarse material, as we have seldom found need for retreatment.[198] In case of doubt, the residual matter should be

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[197] J. W. Mellor, *Quantitative Inorganic Analysis*, pp. 225–47; M. Dittrich, *Neues. Jahrb.*, *2*, 69 (1903); and M. F. Connor, *Congr. Geol. Intern. 12e Sess. Canada*, 885 (1913).

[198] For example, in tests made by J. I. Hoffman, the same results for K_2O and Na_2O were obtained in single and double treatments of a feldspar containing 12.58 per cent K_2O and 2.37 per cent Na_2O, and of refractories containing 1.43 to 2.90 per cent K_2O

dried and mixed with more ammonium chloride but no additional carbonate and the whole treatment repeated. In this case, the water extract of the sintered mass should be carried along separately up to the point at which the last calcium is thrown out.

d. *Removal of Calcium and the Sulfate Ion.* The solution obtained as described contains a large amount of calcium, more or less of any sulfate or borate that the sample may have held, and possibly magnesium if much of it was originally present. In the latter case, to make sure of the removal of magnesium, evaporate the solution to approximately 100 ml, filter, wash the residue with a saturated solution of lime water, treat the filtrate as to be described, and add the residue to the original residue in case this is to be worked over for a possible alkali content.

Remove the calcium by precipitating with ammonium carbonate and ammonium hydroxide at a boiling temperature in a large dish (platinum if possible) which should be kept covered because of the effervescence caused by escape of ammonium carbonate from the hot solution. Filter, wash the precipitate with hot water, redissolve it in little more than enough hydrochloric acid, and repeat the precipitation and filtration. Evaporate the combined filtrates to dryness, carefully drive off the ammonium salts at a temperature short of dull redness, dissolve the residue in 25 ml of water, and throw out the last of the calcium by the addition of a few crystals of ammonium oxalate and a drop or two of ammonium hydroxide. Digest at the side of the steam bath for at least 30 minutes, cool, filter through a small filter, and wash with a 0.1 per cent solution of the oxalate, catching the filtrate in an untared platinum crucible or small dish. Evaporate the liquid to dryness, and ignite the residue at a temperature short of dull redness. Moisten it with a drop of hydrochloric acid to convert to chloride any alkali carbonate that may have been formed by action of the ammonium oxalate during the ignition, and again evaporate, cover with a glass, heat at 110° C for 30 minutes, and then cautiously (and while still covered) continue to heat over a slowly moved free flame until the salts just melt. Cool in a desiccator, and weigh.[199] Dissolve in very little water,

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and 0.36 to 0.89 per cent Na_2O; H. B. Knowles obtained similar results with a soda-lime glass containing 16.63 per cent Na_2O and 0.04 per cent K_2O. In analyses of a diorite, however, he obtained 3.55 per cent K_2O by a single, and 0.08 per cent more, or a total of 3.63 per cent by a double fusion. For Na_2O, the single treatment gave 4.16 per cent and the double 0.05 per cent more or a total of 4.21 per cent. It should be noted that the cake formed with high-alumina refractories is hard to disintegrate.

[199] It is difficult to drive out all NH_4Cl from large amounts of the alkali chlorides without also volatilizing the alkalies. In such cases it is better to dissolve the weighed chlorides in water and again evaporate, ignite, and weigh. The ignition should not be carried beyond 500° C. KCl volatilizes slowly from even the semifused state. Lithium chloride is quite hygroscopic, and sodium chloride is slightly so. If appreciable amounts

collect the few tenths of a milligram of fixed residue on a small filter, and wash, catching the filtrate in a 3-inch dish of porcelain.[200] Ignite and weigh the residue in the crucible or dish from which it came in order to arrive at the weight of the chlorides. These treatments do not take care of any magnesium which may have crept through. In case there is any doubt, test should be made, and correction should be applied as described on page 651; this applies to the blank determinations as well.

If the sample contains sulfur, this will be found in part if not wholly with the chlorides as sulfate. Therefore, if at all large, it must be removed by a suitable amount of a 10 per cent solution of barium chloride (one drop is often more than enough) before the second precipitation of the calcium. The excess of barium added is then to be removed by ammonium carbonate and the last of the calcium by ammonium oxalate as above. If the sulfur is not thus removed, the weight of the chlorides will be slightly in excess, and there is danger if not certainty of sodium sulfate contaminating the potassium chloroplatinate later. A faint reaction for sulfate can usually be obtained, anyway, if the evaporations have been made on a water bath heated by gas.

C. THE BERZELIUS METHOD OF ATTACK AND COLLECTION OF THE ALKALIES AS CHLORIDES

a. *General Considerations.* For treatment by the Berzelius method with hydrofluoric and sulfuric acids, the sample does not have to be so finely ground as a rule as for the Smith method, and most silicates yield to it, that is, to the action of the hydrofluoric acid, the sulfuric acid being used mainly to convert the fluorides and silicofluorides that are formed into sulfates. Among the comparatively few silicates that yield incompletely are andalusite, topaz, and some varieties of tourmaline. Spinel, graphite, and pyrite, which are found in some rocks, are also refractory, but are not silicates and contain no alkalies, and hence may be disregarded if identified. For the first three named, Jannasch recommended to ignite the mineral powder sharply in a platinum crucible, to decompose it with molten ammonium fluoride, to expel the excess of this by heat, and to convert the fluorides

to sulfates by heating with sulfuric acid.[201] For minerals that are completely decomposed by hydrofluoric acid, the attack and first part of the subsequent treatment are as next described, it being assumed that there are elements present that call for all of the operations enumerated, as for instance in silicate rocks. The procedure may be shortened when certain elements are absent, but this condition will seldom arise.

b. *The Attack.* Upon about 1 g of mineral powder in a platinum crucible or small dish, pour about 5 ml of dilute sulfuric acid (1 + 5), mix it with the powder by means of a spatula or stout wire of platinum, add 5 ml of pure concentrated hydrofluoric acid,[202] and evaporate until the sulfuric acid begins to escape. If at this stage gritty particles can still be felt, repeat the evaporation with more hydrofluoric acid until the mineral is wholly decomposed. Then expel most of the sulfuric acid by heating over the radiator (p. 24). The expulsion of fluorine should be thorough, and it may be necessary to add more dilute sulfuric acid and to expel most of it as before. E. Selch [88] brought the residue of sulfates into clear solution with the dilute acid before beginning the second evaporation and claimed thus to effect removal of all fluorine in two treatments.

It is well to bear in mind that, long after every trace of fluorine seems to be gone, so far as the sensitive nose can determine, the formation of a crust on the slowly evaporating solution sometimes allows enough hydrofluoric acid to accumulate to become plainly manifest by its peculiar sharp odor on breaking the crust.

From this point the procedure varies. (*a*) The older analysts did not expel so much of the sulfuric acid as to give rise to the formation of oxides, basic sulfates, or anhydrous sulfates, but kept the residue moist so that, on warming with sufficient water, a clear solution resulted.[203] Some use a little hydrochloric acid to aid solution. (*b*) In order to shorten the time required for the subsequent removal of all but the alkali metals, A. H. Low [204] heated the sulfate residue until fumes of sulfuric acid nearly ceased, and H. V. Krishnayya [205] until they ceased entirely. Thus oxides, or salts

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of lithium are present, the mixed chlorides must be protected from moisture during weighing. Potassium, rubidium, and cesium chlorides are not hygroscopic if pure and properly dried. Traces of impurities, as, for example, magnesium chloride, may increase the hygroscopicity very markedly. G. F. Smith, F. M. Stubblefield, and E. B. Middleton [*Ind. Eng. Chem. Anal. Ed.*, 6, 314 (1934)] point out that more or less water is still retained by mixed chlorides that have been heated at 550° C and that heating should be carried to fusion with precautions to prevent volatilization.

[200] Preferred to platinum because of the possibility under certain undetermined conditions of the formation of an insoluble platinous compound. See also F. Bolm, *Z. anal. Chem.*, 38, 349 (1899).

[201] A. C. Shead and G. F. Smith [*J. Am. Chem. Soc.*, 53, 483 (1931)] recommend fusion with ammonium fluoride for the decomposition of refractory silicates and for the determination of silica, by difference, in glass sands.

[202] In the United States a concentrated and pure acid is obtainable in bottles of ceresin or polyethylene. In lack of this, the crude acid must be distilled from a platinum retort or a blank test made for alkali metals. A slight content of organic matter is not prohibitory as it is when making a ferrous iron determination.

[203] Unless barium or other alkaline earth sulfates show as a white sediment. If they do, they are to be filtered off, washed with cold water, and discarded. Or, if to be used for the determination of barium, either weighed as $BaSO_4$ if pure, or purified if contaminated.

[204] *Chem. News*, 67, 185 (1893).

[205] *Ibid.*, 107, 100 (1913).

of iron, aluminum, titanium, and phosphorus (of the commonly occurring elements) are rendered insoluble in water.

c. *Subsequent Treatment.* α. *Usual procedure.* Once a clear solution has been obtained from the moist residue, the procedure again varies with different analysts. Probably that most used is Bunsen's which as given by Dittrich is substantially as follows when only the alkalies are sought:

Precipitate the sulfate ion by barium chloride solution in slight excess. Without filtering, evaporate the liquid to dryness, take up with a little hot water, and add alkali-free barium hydroxide solution until the reaction is alkaline. In order to render the magnesium more insoluble, again evaporate to dryness without filtering, stir the residue up with water, filter, and wash with a dilute alkali-free barium hydroxide solution.[206] Warm the filtrate, and precipitate most of the excess barium by ammonium hydroxide and ammonium carbonate.[207] Warm for half an hour, filter, wash, evaporate the filtrate to dryness in a platinum dish, and remove the last traces of ammonium salts by gentle ignition. Take up the residue with a little water, treat again with ammonium hydroxide and ammonium carbonate, filter, etc., and repeat all these operations as long as any precipitate of barium carbonate appears. Then evaporate the final filtrate to dryness, moisten the residue with a drop of hydrochloric acid, evaporate, ignite very carefully, and weigh the alkali chlorides, which still may contain a little magnesium as a basic chloride. This last comes from decomposition of the chloride during the preceding ignition. If on solution of the chlorides in a little water any residue is seen, collect, ignite, and weigh it, and deduct its weight

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[206] The removal of magnesium is not perfect, probably because the precipitated hydroxide is redissolved in part by the wash water. It is probable that calcium hydroxide in the form of milk of lime would serve better as a precipitant than barium hydroxide. H. Neubauer [*Z. anal. Chem.*, **43**, 14 (1904)] recommended the following procedure: To the neutral aqueous solution of the chlorides or sulfates in a 125-ml measuring flask, add a drop of phenolphthalein and then so much milk of lime (free from alkalies) that a solution saturated with calcium hydroxide will result. Fill to the mark with water, and mix thoroughly. The solution must still be deep red which shows saturation. After half an hour filter through a dry filter into a dry vessel. Sufficiency of milk of lime is shown by a strong film of calcium carbonate on the liquid, in the filtrate and funnel. To an aliquot taken without regard to the volume occupied by the precipitate, say 100 ml, add oxalic acid, warm, and then add ammonium hydroxide slowly until in slight excess. Let settle for 1 or 2 hours, and filter. If much alkali is present, the precipitate must be dissolved and reprecipitated and the filtrates combined.

[207] To determine the effectiveness of this procedure when appreciable lithium is present, H. B. Knowles made for us three tests on solutions containing 0.0035 g Li_2O, 0.01 g CaO, 0.005 g MgO, and 0.2 g Al_2O_3. He found 0.0036, 0.0036, and 0.0037 g of Li_2O, and that the separated precipitates were spectroscopically free from lithium. He also found that lithium is not carried down by aluminum when the latter is precipitated from a chloride or sulfate solution, or by magnesium when it is precipitated as magnesium ammonium phosphate in cool solution.

from that of the mixed chlorides. Any dissolved magnesium chloride can be determined later and its weight also deducted.

β. *Modified procedures.* Krishnayya, after heating the sulfates until fumes ceased, broke up the crusts, boiled them with a little water for a few minutes, and then, without filtering, followed the usual procedure. His reported results are in excellent agreement with those he obtained by the usual treatment. Low, having carried the heating of the sulfates nearly to cessation of fumes, drenched the residue with a little strong ammonia water and boiled. The products of reaction with the ammonium hydroxides are compact and filter well. When the crusts were well softened and disintegrated, Low filtered, washed with not much hot water, acidified the filtrate with hydrochloric acid, and proceeded as in the usual way, omitting, however, the treatment with barium hydroxide. This omission may be permissible for quick or approximate work, but is hardly justifiable if much magnesium is present or if results of high accuracy are desired, notwithstanding the good agreement of the two comparative determinations given in Low's note.[204]

For the determination of potassium in silicate materials, the sample can be decomposed by attack with hydrofluoric and perchloric acids, the solution heated to fumes of perchloric acid, distilled as in the Willard-Winter method (p. 742) to insure complete expulsion of fluorine, and evaporated to expel water and most of the perchloric acid, and the potassium then precipitated as the perchlorate in anhydrous ethyl acetate solution.[208] Such fluorine as may remain after two evaporations with perchloric acid does not interfere in the triple acetate method for sodium. In this case, the distillation can be omitted and the precipitation made directly in the water solution of the residue obtained after the second dehydration with perchloric acid, which should be stopped when the residue is still moist.

For the determination of alkalies in feldspars, Koenig[209] recommends an initial attack with hydrofluoric acid alone, followed by evaporation to dryness, taking up the residue with water, and treating with calcium oxide to precipitate aluminum, iron, magnesium, fluorine, and residual silicon. After filtration and washing with hot water, most of the calcium is removed by precipitating with ammonium carbonate and filtering, and the remainder by precipitating with ammonium oxalate and again filtering. The filtrate is then acidified with hydrochloric acid and evaporated to dryness, and the residue gently ignited to destroy ammonium salts as usual. In this as in the J. L. Smith method, the weight of the mixed chlorides had better be obtained after treating the residue with a little water, filtering into a

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[208] H. H. Willard, L. M. Liggett, and H. Diehl, *Ind. Eng. Chem. Anal. Ed.*, **14**, 234 (1942).

[209] E. W. Koenig, *ibid.*, **7**, 314 (1935).

weighed platinum dish, washing the residue with hot water, evaporating, igniting until the salts just melt, and cooling.

γ. *Special methods for removing magnesium.* Certain methods aim specifically at the removal of magnesium and are described under Magnesium (p. 633).

D. SEPARATION OF THE ALKALI METALS FROM ONE ANOTHER AND THEIR DETERMINATION

For the separation of the alkali metals from one another and for their determination, see the section on the Alkali Metals (p. 647).

17. Carbon Dioxide, Carbon

A. QUALITATIVE TEST FOR CARBON DIOXIDE

In the preliminary qualitative test for carbon dioxide, it must be remembered that, although calcite gives off its carbon dioxide on treatment with cold acid, dolomite and siderite do not, and hence warming should not be omitted; otherwise a few tenths per cent of carbon dioxide can be overlooked. Moreover, the powder should first be agitated with a little hot water, to remove all enclosed air which might otherwise be mistaken for carbon dioxide. In order not to overlook traces the test should be made in a test tube, by first boiling the powder with a little water, and then cooling and adding dilute hydrochloric acid. If effervescence is immediate, the presence of calcite is assured; if escape of bubbles takes place only on warming, the carbonate is not calcite. In order to make sure of the reaction, it may be necessary to use a pocket lens, holding the test tube in an inclined position and looking down in order better to see the minute bubbles as they stream up along the upper glass wall. It is, of course, important not to mistake escaping hydrogen sulfide for carbon dioxide.

B. QUANTITATIVE TEST FOR CARBON DIOXIDE

For the quantitative determination of carbon dioxide, an apparatus permanently set up is used, of which several forms have been described by different writers. One form is shown under Carbon (p. 769).

In the usual case, place 1 to 5 g of the accurately weighed rock powder in the flask, and cover with hot water. Insert the stopper carrying the separatory funnel and the condenser, and connect the latter with the portion of the chain to the weighed absorber. Force air that is free from carbon dioxide through the system until it is judged that all carbon dioxide has been removed. Close the stopcock in the separatory funnel, and insert the weighed bulb in the train. Half fill the funnel with dilute hydrochloric acid (1 + 1), replace the stopper carrying the air, and see that there is free passage for gases through the train. Open the stopcock in the separatory funnel, and allow acid to flow into the flask, slowly if there is much carbon dioxide, rapidly if there is but little. When effervescence diminishes in the former case, at once in the latter, light the burner, and start the flow of water through the condenser. Keep the flame low, so as to have steady but quiet ebullition, and reduce the current of air, but do not stop it entirely. When it is judged that carbon dioxide has been boiled out, 5 to 10 minutes boiling, remove the heat, increase the air current, and sweep out all carbon dioxide into the weighed bulb. Disconnect and stopper the latter, and stop the current of air. Place the bulb in the balance case. When cool, open the stopper momentarily and weigh against a similar bulb used as a counterpoise.

For the simultaneous determination of carbonates and the carbon of carbonaceous matter see C, below.

It has been shown already under Water (p. 834) how in case of need, as because of paucity of material, the determination of carbon dioxide can be combined with that of water by fusion with lead chromate, provided that free carbon or organic matter is absent. Absorption tubes for carbon dioxide then follow the calcium chloride tube in carrying out the determinations there referred to.

L. H. Borgström[210] called attention to the difficulty of decomposing by hydrochloric acid some minerals that contain carbon dioxide, especially certain scapolites. When these were present he added to the hydrochloric acid 30 ml of a mixture of 1 part strong hydrofluoric acid and 4 parts water. He recommended also to pass hydrochloric acid gas through calcium chloride before use, in order to neutralize any alkalinity it may have and so prevent retention of some of the carbon dioxide by it.

C. CARBON

Fusion with lead chromate is commonly resorted to in order to determine the carbon of graphite or carbonaceous matter in rocks and ores, though boiling in the presence of sulfuric and chromic acids can be made to yield good results.

If carbonates are at the same time present, they can be determined as in B (p. 934), and, by a second determination, as just referred to, the total carbon in both forms can be found as CO_2, whence that of the graphite is derived by difference. Or, according to G. T. Morgan,[211] the carbonates are first decomposed as in B by orthophosphoric instead of hydrochloric acid, whereupon chromic acid is added and the carbon oxidized and determined as CO_2.

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[210] *Z. anal. Chem.*, **53**, 685 (1914).

[211] *J. Chem. Soc.*, **85**, 1001 (1904).

A. C. Fieldner, W. A. Selvig, and G. B. Taylor[212] described a procedure for determining the carbon and hydrogen of combustible matter in shales, clays, and limestones, which seems to afford results as satisfactory as could be expected. It does not take account of volatile or soluble components of the combustible matter that might be driven off in the preliminary treatment of the rock. The procedure is as follows:

Place 0.2 to 1 g of the finely ground rock in a 100-ml platinum dish, treat with 15 ml of hydrochloric acid, and heat below the boiling point on the hot plate for 10 minutes. Add 20 ml of hydrofluoric acid, and heat at *incipient* boiling until the inorganic matter is decomposed. From ½ to 2 hours are usually required, and the volume of the liquid must be maintained above 15 ml by addition of hydrochloric and hydrofluoric acids in the proportion of 3 to 4 from time to time. When the decomposition is complete, evaporate the solution to a volume of 15 ml, add 25 ml of hydrochloric acid, and heat to boiling. Add an equal volume of hot water to the boiling solution, again heat to boiling, and filter while hot, through a filter of ignited asbestos or platinum sponge. Wash with hot water until free from chlorides. Transfer the filter and residue to a porcelain or platinum boat, dry for 2 hours at 105° C, and transfer directly to the combustion tube (see Carbon, p. 773) so that no moisture may be reabsorbed. Determine the percentage of carbon and hydrogen in the usual manner.

18. Chlorine

A. CONDITION IN ROCKS

Chlorine may exist in rocks in a water-soluble condition, in minerals that are decomposed by nitric acid, and in those not attacked by this acid. In the first form, it doubtless exists as infiltrated sodium chloride or as original inclusions in one or more of the constituent minerals; in the second, in minerals of the sodalite group and sometimes apatite; in the last, chiefly in the scapolites. Where a qualitative test shows the water-soluble form to be present in determinable amount, it must be extracted separately and the amount found deducted from the total as determined in a second portion. Sometimes it may be possible to use the extracted material for the determination of the rest of the chlorine.

B. DETERMINATION OF WATER-SOLUBLE CHLORINE

A suitable amount, which may be several grams, of the powder is extracted with water. Very often the filtrate is turbid, a condition that may sometimes be prevented by using double filters or by adding some chlorine-free salt, like sodium nitrate, to the wash water. If the filtrate remains persistently cloudy, the precipitation of silver chloride may be proceeded with as usual, after acidifying with nitric acid. It is best to let the precipitate settle overnight in order to obtain a clear filtrate on the morrow. It is collected on a small filter, washed with water acidified with nitric acid, dried, and ignited in a very small porcelain crucible without allowing the paper to burst into flame. Most of the chloride will be reduced to metal. On disappearance of all carbon, a drop of nitric acid is added and evaporated, then similarly a drop of hydrochloric acid, and the crucible heated gently, but not to fusion of the silver chloride, and weighed. The chloride is then dissolved in a few drops of warm ammonia water and separated by filtration from the siliceous matter, which latter is ignited and weighed in order to get the weight of the chloride.

This method of procedure is permissible even when the original aqueous extract was quite clear, though the operation then stops with the weighing of the chloride. Or, if very small in quantity, the dry paper with its contents is wound up in a tared platinum wire and carefully ignited after Bunsen's manner. The increased weight of the wire is due to the metallic silver of the chloride which has alloyed with the platinum.

C. DETERMINATION OF ACID-SOLUBLE CHLORINE

a. *By Nitric Acid.* If nitric acid will decompose the chlorine-bearing minerals, or if it is desired to distinguish between the chlorine in soluble and in insoluble minerals, the rock powder may be boiled for a few minutes with dilute chlorine-free nitric acid. The acid should be very dilute in order to cause no loss of chlorine, and the boiling should be as brief as possible for the same reason and also to prevent gelatinization of the silica from soluble silicates. Acid as dilute as 1 + 40 will decompose apatite readily and probably the minerals of the sodalite group, but it is doubtful if anything like this dilution is called for.

The filtrate does not require evaporation for the removal of dissolved silica but may be precipitated at once with silver nitrate. The precipitate is treated as in B, or, if at all appreciable in amount, may be collected on a Gooch crucible.

b. *By Nitric and Hydrofluoric Acids.* In many cases, in order to obtain all the chlorine, it is sufficient to attack the powder (which must be much finer usually than the coarse bulk sample) by chlorine-free hydrofluoric and nitric acids in the cold, with occasional stirring, and, after filtering through paper fitted into a rubber funnel or large platinum cone, to throw down the chlorine by silver nitrate. The presence of nitric acid is necessary, since, in its absence, ferrous iron in the presence of fluorine reduces silver nitrate with deposition of crystallized silver. It may be advisable to redissolve the chloride on the filter in ammonia and to reprecipitate by nitric acid and a drop of silver nitrate.

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[212] *Bur. Mines Tech. Paper* 212, 1919.

D. DETERMINATION OF CHLORINE BY ALKALI FUSION

Chiefly because of the difficulty just mentioned, in order to make sure of getting all the chlorine, it is best to fuse with chlorine-free sodium potassium carbonate, or even sodium carbonate alone, first over the full burner and then for a moment or two over the blast, and to extract the melt with hot water. The solution is then cooled, treated with methyl orange, and just acidified with nitric acid. If the solution is perfectly clear, proceed with the precipitation of the chloride. If the solution is not clear, let it stand overnight. Add ammonium hydroxide in slight excess, boil, filter, and wash the precipitate with hot water. Cool the filtrate, acidify with nitric acid, and proceed with the precipitation of the chloride.[213]

19. Fluorine (Silica in Presence of Fluorine)

A. GENERAL REMARKS

There is no direct qualitative test that will reveal with certainty the presence of fluorine in rocks. Heating the powder before the blowpipe with sodium metaphosphate on a curved piece of platinum foil inserted into one end of a narrow glass tube or in a bulb tube and noting the presence or absence of etching on the glass where water from the flame condenses, after the tube has been dried, is not to be relied on in all cases. Although in some rocks as little as 0.1 per cent of fluorine can be detected thus with ease, in rocks of another class much larger amounts may fail to show.

The same is true of the direct quantitative methods. The result obtained by the Berzelius method is almost certain to be low and may even be negative if very little fluorine is present. For small amounts of fluorine (<10 mg), those who have given most attention to the subject therefore seem to favor indirect determination, for which the method given under C below is satisfactory. The preliminary attack of the rock, and the subsequent treatment, up to a certain point, are alike for both methods, and, since one may be used as a check upon the other, both will be described in detail.

For the reason that most fluorine minerals occurring in rocks are attacked but partly, if at all, by strong sulfuric or perchloric acid, none of the methods depending on volatilization of the fluorine can be used directly without preliminary fusion of the material. With decomposable fluorides or after fusion of the material with sodium carbonate, the fluorine may be distilled, but, if amorphous silica is present, it must be removed (p. 742) or more distillate must be collected than if silica in the form of quartz powder is present (see p. 741). The method generally followed is that of Berzelius in which the material is fused with a mixture of sodium and potassium carbonate, and the fluorine is extracted from the melt with water. This method admits of the determination of silica at the same time. It should be noted, however, that all the fluorine cannot be extracted by this procedure from materials such as phosphate rock which contain fluorine and also large amounts of calcium and phosphate.[214] With such materials, distillation seems to be the only means of separation.

B. DIRECT QUANTITATIVE DETERMINATION OF FLUORINE

a. *Method of Berzelius.* α. *Procedure.* Fuse 2 g of the rock powder with 4 or 5 parts of sodium potassium carbonate free from fluorine, avoiding the use of a blast if possible (see Fluxes, p. 847). For minerals rich in fluorine and low in silica, it may be necessary to add pure silica before fusing in order to effect complete decomposition of the fluoride, just as with the alkaline earth phosphates. But probably this will never be required in ordinary rock analysis. Extract the melt with 100 ml of water, filter, and wash the residue with hot water. If the highest accuracy is desired, or the amount of fluorine is large, reserve the insoluble residue, and ignite it together with the precipitates obtained with ammonium carbonate and zinc oxide. To the aqueous extract, containing the fluorine and usually much of the silica besides other bodies, add 2 to 5 g of ammonium carbonate, digest the liquid at a gentle heat (40°) for some time, and, on cooling, introduce more carbonate.[215] After 12 hours, collect the precipitate, and wash with water containing ammonium carbonate. From the filtrate expel the excess of the latter by evaporating nearly to dryness, and bring the somewhat diluted solution toward neutrality as follows, according to the directions of Treadwell. Add a few drops of phenolphthalein, and then nitric acid (not hydrochloric in this case, see below) until the red color disappears. Boil the solution, cool, and again discharge the color by acid as before. Repeat these operations until it requires but 1 to 1.5 ml of 2 *N* acid to discharge the color. Now add 1 to 2 ml of an ammoniacal solution of zinc carbonate,[216] and boil the liquid till the ammonia is wholly expelled.

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[213] According to E. Wilke-Dörfurt [Z. *angew. Chem.*, 40, 1478 (1927)], the iodine in rocks can be distilled off as I_2 or HI by treating the powdered rock with H_2SO_4 in an all-glass apparatus and heating for 3 hours at 220 to 230° C as a stream of air is bubbled through the liquid.

[214] D. S. Reynolds and K. D. Jacob, *Ind. Eng. Chem. Anal. Ed.*, **3**, 366 (1931); and J. I. Hoffman and G. E. F. Lundell, *J. Research NBS*, 20, 607 (1938).

[215] The use of ammonium nitrate or chloride, instead of carbonate, for throwing out the silica and aluminum is not to be recommended because of loss of fluorine on subsequent evaporation (H. Rose).

[216] Made by dissolving zinc oxide in a solution containing ammonium hydroxide and ammonium carbonate. If the rocks are very basic, it may happen that the amount of silica in the alkaline solution of the fusion is so small that ammonium carbonate may be dispensed with for its precipitation and the zinc oxide solution added at once, after neutralizing as above. The smaller the excess of zinc that is used, the better. Instead of the ammoniacal zinc oxide solution F. Seemann [*Z. anal. Chem.*, **44**, 343

The precipitate contains the last of the silica and some phosphorus, in addition to that thrown down with alumina by ammonium carbonate. Filter, and wash with a 2 per cent solution of potassium nitrate.

The above prescribed use of nitric instead of hydrochloric acid for neutralizing is necessitated by the fact that phosphorus, which is almost invariably present, and chromium, must still be removed, and this can be done only from a nitric solution, as follows: To the still alkaline solution, add silver nitrate in excess, whereby phosphate, chromate, chloride if chlorine is present, and hydroxide or carbonate of silver are precipitated. The last serves to correct any acidity resulting from the reaction between the alkaline phosphate and the silver salt, thus producing the neutral solution needed for complete precipitation of the phosphate and chromate.

Heat slightly, filter, wash the precipitate with a little water, and remove the excess of silver by adding sodium chloride, warming, filtering, and washing with a little water. Add 2 ml of a 2 *N* solution of sodium carbonate,[217] evaporate to reduce the volume of the solution to 100 ml, and filter if necessary. Add 15 ml of a 20 per cent solution of calcium chloride, $CaCl_2 \cdot 6H_2O$ (enough for 0.1 g of fluorine), drop by drop to the hot solution, heat near the boiling point for a few minutes, and cool the solution. At this stage there must be no ammonium salts in solution; otherwise calcium fluoride may be held up. Filter through an ashless paper, wash moderately with water, and dry the paper and contents at 110° C.

Transfer the residue as completely as possible to a 100-ml platinum dish, burn the paper in a platinum spiral, and transfer the ash to the dish.[218] Add

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(1905)] advocated Schaffgotsch's solution (*U. S. Geol. Surv. Bull.* 700, p. 213) in which has been dissolved, in the cold, 20 g of freshly precipitated mercuric oxide to the liter. For every 0.2 g of dissolved silica, 100 ml of this reagent are to be used. The solution is then to be evaporated to complete dryness, the residue taken up with water, filtered, and washed, the filtrate again neutralized with hydrochloric acid (nitric in rock analysis —W. F. H.) and again evaporated, after the addition of 20 ml of the reagent, to remove the last of the silica. Where silica is to be determined at this stage, this reagent has the advantage over the zinc solution that direct ignition of the precipitates (under a good draft hood) yields silica at once. Its use is manifestly allowable in rock analysis only after the alumina has first been separated by ammonium carbonate.

[217] The coprecipitation of calcium carbonate and calcium fluoride originated with H. Rose, *Ann.*, 72, 343 (1849). G. Starck and E. Thorin [*Z. anal. Chem.*, 51, 14 (1912)] preferred to add a known amount of oxalate and then calcium chloride in excess, in order to get a precipitate that is less soluble and more easily filtered. The weighed precipitate is then corrected for the amount of calcium oxalate that is equivalent to the amount of oxalate added. In our hands the method has proved much more difficult to carry out than would be expected from the literature on the subject.

[218] If the dish used for the precipitation was of platinum, it is not necessary to cleanse it from adhering precipitate, but the contents of the filter are washed back into the dish, and the liquid in this is evaporated and the ash of the filter added.

10 ml of water and then a 10 per cent solution of acetic acid until effervescence ceases.[219] Evaporate on a hot plate until the odor of acetic acid is gone, and then continue the heating for 30 minutes to convert the calcium fluoride to the granular form. Treat the residue with 10 ml of water, and stir to dissolve the calcium acetate. Decant the solution on an ashless filter, wash the residue with 10 ml of water, and then collect it on an ashless filter by the aid of very small portions of water. Continue the washing with small portions of water until no turbidity is obtained with a solution of sodium fluoride. Transfer the paper and precipitate to a platinum crucible, dry, and ignite at a low heat until carbon is gone and then at 800 to 900° C to constant weight.[220]

The amount of fluoride obtained from rocks being usually very small, a single treatment as above suffices, but, for the larger amounts obtained from fluorine minerals, a second and even third treatment with acetic acid may be needed, filtering and igniting after each. S. L. Penfield and J. C. Minor [221] found in such cases that, if a great excess of acetic acid is used at the start, the results are lower than by the repeated treatment. For considerable amounts, when the loss between two treatments is reduced to not more than half a milligram, F. P. Treadwell and A. A. Koch [222] took the next to the last weight as correct.

β. Testing of the calcium fluoride. The well-washed and gently ignited calcium fluoride finally obtained in the course of this method should be converted to sulfate as a check on its purity, and at the same time as a qualitative test to ascertain if it really is calcium fluoride by the characteristic odor of the gas given off. Should fluorine be found, and the weight of sulfate not correspond to that of the fluoride, the sulfate should be dissolved in hot nitric acid and tested for phosphorus by ammonium molybdate solution. If phosphate is absent, the impurity may have been silica or calcium silicate—which of these it would be difficult to decide. In the former case the fluorine might be safely deduced from the weight of the sulfate, but not in the latter. If the rock were rich in sulfur, it might happen that calcium sulfate would be thrown down with the fluoride, but this should be removed by thorough washing. If not, and it were certainly

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[219] Ten milliliters of a 10 per cent solution of acetic acid dissolve approximately 1.5 mg of pure freshly precipitated calcium fluoride, but the amount is considerably less than this in the presence of the calcium acetate that is formed when a mixture of calcium fluoride and carbonate is treated. Approximately 1.6 mg of calcium fluoride are dissolved by 100 ml of water.

[220] Whenever pure calcium fluoride has been ignited, it is desirable to treat the residue with hydrofluoric acid and again ignite.

[221] *Am. J. Sci.*, [3] 47, 389 (1894).

[222] *Z. anal. Chem.*, 43, 469 (1904).

the only impurity present, the fluorine, x, could be calculated, after conversion of the fluoride into sulfate, by the formula

$$(CaSO_4 - CaF_2):2F::(b - a):x$$

in which b is the weight of the sulfate after conversion and a that of the impure fluoride.

It is an exceptional case when there is exact agreement between the weight of fluoride and of sulfate, and, with the small amounts usually found in rocks, the error may be an appreciable one in percentage of fluorine, though of no great significance otherwise.

γ. *Accuracy of the method.* It is evident from the above that, if the greatest care is not taken to prevent any kind of contamination of the weighed fluoride, the error in the small amounts in question may be very great. If phosphate were present, it would not do to apply the check by conversion to sulfate, because the evaporation with sulfuric acid, following ignition, would volatilize metaphosphoric acid.

There is another source of error due to the solubility of the fluoride itself in water and acetic acid. F. P. Treadwell and A. A. Koch[222] investigated the solvent effect of these and some other reagents. They found that it is possible to detect additional fluorine by repeating the precipitation with calcium chloride in presence of sodium carbonate, and that the total errors are such that, for 5 mg of CaF_2 or less, the results are much too low, though the qualitative detection still can be made in 100 ml of solution with only 0.0009 g of CaF_2, notwithstanding the fact that the quantitative tests had seemed to indicate that the loss would be about 0.0015 g of CaF_2 for every 100 ml, including wash water. It thus appears that, with 1 g of sample, amounts of less than 0.04 to 0.05 per cent of fluorine will escape observation entirely.

A source of error not generally known arises whenever calcium fluoride is ignited in contact with paper. Fluorine escapes to a slight extent and is replaced by oxygen, this reaction being doubtless due to the action of water vapor and not to oxygen of the air.

F. Seemann[223] subjected all the known methods of determining fluorine to extended examination, using calcium fluoride as his test material, and declared the Berzelius method to be far inferior to those based on volatilization of the fluorine as silicon fluoride, by reason of great and varying losses, the causes of which he was unable to trace satisfactorily. He was unable to recover by it more than about 87 to 89 per cent of the fluorine. Tests made by us, confirmed by other workers, do not support his very unfavorable results. From 95 to 98 per cent of the fluorine was repeatedly regained. To do so requires, however, refusion of the residue left after leaching the alkali carbonate melt, including in the same refusion the silica precipitated by ammonium carbonate and ammoniacal zinc oxide, the treatment of the filtrate from the precipitate of calcium carbonate and calcium fluoride with additional sodium carbonate and calcium chloride, and the re-evaporation of the acetic acid solutions of the precipitated calcium carbonate.

b. *Determination of Silica in the Method of Berzelius.* Treat the several precipitates obtained by ammonium carbonate and zinc carbonate, together with the residue from the original alkaline fusion, as follows: Before assembling the precipitates in one solution to be treated as described under Silicon (p. 860), remove the zinc derived from the zinc oxide solution as follows: Evaporate the precipitate containing it to complete dryness with nitric acid, take up with nitric acid, filter, wash the silica, and unite it with that obtained by dissolving the other precipitates in hydrochloric acid and treating the solution by the regular method for silicon (p. 860).[224]

If, as is the usual case, a complete analysis of the mineral or rock is being made, it becomes necessary to recover by the molybdate method (Phosphorus, p. 699) and determine the phosphorus that may be in the zinc nitrate solution and also the phosphorus and chromium that may be in the filtrate from the zinc silicate. The chromium in most cases can best be determined colorimetrically (Chromium, p. 531), and then, from the same solution made acid with nitric acid, the phosphorus can be precipitated by ammonium molybdate and determined. The joint weight of the chromium calculated as Cr_2O_3 and the two recoveries of phosphorus counted as P_2O_5 is to be added to the weight of the composite precipitate produced by ammonium hydroxide in the regular course of analysis of the precipitates referred to in the foregoing paragraph.

c. *Method of Hoffman and Lundell.*[225] In the following method for the determination of silica and fluorine in fluorine minerals, the silica is separated by a modification of the Berzelius method that is more rapid and is fully as accurate, and the fluorine is then precipitated as lead chlorofluoride and determined volumetrically by a modification of the method originally proposed by Starck.[226] The precipitate is titrated instead of weighed because contaminants have no effect unless, as is not likely, they contain chlorine.

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[223] *Ibid.*, **44**, 343 (1905).

[224] A weakness of the method lies in a slight retention of fluorine by the precipitate which subsequently causes a slight loss of silica when the precipitate is dissolved in acid and the solution is evaporated to dehydrate silica. This is especially true and may be quite serious with materials like phosphate rock which contain large amounts of calcium and phosphate (see p. 939).

[225] *Bur. Standards J. Research*, 3, 581 (1929).

[226] G. Starck, Z. *anorg. Chem.*, 70, 173 (1911).

PROCEDURE. Fuse 0.5000 g[227] of the dried sample with 5 g of sodium carbonate, leach the cooled melt with hot water, and filter when disintegration of the melt is complete. Reserve the filtrate *A*. Transfer the insoluble residue back into the dish by the use of a jet of water, add 50 ml of a 2 per cent solution of Na_2CO_3, boil for a few minutes, filter, and wash the residue thoroughly with hot water.[228] Reserve the residue *B* for the determination of silica, and combine the filtrate with the reserved filtrate *A*. To the combined filtrates, which should have a volume of approximately 300 ml, add a solution of 1 g of zinc oxide in 20 ml of dilute nitric acid $(1 + 9)$. Boil the solution for 1 minute, filter, and wash the residue thoroughly with hot water. Reserve the residue *C* for the determination of silica. Add a few drops of methyl red to the filtrate, nearly neutralize with nitric acid, and evaporate to a volume of 200 ml, taking care that the solution remains alkaline throughout the evaporation. Cool somewhat, add dilute nitric acid $(1 + 1)$, dropwise until a very faint pink color just appears. Treat with 1.0 g of zinc oxide that has been dissolved in ammonium hydroxide with the aid of a little ammonium carbonate, and boil in a covered dish (preferably of platinum) until the odor of ammonia can no longer be detected. This usually requires concentration to about 50 ml. After the ammonia has been expelled, add about 50 ml of warm water, stir, allow to settle for a few minutes, and filter. Wash the residue *D* with cold water. Reserve the filtrate *E*.

α. Silica. With the aid of a jet of dilute hydrochloric acid $(1 + 20)$, transfer the residues *B*, *C*, and *D* from the papers to the vessel in which the last precipitation was made. Ignite all papers, and add any residue so obtained to the contents of the vessel. Add 25 ml of hydrochloric acid, and determine silica by double evaporation and intervening filtration as described under Silicon (p. 860). In the second dehydration, it is advisable to add 10 ml of sulfuric acid and to evaporate to fumes, because it is difficult to dry zinc chloride in the absence of appreciable amounts of silica. A small amount of silica (usually less than 1 mg) remains in solution and can be recovered as follows: Add about 0.04 g of aluminum as aluminum chloride and 10 g of ammonium chloride to the filtrate obtained after the second dehydration. Heat to boiling, precipitate with ammonium hydroxide, and filter. Dissolve the precipitate in 50 ml of dilute sulfuric acid $(1 + 10)$, evaporate to fumes of the acid, dilute, filter, and add the small residue to the silica already obtained.

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[227] The size of the sample should be so governed that the amount of fluorine in solution lies between 0.01 and 0.1 g.

[228] This treatment of the insoluble residue aids in the complete extraction of fluorine. It can be omitted if it is intended to ignite the residue together with the first zinc precipitate and again fuse with sodium carbonate.

β. Fluorine. Treat the reserved filtrate *E* as described under Fluorine (p. 744).

d. *Other Direct Methods for Fluorine.* For other methods for the ultimate determination of fluorine in minerals that are decomposed by concentrated sulfuric acid—fluorides and fluophosphates—as well as for fluorides soluble in water, see the chapter on Fluorine (p. 742).

C. INDIRECT QUANTITATIVE DETERMINATION OF SMALL AMOUNTS OF FLUORINE

a. *Steiger's Method.* The indirect method[229] for the determination of fluorine devised by George Steiger in the laboratory of the Geological Survey has met with much favor, although it is not suited for large amounts.

It is based on the well-known fact that fluorine has a powerful bleaching effect on the color that is produced when a solution of titanium is treated with hydrogen peroxide. A solution of definite volume is made, containing the fluorine to be estimated and a known amount of titanium; this is compared in a colorimeter with a second solution, containing an equivalent amount of titanium per milliliter, and the bleaching effect is recorded. From the extent of this bleaching, the percentage of fluorine can be calculated.

Although the results obtained are not so accurate as those given by many methods for the estimation of other elements, yet considering the difficulty of the fluorine determination, and the time and labor required by methods now in use, the indirect method may well be employed, where small quantities of fluorine are to be determined. The operations not only require less skill to carry out but also are fewer in number and take much less time.

Traces of fluorine amounting to several hundredths of 1 per cent are easily detected, and an approximation to the quantity can be made. In amounts up to a few tenths of a per cent, this method seems to be more reliable, and, if not more than 2 per cent is present, the results compare favorably in accuracy with the standard methods. It is hardly to be expected, however, to find a colorimetric method, in which only a few milligrams of the material are used, that will compare in accuracy with gravimetric methods in which larger amounts of sample are used and considerable percentages of fluorine are concerned.

Sodium salts in large amount make the observed reading for the titanium somewhat low[230] but not enough to affect the results seriously. Silica in amounts up to 0.1 g has but little effect, and, by the treatment employed, its amount is reduced to at most 2 or 3 cg. Alumina, which exerts a marked effect, even in small quantities, is readily removed by the preliminary treat-

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[229] *J. Am. Chem. Soc.*, 30, 219 (1908).

[230] H. E. Merwin, *Am. J. Sci.*, [4] 28, 119 (1909).

ment. Phosphoric acid, which bleaches like fluorine, does not interfere unless present in larger amounts than are likely to be encountered in rock analysis.

b. *Merwin's Modification of Steiger's Method.* *α. Introductory remarks.* Merwin, in the paper just cited, not only defined the effect of alkali salts but also showed that the concentration of the acid as well as the temperature affects the color of titanium solutions peroxidized by hydrogen peroxide. The salts cause bleaching, whereas addition of acid counteracts this effect to a considerable degree. Merwin's statements were confirmed by tests made by William Blum at the Bureau of Standards. Steiger's observations on the effect of compounds other than alkali salts were in general accord with those of Merwin. Blum further observed that, with little acid present, the color of the standard and of the bleached test solution cannot be matched under certain conditions. This was so, for instance, with 3 mg of fluorine and 2 per cent sulfuric acid, but, with 10 per cent acid, a fairly satisfactory comparison was possible with as much as 5 mg of fluorine.

Merwin gave formulas for computing fluorine in the presence of known amounts of alkali sulfates and acid and modified accordingly the previous methods of getting the fluorine into final solution.

PROCEDURE. Fuse 2 g of rock powder with 8 g of mixed sodium and potassium carbonates, and take up the fusion with hot water. When leached, and without the necessity for filtering, add 3 or 4 g of powdered ammonium carbonate. Warm the mixture for a few minutes, and then heat on the water bath until the ammonium carbonate is destroyed and the bulk of the liquid is small. In this way the silica, which otherwise might render the final solution turbid, is thrown down, together with the disturbing alumina and ferric oxide. The destruction of the ammonium carbonate is necessary because ammonium sulfate bleaches the final solution. Filter, and add to the filtrate—which should not exceed 75 ml in volume—3 or 4 ml of hydrogen peroxide, and then cautiously 10 ml of standard titanium solution [231] (containing 0.01 g of TiO_2). Including the acid in the titanium solution, about 3.5 ml of strong sulfuric acid are required to be added to neutralize the alkali carbonates. As soon as neutrality is reached, the solution acquires a light orange color. Test for neutrality by adding a little sodium carbonate solution to discharge the color, and then a drop or two of acid to restore it. The further treatment depends upon the amount of fluorine expected and the type of colorimeter used. The amount of acid to be added to the neutralized solution depends upon the amount of fluorine present. Therefore, add first 3 ml of concentrated sulfuric acid, make the solution up to 100 ml at a temperature of about 22°, and compare at the same temperature with a 100-ml solution containing 0.01 g of TiO_2, 4 ml of H_2O_2, and about 3 ml of concentrated sulfuric acid. The fluorine content of the test solution can then be read off on the curves in Fig. 45. If the ratio is greater than about 0.40, the amount of fluorine can be read off accurately. For smaller ratios (more fluorine), more acid should be added to the test solution, a new color comparison made, and a new reading taken from the chart.[232] The chart is made on the assumption that the alkali sulfate corresponds to 8 g of the half-and-half mixture of potassium and sodium carbonates, or 7 g of sodium carbonate, used in the fusion. The chart shows, on the zero line of fluorine, the average color ratio for 8 g of carbonates. The carbonates used for the fusion should be tested in the

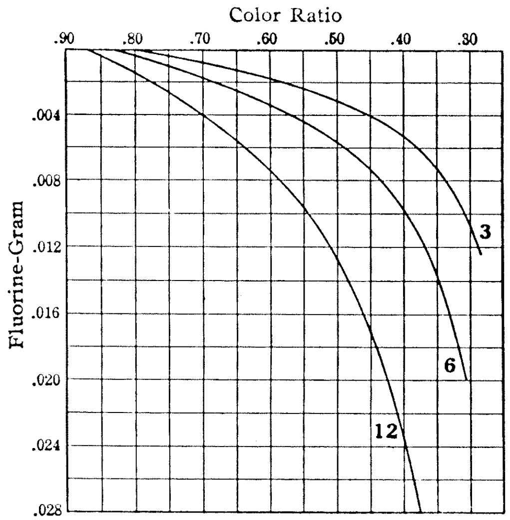

FIG. 45. Merwin's diagram for fluorine. Color ratio $= \frac{\text{depth of standard solution}}{\text{depth of test solution}}$. Each solution is peroxidized and made up to 100 ml and contains 0.01 g of TiO_2. The test solution contains the number of millimeters of concentrated sulfuric acid indicated by the numbers near the curves, and the amounts of fluorine shown, besides sulfates equivalent to 4 g each of sodium and potassium carbonates. The standard solution contains an indefinite amount of acid between 3 and 5 ml. The chart was made at 22°, but it is not significantly different at any temperature between 19 and 25° if both solutions are at the same temperature. If the test solution is 5° warmer than the standard, the curves are displaced toward the left hand about 0.02 for 12 ml of acid, and 0.01 for 3 ml of acid. The total color of the solutions is not significantly affected by 10 per cent change of water content.

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[231] The hydrogen peroxide prevents the precipitation of the titanium by the alkali carbonate.

[232] For certain forms of colorimeter, a correction corresponding to the increased volume of the test solution must be made.

same way as the filtered solution for the fluorine test. These ratios will probably not differ more than 0.03 from those on the chart. This difference represents about 0.5 mg of fluorine, which is about the limit of accuracy of the method for amounts of fluorine below 0.006 g. At about 0.025 g, this limit is about 0.002 g.

It is very evident that the analyst must take into account the amounts of alkali salts and of acid and must always take his readings at about the same temperature. Anyone who has frequent occasion to determine fluorine in this indirect way should prepare diagrams indicating the corrections to be made under his own conditions of operation.

H. J. Wichmann and Dan Dahle[283] have modified and improved the Steiger-Merwin procedure. They used a photometer for making their measurements and determined more exact data on the optimum *p*H for the development of the color. They also give the influence of interfering elements, such as aluminum, phosphates, and alkali sulfates.

L. A. Steinkönig[284] determined the fluorine in a number of soils by a slight modification of the Merwin procedure. The amounts found were as high as 0.05 per cent. The method as used "is not delicate enough to indicate with certainty the presence of 0.01 per cent of fluorine," but even so it is a great advance over the gravimetric method for such small quantities.

20. Sulfur

A. DETERMINATION OF THE CONDITION OF SULFUR IN ROCKS

Before proceeding to the determination of sulfur, when it is present, its condition should be ascertained, both by microscopic identification of the sulfur-bearing minerals, when this is possible, and by qualitative tests. The importance of a microscopic examination cannot be too strongly emphasized, for it may give the analyst most useful information.

Evolution of hydrogen sulfide on boiling with dilute hydrochloric acid is evidence of a soluble sulfide, usually pyrrhotite, but possibly lazurite. Extraction of magnetic particles reacting for sulfur shows pyrrhotite to have been in part at least the source of the hydrogen sulfide. A reaction for sulfuric acid in the filtered solution indicates a soluble sulfate, usually a silicate sulfate, noselite, or haüynite. If the residue, when well washed and treated with aqua regia or hydrochloric acid and bromine, gives more sulfuric acid, the probable presence of pyrite is shown. Should this solution likewise show arsenic, the sulfide may be arsenopyrite, which, however, is found very rarely if ever in igneous rocks.

It is most uncommon to find any sulfur in rocks in the ordinary simple sulfate condition, except sometimes water-soluble traces, even when considerable pyrite is in evidence. The barium of fresh and even moderately decomposed rocks is apparently always in silicates and not in combination with sulfur.

In mineral analysis it is desirable to avoid an alkali fusion whenever possible, but it must not be overlooked that direct treatment of the mineral with hydrochloric acid or oxidizing agents will extract certain amounts of salts, one or another of which may be fatal to the attainment of acceptable results.

B. QUANTITATIVE DETERMINATION IN ROCKS

a. *Total Sulfur.* Before proceeding with the quantitative determination of sulfur, consult the chapter on Sulfur (p. 711).

In rocks, sulfur is not often present in large amounts; hence special precautions in making the precipitation or special purification of the barium sulfate are hardly ever necessary, especially as the precipitation is usually made in the absence of iron.

Although sometimes the sulfur of sulfides may be extracted wholly with aqua regia or some other powerful oxidizer, in the wet way, this is not always so. Therefore it is generally better by far to fuse with sulfur-free sodium carbonate and a little niter over the Bunsen burner, and for a few moments over the blast, using throughout the heating the arrangement shown in Fig. 6 (p. 25), in order to prevent access of sulfur from the flame gases. This determination may be combined very conveniently with that of barium, titanium, zirconium, and rare earths (p. 888). After thorough disintegration of the fusion in water, to which a drop or two of alcohol has been added for the purpose of reducing and precipitating any manganese dissolved as manganate, the solution is filtered and the residue washed with a dilute solution of sodium carbonate. In the filtrate (100 to 250 ml in bulk) the sulfur is precipitated at boiling heat or on the steam bath by barium chloride in excess, after slightly acidifying in the cold by hydrochloric acid. Evaporation to dryness first with acid, in order to eliminate silica, is needless, for, in the above bulk of solution, there will almost never be the least separation of silica with the barium sulfate.[285] It is well that this is so, for evaporation on a bath heated by gas, in order to remove silica, would involve in many cases an error fully equal to the sulfur present, by contamination from the sulfur of the gas burned. With a steam bath, this difficulty does not present itself. Should there be fear

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[283] *J. Assoc. Offic. Agr. Chemists*, **16**, 612 (1933); **20**, 505 (1937).

[284] *J. Ind. Eng. Chem.*, **11**, 463 (1919).

[285] The results of C. W. Stoddart [*J. Am. Chem. Soc.*, **24**, 852 (1902)] showed, in the determination of sulfur in coals by the Eschka method, often higher sulfur when silica is not removed by evaporation in the usual way, but this is contrary to all our experience in silicate work, where duplicates agree usually exactly, and, if they differ, are as likely to be high by one way as by the other. The explanation may be that Stoddart acidified his solutions hot or used too strong an acid and had some silica precipitated.

of a trace of silica being present, it can be removed by a drop of hydrofluoric and sulfuric acids before the barium sulfate is weighed.

In order to reduce greatly the error caused by the presence of sodium chloride resulting from the sodium carbonate used in the fusion, W. A. Turner[236] reduced the solution to a small volume (25 cm), saturated it with hydrochloric acid gas, or added concentrated hydrochloric acid (five times the volume of the solution concentrated to 10 ml), filtered through a Gooch crucible, washed the precipitated sodium chloride with strong hydrochloric acid, evaporated the filtrate, filtered again if necessary, and precipitated with barium chloride.

Errors due to the solvent action on the barium sulfate of hydrochloric acid or of ammonium or fixed salts in the solution can usually be corrected by evaporating the filtrate from the barium sulfate, destroying or expelling ammonium salts if present, treating the residue with water slightly acidified with hydrochloric acid, and collecting and purifying the barium sulfate that may be left undissolved.

b. *Fractional Determination.* When sulfur is present in more than one condition, it is usually desirable to know the respective amounts; hence fractional determinations must be made.

If traces of sulfates soluble in water are present, they can be removed by extraction with boiling water.

For the quantitative extraction of the sulfur of all soluble sulfates, simple boiling with hydrochloric acid suffices, which should be done in an atmosphere of carbonic acid if pyrites or other oxidizable sulfides are present, and should be finished as quickly as possible in order to minimize the error resulting from oxidation to sulfuric acid of the sulfur of sulfides, if present, by any ferric salts that may have been dissolved.

If soluble sulfates and sulfides as well as insoluble sulfates and sulfides are present together, the sulfur of the first is found in solution after extraction by hydrochloric acid in a carbon dioxide atmosphere, and that of the decomposable sulfides by collecting the hydrogen sulfide evolved.[237] Then, in the residue, the sulfur of the insoluble sulfides can be determined after suitable oxidation, and, in the resulting residue, that of the insoluble sulfates after fusion with sodium carbonate. The sulfur of the insoluble sulfates can, however, be calculated by subtracting the barium sulfate equivalent of the preceding fractional determinations from that found for the total sulfur.

The error involved in the above estimation of the sulfur of soluble sulfides, due to the possible reducing effect of hydrogen sulfide on ferric salts, is probably negligible. Most of the hydrogen sulfide would be expelled before any such action could take place and probably before the ferric salts were largely attacked, but of course the small proportion of sulfur set free as such from pyrrhotite would escape estimation and introduce further uncertainty. In general, it would be safe enough to assume the composition Fe_7S_8 for pyrrhotite.

Obviously, such a procedure as that given above is open to many errors, especially with the more complex mixtures, and, however carefully all these separate determinations may be carried out, the final figures for ferrous and ferric oxides can hardly be regarded as more than approximations when much sulfide is present (see p. 916).

21. Boron

A. GENERAL REMARKS

No doubt boron occurs occasionally in rocks in amounts superior to those of some of the other constituents that are habitually determined. But the lack of precision of the methods that are at all applicable to mineral substances not directly soluble in acids other than hydrofluoric acid is accountable for the fact that no one has ever sought to apply these methods to rocks, unless boron was supposed to be present in appreciable amount. When this condition is fulfilled, it is customary to fuse with an alkali carbonate and then apply in one of its numerous modifications the Rosenbladt-Gooch method.

The method depends on expelling the boron as methyl ester by distillation with methyl alcohol from an acid solution, collecting the ester in some suitable manner, and then determining the boron gravimetrically or volumetrically. For simple borates, especially the soluble ones, the method gives satisfaction when all needful precautions are carefully observed, and that it may do so also with refractory borosilicates has been shown by Chapin.[238] Before Chapin's work it was considered necessary to extract with water the alkaline fusion of a mineral and to treat the extract for the boron. The wide divergence of results obtained by different chemists, even between duplicate results by the same analyst, is probably referable to the employment of only a single fusion and extraction, for it was shown by S. L. Penfield and H. W. Foote,[239] by G. W. Sargent,[240] and by W. E. Ford[241] that these operations must be repeated. A decided advance seems to have been scored by Chapin, who showed that aluminum and iron need not be removed but that the carbonate melt may be dissolved directly in acid without prej-

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[236] *Am. J. Sci.* [4] **38**, 41 (1914); *Z. anorg. Chem.*, **88**, 412 (1914); *Chem. News*, 111, 100 (1915).

[237] With pyrrhotite, a small fraction of its sulfur—one eighth if the formula Fe_7S_8 is adopted—is liberated as free sulfur and not as hydrogen sulfide.

[238] *J. Am. Chem. Soc.*, 30, 1691 (1908).

[239] *Am. J. Sci.*, [4] 7, 97 (1899).

[240] *J. Am. Chem. Soc.*, 21, 858 (1899).

[241] *Am. J. Sci.*, [4] 14, 195 (1903).

udice to the accuracy of the method as carried out by him. Furthermore, the presence of chlorine, even of fluorine, does not seem to be detrimental. For a description of the procedure, see under Boron (p. 754).

B. QUALITATIVE TESTS FOR BORON

The detection of very small amounts of boron in rocks is not a simple test. E. T. Wherry and W. H. Chapin[242] found the limit of sensibility of the direct flame test to be 0.2 per cent. The test is made by mixing the mineral powder with potassium bisulfate and calcium fluoride and introducing it on a clean platinum wire into the nonluminous Bunsen burner flame. A green color imparted to the flame, appearing only as evanescent flashes toward the lower limit of sensitiveness, is indicative of boron if no other elements are present that might give a green color.

Applied to distillates as obtained under A above, the color imparted to the flame of burning alcohol by its boric ester affords a much more delicate test, as was shown by C. Mannich and H. Priess,[243] V. Lenher and J. S. C. Wells,[244] and others.

The turmeric paper test as carried out by W. W. Low[245] gave Wherry and Chapin a distinct positive test for boron in a mineral carrying 0.08 per cent B_2O_3. Low's procedure is as follows: In the boric solution acidified with hydrochloric acid and contained in a shallow dish (not glass of the borosilicate type) is placed a piece of turmeric paper. The solution is then evaporated to complete dryness in a desiccator. Boron imparts a pinkish-red color to the paper if no interfering element, such as titanium, or too much hydrochloric acid, is present. The test is not applicable directly to the solution of a mineral, but only to distillates obtained as described under A above, and forms the basis of an accurate quantitative determination of small amounts of boron (see p. 764).

The turmeric test is the most delicate of all when made with the precautions taken by G. Bertrand and H. Agulhon,[246] for which reference must be made to the original publications. These authors applied the tests for amounts of boric oxide ranging from 0.1 mg down to 0.0005 mg. Specially prepared reagents must be used. E. T. Allen and E. G. Zies[247] have used the method with success. The basis of the test is the length of coloration imparted to small strips of turmeric paper dipping into like volumes of the test solution and of several standard solutions contained in small graduates. The solutions drawn up by capillarity evaporate at the exposed

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[242] *J. Am. Chem. Soc.*, **30**, 1684 (1908).

[243] *Chem. Ztg.*, **32**, 314 (1908).

[244] *J. Am. Chem. Soc.*, **21**, 417 (1899).

[245] *Ibid.*, **28**, 807 (1906).

[246] *Compt. rend.*, **157**, 1433 (1913); *Bull. soc. chim.*, **7**, 90–125 (1910); **13**, 396 (1913).

[247] *J. Am. Ceram. Soc.*, **1**, 739 (1918).

ends of the strips, and after some hours these appear colored for different lengths according to the amounts of boron present in the different solutions. With a sufficient number of standard solutions, the test yields fairly accurate quantitative results. Application of ammonia turns the color blue.

22. CERTAIN CONSTITUENTS IN MINUTE TRACES

If, as sometimes may happen, the problem is presented of examining rocks for traces of gold, silver, and other elements which are not ordinarily looked for, as in F. Sandberger's investigations bearing on the origin of the metalliferous contents of veins, large weights of material must be taken, up to 50 g or more. This involves the use, also, of large quantities of reagents, the purity of which must be looked to with the utmost care. Special directions to meet such cases cannot then be given here, nor even a complete reference list of the scanty and scattered literature on this subject. Sandberger's own writings dealt but little with its analytical side, as did also the report by H. von Foulton,[248] Über den Gang und die Ausführung der chemischen Untersuchung, following Sandberger's own paper[249] in the general report, Untersuchungen der Nebengesteine der Pribramer Gänge. A few data on gold, silver, lead, zinc, etc.,[250] were given in S. F. Emmons' report on The Geology and Mining Industry of Leadville; J. S. Curtis,[251] in his report on The Silver-Lead Deposits of Eureka, Nev., gave his method of assaying rocks for traces of gold and silver; in Volume 7 of the Reports of the Missouri Geological Survey, page 740, are to be found the methods used by James D. Robertson for the determination of lead, zinc, and copper in silicate and carbonate rocks of Missouri. The earlier work of J. G. Forchhammer[252] and L. Dieulafait,[253] the latter of whom examined many hundreds of Archean rocks, was of a qualitative nature. Later papers on the dissemination and determination of traces of gold are those of J. R. Don[254] and L. Wagoner.[255] O. Hackl[256] gave precise directions for the

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[248] *Jahrb. Bergakad, Leoben u. Pribram*, 363 (1887).

[249] From Sandberger's report, it appears that the rocks were treated successively with water, acetic acid, boiling dilute hydrochloric acid for two days, and finally hydrofluoric acid, the several extracts and final residue of fluorides (and pyrite) being separately examined for heavy metals. The products of distillation were also examined. A striking fact observed in all cases was the complete insolubility of the pyrite, even after the severe treatment mentioned. This speaks strongly in favor of the correctness of ferrous iron estimations in silicates by the hydrofluoric and sulfuric acid method when pyrite is present unaccompanied by other sulfides (see a, p. 916).

[250] *U. S. Geol. Survey Mono.* **12**, Appendix B, 592–96 (1886).

[251] *Ibid.*, **7**, 120–38 (1884).

[252] *Pogg Ann.*, **95**, 60 (1855).

[253] *Ann. chim. phys.*, **15**, **17**, **18**, **21** (1878–80).

[254] *Trans. AIME*, **27**, 564 (1897).

[255] *Ibid.*, **31**, 808 (1901).

[256] *Chem. Ztg.*, **45**, 1169 (1921); **46**, 385 (1922).

detection and determination of traces of arsenic, nickel, and cobalt in silicate rocks, the former after volatilizing the arsenic in a current of carbon dioxide saturated with bromine.

E. B. Sandell and R. W. Perlich[257] describe methods for the determination of nickel and cobalt in silicate rocks. The first is based on precipitation with dimethylglyoxime, in an ammoniacal citrate solution of the rock, extraction of the salt in chloroform, shaking the extract with hydrochloric acid to bring the nickel in the aqueous phase, and then determining the nickel colorimetrically by Rollet's method in a concentration not exceeding 6 micrograms per ml (p. 416). As little as 0.0001 per cent of nickel in a 0.5-g sample can be detected, and copper, cobalt, manganese, chromium, and vanadium, in amounts likely to be encountered in most igneous rocks, do not interfere.[258] The determination of cobalt is based on the extraction of the element with a carbon tetrachloride solution of dithizone from an ammoniacal citrate solution of the sample and evaporation of the extract, followed by ignition, solution of the residue in aqua regia, reduction with stannous chloride, and colorimetric determination with thiocyanate and acetone by Tomula's method (p. 423). As little as 0.0001 per cent of cobalt can be detected in a 1-g sample.

E. B. Sandell[259] also describes colorimetric methods for the determination of copper, zinc, lead, and cadmium in silicate rocks which are based on preliminary extraction by means of dithizone (diphenylthiocarbazone)-carbon tetrachloride solution. These methods are suitable for percentages as small as 0.002, 0.0025, 0.0005, and 0.00005 of copper, zinc, lead, and cadmium, respectively.

23. THE GASES AND VAPORS EXPELLED BY HEAT

That rocks and minerals evolve large quantities of gases and vapors when heated is a well-recognized fact. Numerous analyses have shown that the volatile products usually comprise hydrogen and carbon dioxide as preponderating constituents, with carbon monoxide, methane, nitrogen, hydrogen sulfide, etc., in smaller amounts. The total volume may be many

times that of the solid. To a certain extent, sometimes a large extent, especially with carbon dioxide, the source of these is entrapped fluid inclusions, whose origin was contemporaneous with that of the containing minerals. A further portion may have been held dissolved in the rocks, particularly in those not wholly crystallized. But from the experiments of some investigators, especially Morris W. Travers,[260] A. Gautier,[261] K. Hüttner,[262] and R. T. Chamberlin,[263] it is very evident that the gases are often produced by chemical changes resulting from the heat used for their expulsion. Thus, hydrogen may be due to reduction of water by minerals susceptible of oxidation at high temperatures, as ferrous silicates; the carbon monoxide to reduction of carbon dioxide in a like manner or by the hydrogen formed by the first reaction; the methane might arise from interaction between water and traces of metallic carbides, etc.[264]

Free oxygen is not reported as one of the evolved gases, and from the nature of the case it should hardly be expected.

Nitrogen, though found in but small relative amount in the free state in the earth's crust, is comparatively abundant and easily detectable as ammonia or ammonium salts in certain classes of rocks and long since was thus recognized. H. Rose[265] said that pitchstone gives off ammoniacal water on heating; A. Delesse[266] found ammonia in rocks, and A. Gautier later made quantitative tests; H. Erdmann[267] found that ammonia was obtained by acting on various minerals of ancient igneous rocks with a caustic alkali; C. Luedeking and H. A. Wheeler[268] found ammonium sulfate in a barite from Missouri, the presence of which one of us (W. F. H.) was able to confirm.

It has been noted in the U. S. Geological Survey laboratory on three separate occasions, when series of ores, roofing slates, and eruptive rocks were analyzed, that ammonia, in the form of either chloride or sulfate, or even as free ammonia, was given off on heating. Its appearance was not limited to one or a few specimens of a series but seemed to be characteristic of all and to be afforded by the unbroken rock as well as by the powdered sample. The precise conditions under which the specimens were collected

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[257] *Ind. Eng. Chem. Anal. Ed.*, **11**, 309 (1939).

[258] H. F. Harwood and L. T. Theobald [*Analyst*, **58**, 673 (1933)] describe a direct method intended for use with larger amounts of nickel (0.01%) in which a 2-g sample of finely powdered rock is decomposed by attack with hydrofluoric and sulfuric acids (with fusion of the residue if necessary), and the nickel is precipitated twice with dimethylglyoxime in ammoniacal citrate solution. α-Furil dioxime is substituted for dimethylglyoxime if the percentage of nickel oxide is less than 0.02 per cent.

[259] *Ind. Eng. Chem. Anal. Ed.*, **9**, 464 (1937); **11**, 364 (1939). See E. B. Sandell, *Colorimetric Determinations of Traces of Metals*, 2d ed., Interscience Publishers, New York (1950).

[260] *Proc. Roy. Soc.*, **64**, 130 (1899).

[261] *Compt. rend.*, **131**, 647 (1900); **132**, 58, 189 (1901); **136**, 16 (1903); *Ann. chim. phys.*, [7] **22**, 97 (1901); *Ann. mines*, [10] **9**, 316 (1906).

[262] *Z. anorg. Chem.*, **43**, 8 (1905).

[263] The gases in rocks, Carnegie Institution of Washington (1908). This is a very complete discussion of the subject, supplemented by a mass of experimental data.

[264] For the methods of collecting and analyzing such gaseous mixtures, consult the above cited papers by Gautier, and Charles Moureu, *Compt. rend.*, **142**, **44** (1906).

[265] *Quantitative Analyse*, Finkener ed., p. 673.

[266] *Ann. mines*, **18**, 151 (1860).

[267] *Ber.*, **29**, 1710 (1896).

[268] *Am. J. Sci.*, [3] **42**, 495 (1891).

not being known, it is impossible to affirm positively that the ammonia may not have been due to recent organic contamination of some sort, especially in the slates, but it is believed that a more critical collection of material will not alter the general result. Its amount was sometimes readily determinable by nesslerization, being as high as 0.04 per cent in some slates. Carbonaceous organic matter was absent from most of these, but doubtless existed in them in their early history. In their case, the ammonia was evolved as such in part, at least, and imparted a strong alkaline reaction to the water in the upper part of the tube. The presence of sulfides, fluorides, or chlorides in the rock might cause the ammonia to appear as a sublimate of sulfate, fluoride, or chloride. It has been suggested that ammonia might result from the action of water on metallic nitrides, O. Silvestri[269] having observed a nitride of iron in a lava from Etna.

24. Special Procedures

The problem presents itself often of ascertaining the composition of that portion of a rock powder which is soluble in special reagents or in a reagent of a particular concentration. No precise directions can be formulated to meet such cases. The procedure must vary with the character of the constituents of the rock and with the object that it is sought to attain, and only in exceptional cases can a separation of this kind be sharp. Much depends on the degree of fineness of the powder and on the length of time it is exposed to the action of the reagent.

A. DETECTION OF NEPHELINE IN PRESENCE OF OLIVINE

For confirmation of the microscopic diagnosis, L. V. Pirsson[270] has indicated a means of detecting nepheline in the presence of olivine, as in nepheline basalts, based on the very ready solubility of nepheline, as compared with olivine, when boiled for but 1 minute with a sufficiency of very dilute nitric acid (1 + 40). Gelatinization of the filtrate on evaporation is taken as evidence of the presence of nepheline. If olivine is present in quantity, however, this test must not be accepted at once as final, for some if not all olivines are much more soluble in nitric acid of the above strength than Pirsson was led to believe from his original tests. If, therefore, on evaporation of the filtrate, much iron is indicated, the gelatinization may be due to olivine alone or in part, and then the quantitative relation of silica to iron plus magnesium should be ascertained. It must be borne in mind also that any other very soluble silicates present will be more or less affected, and that apatite is largely or wholly dissolved. It is possible that still more dilute nitric or perhaps some other acid may exert a slighter solvent action on olivine without being appreciably less effective in dissolving nepheline, etc. In combination with a quantitative analysis of the extract the method is perhaps susceptible of a wider application than the particular case for which it was first used. It is well worth further study.

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[269] *Gazz. chim. ital.*, 5, 301 (1875).
[270] *Am. J. Sci.*, [4] 2, 142 (1896).

B. DETERMINATION OF "SOLUBLE" SILICA

For the determination of so-called "soluble" silica see under Silica (p. 852).

PART IV

CARBONATE ROCK ANALYSIS

I. INTRODUCTION

1. Qualitative Comparison of Carbonate and Silicate Rocks

The analysis of an ideally pure carbonate of any one metal is of great simplicity. The carbonates met with in nature occasionally approach but probably never fully reach this condition of purity, as when we find them in the form of well-crystallized mineral species, like calcite, magnesite, siderite, and cerusite. Even in such cases it is usually true that the crystals either contain included foreign matter to a slight extent or are composed of more than one carbonate in isomorphous mixture, and then the separation of the different metals may demand considerable skill and time. The great carbonate formations of the earth's crust are never of this simple character, however; even the most dazzling white marble contains other ingredients than calcium carbonate, and the degree of admixture may vary from almost nothing up to that indefinite point beyond which the rocks are not classified as limestones or dolomites, but rather as calcareous shales, calcareous sandstones, etc.

The matters other than carbonates that these rocks may contain are in the main original constituents, having been introduced at the time the carbonates were themselves deposited. They may consist of the detritus of earlier geologic formations in the form of sand or clay that has undergone little or no alteration in the subsequent passage of time, besides carbonaceous matter derived from the marine life existing during their formation. But besides these there may be found secondary minerals that have resulted from chemical transformation in the mass of the accumulated sediments, either with or without the powerful aid of dynamic forces like long-continued movements of the crust or the intrusion of hot igneous rocks. The metamorphism produced by these last agencies is often of a most profound character and may result in the production of a great variety of minerals altogether foreign to the original sediments. The metamorphism may have been accompanied by the introduction and incorporation of new material, but even in the contrary case all the chemical constituents of the original detrital foreign matter have necessarily become a part of the carbonate rock. These constituents are furthermore necessarily those common to silicate rocks of the earth's crust; hence the carbonate rocks differ qualitatively in no essential respect from their silicate associates, except in the more common

occurrence of carbonaceous matter; and a complete analysis of one of them involves most of the determinations and separations described in Part III. The analytical procedure differs, however, in some respects, owing to the great preponderance in most cases of components easily soluble in the common mineral acids, which either renders it unnecessary to use an alkaline flux or enables the analyst to reduce its amount very materially, thereby simplifying subsequent operations. The analysis is further simplified by the occurrence in reduced amounts, as a rule, of those elements that most complicate the analysis of a silicate rock. Only in the very purest carbonate rocks are some of them nearly or entirely lacking, as silicon, aluminum, and the alkalies, but the minor constituents zirconium, barium, and strontium are often not present in readily determinable amount.

In the following pages the descriptions will apply especially to those large deposits of carbonate materials denominated limestones, magnesian or dolomitic limestones, and dolomites, many of which are of great and growing economic importance. For the purpose of the analyst, an exact definition of these terms is of minor significance. Indeed, among geologists there has been no uniform rule for the delimitation of these rocks, and any rule made must be purely arbitrary, since there is absolutely no break in the series between limestones and dolomites. The last name applies strictly only to the equiatomic double salt of calcium and magnesium, $CaMg(CO_3)_2$, and by some it is held that this should be its only application. On the other hand, the opposite extreme has been approached by those who contend that all limestones with as much as 1 or 2 per cent of magnesium carbonate should be classed as dolomites. According to H. Ries,[1] the most prevalent practice among geologists seems to be to call all limestones with 5 to 18 per cent of magnesium carbonate magnesian limestones and the rest limestones or dolomites, according to whether their magnesium carbonate contents lie below or above these limits. Some, however, although subscribing to the above definition of magnesian limestones, would and do call those rocks, with from 20 per cent of magnesium carbonate up to the dolomitic ratio, dolomitic limestones. F. W. Pfaff[2] called limestones with 11 to 46 per cent of $MgCO_3$ dolomites, since these are common, whereas those with 7 to 11 per cent, he says, are very rare, if indeed they occur at all.

It has seldom been considered necessary to analyze the carbonate rocks with any great attention to detail. The majority of analyses have been made with reference to their technical utilization and with determination of only the more important constituents. In such cases it has been a common practice to omit direct determination of the carbon dioxide and

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[1] *Bull. N. Y. State Mus.* **44**, 644 (1901).

[2] *Neues Jahrb. Beilage Bd.*, **23**, 529 (1907).

either to calculate its supposed amount on the basis of the total lime and magnesia found or to regard the loss on ignition as representing the carbon dioxide. The portion insoluble in hydrochloric acid has been frequently stated as silica. Any iron that may have been determined has been reported as Fe_2O_3; water and carbonaceous matter have been overlooked entirely or neglected, as also titanium, phosphorus, and the rarer constituents; and sulfur has been reported almost uniformly as SO_3. Such practice has repeatedly involved very gross errors of omission as well as of commission, which, though of little moment in many cases from the commercial point of view, detract much from the value of all these analyses in the eyes of the geologist intent on gaining an exact knowledge of an important formation and of the possible sources of metallic ore deposits of economic value, whether these last are residual soils resulting from the subaerial decomposition of limestone formations or whether they are deposits of the ores of lead, zinc, vanadium, etc., that have been formed beneath the surface by the agency of circulating waters.

2. Mineral Composition of Carbonate Rocks

The chief mineral compounds entering into the make-up of the carbonate rocks are of course calcium carbonate for the limestones proper, with the double carbonate, the mineral dolomite, in increasing proportions through the magnesian limestones and dolomites; but it is the exception to find them free from other carbonates as essential components, chiefly those of iron and manganese, which are usually in isomorphous combination with the constituents of one or the other of the above minerals. The proportion of these is far less than that of the others but sometimes aggregates several per cent. When they predominate, the rock is no longer a limestone but becomes an ore of iron or manganese.

Neglect to take account of these minor carbonate constituents is a frequent source of error in the statement of analyses, where it is very common to find reported as carbonates only calcium and magnesium, and perhaps a considerable amount of iron as Fe_2O_3 and manganese as one of its higher oxides, although it is practically certain that these must have existed in large part as ferrous and manganous carbonate. A careful determination of the carbon dioxide will often tell whether this is so or not, for it will perhaps be found in excess of that required for lime and magnesia. A negative result, however, is not to be taken as proof of the absence of iron or manganese carbonate or both, for very often a small portion of the magnesia may be in silicate combination, or in some formations there may be a little gypsum to claim a portion of the lime. This last is not likely to be the case in the average hard rock that is used for the manufacture of cement. In such the sulfur often reported as SO_3 is likely to come from iron pyrites and perhaps to a limited extent at times from carbonaceous matter. Hence it is easy to see that, except in absence of iron and manganese, it is not possible to ascertain the exact proportions of calcium and magnesium carbonates, and in some of the excepted cases it is possible only after separate analyses of the parts soluble and insoluble in dilute acid have been made.

The commonest sulfide in limestone formations is pyrite, though often its presence is obscured by its extremely fine state of division or by carbonaceous matter. In the metamorphosed limestones, especially those altered by intruded igneous bodies, other sulfides, as sphalerite, and galena, are not uncommon, and these and still other sulfides may form important ore bodies or again give rise by oxidation to equally or even more valuable ores of a different sort. The strongly metamorphosed siliceous limestones, however, are seldom subjected to chemical analysis, especially for commercial purposes.

The siliceous components may be of the most varied character. Their names alone might fill a page. Suffice it to mention for the metamorphosed rocks garnet, vesuvianite, wollastonite, tremolite, diopside, the scapolites, tourmaline, apatite, and silica, in the form of chert. Cherty limestones are extremely common, and their silica was doubtless introduced during metamorphism. The chief siliceous components of unmetamorphosed limestone rocks are, as said before, sand and a clay. The latter particularly, since it is a clay, carries water, and this fact is usually overlooked in ordinary analyses. The analytical statements may show no water, though clayey matter is present to a large extent. The sand may be largely or altogether quartz, or it may be composed in part of such other minerals as are commonly found in sands, like mica, garnet, and zircon. The latter may often be detected, even in the less siliceous and clayey limestones, by dissolving large amounts in hydrochloric or acetic acid and subjecting the residue to microscopic examination, after burning off obscuring carbonaceous matter, if necessary. The unignited residue will, needless to say, contain the pyrite of the rock and any other sulfides not attacked by dilute acid. In some nonsiliceous rocks, it may even consist to a considerable extent of iron oxide, probably in most cases one of the hydrated oxides, but perhaps often hematite. The presence of such a constituent in a limestone is occasionally indicated by a reddish cast of color in the fresh rock, provided there is not enough carbonaceous matter to obscure it. The existence of a ferric oxide is not always incompatible with the simultaneous presence of this carbonaceous matter.

A purple color may be due, as in some slates, to admixture of a ferric oxide or hydroxide with carbonaceous matter, whereas to the latter component are due the gray and black colors often encountered. The color of greenish sedimentary limestones may be caused by certain minerals of the mica family, as the chlorites.

The condition of phosphorus when it occurs in only minute amounts is not determinable with certainty. Doubtless it may be found sometimes in traces in the form of heavy phosphates like monazite and xenotime in the insoluble residues, and again it is held by iron and aluminum, but in the highly phosphatic rocks its usual form is overwhelmingly that of phosphorite or apatite, which may in fact become the predominating constituent.

It is known that vanadium is a regular though very minor constituent of limestones as well as of sandstones and igneous rocks generally. Tests on 100-g lots of a great limestone formation in northwestern Mexico show that it at least carries molybdenum as well as vanadium, and also nickel. Nothing is known with certainty regarding the mode of combination of these elements in limestones, though it is quite possible, of the vanadium at least, that it was an original ingredient of the aluminous silicates of the clayey matter, and that nickel, zinc, and lead when present are mainly in the form of carbonate or sulfide.

Carbonaceous matter has been alluded to frequently as a common constituent of secondary importance. It is absent from the white marbles and some colored decorative stones but forms an appreciable percentage of other limestones in extreme cases.

Some kinds of bituminous limestone are characterized by a fetid odor when struck or abraded. This is perhaps due in most cases to hydrogen sulfide, either original or resulting from decomposition of organic matter. The presence of hydrogen sulfide is sometimes unmistakable, and B. J. Harrington determined its amount at about 0.02 per cent in the form of liquid inclusions in a fetid calcite from Canada.

The above remarks do not exhaust the subject of the mineral composition of limestone rocks, this term being used here and elsewhere in its generic sense to include the magnesian varieties. They may serve as a sufficient guide, however, to chemists undertaking the analysis of these rocks. Ignorance of the minor mineral components has been a prolific source of error in these analyses.

3. BEHAVIOR TOWARD DIFFERENT REAGENTS AS A MEANS OF DISTINGUISHING DIFFERENT CARBONATES

Although, for the analyst provided with laboratory facilities, it is usually of little importance to possess other means for identifying qualitatively the different varieties of carbonate rocks than the conventional methods of qualitative analysis, some of the rapid methods for so doing may serve a most useful purpose at times, especially in the field, where transport of bulky apparatus and quantities of liquid reagents is difficult or impossible.

A. DIFFERING SOLUBILITY IN TARTARIC AND CITRIC ACIDS AND IN ACID POTASSIUM SULFATE

This subject, touched on now and then by earlier writers, was first studied by H. C. Bolton,[3] and many of his results were long afterward confirmed by J. W. Richards and N. S. Powell.[4] Solid organic acids like citric and tartaric were found to be well adapted for distinguishing between many carbonate minerals by the difference in the degree of action on them. Potassium acid sulfate had been used earlier to some extent by E. Jannettaz,[5] and Richards and Powell gave data on this reagent for carbonates. It will suffice here to refer to the originals, especially Bolton's papers, where will be found data as to the solubility of a great variety of minerals in the abovenamed solvents as well as in others of inorganic nature.

B. DISTINGUISHING CALCITE FROM ARAGONITE

In the opinion of J. Johnston, H. E. Merwin, and E. D. Williamson,[6] chemical tests used alone for distinguishing qualitatively calcite from aragonite are indecisive, "particularly so where they would be most useful, namely, for the characterization of fine-grained material which may carry something that interferes with the test." Hence their description is omitted. Optical methods in experienced hands are more trustworthy.

C. DISTINGUISHING BETWEEN CALCITE AND DOLOMITE

It must be understood that magnesian and dolomitic limestones represent, as a rule, mixtures of the double carbonate dolomite with calcite, and not of calcite with magnesite. Calcite is easily soluble in dilute hydrochloric and acetic acids; dolomite and magnesite are nearly insoluble. Hence calcite effervesces strongly with these acids, even in lump form, whereas dolomite shows little or no effervescence. An easy means is thus afforded for distinguishing the two. Dolomitic limestones are also but feebly attacked, according to their content in calcite, so that in powder form it is not difficult to make a fair separation of calcite from dolomite and magnesite, but not from magnesian hydrocarbonates, which last, however, are never essential components of the great carbonate formations.

The behavior toward heat alone is sometimes useful as a distinguishing test, for dolomite loses its carbon dioxide so easily that the powder is

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[3] *Ann. N. Y. Acad. Sci.*, 1, 1–153 (1877–80); 2, 1; *Proc. Am. Assoc. Advancement Sci.*, 31, 271 (1883); *Chem. News*, 36, 37, 38, 43, 47 (1877–83); *Brit. Assoc. Advancement Sci. Rept.* 506 (1880); *Mineralog. Mag.*, 4, 181 (1880–81); *Ber. deut. chem. Ges.*, 13, 726 (1880).

[4] *J. Am. Chem. Soc.*, 22, 117 (1900).

[5] *Compt. rend.*, 77, 838 (1873); 78, 852 (1874).

[6] *Am. J. Sci.*, [4] 41, 473 (1916). This article contains a summary of the literature upon the subject.

violently projected from the crucible if the heat is not very cautiously applied, whereas calcite can be strongly heated at the start without danger of loss of solid matter.

J. Lemberg[7] found that calcite responds by the formation of a violet color in its powder when treated with a solution of aluminum chloride and hematoxylin (extract of logwood) but that dolomite remains unaffected. The solution is prepared by dissolving 4 parts of dry aluminum chloride in 60 parts of water, adding 6 parts of logwood, and boiling for 25 minutes with replacement of the escaping water. The deep-violet solution is then filtered. Coarsely powdered Iceland spar and Carrara marble became violet after 5 to 10 minutes immersion and subsequent removal of the adhering solution with water. In the powder of a dolomitic limestone the calcite grains were easily distinguishable from those of dolomite by this means. It is not advisable to prolong the treatment unnecessarily, for after 20 minutes the dolomite surfaces may show occasional pale-blue spots. The reaction is caused by precipitation upon the calcite of aluminum hydroxide, which forms, with the coloring matter, a lake.

F. Hinden[8] found that limestone (calcite) at room temperature gives carbon dioxide with 10 per cent solution of ferric chloride, but dolomite does so only on warming. A second reagent mentioned by him is copper sulfate solution, from which basic copper carbonate is separated by calcite, but is not by dolomite.

It is not known if objections similar to those mentioned in the foregoing section B apply to the procedure of Lemberg and Hinden. The possibility, however, should be borne in mind.

II. REFINED METHODS FOR THE ANALYSIS OF CARBONATE ROCKS

1. Silica, Its Separation from Alumina, etc.

A. METHODS OF DECOMPOSING THE ROCK

Few limestones are so pure that they leave no residue on treatment with hydrochloric acid. The residue may consist of quartz, clay, or other silicates, carbonaceous matter, pyrite, etc., and the mode of attack employed will depend on the amount of insoluble matter and whether or not it is desired to know its composition separately from that of the soluble portion.

a. *When the Inorganic Residue Is to Be Separately Analyzed.* A gram[9] of the rock powder is moistened with water and dissolved in dilute hydrochloric acid (or acetic, if the former acid is likely to act appreciably on the silicates) in a covered beaker till all effervescence ceases. Moderate heat is needed if the effervescence is so weak as to indicate a rock of dolomitic character. The solution is filtered through a 7-cm filter, and the residue is washed with water, or hot dilute hydrochloric acid if gypsum is present and the silicates are resistant. The paper, with its contents, is ignited moist in platinum (blast needed only if the amount is considerable), and, after weighing, it is fused with sodium carbonate and analyzed like a silicate rock (p. 859 et seq.). If it contains hydrous minerals, the original water content of the residue is best determined by a separate test on a fresh portion of the sample and not by drying and weighing on a counterpoised filter and then igniting. The weight of water found should be added to that of the ignited residue in order to get the true weight of the insoluble matter.

If the ignited residue is wholly quartz, or is very insignificant in amount, it may be treated at once with a drop of sulfuric acid and a few drops of hydrofluoric acid, and the acids removed in the radiator shown in Fig. 5 (p. 24). If then a slight residue still is visible, it is well to repeat the treatment with acids and evaporation, for it cannot be too insistently pointed out that quartz resists the action of hydrofluoric acid far more than many silicates, and several evaporations may be needed to volatilize the crystallized mineral unless it has first been reduced to a most impalpable state of division. When the weight after exposure for a few minutes to the full burner heat no longer changes, the loss represents silica. If a slight residue still shows, it is to be fused with a little carbonate and dissolved in hydrochloric acid and the solution added to the original acid filtrate, which is best treated for iron, aluminum, etc., as in 2, A (p. 968).

If the original residue is small, and accurate knowledge of its composition is desired, several grams of the rock may be dissolved. In this case the whole filtrate from the insoluble matter is best treated for dissolved iron, aluminum, and manganese as in 2, A (p. 968), but then only an aliquot part of the subsequent filtrate should be used for the determination of calcium and magnesium.

In case the filtrate from the residue is colored perceptibly by dissolved organic matter, a condition that may arise occasionally, this organic matter must be effectually destroyed before proceeding to the precipitation of iron and aluminum, for otherwise incomplete precipitation of one or both will be the result. The complete removal of this disturbing material cannot always be effected by ordinary oxidizing agents, but only by evaporation and heating to its carbonization point. In doing this, it is necessary, in order to avoid possible loss of iron as chloride, to evaporate with nitric acid to dryness a couple of times and then to heat over a free flame gently until the desired result is achieved. If this seems undesirable for any reason, it may be better to start with a fresh portion of the limestone and

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[7] *Z. deut. geol. Ges.*, 40, 357 (1888).

[8] *Verhandl. naturforsch. Ges. Basel*, 15, 1 (1905).

[9] For the determination of constituents that amount to over 5 per cent, individual samples should be dried at 105 to 110° C in weighing bottles, weighed, and poured out as completely as possible, and the bottle reweighed.

to treat it by one of the methods given under b, below, for the bulk analysis.

b. *When the Inorganic Residue Is Not to Be Separately Analyzed.* The usual case does not involve separate analysis of the inorganic residue. As said above, the residue may consist of clay or other silicates, carbonaceous matter, pyrite, etc., with or without quartz. There are two ways open to render the noncombustible part of this soluble.

α. By solution in acid after strong ignition. Solution in acid after strong ignition is the best method to employ if the ratio of insoluble to soluble compounds is not less than that in an argillaceous limestone which is directly suited for burning to Portland cement—that is to say, if the silica does not much exceed 15 per cent and the oxides of iron, aluminum, and titanium together are not in excess of 6 per cent. The exact allowable limits have not yet been determined, nor is it known what the proportions may be in dolomites and dolomitic limestones. This is a subject for further investigation.

Limestone, however, in which the above percentages of silica, alumina, etc., are not exceeded may be converted in 10 to 15 minutes by a burner capable of giving an effective temperature of 1100 to 1200° to a product that is wholly soluble in hydrochloric acid, provided the rock was first reduced to a very fine powder.

A gram of the powder is heated at 1100 to 1200° C in a covered platinum crucible. If a limestone, the heat may be applied at once, as a rule, without fear of loss, or after short heating at 700 to 900° C. Highly magnesian limestones, if this method is applicable to them, must, however, be heated with the greatest caution, for their temperature of decomposition is far below that of limestones, and violent projection of material often begins far short of visible redness.

The strong heating is usually stopped after 10 or 15 minutes, when the shrunken product may have the appearance of a sintered or even clinkered mass that detaches for the most part readily from the crucible.[10] It is transferred to a beaker or evaporating dish and moistened with water. The crucible is then cleaned with hydrochloric acid (1 + 1), and the contents are poured into the beaker or dish. By gentle heat and cautious pressure with the flattened tip of a rod, the lump or lumps are caused to disintegrate and pass largely into solution in a few minutes. A certain

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[10] The changes that take place during the ignition comprise loss of all carbon dioxide, water, and carbonaceous matter; oxidation of all pyrite, with retention of the whole of the sulfur as calcium sulfate. Prolonged heating will gradually expel all the sulfur trioxide from the calcium sulfate and later the alkalies, which can be wholly volatilized in an hour or less by a powerful blast. With an inclined blast, the alkalies condense in part on the under side of the lid as a soluble and powerfully alkaline deposit, sometimes weighing several milligrams, but, in the time above set, no loss of alkali appears to occur.

amount of silica may remain undissolved in a flocculent state, but this is of no moment. When all grit has disappeared, the liquid, if in a beaker, is washed into a dish and evaporated to dryness. If solution was made directly in the dish, the volume of liquid need not exceed a few milliliters, and the evaporation takes but a short time. A much smaller dish is allowable than in the case of wholly siliceous minerals, because of the small bulk of solution and the entire absence of added fixed salts.

β. By solution in acid after heating with sodium carbonate. When the siliceous components are in such amount as not to permit the formation of a wholly soluble product by strong ignition, it is necessary to mix sodium carbonate with the powder and decompose the silicates by its aid over the blast lamp. This procedure may be adopted with all siliceous limestones if desired. The amount of flux to be used is but a fraction of that needed for a silicate analysis. One-fourth to one-half gram for one gram of limestone suffices, for the lime formed by ignition is itself a powerful flux, and it is quite unnecessary to have here a liquid fusion. A sintering suffices. This proportion holds also for highly magnesian limestones and for cement rocks containing as little as 50 per cent of lime.

B. SEPARATION OF SILICA

In this connection the remarks on page 860 should be carefully read.

Because of the absence of large amounts of alkali salt and of much silica, the evaporation of the hydrochloric acid solution obtained on pages 964 and 966 takes little time compared with a silicate analysis. When dry, or nearly so, on the steam bath, the dish may be placed in an air bath or (covered) on a platinum triangle resting on a hot plate, and heated at not over 110° C for an hour. Higher temperatures or longer heating should be avoided because of recombination of silica and magnesia, with subsequent resolution of the silica when acid is added.

Bertram Blount[11] declared that, by heating to 200°, the silica is completely separated by a single treatment, but we have not found it so, though the amounts going into solution on subsequent addition of acid are small, seldom over 2 or 3 mg. Therefore, for exact work with silica present to the amount of 2 to 4 per cent and over, that already rendered insoluble should be filtered off and the solution again evaporated. With this end in view, the dry mass is drenched with 10 ml of hydrochloric acid and then with 100 ml of hot water, and the dish covered and placed on the bath for 10 minutes. The silica is then separated by filtration on a filter of suitable size and washed thoroughly with dilute hydrochloric acid (1 + 99) and then twice with hot water. The filtrate is evaporated again to dryness and the residue extracted with hydrochloric acid as before, but with half the

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[11] *J. Soc. Chem. Ind.*, 21, 1217 (1902).

quantity of acid and water and the allowance of only a few minutes' time. The solution is then filtered once more through a second and smaller paper and the paper and residue washed first with cool dilute hydrochloric acid (1 + 99) and then with hot water. The two papers with their contents are slowly dried, charred, and ignited in platinum, finally at 1200° C for 10 minutes. The weighed silica is to be corrected for foreign matter by evaporating with 5 ml of hydrofluoric acid and 1 or 2 drops of dilute sulfuric acid (1 + 1) as directed on page 863. The residue obtained after ignition is almost always considerably less than that found in analyzing a silicate rock, and an ignition of a minute or two over a full burner (1000° C), after expulsion of the sulfuric acid, is in almost all cases sufficient. The composition of this residue is similar qualitatively to that derived from silicate rocks. It should never contain calcium or magnesium but consists mainly of alumina, with a little ferric, titanic, and phosphoric oxides. It should be fused with a little carbonate, dissolved in hydrochloric acid, and added to the filtrate from the silica.

2. Aluminum, Total Iron, Titanium (Silica, Manganese); Precipitation in Company with Phosphorus [12]

The next steps differ widely, according to the relative amounts of iron, aluminum, etc., taken collectively, and according to whether it is intended to precipitate manganese with these or after separation from them. The individual preferences of experienced analysts will often differ in the selection of the particular method, and it is not intended here to prescribe definitely the course that anyone should follow. Nor in the following paragraphs are all methods of separation that may be capable of affording good results noticed. There are some that seem promising but that have not yet been studied sufficiently to justify description. A method that may be well adapted to a certain combination of elements may be valueless if to that combination a single other element is added,[13] or it may be that the possible disturbing influence of that element has not yet been ascertained.

A. PRECIPITATION OF ALUMINUM, IRON, ETC.

a. *Collective Precipitation of Aluminum, Iron, Manganese, Titanium, and Phosphorus by Ammonium Sulfide.* If aluminum, iron, manganese, titanium, and phosphorus collectively represent 2 or 3 per cent or less of the rock, the filtrate from the silica (1, B, p. 967), reduced in bulk, if need be, is put into a flask of 150 ml capacity with enough hydrochloric acid to prevent precipitation of magnesium when made ammoniacal. This last is a most important point. Ammonia free from carbonate is then added to strong alkalinity, and hydrogen sulfide is introduced to saturation, followed by a fresh addition of ammonia equal to the excess first used. Boiled water is then poured in until it is well up in the neck, the cork is inserted, and the flask is set aside for 12 to 24 hours. Its contents are then collected on a filter of small size (7 cm) and washed with water containing a little ammonium sulfide and chloride. Precipitation is not absolute as to one or more of the constituents of the separated mixture, but the amounts recoverable from the filtrate are usually very minute. (For treatment of the filtrate, see 5, p. 973.)

The paper and its contents, having been washed with ammonium chloride, may be safely charred and ignited as they are. The final weight after ignition in full contact with air, followed by application of the inclined blast for not over 5 minutes, represents Al_2O_3, Fe_2O_3, Mn_3O_4, TiO_2, P_2O_5, and other oxides such as ZrO_2 if these are present in the rock. (For the separation of these, see C, p. 970.)

This method is inapplicable for phosphatic limestones containing insufficient aluminum to more than combine with the phosphorus, for then calcium and magnesium phosphates would be precipitated also. In such case method b or c would apply if the iron and aluminum together more than sufficed to carry down the phosphorus, but in general it would be necessary to add a known amount of pure iron oxidized to the ferric state, then to precipitate by ammonium hydroxide or the basic acetate process, and to deduct the added iron oxide from the weight obtained.

b. *Precipitation of Aluminum, Iron, Titanium, and Phosphorus by Ammonium Hydroxide.* The filtrate from silica is boiled, with addition of a few drops of bromine water or 2 or 3 drops of strong nitric acid, until all trace of bromine or chlorine is gone. Then hydrochloric acid is added, if not already present, in amount sufficient to prevent precipitation of magnesium when rendered ammoniacal. A few drops of methyl red solution are added, and the liquid (100 to 200 ml in volume) is heated just to boiling. Neutralization is then brought about by means of ammonium hydroxide (dilute toward the end) until the color of the solution changes to a distinct yellow. It is then boiled for 1 or 2 minutes, allowed to settle a bit, filtered, then at once washed two or three times with hot ammonium chloride solution (2 per cent), and sucked dry (consult p. 869). The precipitate is then redissolved in hot and moderately strong hydrochloric acid, the solution is boiled to drive out the trace of chlorine derived from solution of any precipitated manganese dioxide, and the precipitation is repeated one or more times just as described, according to the amount of manganese in the rock. Macerated filter paper is added before the last precipitation if the oxides are in large amount. The final precipitate is washed with the ammonium chlo-

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[12] See also p. 868.

[13] For example, precipitation by an excess of sodium hydroxide and carbonate (p. 85) serves satisfactorily for the separation of iron from aluminum in the presence of calcium but not of magnesium.

ride solution. (For treatment of the combined ammoniacal filtrates, see B, below.)

The precipitate is ignited moist in the crucible containing the residue from volatilization of the silica by hydrofluoric acid (if this was not fused and dissolved), and the combined weights, increased by traces subsequently recovered (B, below), represent all iron as Fe_2O_3, Al_2O_3, TiO_2, P_2O_5, and possibly other oxides such as ZrO_2. (For separation of the ignited oxides, see C, below.)

c. *Precipitation of Aluminum, Iron, Titanium, and Phosphorus by the Basic Acetate Method.* The basic acetate method of separation is less employed in limestone analysis than in that of silicate rocks, by reason of the relatively smaller amounts of those elements that precipitate in the basic acetate process, and hence of their more ready separation by ammonium hydroxide from appreciable quantities of manganese. (For its application, see p. 870, giving due regard to the smaller amounts of iron, etc., involved in the case of limestones.)

B. TREATMENT OF THE FILTRATES FROM ALUMINA, ETC.

The combined filtrates obtained in A, b (or c), above, which, besides all the calcium and magnesium, will contain the manganese and usually traces of aluminum and even iron, are acidified with hydrochloric acid, evaporated to a small volume in platinum, treated with ammonium hydroxide until the solution is just alkaline to methyl red and any precipitate that separates is collected. This is washed a little, redissolved in hydrochloric acid (with addition of a drop or two of sulfurous acid if its color indicates precipitation of some manganese), and reprecipitated by ammonium hydroxide at boiling heat in a very small beaker. If need be, the precipitation is to be again repeated, but this will seldom be the case. The alumina and perhaps trace of iron oxide thus obtained are added to that already found (A, p. 968). (For treatment of the filtrate, see 3, p. 971.)

C. SOLUTION AND SEPARATION OF THE OXIDES OBTAINED IN A AND B

The same course is followed, whether method a, b, or c under A (pp. 968–970) has been employed for precipitating aluminum, iron, etc. According to the weight of the ignited oxides, these are fused with from one to several grams of potassium or preferably sodium pyrosulfate[14] in the covered crucible over a low flame. If pyrosulfate is used instead of acid sulfate, the time of fusion is greatly shortened, especially when the oxides are in a finely divided state, as after precipitation in the presence of macerated filter paper.

When decomposition is complete, the cooled melt is dissolved in 50 ml of hot dilute sulfuric acid (5 + 95), the solution is transferred to a platinum dish and evaporated as far as practicable on the bath. Add 10 ml of dilute sulfuric acid (1 + 1), and continue the evaporation over a radiator, or on a sand bath, or by aid of a free flame applied with care to prevent spattering, until fumes of acid appear freely. When cool, the melt should be rather pasty and not hard and dry. It is dissolved by the aid of heat in 100 ml of water, and the solution is allowed to digest for 10 to 15 minutes on the bath. A few flocks of silica will then generally be apparent at the bottom of the dish. Whether visible or not, the solution is passed through a 7-cm filter, which is then washed with hot water until free from salts.

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[14] For its preparation, see p. 36.

a. *Silica (Barium).* The paper with the silica is ignited, weighed, and then treated with a drop of sulfuric acid and a few drops of hydrofluoric acid, and the crucible, after ignition, is again weighed. The loss represents silica that escaped earlier separation, and its amount is to be added to that already found.

If the final residue is reddish, it is to be brought into solution by a little pyrosulfate, and its solution, if clear, is added to the main filtrate containing the mass of the iron. If it is not clear, the turbidity may be due to a trace of barium sulfate, which should of course be separated and deducted from the weight of the alumina plus other oxides.

b. *Iron.* In this solution the iron is to be determined by potassium permanganate after reduction as in α on page 877. The amount of vanadium present is, so far as known, always so small as to make it unnecessary to follow procedure β, on page 877.

c. *Titanium.* After titration of the iron, the solution is treated as prescribed on page 879, and the titanium is determined colorimetrically (p. 885).

d. *Aluminum.* The aluminum is determined by difference after subtracting the weights of iron and titanium oxides found as above, and also the phosphoric oxide found in a separate portion of the sample (6, p. 974), and further the manganosomanganic oxide, if this had intentionally been precipitated along with the iron and aluminum as in A (p. 968). (For the discussion of the relative merits of this indirect and the direct methods for arriving at the aluminum, see pp. 874 and 879.)

3. MANGANESE

A. IN THE FILTRATES FROM 2 B (p. 970)

The filtrates containing the calcium, magnesium, and manganese are caught in a flask of about 150 ml capacity, 2 ml of ammonium hydroxide is added, hydrogen sulfide gas is introduced to saturation, and then additional ammonium hydroxide is added to equal that just prescribed. The flask is filled with recently boiled water, stoppered, and set aside for 12 to 24 hours; the precipitate (perhaps colored dark by a little platinum, iron, or other heavy-metal sulfide[15]) is collected on a 7-cm filter and washed with a dilute solution of ammonium chloride carrying a little ammonium sulfide.[16] (For treatment of the filtrate see 5, p. 973.)

If the manganese is not to be determined in a separate portion of the rock, the flask is then cleaned from possibly adhering sulfide with a solution of half-strength hydrochloric acid diluted with five times its volume of hydrogen sulfide water, which is then passed through the filter in order to dissolve the manganese sulfide. The filtrate is treated as in β, page 881 if the gravimetric method of determination is chosen. In view of the relatively enormous errors affecting this method when small amounts are in question (see p. 879), it is far safer to evaporate the hydrochloric acid solution with sulfuric acid, until no trace of chlorine is left, and to apply the colorimetric method (p. 882).

If the manganese is to be determined in a separate portion, the sulfide precipitate is discarded; indeed, if it is known that but a few hundredths of 1 per cent are present, its separation at this stage may be altogether omitted.

B. SEPARATE DETERMINATION OF MANGANESE

Small amounts of manganese are always determined best by colorimetry, and then with greatest accuracy in a separate portion of the sample. This, if wholly soluble in acid, is to be dissolved by dilute nitric acid free from hydrochloric acid and further treated, in whole or in an aliquot part, as on page 882. If it is not altogether soluble in acid or if the solution is colored by organic matter, it is best to heat the powder with half its weight of sodium carbonate (itself free from manganese) over a strong blast, to digest the cooled mass with nitric acid until any residue that may remain is entirely colorless, and to filter into a suitable-sized flask before proceeding with the determination.

4. Copper, Nickel, Cobalt, Lead, Zinc, Rare Earths, Chromium, Vanadium, Molybdenum

It is commonly useless to look for copper, nickel, cobalt, lead, zinc, rare earths, chromium, vanadium, or molybdenum in a sample as small as that

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[15] More than a negligible trace of iron should not appear at this point. If, however, the organic matter of the limestone is at all soluble in acids and the method of direct solution has been employed, it may very well happen that some iron (aluminum likewise) will fail of precipitation by ammonium hydroxide. The former will then appear at this stage. Hence, prior ignition of the limestone is imperative in such cases.

[16] This is best prepared by overneutralizing a little hydrochloric acid in a small beaker, and then adding hydrogen sulfide water or introducing hydrogen sulfide gas for a few moments, and further diluting if need be.

taken for the general analysis. To detect these from 50 to 500 g of material will be required, which should be dissolved in hydrochloric acid and the residue separated by filtration. If it is desired to examine this residue, it is analyzed separately, after fusion with sodium carbonate and leaching with water. Chromium, vanadium, and molybdenum will then be found in the filtrate, the other metals in the residue. The former can be determined according to page 901, the latter by the usual methods.

For the hydrochloric acid solution, which will contain the above elements mainly or wholly, the treatment given under 2, A (p. 968) is probably best adapted, and the following outline may serve as a guide:

The precipitate produced by ammonium sulfide is to be dissolved, the copper and perhaps some molybdenum precipitated by hydrogen sulfide, the filtrate oxidized and evaporated to dryness, and the residue boiled with a solution of oxalic acid. The rare earths, perhaps contaminated by silica, will be thrown out and are to be washed with dilute oxalic acid solution, ignited, treated with sulfuric and hydrofluoric acids, redissolved, and reprecipitated in neutral or nearly neutral solution by oxalic acid, ignited, and weighed. They can then be tested for character as described under Rare Earths (p. 561). The filtrates are freed from oxalic acid by evaporation and gentle ignition, and the residue is redissolved and tested for nickel, cobalt, zinc, and chromium by approved methods. It must not be forgotten that the filtrate from the original precipitation by ammonium sulfide may hold most of the vanadium and molybdenum, and perhaps nickel, which are to be recovered by acidifying with dilute acetic acid.

Vanadium may usually be found and determined with sufficient accuracy in 5 g of the limestone by fusing with sodium carbonate and further treating as described on page 902.

5. Calcium, Strontium, Barium, Magnesium (Manganese)

A. ORDINARY PROCEDURES

The filtrate obtained on page 968 or page 971 is treated for the most part as in silicate analysis (p. 883).

With dolomitic limestones and dolomites it will be usually impossible to obtain a correction by the second method given under Magnesium (p. 640) for the small amount of calcium with the magnesium pyrophosphate. Method A, The Alkaline Earths (p. 612), is to be followed.

The accurate determination of barium in a limestone is more difficult than in a silicate rock. It is perhaps best to recover it, if it is present, from the filtrates from the calcium oxalate, after evaporating them and expelling ammonium salts (p. 133) by taking up the residue in as little hydrochloric acid as possible and, without filtering, adding a few drops of sulfuric acid

C. SIMULTANEOUS DETERMINATION OF WATER AND OF TOTAL CARBON

In the presence of sulfides or soluble organic matter, the following method will sometimes answer for the simultaneous determination of water and of the carbon of carbonates and organic matter.

Ignite in a current of air 1 g of the rock in a tube of very hard glass, or in the tubulated crucible of Gooch (Fig. 39, p. 831), and collect the water and the carbon dioxide. The sulfur of sulfides will be retained as calcium sulfate. It is necessary for the success of this operation that the temperature be sufficient to drive out all carbon dioxide from the carbonates, but insufficient to decompose calcium sulfate. The water found represents that in the minerals of the rocks as well as that derived from the hydrogen of the organic matter.

A separate determination of the carbon dioxide (see B, p. 934) gives the data for calculating the carbon of the organic matter.

According to G. T. Morgan,[19] the two conditions of carbon can be determined successively on the same portion of sample by first finding the carbon dioxide as in A, but with substitution of orthophosphoric for hydrochloric acid, and then, after weighing and replacing the absorption tubes, adding chromic acid and renewing the boiling to oxidize the organic matter and liberate its carbon as CO_2.

10. CHLORINE

Several grams of the rock are dissolved in the cold, or with as low a heat as may be, in dilute nitric acid free from chlorine, the solution is filtered, silver nitrate added, and the precipitate collected and treated as usual (see pp. 936–938).

If the rock is likely to contain chlorine-bearing silicates, it is decomposed with its own weight or less of chlorine-free sodium carbonate in a platinum crucible over the burner or moderate blast without undue prolongation of the heating. The mass is extracted with hot water and the filtrate acidified with cold dilute nitric acid, or it may be decomposed directly with the acid and the solutions filtered. The further treatment is as above given.

11. FLUORINE

As with silicate rocks, an exact determination of fluorine in carbonate rocks is difficult. Probably the best procedure is to separate the fluorine from most of the other constituents of the rock by the Willard and Winter distillation (p. 742), and then to titrate the fluorine in the distillate with thorium nitrate (p. 744) or to determine it colorimetrically by the Steiger-Merwin method or one of its modifications. If the material is not completely soluble in the acid prescribed in the method, the residue should be examined for fluorine, or the whole sample may be fused with sodium carbonate before distillation.[20]

12. SULFUR

A. TESTS AS TO ITS CONDITION; DETERMINATION OF SULFATE SULFUR

In very many, perhaps most, carbonate rocks, any sulfur present is chiefly if not wholly in the sulfide condition, and then usually as pyrite. In what condition it may be is readily ascertainable. If moistened lead acetate paper is blackened when held over the mouth of a test tube in which some of the rock powder is being boiled with dilute hydrochloric acid, a soluble sulfide is indicated, but it is seldom more than a negligible trace. If the filtrate after approximate neutralization with ammonia gives a precipitate with barium chloride there is sulfate present. If the total sulfur obtained as in B, below, is in excess of that in the sulfate and soluble sulfide states, the difference may safely be calculated to iron disulfide.

In the presence of much sulfide and also of sulfate sulfur, the extraction of the latter should be made in an atmosphere of carbon dioxide, but usually this precaution is quite unnecessary. For details of the determination of sulfur, consult page 948.

B. DETERMINATION OF TOTAL SULFUR

a. *Methods of Converting Sulfides to Sulfates.* α. *By ignition without flux.* In a rock that is not heavily charged with sulfides, the following method has afforded excellent results, even in the presence of 1 per cent of organic matter, though its range of application has not been ascertained:

The platinum crucible containing 1 to 2 g of the rock powder is placed in the perforated disk (Fig. 6, p. 25) and exposed to the heat of a burner for 15 minutes or to that of an inclined and moderate blast for 10 minutes. So far as present experience teaches, it is not at all necessary to begin with a gentle heat. All sulfide sulfur is oxidized and retained by the lime as sulfate without any loss by volatilization, all organic matter is removed, and the silicates are rendered soluble in acid if they are not in excess (see p. 966)..

β. *By ignition with sodium carbonate.* From 1 to 2 g of powder is mixed with half the weight of sulfur-free sodium carbonate in a platinum crucible and heated in the perforated disk, as in α. It is not probable that the addition of niter is called for, even when a good deal of carbonaceous matter is present. Since not enough flux is used to produce more than a sintering,

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[19] *J. Chem. Soc.*, **85**, 1001 (1904).

[20] James I. Hoffman and G. E. F. Lundell, Analysis of Phosphate Rock, *J. Research NBS*, 20, 610 (1938).

the air entering the crucible after the bulk of the carbon dioxide has passed off effects very speedy oxidation in the porous mass.

With highly impure limestones it may be necessary to increase the amount of flux and to use a little niter as well.

b. *Treatment after Ignition.* The ignited mass obtained in a, α or β will usually separate easily from the crucible. It is transferred to a small beaker and covered with water. The crucible is cleansed with dilute hydrochloric acid and the solution poured into the beaker. More acid is added until decomposition is complete in the cold or on gently warming. The solution is then filtered, diluted if need be to 150 or 200 ml containing 1 to 2 per cent of hydrochloric acid by volume, brought to boiling or simply placed on the steam bath; barium chloride is added, and the precipitated sulfate is collected in due time and weighed as described under Sulfur (p. 719).

Evaporation to dryness to separate the dissolved silica is quite unnecessary. After decomposition with acid, the solution should never be permitted to gelatinize, and it needs but little practice on the part of the operator to insure unfailing success in preventing this. If it should happen, however, it is generally best to begin over, but the difficulty may be overcome if but little free acid is present by dissolving the gelatinized silica in sulfur-free fixed alkali and reacidifying in the cold with hydrochloric acid.

13. Water

A. HYGROSCOPIC WATER

From one to several grams of the air-dry powder are heated in a current of air dried by calcium chloride in a glass tube at 100° to 105°, and the escaping water is collected in a calcium chloride tube, or the air may be dried by sulfuric acid or magnesium perchlorate trihydrate and the water collected in the same kind of desiccant. This direct determination of the water is certain to give a higher and more correct result than that obtained by drying in a crucible at the above temperature.

B. FIRMLY HELD WATER

Combined water may be determined ordinarily on the air-dry sample by heating in a tube of combustion glass and collecting the water in a calcium chloride tube with the above-mentioned precautions. Or the powder may be mixed with dry sodium carbonate and heated in the apparatus of Gooch (p. 830). From the result thus found, the separately determined hygroscopic water is to be deducted. It is to be remembered that the result will be in error by the amount of water afforded by the hydrogen of any organic matter there may be in the limestone.

III. CONDENSED ANALYSIS

For many purposes, especially those with a technical end in view, a highly refined or detailed analysis is not called for. The analyses of this kind that are now made vastly exceed in number those demanding the kind of work provided for in many of the subdivisions of Section II. To meet the needs of those having work of this kind to do, procedures are here given in brief that cover the important constituents of limestones. The operations are generally given without explanations. Those who seek reasons for one or another procedure or details of manipulations are referred to the corresponding parts of Section II.

1. Decomposition and Solution

If the substance is convertible by heating at 1000 to 1200° C into a condition wholly decomposable by hydrochloric acid, heat 0.5 to 1 g of the fine powder in a covered platinum crucible at 1200° C for 15 minutes, or longer if the temperature is lower.

If the material is very impure, mix 0.5 to 1 g with half its weight of pure sodium carbonate, and ignite until well sintered together.

Transfer the ignited material obtained in either of the above ways to an evaporating dish, preferably of platinum, and moisten with a few milliliters of water. Clean the crucible with dilute hydrochloric acid, pour the solution into the dish, which is to be kept covered if sodium carbonate was used, and add more acid. Solution of the mass may be aided by gentle pressure with the flattened end of a glass rod. Evaporate the solution to dryness on the steam bath.

2. Silicon

Drench the residue with 5 to 10 ml of hydrochloric acid, and dilute with 50 ml of hot water. Cover the dish, and digest for 10 minutes on the bath, after which filter the solution through a 7-cm paper. Wash the silica with hot dilute hydrochloric acid (5 + 95) at first, followed by a little hot water. Evaporate the filtrate to dryness on the steam bath, and then heat for 1 hour at 105 to 110° C. Treat the residue with acid and water, but in smaller amounts, and digest as before. Collect the second portion, of usually dark-colored silica, on another small paper, and wash first with cold dilute hydrochloric acid (1 + 99) and then with hot water. Reserve the filtrate *A*. Heat the filter papers with their contents slowly in a platinum crucible, and then ignite, first over the burner and finally at 1200° C for 5 to 15 minutes, according to the amount of the silica. Repeat the heating until constant weight is obtained. Moisten the weighed silica with water, and add

1 drop of dilute sulfuric acid (1 + 1) and 5 to 10 ml of pure hydrofluoric acid. Place the crucible in a radiator (Fig. 5, p. 24), and evaporate the liquid. Heat the residue at 1000 to 1100° C for a minute, and in due time weigh. It is better not to make this correction if it is not intended to separate and determine also the silica always accompanying the iron and aluminum oxides, for the reason that, with the small amount of silica in limestones, the nonvolatile residue compensates more or less for the silica remaining in solution after the second evaporation; but it should never be omitted if this latter correction is contemplated. If a correction is made and the residue weighs more than 1 to 2 mg, it is safer to fuse it with a little sodium carbonate and to add a solution of the melt to the filtrate from the silica than to weigh the residue with the ammonia precipitate.

Results obtained by a single evaporation for silica are always low if treatment with sulfuric and hydrofluoric acids is carried out, even though the silica content of the ammonia precipitate is afterwards determined.[21]

3. ALUMINUM, IRON, ETC.

Treat the filtrate *A*, which need not exceed 100 ml in bulk if the limestone is fairly pure, with a few drops of methyl red, heat to boiling, and then add dilute ammonium hydroxide (1 + 1), slowly until the indicator just turns yellow. Boil for 1 to 3 minutes, filter at once, wash the beaker and paper once or twice with a hot 2 per cent solution of ammonium chloride, and set the filtrate *B* aside. If the precipitate is small and well washed, reprecipitation can be omitted. If it is large, place the original beaker under the funnel, dissolve the precipitate in hot dilute hydrochloric acid (1 + 1), thoroughly wash the paper with hot water, and set it aside. Dilute the solution to approximately 75 ml, add methyl red, precipitate with ammonium hydroxide as before, stir in the reserved paper, and filter through a new paper. Transfer the precipitate completely to the paper, and wash with the hot solution of ammonium chloride. Combine the filtrate with filtrate *B*. A third precipitation is rarely necessary.

Place the paper and precipitate in a platinum crucible, char the paper slowly as the heat is gradually increased, and finally heat under good oxidizing conditions at approximately 1200° C for 5 to 10 minutes. The weight found represents the oxides of ferric iron, aluminum, titanium, phosphorus, and the like, but not of manganese.

If the weighed precipitate is small, as is often the case, a correction for its silica content can be made as follows: Treat with a drop of dilute sulfuric acid (1 + 1) and then with 5 to 10 ml of hydrofluoric acid, and evaporate to dryness. Heat, gently at first, until sulfates are decomposed, then at approximately 1000° C for 3 to 5 minutes and weigh.

The iron and titanium in the weighed oxides can be determined after fusion with pyrosulfate as directed on page 877, but in the general case are more expeditiously determined in fresh samples, as is also the case with phosphorus. Aluminum oxide is gotten by subtracting all of the oxides found from the weight of the mixed oxides. If a deduction for iron alone is made, the percentage reported for alumina may be entirely misleading. The percentage of mixed oxides obtained after a single precipitation with ammonium hydroxide is normally high, and so is the percentage of alumina.[22]

4. MANGANESE

If manganese is present in the limestone, it falls in part with calcium and in larger part with magnesium unless prior removal is made. It can be precipitated and removed by treating filtrate *B* with ammonium sulfide, or caught in the ammonia precipitate as follows: Dilute filtrate *A* to 150 to 200 ml, add 10 to 15 ml of hydrochloric acid if not already present, nearly neutralize with ammonium hydroxide, add 1 g of solid ammonium persulfate, and continue the addition of ammonium hydroxide until the solution is just alkaline to litmus. Heat the solution to boiling, boil for 2 minutes, and add ammonium hydroxide until the solution is again alkaline to litmus.[23] Filter immediately, wash moderately with a hot 2 per cent solution of ammonium chloride, and reserve the filtrate *B*. Dissolve the precipitate in hot dilute hydrochloric acid, cool, reprecipitate as before, filter, wash, and combine the filtrate with the reserved filtrate *B*.

The actual determination of manganese had better be made as described

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[21] For example, after a single evaporation for silica in a sample of glass containing 74.1 per cent of SiO_2, the percentage of SiO_2 indicated was 73.7 when no corrections were made, 73.5 when treatment with $HF—H_2SO_4$ was carried out, and 73.7 when the latter result was corrected by the silica carried down by the ammonia precipitate. Similar procedures applied to a sample of argillaceous limestone containing 18.08 per cent of SiO_2 gave 17.80, 17.71, and 17.90 respectively. It is evident that very little, if anything, is gained by applying corrections after a single evaporation, and that all of the silica that escapes is not caught by the ammonia precipitate.

[22] For example, after a single precipitation with ammonium hydroxide following a single evaporation for silica in the analysis of a soda-lime glass containing 0.42 per cent of "R_2O_3," the percentage indicated was 0.58 when the precipitate was weighed by itself, 0.78 when it was weighed with the nonvolatile residue left from the silica, and 0.63 when the last result was corrected for silica. Similar treatments applied in the analysis of an argillaceous limestone containing 7.86 per cent of "R_2O_3" indicated 8.09 per cent when the nonvolatile residue was not included and 7.91 per cent when this result was corrected for silica.

[23] Litmus is not an ideal indicator for use in the precipitation of aluminum, but is specified because indicators such as methyl red are destroyed in the hot oxidizing solution. The amount of aluminum left in solution is negligible in ordinary analyses.

under Manganese (p. 443 or p. 451), in a separate portion of material, and its effect, as Mn_3O_4, deducted from the weighed mixed oxides if persulfate has been used.

5. Calcium

Concentrate the reserved filtrate *B* if need be to a bulk of 200 to 250 ml with occasional addition of a few drops of ammonium hydroxide. If a slight precipitate separates, collect it on a small filter, wash with a hot 2 per cent solution of ammonium chloride, redissolve in dilute hot hydrochloric acid, reprecipitate, filter, and add the precipitate to the main quantity of iron and aluminum oxides. Combine the filtrates, boil, and slowly add 40 ml (for 1 g of sample; 20 ml if but 0.5 g is under analysis) of a hot 4 per cent solution of ammonium oxalate. Continue the boiling until the precipitated calcium oxalate assumes a well-defined granular form, and set aside to cool for 1 hour. Filter and wash a few times with a 0.1 per cent solution of ammonium oxalate. Reserve the filtrate *C*. Place the beaker under the funnel, dissolve the precipitate in 25 to 50 ml of hot dilute hydrochloric acid (1 + 9), and wash the paper with hot water. Dilute to 100 ml, add 5 ml of the 4 per cent oxalate solution, boil, and then slowly stir in ammonium hydroxide until in slight excess. Filter after 1 hour, wash beaker, paper, and precipitate moderately at first with the dilute oxalate solution and then with no more hot water than is necessary to wash out the excess oxalate (approximately 50 ml, used in small portions). Drain, combine the filtrate with filtrate *C*, and reserve for the determination of magnesium. Sluice as much of the precipitate as possible back into the beaker, and spread the opened filter on the inside of the beaker near the top. Add sulfuric acid, and titrate with permanganate as described under The Alkaline Earths (p. 627).

If desired, the final precipitate can be ignited and weighed as the oxide as described under The Alkaline Earths (p. 624). Results obtained by single precipitations of the oxalate are high, no matter whether the precipitate is ignited or titrated, the former as a rule giving a higher result than the latter.[24] The oxalate precipitate contains practically all of any strontium originally present in the material, part of the manganese if it was not removed, and no barium. If strontium is to be sought, the oxalate precipitate must be ignited, weighed, and converted to nitrates and strontium separated by ether alcohol as described under The Alkaline Earths (p. 615).

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[24] For example, in the analysis of a soda-lime glass after a single precipitation with ammonium oxalate, following a single evaporation for silica and a single precipitation with ammonium hydroxide, the percentage of CaO indicated was 5.11 when the precipitate was ignited to oxide, and 4.81 when it was titrated with permanganate, as against the true value 4.65. Ignition to the oxide after similar treatment of a limestone gave 38.7 per cent of CaO as against the actual content 37.7.

6. Magnesium

To the filtrate *C* reserved in the determination of calcium, add 2 g of diammonium phosphate, $(NH_4)_2HPO_4$, and then 1 g extra for each 100 ml of solution. Stir until dissolved, add sufficient ammonium hydroxide to give an excess of 5 per cent by volume, again stir thoroughly, and set aside for at least 4 hours, preferably overnight if the precipitate is very slight or the volume of the solution exceeds 400 ml. Filter, wash the beaker, paper, and precipitate moderately with dilute ammonium hydroxide (5 + 95), and discard the filtrate. Place the beaker under the funnel, and dissolve the precipitate in 25 to 50 ml of hot, dilute hydrochloric acid (1 + 9). Add 0.1 g of diammonium phosphate, dilute to 75 ml, cool, and then add ammonium hydroxide, drop by drop with constant stirring until the solution is alkaline. Finally add 5 ml in excess, and let stand 4 hours. Decant the solution through a fresh paper, wash the precipitate once by decantation with the cool 5 per cent ammonium hydroxide, and then transfer the precipitate quantitatively to the paper and continue the washing until chlorides are removed.

Dry the precipitate, wrapped in its moist paper, in a weighed platinum crucible, char the paper slowly without letting it ignite, burn the carbon over a gradually increased flame, and finally heat for 15 to 30 minutes at 1000 to 1050° C. Cool in a desiccator, and weigh as $Mg_2P_2O_7$.

The weighed residue contains any lime that escaped precipitation as oxalate, all of any barium originally present in the sample, and practically all of any manganese present in the filtrate from the calcium.

Results obtained by a single precipitation of magnesium in the solution left after the determination of calcium are normally high in any precipitation procedure, hot or cold, that gives complete precipitation of the magnesium that is present.[25] If many determinations are to be made, the final precipitate can be titrated as described under Magnesium (p. 644).

7. Alkalies

See 8 (page 976).

8. Carbon Dioxide

See 9 (page 977).

9. Sulfur

See 12 (page 979).

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[25] For example, in analyses in which but single treatments were made for the separation of SiO_2, "R_2O_3," and CaO, single precipitations of the magnesium phosphate indicated 3.31 per cent of MgO as against the true content 3.23 in a soda-lime glass, and 5.46 instead of 5.08 in a limestone.

10. Water

See 13 (page 980).

11. Ignition Loss

The determination of ignition loss has little significance, though it affords a more or less correct indication of the proportion of carbonates in the rock. As it is a determination commonly made in commercial laboratories, some space will be devoted to it.

Loss on ignition with carbonate rocks represents, as with those of a silicate nature, the algebraic sum of a number of chemical changes involving both losses and gains, and its amount will depend largely on the temperature employed. At the temperature of a moderate blast (1100° C), with crucible covered, carbon dioxide, water, and carbonaceous matter escape wholly. Sulfides are oxidized to sulfates, and all the sulfur is retained as sulfate by the calcium. With a powerful blast (1200 to 1300° C) the sulfate is decomposed gradually, with eventual loss of the entire sulfur. At this point the alkalies begin to escape as oxides, the potassium relatively faster than the sodium, and they may be found in part condensed on the lid of the crucible. If the heating is long continued, they can be wholly volatilized. As a small offset to these losses, the iron of pyrite and the iron and manganese of ferrous and manganous carbonates take up oxygen and unite with the lime. By proper control of the temperature it is not difficult to prevent loss of sulfur and alkalies, and this is the object to be sought in making the determination.

From 0.5 to 1 g of the powder is placed in a platinum crucible of 20 to 25 g weight, the crucible is inserted to three fifths of its depth in a perforated platinum disk or asbestos board (Fig. 6, p. 25), and an inclined blast flame of considerable intensity is caused to play against the bottom of the covered crucible for 15 or 20 minutes. A repetition of the heating for 5 minutes will usually cause little or no further loss. Duplicate determinations should agree within 0.2 per cent, and, after the operator becomes skilled, probably within 0.1 per cent. A muffle can be substituted for the blast. It is important that each operator should ascertain just what the proper conditions may be for his particular blast or muffle. They are right if after the ignition he finds exactly the whole of the sulfur in the ignited powder in the sulfate state.

TABLE 35

International Atomic Weights,* 1951

	Symbol	Atomic Number	Atomic Weight †		Symbol	Atomic Number	Atomic Weight †
Actinium	Ac	89	227	Molybdenum	Mo	42	95.95
Aluminum	Al	13	26.98	Neodymium	Nd	60	144.27
Americium	Am	95	[243]	Neptunium	Np	93	[237]
Antimony	Sb	51	121.76	Neon	Ne	10	20.183
Argon	A	18	39.944	Nickel	Ni	28	58.69
Arsenic	As	33	74.91	Niobium	Nb	41	92.91
Astatine	At	85	[210]	Nitrogen	N	7	14.008
Barium	Ba	56	137.36	Osmium	Os	76	190.2
Berkelium	Bk	97	[245]	Oxygen	O	8	16
Beryllium	Be	4	9.013	Palladium	Pd	46	106.7
Bismuth	Bi	83	209.00	Phosphorus	P	15	30.975
Boron	B	5	10.82	Platinum	Pt	78	195.23
Bromine	Br	35	79.916	Plutonium	Pu	94	[242]
Cadmium	Cd	48	112.41	Polonium	Po	84	210
Calcium	Ca	20	40.08	Potassium	K	19	39.100
Californium	Cf	98	[246]	Praseodymium	Pr	59	140.92
Carbon	C	6	12.010	Promethium	Pm	61	[145]
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium (see Niobium)				Rubidium	Rb	37	85.48
Copper	Cu	29	63.54	Ruthenium	Ru	44	101.7
Curium	Cm	96	[243]	Samarium	Sm	62	150.43
Dysprosium	Dy	66	162.46	Scandium	Sc	21	44.96
Erbium	Er	68	167.2	Selenium	Se	34	78.96
Europium	Eu	63	152.0	Silicon	Si	14	28.09
Fluorine	F	9	19.00	Silver	Ag	47	107.880
Francium	Fr	87	[223]	Sodium	Na	11	22.997
Gadolinium	Gd	64	156.9	Strontium	Sr	38	87.63
Gallium	Ga	31	69.72	Sulfur	S	16	32.066
Germanium	Ge	32	72.60	Tantalum	Ta	73	180.88
Gold	Au	79	197.2	Technetium	Tc	43	[99]
Hafnium	Hf	72	178.6	Tellurium	Te	52	127.61
Helium	He	2	4.003	Terbium	Tb	65	159.2
Holmium	Ho	67	164.94	Thallium	Tl	81	204.39
Hydrogen	H	1	1.0080	Thorium	Th	90	232.12
Indium	In	49	114.76	Thulium	Tm	69	169.4
Iodine	I	53	126.92	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.90
Iron	Fe	26	55.85	Tungsten	W	74	183.92
Krypton	Kr	36	83.80	Uranium	U	92	238.07
Lanthanum	La	57	138.91	Vanadium	V	23	50.95
Lead	Pb	82	207.21	Xenon	Xe	54	131.3
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.99	Yttrium	Y	39	88.92
Magnesium	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mercury	Hg	80	200.61				

* Adopted by International Union of Chemistry at New York, September 1951.

† A value given in brackets denotes the mass number of the isotope of longest known half-life.

Owing to the isotopic nature of the oxygen standard, physicists are using atomic weights slightly different from those given in the table. To convert from the chemical atomic weights to the physical, multiply by 1.000278. Because of natural variations in the abundance ratio of the isotopes of sulfur, the atomic weight of this element has a range of ±0.003. The table is given for the reader's convenience, but the new atomic weights, published periodically by the American Chemical Society, should always be consulted.

INDEX OF SUBJECTS