MANUAL OF FIRE ASSAYING

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SUN VALLEY, CALIFORNIA
1977

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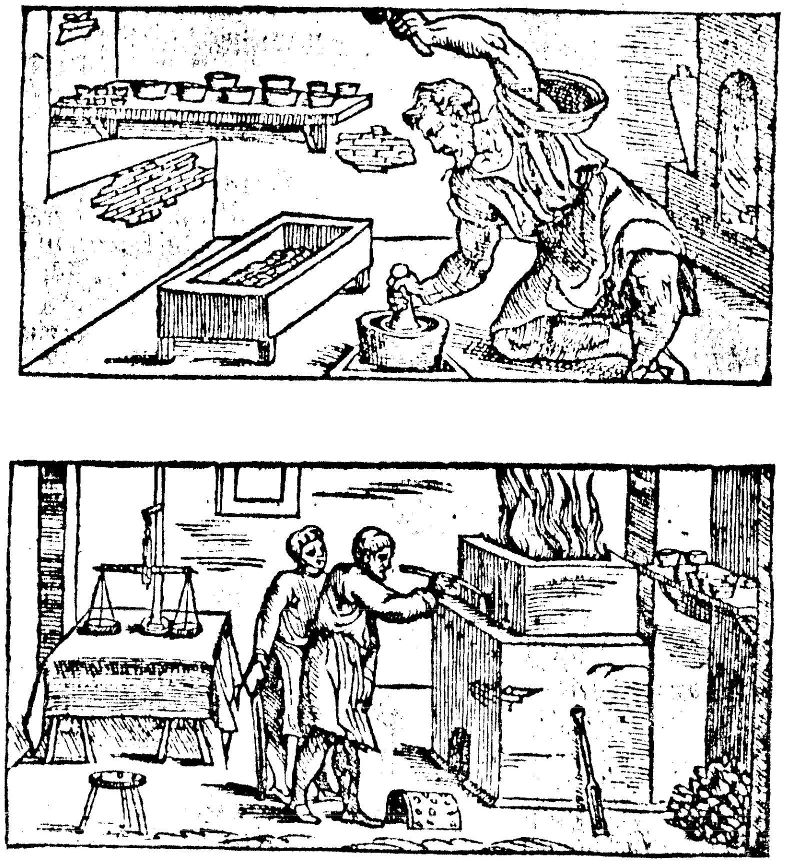

The Assayer.—From Pirotechnia, Li Diece Libri Della Pirotechnia, by Vannuccio Biringoccio, Venice, MDLVIII.—(3rd edition),

CHAPTER I.

ASSAY REAGENTS AND FUSION PRODUCTS.

Assaying is a branch of analytical chemistry, generally defined as the quantitative estimation of the metals in ores and furnace products. In the western part of the United States, the term is employed to include the determination of all the constituents, both metallic and non-metallic, of ores and metallurgical products.

Fire assaying is the quantitative determination of metals in ores and metallurgical products by means of heat and dry reagents. This involves separating the metal from the other constituents of the ore and weighing it in a state of purity.

An **ore** is a mineral-bearing substance from which a metal, alloy or metallic compound can be extracted at a profit. The term is loosely used to include almost any inorganic substance that may occur in nature. An ore generally consists of two parts, the metalliferous or valuable portion, and the " gangue " or valueless portion. Gangue minerals are divided, according to their chemical composition, into two classes, acid and basic. Silica is a type of the former; lime, magnesia, and the oxides of iron, manganese, sodium and potassium are examples of the latter.

An ore may be acid, basic or " self-fluxing " according to the preponderance of one or the other group of slag-forming gangue constituents. A self-fluxing ore is one which contains acid and basic material in the right proportion to form a slag.

The metallurgical products which come to the assayer include bullion, matte, speiss. drosses and crusts, litharge, flue-dust and fume, as well as solutions and precipitates resulting from hydrometallurgical operations.

The reagents used in fire assaying may be classified as fluxes, acid, basic or neutral, and as oxidizing, reducing, sulphurizing or desulphurizing agents. Some reagents have only one property, as for instance silica, an acid flux, others have several different properties, as litharge, a basic flux but also an oxidizing and desulphurizing agent.

A **flux** is something which converts compounds infusible at a certain temperature into others which melt at this temperature. For instance, **quartz** by itself is fusible only at a very high temperature, but if some sodium carbonate is added to the pulverized quartz it can be fused at a temperature easily obtained in the assay furnace.

The student should remember that to aid in the fusion of an acid substance, a basic flux such as litharge, sodium carbonate, limestone, or iron oxide should be added while for a basic substance an acid flux such as silica or borax should be used.

A **reducing agent** is something which is capable of causing the separation of a metal from the substances chemically combined with it or of effecting " the stepping down " of a compound from a higher to a lower degree of oxidation.

An **oxidizing** agent is one which gives up its oxygen readily.

A **desulphurizing agent** is something which has a strong affinity for sulphur and which is therefore capable of separating it from some of its compounds.

The principal reagents used in assaying follow:

Silica, SiO_2, is an acid reagent and the strongest one available. It combines with the metal oxides to form silicates which are the foundation of almost all slags. It is used as a flux when the ore is deficient in silica and serves to protect the crucibles and scorifiers from the corrosive action of litharge. Care must be taken to avoid an excess of silica, as too much of it will cause trouble and losses of precious metals by slagging or by the formation of matte. Silica melts at about 1625° C. to an extremely viscous liquid. It should be obtained in the pulverized form.

The fluxing effect of silica is shown in the accompanying freezing-point curve* of the lime-silica series. The series shows three eutectics and two compounds. The combination having the lowest melting-point is the eutectic with 37 per cent of CaO which melts at 1417° C. Another eutectic containing 54 per cent CaO melts at 1430° C. Lying between these is the compound calcium bi-silicate, corresponding to the formula $CaSiO_3$, which fuses at

1512° C. A second compound, corresponding to the formula Ca_2SiO_4, the calcium singulo-silicate melts at 2080° C. A cursory glance at this curve will be sufficient to suggest the desirability of trying to make approximately a bi-silicate slag when assaying ores which contain considerable lime

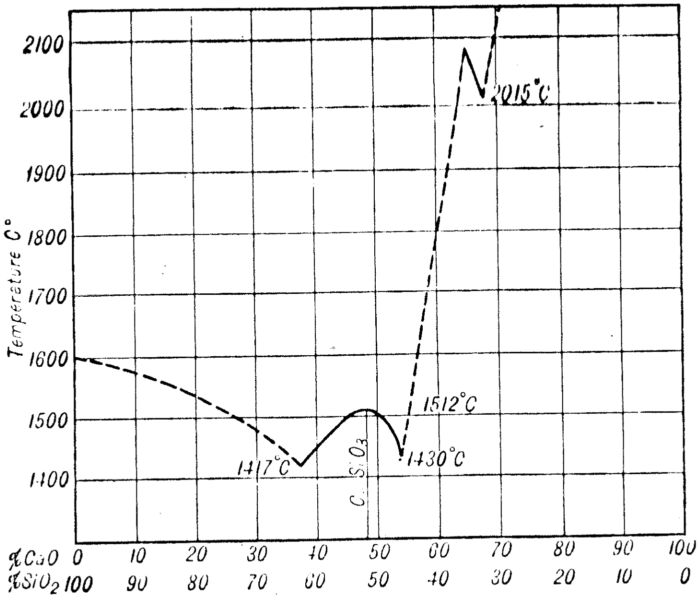

FIG. 1. — Freezing-point curve of lime-silica series.

Glass is used by some in place of silica. Ordinary window-glass, a silicate of lime and the alkalies with the silica in excess, is best. Its acid excess is always doubtful and so is not commonly used. If used, a blank assay should be run on each new lot to insure against introducing precious metals into the assay in this way. Its chief advantage is that 5 or 10 grams too much glass will ordinarily do no harm in a fusion whereas 5 or 10 grams of silica in excess might spoil the assay.

Borax. — $Na_2B_4O_7$, $10H_2O$, is an active, readily fusible, acid flux. It melts in its own water of crystallization, beginning at the lowest visible red heat, and becomes anhydrous at a full red heat. It intumesces in fusing and on account of this behavior may, if used in large amounts, tend to force part of the charge out of the crucible, especially if not thoroughly mixed with the charge.

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* Day and Shepard Am. Jour. Sc. **22**, p. 255.

results a very tough, glassy or stony slag which holds tenaciously to the lead button. This is probably due partly to the effect of borax in reducing the coefficient of expansion of the slag and partly to its action in preventing crystallization. When the attempt is made to separate the lead and slag, a film of lead will often adhere to the slag and give the assayer much trouble.

The remedy for this condition is, first, to reduce the quantity of borax used and then, if necessary, to increase the bases. No more than 5 or 10 grams of common borax or its equivalent in borax-glass should be used per assay-ton of siliceous ore.

The melting-point curve of the sodium meta-borate — sodium bi-silicate series, according to Van Klooster[*], is shown in Fig. 2. The melting-point of sodium bi-silicate does not agree exactly with that given by Niggi but, none the less, the diagram serves to illustrate the effect which borax has in reducing the melting-point of assay slags.

The eutectic containing 56.5 per cent of Na_2SiO_3 freezes at 814° C.

Sodium bicarbonate, $NaHCO_3$, is still used by some assayers as an alkaline flux, mainly because of its cheapness and purity. It is, however, decomposed when heated to 276° C., forming the anhydrous normal carbonate with the liberation of water vapor and carbon dioxide. The large volume of water vapor and carbon dioxide released, passing up through the charge before it has softened, is bound to carry off more or less of the fine ore and thus contributes to the so-called "dusting" loss.

The bicarbonate contains but 63.1 per cent of Na_2CO_3 and therefore when it is used as a substitute for the normal carbonate 158 parts are required for each 100 parts of the normal carbonate. Because of the above serious disadvantages the use of the anhydrous normal carbonate is recommended in all cases. The only advantage which can now be claimed for the bicarbonate is that it does not deliquesce.

Sodium carbonate, Na_2CO_3, is a powerful basic flux and by far the cheapest one available for assay purposes. Owing to the ease with which alkaline sulphides and sulphates are formed it also acts to some extent as a desulphurizing and oxidizing agent. Pure anhydrous sodium carbonate melts at 852° C. When molten it is very fluid and can hold in suspension a large proportion of

Note Sulphides

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[*] Zeitschr. anorg. Chemie, 69, p. 122 (1910).

finely ground, infusible and inactive material such as carbon or bone-ash.

The commercial normal carbonate of this country, made by the Solvay process from the bicarbonate, is easily obtained in a pure state. It tends to absorb water from the air and is, therefore, unsatisfactory for use in some climates. The variety known by the trade as 58 per cent dense soda-ash has been found particularly satisfactory for assay purposes, and is but little affected by atmospheric moisture.

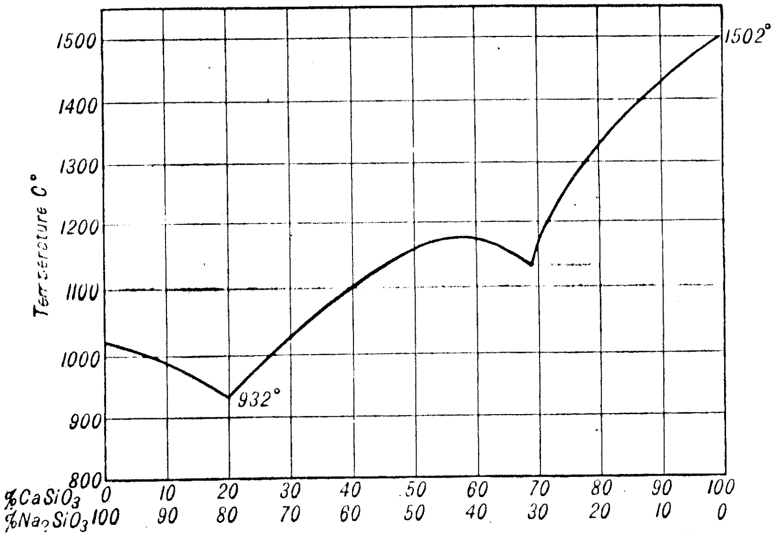

Fig. 3. — Freezing-point curve of calcium bi-silicate — sodium bi-silicate series.

When sodium carbonate is heated to about 950° C., it undergoes a slight dissociation with the consequent evolution of a small amount of carbon dioxide. Analysis of sodium carbonate which has been melted shows it to contain about 0.4 per cent of free alkali. When silica is added to the fused carbonate this free alkali first disappears and then a reaction takes place between the silica and sodium carbonate and a certain amount of carbon dioxide is evolved. The amount evolved is directly proportional to the amount of silica added and to the temperature. Niggi[*] showed that the system $Na_2CO_3 - SiO_2$, for a constant temperature and

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[*] Jour. Am. Chem. Soc. 35, pp. 1693–1727.

pressure of CO_2, reaches a state of equilibrium, which condition may be expressed by the equation:

$$Na_2CO_3 + Na_2SiO_3 \rightleftarrows Na_4SiO_4 + CO_2.$$

He found that in order to displace all the CO_2, at least one mol of SiO_2 for each mol of Na_2O must be added. Combinations less acid than the bi-silicate retain CO_2 indefinitely. The bi-silicate melts at about 1018° C.

The fluxing effect of sodium carbonate is shown in the accompanying freezing-point curve* of the calcium bi-silicate — sodium bi-silicate series.

Between the melting-point of sodium bi-silicate, 1018° C. and that of calcium bi-silicate, 1502° C., Wallace found indications of a eutectic containing 20 per cent $CaSiO_3$ which melted at 932° C. It may be concluded from this that if we are to flux limestone with soda and silica alone, we should add 4 mols of Na_2CO_3 for each mol of $CaCO_3$, or roughly 60 grams of Na_2CO_3 for ½ A.T. of pure $CaCO_3$, together with sufficient silica for a bi-silicate. The addition of borax will materially reduce the melting-temperature of the mixture.

Potassium carbonate, K_2CO_3, is a basic flux, similar in its action to sodium carbonate. It melts at 894° C. It has the disadvantage of being more expensive, weight for weight, than sodium carbonate, and because of its greater molecular weight more of it is required than of sodium carbonate to produce a given result.

Niggi† showed that a small amount of silica displaces an almost equivalent amount of CO_2 from fused potassium carbonate, and that successive additions of silica displace a progressively smaller quantity of CO_2, until when the proportions are 2 mols of SiO_2 to 1 mol of K_2O, the silica displaces only half the equivalent amount of CO_2, at which condition the last of the CO_2 passes off. He gives the following equation as expressing the conditions of equilibrium:

$$K_2CO_3 + K_2Si_2O_5 \rightleftarrows 2K_2SiO_3 + CO_2.$$

Willorf‡ contends that diminution of the partial pressure of CO_2 causes considerable displacement of the equilibrium toward the right-hand side of the equation. With this, Niggi does not agree and argues that the influence of the partial pressure of CO_2 is inconsiderable. He cites experimental data as well as theoretical grounds for this belief.

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* Zeitschr. anorg. Chemie, **63**, p. 1 (1909).

† loc. cit.

‡ Zeitschr. anorg. Chemie, **39**, 187 (1904).

As is the case with a mixture of sodium and potassium carbonates, a mixture of sodium and potassium silicates melts at a lower temperature than either one alone, and for this reason the mixture is used whenever it is desired to maintain a low temperature during the assay. The lead assay is an example and in fact is now about the only case in which it is still customary to use potassium carbonate in fire assaying.

Litharge, PbO, is a readily fusible basic flux. It acts also as an oxidizing and desulphurizing agent and on being reduced it supplies the lead necessary for the collection of the gold and silver. ← ✗ It melts at 883° C., and contains 92.8 per cent of lead.

Not sulphur

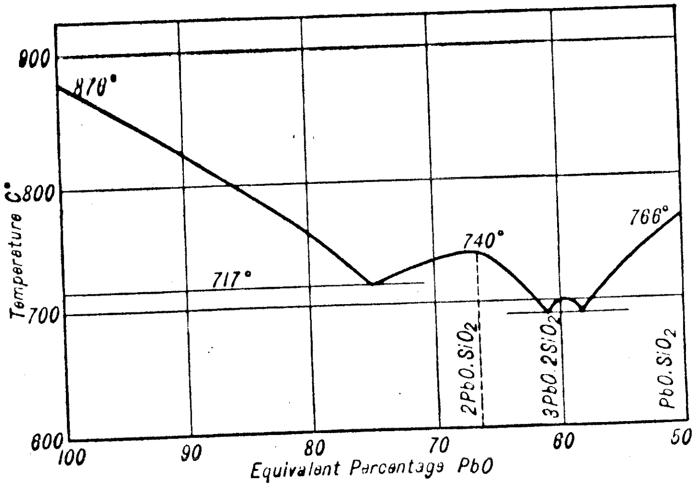

Fig. 4. — Freezing-point curve of litharge-silica series.

Mixtures of finely pulverized litharge and silica, ranging from $6PbO.SiO_2$ to $PbO.SiO_2$, begin to sinter at about 700° C. According to Mostowitch* the sub-silicate, $4PbO.SiO_2$, is completely liquefied at 726°; the singulo-silicate, $2PbO, SiO_2$, forms a viscous liquid at 724° but does not flow readily until heated to 940° C. The bi-silicate, $PbO.SiO_2$, melts at 770° and eutectic mixtures both lower and higher in silica fuse at lower temperatures.

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* Trans. A.I.M.E. **55**, p. 744.

the iron oxide formed acts as a basic flux. Iron decomposes all fusible lead silicates by replacing the lead, thus:

$$xPbO.SiO_2 + xFe = xFeO.SiO_2 + xPb.$$

It should therefore always be used in the lead assay.

It is used in the form of spikes or nails, and sometimes, especially in Europe, an iron crucible is employed.

Potassium nitrate, KNO_3, commonly known as niter, is a powerful oxidizing agent. It melts at 339° C. and fuses at a low temperature without alteration, but at a higher temperature it breaks up, giving off oxygen, which oxidizes sulphur and many of the metals, notably lead and copper.

It is used in the fire assay especially to oxidize sulphides, arsenides, antimonides, etc.

If fused alone it is stable until a temperature of 530° C. is reached, when it begins to decompose, giving off oxygen. When it is fused with charcoal, the two begin to react at about 440° C. The reaction between niter and carbon, according to Roscoe and Schoerleman, is as follows:

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2$$

According to the same authority, sulphur and niter react as follows:

$$2KNO_3 + 2S = K_2SO_4 + SO_2 + N_2.$$

Niter begins to react with silica at about 450° C.,* probably according to the following reaction:

$$4KNO_3 + 2SiO_2 = 2K_2SiO_3 + 5O_2 + 2N_2.$$

In a charge containing a large excess of soda and litharge the reaction with pyrite is as follows:

$$6KNO_3 + 2FeS_2 + Na_2CO_3 = \\ Fe_2O_3 + 3K_2SO_4 + Na_2SO_4 + CO_2 + 3N_2.$$

Many assayers object to the use of niter because of its oxidizing effect on silver. Large amounts of niter cause boiling of the crucible charge and necessitate careful heating to prevent loss. It is found to give less trouble when the crucible is uniformly heated, as in the muffle, than when the charge begins to melt first at the bottom, as in the pot-furnace.

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* Fulton, A Manual of Fire Assaying, p. 59

Potassium cyanide, KCN, is a powerful reducing and desulphurizing agent. It combines with oxygen, forming potassium cyanate, thus:

$$PbO + KCN = Pb + KCNO \text{ (reducing action)},$$

and also with sulphur, forming sulphocyanide, as follows:

$$PbS + KCN = Pb + KSCN.$$

It is sometimes used in the lead assay and usually in the tin and bismuth assays. It is extremely poisonous, and should be handled with great care. It fuses at 526° C.

Salt, NaCl, is used as a cover to exclude the air, and to wash the sides of the crucible and prevent small particles of lead from adhering thereto. It melts at 819° C.

It does not enter the slag, but floats on top of it. It is often colored by the different metallic oxides of the charge and sometimes helps to distinguish assays which have become mixed in pouring.

TABLE II.

ASSAY REAGENTS.

Name	Formula	Properties in order of their importance
Silica	SiO_2	Acid flux
Glass	$xNa_2O.yCaO.zSiO_2$	Acid flux
Borax	$Na_2B_4O_7.10H_2O$	Acid flux
Borax-glass	$Na_2B_4O_7$	Acid flux
Sodium bicarbonate	$NaHCO_3$	Basic flux, desulphurizing
Sodium carbonate	Na_2CO_3	Basic flux, desulphurizing
Potassium carbonate	K_2CO_3	Basic flux, desulphurizing
Litharge	PbO	Basic flux, desulphurizing, oxidizing
Potassium nitrate	KNO_3	Oxidizing, desulphurizing
Argols	$KHC_4H_4O_6 + C$	Reducing agent, basic flux
Cream of tartar	$KHC_4H_4O_6$	Reducing agent, basic flux
Flour		Reducing agent
Charcoal	C	Reducing agent
Lead	Pb	Collecting agent
Iron	Fe	Desulphurizing and reducing agent
Potassium cyanide	KCN	Reducing and desulphurizing agent
Salt	NaCl	Cover and wash
Fluorspar	CaF_2	Neutral flux
Cryolite	$AlNa_3F_6$	Neutral flux

Fluorspar, CaF_2, is occasionally used as a flux in fire assaying. Its melting-point is 1361° C. and it would, therefore, seem to be of doubtful value in fire assay fusions which seldom exceed 1200° C.

When melted it is very fluid and assists in liquefying the charge, although it is inert and does not ordinarily enter into chemical combination with the other constituents of the charge. Karandéeff* shows a melting-point curve of $CaF_2 - CaSiO_3$ series with a eutectic, containing 54 molecular per cent of $CaSiO_3$, which fuses at 1128° C.

Cryolite, $AlNa_3F_6$, is a powerful flux, commonly used in the manufacture of enamels and occasionally in the melting of bullion. It may sometimes be useful in fire assaying. Cryolite melts at about 977° C. and has the property of dissolving alumina. It increases the coefficient of expansion of the slag.

Fusion Products. — Every gold, silver or lead assay fusion, if the charge is properly proportioned and manipulated, should show two products, a lead button and, above it, a slag. Two undesirable products, matte and speiss are occasionally also obtained. When a cover of salt is used, or if niter is used in the assay, a third product will be found on top of the solidified slag. In the first case this is almost entirely sodium chloride, in the latter case it is a mixture of the sulphates of sodium and potassium.

THE LEAD BUTTON should be bright, soft and malleable and should separate easily from the slag. It should contain practically all of the gold and silver which were in the ore taken for the assay.

SLAG is a fusible compound of earthy or metallic oxides and silica or other acid constituents. The slags made in fire assaying are usually silicates or borates of the metallic oxides contained in the ore and fluxes used.

Slags should be homogeneous and free from particles of undecomposed ore. A good slag is usually more or less glassy and brittle. When poured, the slag should be thin and fluid and free from shots of lead. If too acid, it will be quite viscous and stringy, and the last drops will form a thread in pouring. If too basic, it will be lumpy and break off short in pouring. When cold, the neutral or acid slag is glassy and brittle, the basic one is dull and stony-looking.

Slags in the molten state are usually solutions, but in rare cases they may be chemical compounds. In the solid state they are usually either solid solutions or eutectic mixtures; occasionally they may be chemical compounds.

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* Zeitschr. anorg. Chemie, 68, p. 188 (1910).

MATTE is an artificial sulphide of one or more of the metals, formed in the dry way. In assaying it is most often encountered in the niter fusion of sulphide ores when the charge is too acid. It is found lying just above the lead button. It is usually blue-gray in color, approaching galena in composition and very brittle. It may form a layer of considerable thickness, or may appear simply as a granular coating on the upper surface of the lead button. This matte always carries some of the gold and silver and, as it is brittle, it is usually broken off and lost in the slag in the cleaning of the lead button. The student should examine the lead button as soon as it is broken from the slag and if any matte is found, he may be certain that his charge or furnace manipulations are wrong.

SPEISS is an artificial, metallic arsenide or antimonide formed in smelting operations. As obtained in the fire assay, it is usually an arsenide of iron approaching the composition of Fe_5As. Occasionally the iron may be replaced by nickel or cobalt. The antimony speiss is very rare. In assaying, speiss is obtained when the iron method is used on ores containing arsenic. It is a hard, fairly tough, tin-white substance found directly on top of the lead and usually adhering tenaciously to it.

If only a small amount of arsenic is present in the ore, the speiss will appear as a little button lying on top of the lead; if much arsenic is present, the speiss will form a layer entirely covering the lead. It carries some gold and silver. If only a gram or so in weight, it may be put into the cupel with the lead and will be oxidized there, giving up its precious metal values to the lead bath. A large amount of speiss is very hard to deal with as it is difficult to scorify. The best way is to assay again, by some other method.

CHAPTER II

REDUCTION AND OXIDATION REACTIONS

REDUCTION.—A reduction reaction, as particularly defined for assaying, is one in which a metal is reduced from its compounds by some reducing agent. The chemical definition is also applicable in that, in assaying, we frequently reduce a compound from a state of higher oxidation to a lower state of oxidation by means of a reducing agent.

An oxidation reaction is one in which a metal or a compound is changed to a compound of a higher state of oxidation; for example, Pb to PbO, S to SO_2, or PbO to PbO_2. Reduction and oxidation reactions frequently occur in assaying, and it is essential that the assayer be thoroughly familiar with the theory and facts. In speaking of reducing agents and reduction with special reference to assaying, we have chiefly in mind such reagents as reduce metallic lead from litharge in the crucible. The chief of these are: (1) argol, (2) charcoal or coke or coal dust, (3) flour or sugar. These are added to the charge in sufficient quantity to produce the proper size of lead button in the crucible assay. It often happens that an ore will contain reducing agents, chiefly sulphides, so that it becomes unnecessary to add an extraneous agent. In fact, it may contain an excess of reducing agent, requiring an oxidizing agent to destroy the excess.

The reduction of lead by argol is expressed by the following equation:

$$\underset{}{10\,PbO} + \underset{376}{2KHC_4H_4O_6} = \underset{2070}{10Pb} + 5H_2O + K_2O + 8CO_2$$

One gram of argol will reduce 5.50 grams of lead from 5.93 or more grams of PbO. The above formula for argol is that of pure bitartrate of potassium. Argol contains as impurity a certain amount of carbonaceous matter, so that its reducing power will be increased. It will be found that the actual reducing power of 1 gram of argol varies between 7 and 9.5 grams of lead, dependent on the argol used.

The reduction of lead by charcoal is expressed by the following reactions:

$$2PbO + \underset{12}{C} = \underset{414}{2Pb} + CO_2$$

One gram of carbon will reduce 34.5 grams of Pb. As charcoal, coal or coke dust will contain more or less inert ash which has no reducing effect, the actual amount of lead reduced will be materially less. It will usually be found to range between 20 and 30 grams per gram of carbonaceous reducing agent used.

Flour will reduce from 9 to 12 grams of lead per gram, depending on the nature of the flour.

The common sulphides most frequently found in ores, and which give the ores containing them reducing powers, are: Pyrite (FeS_2), pyrrhotite (Fe_7S_8), arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), stibnite (Sb_2S_3), galena (PbS), and sphalerite (ZnS).

The amount of lead reduced per gram of the respective sulphides varies according to the combination of conditions, which will be fully discussed.

Taking pyrite as an example, the following equation expresses the reaction which takes place when it is fused with soda and litharge:

$$(a)\quad \begin{array}{l} 2FeS_2 + 15PbO = Fe_2O_3 + 4SO_3 + 15Pb \\ \;\;240 \qquad\qquad\qquad\qquad\qquad\qquad\quad 3105 \end{array}$$

$$(b)\quad 4SO_3 + 4Na_2CO_3 = 4Na_2SO_4 + 4CO_2$$

One gram of pure pyrite reduces 12.9 grams of lead. The result can readily be obtained by the following charge:

Pyrite	3 grams
Na_2CO_3	10 grams
PbO	100 grams

The result could not be obtained were the pyrite to be fused with litharge alone, as the presence of soda, a strongly alkaline base, induces the formation of sulphuric anhydride (SO_3), which combines with soda to form sodium sulphate (Na_2SO_4). This sodium sulphate will float on top of the slag and is not decomposed by the temperature usually attained in the muffle. It separates out on cooling as a fused white mass. Its melting-point is 885° C.[1] When the oxidizing action in the above charge is diminished by decreasing the litharge[2] to below 70 grams, the iron is only partially oxidized to the ferric condition and the two following equations express the reactions:[3]

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[1] W. P. White, *Am. Jour. Sci.*, XXVIII, 471.

[2] E. H. Miller, "The Reduction of Lead from Litherage," in *Trans.* A. I. M. E., XXXIV, 395.

[3] It must be borne in mind that while we speak of a "reducing" or an "oxidizing" reaction, the reaction is really of both natures, for while litharge is "reduced," the iron pyrite is "oxidized."

$$FeS_2 + 7PbO = FeO + 2SO_3 + 7Pb$$

$$2FeS_2 + 15PbO = Fe_2O_3 + 4SO_3 + 15Pb$$

The first equation will give 12 grams of Pb per gram of pyrite, and the second will give 12.9 grams. The accompanying table gives the reducing powers of the various substances as determined by the litharge-soda charge given for pyrite.

TABLE II.—REDUCING POWERS OF AGENTS

Name of reducing agent	Quantity of lead in grams reduced by 1 gram of reducing agent	
Argol	9.61	
Flour	10.53	
Sugar	11.78	
Charcoal	26.0	
Sulphur	18.11	(See Table III)
Pyrite	12.24	
Pyrrhotite	8.71	
Stibnite	7.17	
Chalcocite	4.38	
Sphalerite	8.16	

When no soda is present to induce the formation of alkaline sulphates, the following reaction takes place, sulphur dioxide (SO_2) being formed:

$$\begin{array}{l} FeS_2 + 5PbO = FeO + 2SO_2 + 5Pb; \\ \;\;120 \qquad\qquad\qquad\qquad\qquad\quad 1035 \end{array}$$

or 1 gram of pyrite reduces 8.6 grams of lead.

In the assay, as ordinarily performed, the foregoing conditions are modified by the presence of other substances, in the main by silica. Lead oxide readily forms silicates with silica, and the mono-, bi-, and tri-silicates are easily fusible, while those of a higher degree are fusible with difficulty. When a reducing agent (argol, sulphides, etc.) is fused with a silicate of lead, or with a charge containing litharge and silica, only a little lead is reduced when the silica is present in amounts to form a trisilicate or above, and only somewhat more when the silica is present in amounts to form a mono- or bisilicate. The reason for this is that the silicates of lead are not reduced by sulphides or carbonaceous reducing agents at temperatures below about 1000° C.[1] Above

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[1] Consult *Metallurgie*, IV, 647.

that temperature reduction takes place more readily. The higher the silicate degree the more difficult is the reduction. If, however, certain other bases, such as ferrous oxide (FeO), soda (Na_2O), or lime (CaO), are present (as is the case with most ores), reduction of lead from the silicate occurs, with ferrous oxide or soda, at a comparatively low temperature; but with lime alone, only at a high temperature. The following equation expresses this condition:

$$Pb_2SiO_4 + 2FeO + C = Fe_2SiO_4 + CO_2 + 2Pb$$

No difficulty is encountered in reducing lead from the borates of lead and soda, by the ordinary reducing agents, at 1100° C. While soda influences the amount of lead reduced from litharge by the sulphides present, it has not that influence on carbonaceous reducing agents, except in so far as it may reduce the acidity of the charge and thus favor reduction.

The following charge gave results as tabulated below:[1]

Reducing agent	1 gram	Sodium carbonate	10 grams
Litharge	45 grams	Silica	7 grams

Pyrite, in this table, shows a reduction of 9.30 grams of lead per gram, a figure to be expected when its sulphur goes off partly as SO_2 and partly as SO_3. If the soda in the preceding charge is increased, the lead button will approach the maximum reducible by pyrite.

TABLE III.—REDUCING POWER OF AGENTS

Name of reducing agent	Quantity of lead reduced by 1 gram of reducing agent
Argol	9.6
Flour	10.92
Sugar	11.74
Charcoal	26.08
Pyrite	9.30
Sulphur	18.11[2]

NOTE.—Compare Table II with this.

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[1] "The Reduction of Lead from Litharge," *Trans.* A. I. M. E. XXXIV, 395.

[2] Due to the ready distillation of sulphur, this figure is difficult to obtain; 1 gram of sulphur will usually reduce 6 or 8 grams of lead.

When carbonaceous reducing agents are used to obtain the required lead button, the nature of the charge, as regards acidity (due to SiO_2 or borax), has little influence on the size of button, provided sufficient bases, outside of PbO, are present to decompose lead silicates formed, and the silicate degree does not exceed a monosilicate. The amount of litharge present has some influence. The quantity of carbonaceous reducing agent remaining constant, the size of button will increase somewhat with increasing amounts of PbO in the charge. When the reducing agent is a sulphide (often a natural constituent of the ore), the acidity of the charge influences, to a certain extent, the size of button obtainable. It is, however, the amount of alkaline base present (K_2O, Na_2O) that exerts the most powerful influence, its presence inducing the formation of SO_3 and, consequently, sulphates, thus reducing larger amounts of lead than when no alkaline bases are present, the sulphur going off as SO_2.

Sulphide →

OXIDATION.—Oxidation of impurities in ores is frequently necessary in order to obtain good results in the assay. When ores contain an excess of sulphides, arsenides, etc. (by an excess is meant a quantity above that which will give the required size of lead button), an oxidizing agent is required to oxidize this excess, enabling it to be volatilized or slagged. Oxidation of impurities is accomplished in one of two ways.

1. By the addition of potassium nitrate (KNO_3) to the charge (or other oxidizing agents).
2. By roasting the ore, thus using the oxygen of the air for the oxidation of impurities.

When niter is added to an assay, it reacts with the most easily oxidizable compound in the charge, which is usually the reducing agent, *i.e.*, the sulphide present. Extraneous reducing agents, such as argol, flour, or charcoal, are present simultaneously with niter only when it is desired to determine the oxidizing power of niter against these reagents. For the sake of convenience, the oxidizing power of niter is expressed in terms of lead. If finely divided lead is fused with niter, the fusion reaching a temperature of 1000° C. after one-half hour, the following reaction takes place, approximately:

$$7Pb + 6KNO_3 = 7PbO + 3K_2O + 3N_2 + 4O_2;$$

or 1 gram of niter oxidizes 2.39 grams of lead. The actual number of grams of lead oxidized, determined by a considerable number of experiments, has been found to be 2.37. The analysis of the gas caught from the fusion showed 10.75 per cent. oxygen, the balance being nitrogen. Oxides of nitrogen were absent. This indicates that when niter is used in the crucible fusion, oxygen is evolved which, under certain conditions, may escape from the charge without reaction. As already stated, the niter will react with the reducing agent; expressing its oxidizing power in terms of lead is merely for convenience. In certain types of charges, *i.e.*, those containing litharge, niter, and reducing agent, or litharge, soda, niter, and reducing agent, practically theoretical results may be obtained; *e.g.*, the oxidizing power of niter as compared to charcoal is expressed by the following equation:

$$4KNO_3+5C=2K_2O+5CO_2+2N_2;$$

or 1 gram of niter oxidizes 0.15 gram of carbon.

Taking the reducing power of pure carbon as 34.5 grams of lead, the oxidizing power of niter against carbon, expressed in terms of lead, is 0.15×34.5, or 5.17 grams. Ten fusions of a charge composed of 85 grams PbO, 1 gram charcoal, 3 grams KNO_3, with 5 grams PbO as a cover, gave very concordant results, and showed the oxidizing power of niter to be 5.10. The reducing power of the charcoal was determined by five fusions with the same charge, omitting the KNO_3.[1] These results, of course, can also be obtained by an impure charcoal, for, taking one which has a reducing power of 26 grams of lead (this was used in the above fusions), it then contains $\frac{26.0}{34.5}$ or 0.765 gram pure carbon. If 3 grams of niter have been added to the charge, the available carbon for reduction will be 0.765−(3×0.15) or 0.315 gram, which will reduce 34.5×0.315, or 10.75, grams of lead. The oxidizing power of niter expressed in lead, then, is

$$\frac{26-10.75}{3}, \text{ or } 5.12 \text{ grams.}$$

Considering a sulphide and niter, and it is in this connection that niter is almost invariably used, the following reaction takes place in the litharge-soda charge already mentioned:

$$6KNO_3+2FeS_2=Fe_2O_3+SO_3+3K_2SO_4+3N_2$$
$$SO_3+Na_2CO_3=Na_2SO_4+CO_2$$

or 1 gram of niter oxidizes 0.39 gram of pyrite. In the litharge-soda charge, 1 gram of pyrite reduces 12.22 grams of lead; therefore, 1 gram of niter in this instance would oxidize 12.22×0.39, or 4.76, grams of lead. The accompanying table[1] shows actual results obtained for the oxidizing power of niter against different reducing agents.

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[1] This finding confirms that of E. H. Miller, in *Trans.* A. I. M. E., XXXIV, 395.

TABLE IV.—OXIDIZING POWER OF NITER

Reducing agent	Oxidizing power of niter in terms of lead
Pyrite	4.73 grams
Charcoal	5.15 grams
Flour	5.09 grams
Argol	4.76 grams

It follows, therefore, that the oxidizing power of niter varies with the reducing agent used.

When the assay charge contains silica and borax glass, the above figures no longer hold, for in their presence oxygen is evolved by the niter, which escapes from the charge, as in the case of the oxidation of metallic lead by niter. The amount of oxygen lost (thus reducing the oxidizing power of niter) is probably a function of the rate of rise of temperature, but evidence also points to the fact that silica reacts with the niter, setting free oxygen, at a temperature very close to that at which niter reacts with charcoal, or at which oxygen will react with carbon. Niter fuses at 339° C., but does not give off oxygen when fused alone until 530° C. is reached. Charcoal ignites at temperatures[2] ranging from 340° C. to 700° C., depending upon the temperature at which it was burnt, while silica begins to react with niter at very nearly 450° C., probably according to the following reaction:

$$2KNO_3+SiO_2=K_2SiO_3+5O+N_2$$

Thus, during the period in which the temperature in the crucible gradually rises to a yellow heat (that of the muffle), oxygen escapes during the range from 400° C. to 500° C., etc., this last being taken as an average temperature at which charcoal will begin actively to oxidize.[3]

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[1] *Ibid.*

[2] From a number of experiments by the author, willow charcoal was found to begin reaction with niter at very close to 440° C.

[3] This is offered tentatively, as an explanation of what occurs.

XLI.—CONVERSION TABLE FOR WEIGHTS

By W. J. Sharwood, Chemist, Homestake Mining Co., Lead, S. Dak.

	Grains	Pennyweights	Troy Ounces	Avoirdupois Ounces	Avoirdupois Pounds	Grams	Fine Gold Value	
							United States	British
1 Grain	1	.041666	.0020833	.00228571	.000142857	.0648	4.306 cts.	2.125 pence
1 Pennyweight	24	1	.0500	.0548571	.00342857	1.5552	$1.0335	4.25 shillings
1 Troy ounce	480	20	1	1.0971428	.0685714	31.104	$20.67	85 shillings
1 Troy pound	5,760	240	12	13.165714	.822857	373.248	$248.04	£51
1 Avoirdupois ounce	437.50	18.22917	.911458	1	.06250	28.35	$18.84	77.474 shillings
1 Avoirdupois pound	7,000	291.666	14.58333	16	1	453.60	$301.4375	£61.97
1 Milligram	.015432	.000643	.00003215	.000035274	.0000022046	.0010	.06645 cts.	.033 penny
1 Gram	15.432	.643	.03215	.035274	.0022046	1	66.45 cts.	2.73275 shillings
1 Kilogram	15,432	643	32.15	35.274	2.2046	1,000	$664.54	£136.64

Parting in Porcelain Capsules. — A glazed porcelain capsule 1$\frac{3}{8}$ inches in diameter and 1 inch high is preferable for this work on account of its broad flat base, but a small porcelain crucible does very well if care is taken not to upset it. Many different strengths of acid and other details of manipulation have been recommended, but the procedure given below is one which has given uniformly satisfactory results to the author in his laboratory. The strength of acid which may be used depends on the proportion of gold and silver in the alloy; the less the ratio of silver to gold, the stronger the acid may be without danger of breaking up the gold. It is not necessary that the method to be described should be followed in every case, but this method is a safe one for the treatment of beads having almost any proportion of silver to gold, from 3 to 1000 or more parts of silver to 1 of gold.

Procedure. — Pour into the capsule about half an inch of dilute nitric acid of 1.06 sp. gr., made by diluting 1.42 acid with seven times its volume of water. Put on the hot-plate and heat until vapor can be seen rising from it, and then drop in the bead which should be free from adhering bone-ash. In case the alloy has only 3 or 4 parts of silver to 1 of gold it must be hammered or rolled out to the thickness of an ordinary visiting card, say to 0.01 inch. The bead should begin to dissolve at once, giving off bubbles of nitrogen oxides. If it does not begin to dissolve, add nitric acid, 1.26 sp. gr., a few drops at a time until action starts. The solution should be kept hot but not boiling. The action should be of moderate intensity. Continue the heating until action ceases and then decant the solution into a clean white evaporating dish in a good light, taking care not to pour off any of the gold. Then add a few cubic centimeters of 1.26 sp. gr. acid, made by diluting strong nitric acid, 1.42 sp. gr., with an equal volume of water, and heat almost to boiling for from two to ten minutes. Decant this solution and then wash three times with warm distilled water, decanting as completely as possible after each washing. Apply the stream of water from the wash bottle tangentially to the sides of the capsule, rotating it meanwhile to prevent direct impact of the stream on the gold. After the final washing manipulate the particles of gold so as to bring them together, decant off the last drops of water as completely as possible and set the cup on a warm plate to dry the gold, but avoid too high a temperature as the sputtering of the last drop of water would tend to break up and possibly throw out the gold. Finally "anneal" the gold by putting the cup in the muffle or over the open flame until the bottom is bright red, when the gold will change from its black amorphous condition to the true yellow color of pure gold. It is now ready to cool and weigh. To transfer the gold from the cup to the scale-pan, bring the scale-pan to the front part of the balance. Gradually invert the cup over the pan, tapping it meanwhile with a pencil. When this is done the gold will usually slide out without difficulty. If any small particles stick to the cup they may be detached by touching them gently with the point of the forceps or a small camel's-hair brush.

The gold should be pure yellow throughout and may be compared with parted gold of known purity. If it is lighter-colored than pure gold it is probable that all of the silver has not been dissolved. If it is dark in spots or if the cup is stained, it indicates incomplete removal of the silver nitrate. The "annealing" causes the gold to stick together, making it easier to handle, tends to burn out any specks of organic matter which may have fallen into the cup, allows the assayer to observe the color of the parted gold and to determine its purity in that way and to distinguish and separate any specks of foreign matter such as fire brick, coke dust etc., which may have found their way into the cup. The "annealing" at a red heat is also necessary in order that the gold may contract and lose most of its porosity, since otherwise it would condense a considerable quantity of gas during weighing.

After the silver has been dissolved from a doré alloy by the acid, the gold remains as a porous mass which is more compact the larger the proportion of gold the alloy contained, the thicker the alloy and the less the mechanical disturbance of the bead during solution. In treating a bead which is near the limiting ratio of silver to gold it is sometimes difficult to determine whether or not it is parted. This may be ascertained by touching it with a glass rod drawn down to a rather small diameter, (approximately 1/32 inch). If it feels soft throughout and can be broken up it is practically parted, but it should be heated almost to boiling with 1.26 sp. gr. acid for at least ten minutes to ensure dissolving the last of the silver. Such a mass of parted gold will require a longer and more careful washing, for on account of its density a longer time is required for the silver nitrate to diffuse through its minute pores. In parting the ordinary bead containing ten, twenty or more times as much silver as gold, it is easy to see when parting is complete by the considerable shrinking of the mass.

Notes: 1. The nitric acid solution should be hot before dropping in the bead as in cold acid the gold tends to break up into extremely fine particles.

2. The violent mechanical disturbance due to boiling or too rapid solution may cause the gold to break up, causing difficulty or actual loss in washing and subsequent handling.

3. If only a few tenths of a milligram of porous gold remains, the ten minutes heating with 1.26 sp. gr. acid is unnecessary.

4. Strong nitric acid (1.46 sp. gr.) should not be used at any time, as gold is slightly dissolved by it.

5. If in doubt at any time as to the purity of the parted gold, wrap it up six times its weight of silver foil and carefully cupel with lead, then repart and weigh.

6. If a small particle of gold is seen floating on the surface of the liquid, it may be made to sink by touching it with a glass rod.

7. The black stain occurring in parting cups after heating is due to metallic silver reduced from silver nitrate by the heat, showing insufficient washing.

Inquartation. — When the bead contains too little silver to part, it is necessary to alloy it with more silver. This process is called inquartation. It originated from the custom of the old assayers of adding silver until the gold was one-quarter of the whole. They considered a ratio of 3 parts of silver to 1 of gold to be necessary for parting. At present, in assaying gold bullion, a ratio of only 2 or $2\frac{1}{4}$ parts of silver to 1 of gold is used, mainly to avoid all danger of the gold breaking up in the boiling acid. In this case some little silver remains undissolved, even though the alloy is rolled out to about 0.01 inch in thickness.

To inquart a bead wrap it with six to ten times its weight of silver in 4 or 5 grams of sheet lead and cupel. Rose* considers that different proportions of silver should be used according to the weight of the gold, and gives the following suitable proportions:

Weight of Gold	Ratio of Silver to Gold
Less than 0.1 mg.,	20 or 30 to 1
About 0.2 mg.,	10 to 1
About 1.0 mg.,	6 to 1
About 10 mg.,	4 to 1
More than 50 mg.,	$2\frac{1}{4}$ to 1

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* Metallurgy of Gold, Sixth Ed., p. 511.

therefore the continuity of the gold, as to prevent its cohesion during the acid treatment.

There is naturally a gradation in the degree of gold disintegration, from its almost complete cohesion when derived from practically "fine" beads, to its completely pulverulent form when derived from beads of 990 fineness.

Indications of Presence of Rare Metals. — As has been indicated in the chapter on cupellation, the assay beads may contain, in addition to traces of lead, bismuth, copper and tellurium, practically all of the platinum, palladium, iridium, iridosmium, as well as more or less of the rhodium, osmium and ruthenium contained in the original material which was assayed. Most of these rare metals make their presence known by the appearance of the bead. If they are not discovered in the bead, indications of their presence may be found during parting.

In nitric acid parting a considerable part of the platinum, palladium and osmium are dissolved, the amount depending on various conditions such as the amount of silver present, the strength of acid, etc.

According to Rawlins,* PLATINUM has a disintegrating effect upon the gold, when the latter does not make up more than 5 per cent of the weight of the bead. As platinum is only partly soluble, the remaining insoluble platinum discolors the gold, leaving it steel-gray instead of yellow. Furthermore, platinum gives the parting acid a brown or blackish color according to the amount present, but small amounts might not be detected this way. If, however, the appearance of the bead leads one to suspect the presence of platinum the above indications would help to confirm its presence.

PALLADIUM yields an orange-colored solution in nitric acid parting. This test is very delicate, so that even 0.05 milligrams in a small bead gives a distinct coloration to the solution.

IRIDIUM appears in the parted gold as detached black specks retaining their color after annealing.

Errors Resulting from Parting Operations. — In addition to platinum, iridium, and other of the rare metals which may be retained and weighed as gold there is always a small amount of silver which persistently resists solution. The amount depends upon a number of factors, chief of which are the ratio of silver to gold in the original bead, the strength of acid used and the time of acid treatment. Under ordinary conditions this silver retained probably amounts to about 0.05 per cent of the weight of the gold.

When gold disintegrates in parting on account of the presence of impurities in the bead, part of it is invariably lost in decantation. This decanted gold is often so finely divided as to be invisible.

If the parting acid contains impurities, particularly chlorine in any form, some of the gold is sure to be dissolved. Even pure nitric acid, if concentrated and boiling, dissolves a small amount, according to Rose* about 0.05 per cent. The silver retained and the gold dissolved in pure acid produce errors so small as to be negligible, but the loss resulting from the use of impure acid and the decantation loss must be carefully guarded against.

There are a number of errors in the determination of gold which should be obvious and which can be either avoided or corrected. Such errors need not be discussed here.

Recovery of Gold Lost in Decantation. — Because of the effect of impurities in the bead or for other reasons, some of the gold may disintegrate in parting and be lost in decantation. This decanted gold is often so finely divided as to be invisible, and is therefore lost in ordinary commercial work. It may be readily collected, however, by the precipitation of a small amount of silver chloride which carries it down in settling. The precipitate containing the gold is then filtered off, dried and scorified with lead. The button is cupeled and the bead parted.

Testing Nitric Acid for Impurities. CHLORIDES. — To test for the presence of hydrochloric acid take about 10 c.c. of acid and pour a few c.c. of silver nitrate solution cautiously down the side of the tube, so that the two liquids do not mix. If chlorides, bromides or iodides are present, a precipitate in the form of a ring will appear where the two liquids come together. This test is more delicate than mixing the two solutions. It is not necessary to try to distinguish between the three haloids, as, if any precipitate is found, the acid must be either rejected or purified.

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* Trans. Inst. Min. and Met. 23, p. 177.

* Metallurgy of Gold, Sixth Ed., p. 541.

Chlorates. — Nitric acid often contains chlorine in the form of chloric acid, and this does not give a precipitate with silver nitrate. The chloric acid must first be decomposed before the chlorine will precipitate as silver chloride. To test nitric acid for chlorates take about 250 c.c. in a beaker and add 1 c.c. of silver nitrate solution. In the absence of any precipitate which would indicate the presence of chlorides, etc., add about 5 grams of some metal to reduce the chloric salt. Silver, zinc or copper will do. Heat nearly to boiling to dissolve the metal. If chloric acid is present a precipitate of silver chloride will form. To confirm, observe solubility in water and in cold dilute ammonia, also effect of sunlight.

Testing Wash Water, etc. — The water used for washing the parted gold and for diluting the nitric acid should be distilled to ensure its purity. Any chlorides in the wash water will of course precipitate in the parting vessel as silver chloride and if not removed will be weighed as gold. The wash water should be carefully tested by slightly acidifying with nitric acid and then pouring in silver nitrate as in testing the nitric acid. If distilled water is not available and water at hand contains a small amount of chlorides the proper combining proportion of silver nitrate may be added, the whole well mixed and then allowed to stand until the silver chloride settles out. Care must be taken to avoid adding an excess of silver nitrate, for obvious reasons. If by any chance silver chloride has been precipitated in the parting cups, the addition of a little ammonia will cause it to dissolve, after which the washing may be completed with pure water.

Testing Silver Foil for Gold. — It is never safe to assume that so-called C. P. silver is free from gold, until it has been tested and proven so. A simple dissolving of the foil in nitric acid is hardly sufficient as small amounts of gold might escape recognition in this way. A better method is to fuse about a gram into a bead and dissolve this slowly in hot dilute nitric acid. The best method is to dissolve about 10 grams in nitric acid, dilute and add a small quantity of a weak solution of sodium chloride. This will precipitate some silver chloride which will collect any finely divided gold. Allow this precipitate to settle, then filter it off, dry and scorify with lead. Cupel the button and part the small bead obtained. This should give all the gold in one piece.

CHAPTER IV

ORE SAMPLING.

A sample is a small amount which contains all the components in the proportions in which they occur in the original lot.

Object. — The object of sampling an ore is to obtain, for chemical or mechanical tests, a small amount which shall contain all the minerals in the same proportion as the original lot. In the subsequent discussion the word "sample" will be taken to mean that fraction which is taken to represent the whole, whether or not it does so. The compound words correct-sample, representative-sample, true-sample, will be used to represent the ideal conditions.

In the intelligent operation of a mine or metallurgical plant, it is necessary to sample and assay continually. In most mines, the different faces of ore are sampled every day. In concentrating plants, it is customary to sample the products of every machine at frequent and regular intervals, to ascertain whether the machine is doing the work expected of it. In smelters, it is necessary to sample and assay every lot of ore, as well as fluxes and fuels, in order to calculate a charge which will run properly in the furnace. The slag, flue dust and metallic products must also be sampled and assayed, with a view to maintaining control of the operations. In lixiviation plants, the ore and tailings, as well as the solutions, must be sampled in order that the daily work of the plant may be controlled and checked. In fact, careful sampling and assaying cannot be disregarded, and are becoming more and more important every day as the grade of ore decreases and the margin of profit becomes less.

The assayer will usually have the major part of the sampling done for him, but he is expected to know how to do it when called upon. He usually has to prepare only the final sample, but will occasionally receive lots of 10 to 100 or more pounds to assay, in which case he will have to do his own sampling. The following discussion will deal principally with the assay laboratory problems of sampling; the question of mine sampling is entirely omitted, but methods used in sampling mills are briefly reviewed for the sake of completeness.

Methods. — The question of ore sampling is probably the most complicated of all sampling problems, because of the great variety of constituents and the lack of uniformity in their distribution throughout the whole mass. It is obvious that, however we may proceed, the problem is to select a method, such that every particle of our non-homogeneous mixture, the ore, shall have nearly the same chance of being included in the sample. Several methods may be followed to secure this result and, assuming the ore to have had a preliminary crushing, the available methods are:

1. Random selection
2. Selection by rule
3. Mixing and cutting

The first two are rough, preliminary methods generally known as "grab-sampling." The last is capable of mathematical precision and may be repeated through all stages of the sampling process. It is the only method which should be used when an exact sample of the precious metal ores is desired. Iron ores are so uniform that "grab-sampling" is likely to yield satisfactory results.

When it is considered that the final sample for chemical analysis usually weighs only half a gram and for fire assay somewhat less than 15 grams, and that each must truly represent from 1 to 5 carloads of ore weighing from 50 to 250 tons, the enormous practical difficulties of the problem may be appreciated.

Precise sampling may usually be considered to consist of three distinct operations, repeated as many times as necessary. These operations are crushing, mixing and cutting. The cutting gives a sample and a reject. By a repetition of the three operations the sample may be further reduced until it has reached the desired weight.

The whole science of ore sampling depends primarily on a correct knowledge of the proper relation between the maximum size of the ore particles and the weight of the sample taken. The problem to be solved in each case is somewhat as follows: when a particular ore has been crushed to a certain size, how small a sample is it safe to take from this and still keep within the limit of allowable error? It is necessary to know the ore, the limit of allowable error, and the mathematical principles involved.

Sampling is classed as hand sampling when the mixing and cutting down is done by men with shovels, and as machine sampling when it is done by some form of automatic machine.

Commercial Considerations. — The most certain method of obtaining a representative sample of a lot of ore would be to crush the whole to 100-, 120-mesh or finer, mix it thoroughly and then cut down to the desired weight. This method can be followed for small amounts of a pound or so, but in the case of large lots it would entail too much labor and would usually unfit the ore for future treatment. The method generally adopted is a compromise and consists in crushing the whole lot to a certain predetermined maximum size and then taking out a certain fraction as a sample. This sample is again crushed to a smaller size and cut down as before, and this process repeated until finally the assay sample is obtained.

The care which is required in sampling, as well as the size to which a lot of ore or other material must be crushed before a sample is taken, depends upon the value and uniformity of composition of the material. The more uniform it is, the smaller may be the sample taken after crushing to any particular size. For instance, in the case of a solid piece of galena containing silver uniformly distributed as an isomorphous silver sulphide, a piece may be broken off anywhere, and after being crushed, will give a lot of ore which is truly a sample of the piece. If, however, the specimen is not solid galena, but is made up of galena and limestone, the silver still being contained in the galena, it will be necessary to crush the whole lot to a uniformly fine size before taking out a fractional part for a sample. Furthermore, it will readily be seen that the greater the difference in the grade of the different minerals in the ore, the finer the ore must be crushed before a sample of a given size should be taken from it.

Since ores are never perfectly uniform in composition, a certain amount of crushing is evidently necessary in every case. To determine the amount of crushing it is important to consider the commercial side of the question, that is, to determine how far it will pay to go with the process. Evidently a mistake of 1 per cent in the iron contents of a carload of iron ore worth $3 a ton is less serious than the same percentage error in the

Machines for crushing should be rapid in action and easy to clean. Jaw breakers and rolls fulfill these requirements; ball mills and pebble mills do not.

Mixing. — This step in the process of sampling is often omitted or allowed to take care of itself. It is a necessary forerunner of quartering and channeling, but is usually omitted before the other methods of cutting. Especially in the handling of small lots of ore in the laboratory, it is best to be over-careful in this particular rather than the reverse, and, as it adds but little labor, to give each lot of crushed ore a thorough mixing before cutting. The mixing of small lots will be discussed under the head of finishing the sample.

The final step in the sequence of sampling operations consists in taking out a fraction of the whole, say a quarter or a half, in some systematic, impartial manner. The part taken out is called the sample, and the operation of taking it is the cutting.

Hand Cutting. — The following methods of hand cutting are occasionally used, but whenever possible are being replaced by machine cutting.

FRACTIONAL SHOVELING. — This is a rough starting method, suited only to large lots of low-grade or fairly uniform ore. When the ore is being taken away from the crusher or shoveled out of cars, as the case may be, every second, third, fifth, or tenth shovelful, depending on the value and uniformity of the ore, is taken and placed in a separate pile, which is afterwards cut down by some of the methods described later. When the ore is being shoveled, care must be taken that each shovelful is taken from the floor. Lumps which are too large for the shovel should be broken and put back on the pile. The method is open to the serious objection that it is a very simple matter for a prejudiced person to make the sample either higher or lower in grade than the average, by selection of his shovel samples.

QUARTERING. — This is the method of cutting which accompanies coning. It presupposes a thorough mixing by coning, as the two always go together.

CONING. — The sample is shoveled into a conical pile, each shovelful being thrown upon the apex of the cone so that it will run down evenly all around. When a large lot of ore is to be mixed by coning, it is first dumped in a circle and then coned by one or more men who walk slowly around between the cone and the circle of ore. The best results are obtained by coning around a rod, as by this means the center of the cone is kept in a vertical line. Coning does not thoroughly mix an ore, but rather sorts it into fine material which lies near the center and coarser material which rolls down the sides of the cone. If the ore is practically uniform in size and specific gravity, the mixing may be more thorough. A slight dampening of the ore is said to allow of better mixing by coning. The floor, for this and other hand sampling operations, should be smooth, and free from cracks which would make good cleaning difficult or impossible. A floor made of sheet-iron or steel plates is preferable.

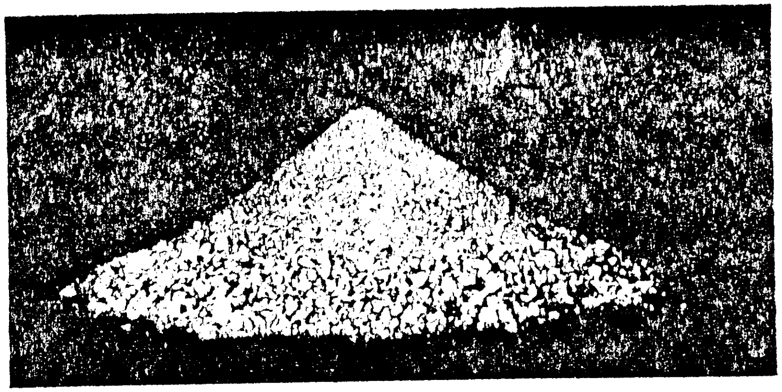

FIG. 22. — Cone of crushed ore.

Figure 22,* a cone of crushed ore, shows clearly the inherent defect of this method of sampling, the segregation of coarse and fine ore, caused by dropping shovelful after shovelful on top of a cone.

When the cone is completed, it is worked down into the form of a flat truncated cone by men who walk around and around, drawing their shovels from center to periphery, or starting at the apex and working the shovel up and down in the path of a spiral. The point to be observed here is not to disturb the radial distribution of the coarse and fine ore. After flattening, the cone is divided into four 90-degree sectors or quarters by means of a sharp-edged board, or better, by a steel-bladed quarterer. These

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* From U. S. Bureau of Mines Technical Paper No. 86: Ore Sampling Conditions in the West.

quarters should, of course, radiate from the position of the center of the original cone. Two opposite quarters are taken out and rejected and the two others are then taken for the sample. Care must be taken at this point to sweep up all dust belonging to the rejected portions before proceeding, so that this dust shall neither be lost nor mixed with the sample. This sample may be again mixed by coning and quartered, or crushed, coned and quartered as the case may require.

Fig. 23. — Partly flattened cone

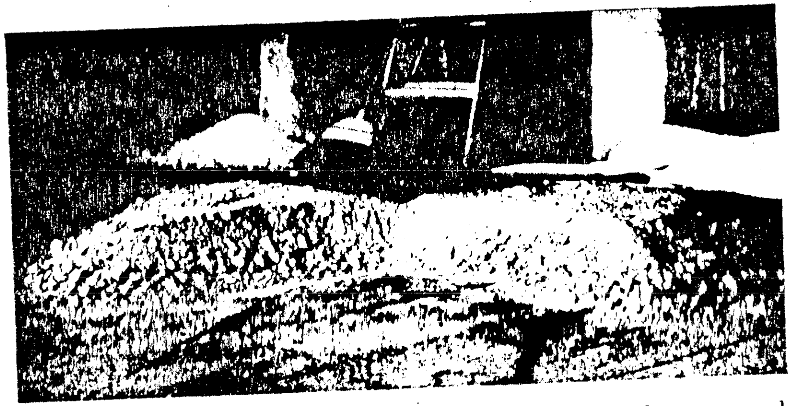

Fig. 24. — Truncated cone from which reject quarters have been removed.

lump ore before it was broken. Therefore as the size of the ore particles is reduced a larger and larger number should be taken for the sample. To conform to this condition the following rule was proposed by Professor R. H. Richards: " For any given ore the weight taken for a sample should be proportional to the square of the diameter of the largest particle. "

The accompanying table, based on figures taken from the practice of several careful managers, to a certain extent conforms to this rule. The table was arranged by and is now published with the permission of Professor Richards.

TABLE V.

Weights to be Taken in Sampling Ore.

Weights of sample pounds	1	2	3	4	5	6
	Diameter of largest particles — millimeters					
	Very low grade or very uniform ores	Low grade or uniform ores	Medium ores		Rich or spotted ores	Very rich and spotted ores
20,000.000	207.00	114.00	76.20	50.80	31.60	5.40
10,000.000	147.00	80.30	53.90	35.90	22.40	3.80
5,000.000	107.00	56.80	38.10	25.40	15.80	2.70
2,000.000	65.60	35.90	24.10	16.10	10.00	1.70
1,000.000	46.40	25.40	17.00	11.40	7.10	1.20
500.000	32.80	18.00	12.00	8.00	5.00	.85
200.000	20.70	11.40	7.60	5.10	3.20	.54
100.000	14.70	8.00	5.40	3.60	2.20	.38
50.000	10.70	5.70	3.80	2.50	1.60	.27
20.000	6.60	3.60	2.40	1.60	1.00	.17
10.000	4.60	2.50	1.70	1.10	.71	.12
5.000	3.30	1.80	1.20	.80	.50	
2.000	2.10	1.10	.76	.51	.32	
1.000	1.50	.80	.54	.36	.22	
.500	1.00	.57	.38	.25	.16	
.200	.66	.36	.24	.16	.10	
.100	.46	.25	.17	.11		
.050	.33	.18	.12			
.020	.21	.11				
.010	.15					
.005	.10					

The first column shows the safe weight in pounds for a sample of ore of any of the six grades shown and for sizes as indicated in the respective columns. Column 1 applies to iron ores, column 2

The following table is probably the best and certainly the most conservative of all. A good deal of intelligent discrimination may often be used, however, and mere formulas can never be made to cover all possible contingencies. For instance, in sampling an ore in which the valuable mineral is finely and uniformly disseminated

TABLE VI.

WEIGHTS TO BE TAKEN IN SAMPLING ORE.

Specific gravity Richest mineral	Size of particles		Grade of richest mineral divided by average grade					
	Mesh	Diam. Inch	10	50	200	600	1,500	2,500
			Safe weight in pounds when largest particles are of size given in second column					
5.0	120	.0043			.003	.010	.025	.043
	100	.0055	.0003	.0018	.007	.021	.053	.089
	50	.0100	.0017	.0095	.030	.116	.201	.485
	14	.0364	.0585	.319	1.29	3.90	9.76	16.3
	4	.145	2.96	16.1	65.5	105.	494.	823.
	2	.338	30.0	163.	664.	2,000.	5,000.	8,340.
		.5	75.9	413.	1,680.	5,050	12,600	21,100,
		1.0	486.	2,650.	10,700.	32,300.	80,900.	140,000.
7.5	120	.0043			.005	.015	.038	.064
	100	.0055	.0005	.0027	.011	.032	.080	.134
	50	.0100	.0026	.0143	.058	.174	.437	.727
	14	.0364	.0878	.479	1.94	5.85	14.6	24.5
	4	.145	4.44	24.2	98.3	293.	740.	1,230.
	2	.338	45.0	245.	996.	3,000.	7,500.	12,500.
		.5	114.	620.	2,520.	7,580.	19,000.	31,600.
		1.0	729.	3,970.	16,100.	48,500.	121,000.	211,000.
10.5	120	.0043	.0005	.0027	.011	.032	.081	.135
	100	.0055	.0010	.0055	.022	.068	.170	.283
	50	.0100	.0041	.0222	.090	.272	.679	1.13
	14	.0364	.148	.804	3.26	9.83	24.6	41.0
	4	.145	7.78	42.4	172.	518.	1,300.	2,160.
	2	.338	78.8	429.	1,740.	5,250.	13,100.	21,900.
		.5	230.	1,250.	5,080.	15,300	38,200.	63,800.
			1,500	3,000	6,000	15,000	30,000	60,000
17.6	150	.0036	.0798	.159	.319	.798	1.59	3.19
	120	.0043	.136	.272	.544	1.36	2.72	5.40
	100	.0055	.284	.569	1.14	2.84	5.69	11.4
	50	.0100	1.14	2.28	4.56	11.4	22.8	45.6
	14	.0364	41.2	82.5	165.	412.	825.	1,650.
	4	.145	2,170.	4,350.	8,600.	21,700.	43,500.	80,900.
	2	.338	22,000.	44,000	88,100.	220,000.	440,000.	881,000.

CHAPTER V

THE SCORIFICATION ASSAY.

The scorification assay is the simplest method for the determination of gold and silver in ores and furnace products. It consists simply of an oxidizing muffle fusion of the ore with granulated lead and borax-glass. The lead oxide formed combines with the silica of the ore and also to a certain extent dissolves the oxides of the other metals. The only reagents used other than lead are borax-glass and occasionally powdered silica, which aid in the slagging of the basic oxides.

The scorifier is a shallow, circular fire-clay dish 2 or 3 inches in diameter. The sizes most commonly used are 2½, 2¾ and 3 inches in diameter.

The amount of ore used varies from 0.05 A. T. to 0.25 A. T., the amount most commonly used being 0.10 A. T. With this is used from 30 to 70 grams of test lead and from 1 to 5 grams of borax-glass, depending on the amount of base metal impurities present. Sometimes powdered silica and occasionally litharge are also used. With nearly pure galena, or a mixture of galena and silica, a charge of 30 to 35 grams of test lead and 1 gram of borax-glass will suffice for 0.10 A. T., of ore, but when the ore contains nickel, copper, cobalt, arsenic, antimony, zinc, iron, tin, etc., a larger and larger amount of lead and borax-glass must be used according to the relative ease with which the metals are oxidized and the solubility of their oxides in the slags formed. Of the above, copper especially is very difficultly oxidized and when much is present in the ore the lead button from the first scorification will have to be rescorified once or twice with added lead. Iron, on the other hand, is comparatively readily oxidized, and except for the necessity of adding an extra amount of lead and borax-glass to make a fluid slag the ore is as readily assayed as galena. Lime, zinc, and antimony require especially large amounts of borax-glass to convert their refractory oxides into a fusible slag.

Solubility of Metallic Oxides in Litharge. — Litharge although a strong base, has the power of holding in igneous solution certain quantities of other metallic oxides. This has an important bearing on the ease or difficulty with which various metals may be slagged in scorification. According to Berthier and Percy, the solubilities of the various metallic oxides in litharge are as shown in the following table:

One part of	Cu_2O	CuO	ZnO	Fe_2O_3	MnO	SnO_2	TiO_2
Requires parts of PbO	1.5	1.8	8	10	10	12	8

Antimony trioxide (Sb_2O_3) dissolves in litharge in all proportions.

Heat of Formation of Metallic Oxides. — Another important factor having to do with the elimination of impurities by scorification is the relative heat of formation of the various metallic oxides. In a mixture of various metallic sulphides, (assuming for a moment the ignition temperature to be the same for all), that reaction in which is evolved the greatest amount of heat would naturally proceed at the fastest rate. The heat of combination of various metals each with 16 grams of oxygen is shown in the following table. This basis is used on the assumption that the amount of oxygen is limited.

TABLE XV.

HEAT OF FORMATION OF METALLIC OXIDES.[1]

Reaction.	Heat of comb. with 16gO		Reaction.	Heat of comb. with 16gO	
Zinc to ZnO		83,260	Bismuth to Bi_2O_3	$\frac{135,500}{3}$	45,167
Tin to SnO_2	$\frac{138,000}{2}$	69,000	Copper to Cu_2O		40,000
Iron to FeO		64,100	Tellurium to TeO_2	$\frac{78,300}{2}$	39,150
Nickel to NiO		57,800	Sulphur to SO_2	$\frac{70,940}{2}$	35,470
Cobalt to CoO		57,600	Copper to CuO		34,900
Antimony to Sb_2O_3	$\frac{165,300}{3}$	55,100	Silver to Ag_2O		6,950
Lead to PbO		52,500	Gold to Au_2O_3	$-\frac{12,900}{3}$	$-4,300$
Arsenic to As_2O_3	$\frac{154,000}{3}$	51,333			

[1] These are heats of formation at room temperature, 15° C. To change to some other temperature such as 800° C., subtract (800 − 15) times the mean molecular specific heat of the oxide. If the specific heat of the compound is not known, add the atomic heats of the elements.

Ignition Temperature of Metallic Sulphides. — The ignition temperature of the metallic sulphides may also be of interest in this connection.

TABLE XVI.

IGNITION TEMPERATURES[1] OF METALLIC SULPHIDES WHEN HEATED IN AIR.

Material	Formula	Ignition Temp.° C.	Material	Formula	Ignition Temp.° C.
Stibnite	Sb_2S_3	290–340	Galena[2]	PbS	554–847
Pyrite	FeS_2	325–427	Millerite	NiS	573–616
Pyrrhotite	Fe_xS_{x+1}	430–590	Argentite	Ag_2S	605–873
Chalcocite	Cu_2S	430–679	Sphalerite	ZnS	647–810

[1] Friedrich, Metallurgie, **6**, p. 170 (1909).

[2] In Oxygen.

The metals in Table XV are arranged in order of their heats of combination with oxygen, expressed in terms of a unit weight of oxygen. This is the order in which they will be removed in scorification or cupellation. In general it may be said that the metals in a molten alloy, such as a lead button on a cupel, or the lead alloy in a scorifier, are oxidized in succession, each partly protecting those which are less easily oxidized than itself. This separation is not quantitative however, owing to the effect of mass action, and in the case under discussion, where we have a large amount of lead and small amounts of other metals, a considerable amount of lead would be oxidized during the complete oxidation of the metals above it in the table.

Those metals which lie below lead in the table will be but slowly slagged in scorification and only at the expense of a large amount of lead. Thus, during scorification or cupellation, bismuth, copper and tellurium are concentrated in the residual unoxidized lead and this explains why it is so difficult to separate these metals from silver by scorification and cupellation. This can only be done by repeated scorification with fresh lead and, as might be expected, this will result in a considerable loss of silver.

From their positions in the table, it is evident that silver is not easily oxidized and that gold is protected by all other metals.

To one who has a knowledge of the mineral character of the ore, a glance at the ignition temperature of the sulphides shown in Table XVI will afford an idea of the initial temperature required for scorification. From a comparison of the heats of oxidation of the metals present with that of lead, the relative brittle it may contain impurities which must be removed by re-scorifying with an additional amount of granulated lead.

Finally cupel and weigh the resultant silver or doré beads. Report in your notes the weight of ore and reagents used, the weight of lead button obtained, as well as the weight and assay in ounces per ton of gold and silver. Note also the time of scorification and cupellation and describe the appear- ance of the scorifier and cupel.

Notes: 1. The ore must be so fine that a sample of 0.1 A. T. will truly represent the whole; 100-mesh may be fine enough for some ores, 170-mesh may be necessary for some others.

2. In weighing out the ore, spread the sample which has been thoroughly mixed, into a thin sheet on the glazed paper at one side of the pulp balance. Place the weight on the right-hand pan and the ore on the left-hand pan. With the spatula mark the ore off into squares 1 inch or so on a side, and then take a small portion from every square for the sample, being sure to take a section from top to bottom of the ore. During this first sampling the scale-pan should be held over the paper in one hand and the spatula in the other. When what is judged to be the right amount of ore is obtained the pan is put back on the balance and the hand with which it was held is used to turn the balance key.

The balance should be turned out of action each time ore is put on or taken off the scale-pan and the pointer need move only 1 or 2 divisions to indicate whether too much or too little ore is on the pan. To obtain the final balance, have a little too much ore in the pan, take off enough on the point of the spatula to reverse the condition of balance. With the balance key lift the beam only enough to allow the pointer to swing 1 or 2 divisions to the left of the center and then hold the key in this position. Hold the spatula over the pan and by tapping it gently with the first finger allow the ore to slide off onto the scale-pan a few grains at a time, until the balance is restored and the needle swings over to the center. By repeating this process, rejecting the ore retained on the spatula each time, an exact weight can soon be obtained.

3. The value of the results depends upon the care which is taken in mixing, sampling and weighing out the charges. Do not attempt to save time by slighting the mixing, for if a true sample is not obtained at this point no amount of subsequent care will avail to give reliable results.

4. Instead of being weighed, the granulated lead may be measured with sufficient accuracy by the use of a shot measure or small crucible. The borax-glass may also be measured.

5. The size of scorifier to be used depends upon the amount of ore, lead, borax-glass and silica used, and should be such as to give a button of approximately 15 to 18 grams. If a large scorifier is used with a small amount of lead the resulting lead button will be very small and a high loss of silver will result. Again, the larger the amount of borax-glass that is used the more slag there will be and the sooner the lead will be covered.

6. If the contents of the scorifiers do not become thoroughly liquid and show a smooth surface of slag after ten or fifteen minutes, the assays require either more heat, more borax-glass or more lead.

7. If the ore contains much tin, antimony, arsenic, nickel or large amounts of basic oxides such as hematite, magnetite, etc., an infusible scoria is almost certain to form on the surface of the slag or on the sides of the scorifier which neither a high temperature nor extra borax-glass will remove. As this scoria is likely to enclose particles of undecomposed ore the only safe procedure is to make a fresh assay with less ore, and with such other changes in charge and manipulation as the experience of the first assay may suggest.

8. Ores containing pyrite require a higher temperature during the roasting period than those containing galena.

9. Some assayers add litharge to the scorification charge, especially with pyritic ores. On heating, the litharge is reduced to metallic lead, the sulphur of the pyrite being oxidized.

10. Litharge, being a strong base, has a great affinity for the silica of the scorifier and, especially when mixed with copper oxide, it attacks this silica readily. When scorifying matte and copper bullion it is often necessary to add powdered silica to the charge to prevent a hole being eaten through the scorifier.

11. The lead button should weigh from 12 to 20 grams. If it is much smaller than this there is danger of a loss of silver due to oxidation, especially when the ore is rich. If the button is too large it may be rescorified in a new scorifier to the size desired.

12. Hard buttons may be due to copper, antimony or in fact almost any metal alloyed with the lead. Brittle buttons may be due to one of many alloyed metals, or to the presence of sulphur or lead oxide.

13. The scorifier slag should be homogeneous and glassy. If non-homogeneous it probably contains undecomposed ore.

14. The white patches occasionally found in the slag are made up mostly of lead sulphate which is formed when the scorification temperature is low.

15. Scorifier slags are essentially oxide slags and consist of metallic oxides dissolved in an excess of molten litharge, together with smaller amounts of dissolved silicates and borates.

16. If too low an initial temperature is employed or if the muffle door is opened too soon, the scorification losses may be considerable, owing to the retention in the slag, or on the sides of the scorifier, of undecomposed silver minerals.

The scorification assay is simple, inexpensive and reasonably rapid. For the determination of silver in sulphide ores having an acid gangue, it is generally satisfactory and widely used. It is particularly suited for the determination of silver in ores containing considerable amounts of the sulphides, arsenides or antimonides of the difficultly oxidizable base metals, particularly copper, nickel and cobalt. It is used in many localities for silver in all sulphide ores, as well as for gold and silver in copper bullion, impure lead bullion, copper and nickel mattes and speiss.

It is not to be recommended for pure ores, low in silver, because of the difficulty of handling and weighing the small beads obtained. Rich ores have to be weighed more carefully for scorification assays, than for crucible assays where usually two and a half to five times as much ore is used, in order to obtain the same precision. The ordinary charge using 0.10 assay-ton of ore, does not give a close enough approximation on a gold ore for commercial purposes. Therefore, in the case of ores, this method is restricted to those containing only silver. Ores containing both silver and gold will ordinarily be assayed by the crucible method so as to obtain gold results of the necessary precision.

There is no good reason for scorifying ores or products which do not require oxidation, and scorification is entirely unfitted for those ores carrying higher oxides such as magnetite, hematite, pyrolusite, etc. It is not suitable for ores having any considerable amount of basic gangue as but a small quantity of acid reagents can be used. It should not be used on ores containing volatile constituents such as carbonates and minerals containing water of crystallization which tend to cause spitting and consequent loss of alloy. Volatile compounds of the precious metals are more likely to escape from a scorifier than from a crucible because of the exposed conditions of the ore in the former.

Chemical Reactions in Scorification. REACTIONS DUE TO HEAT ALONE.—Various chemical changes may be caused by heat alone, so that during the fusion period, even in the absence of oxygen, the hydrates give up their water, most of the carbonates give up their carbon dioxide and are converted into oxides and even some of the sulphates are decomposed.

Chalcopyrite breaks up as follows when heated to 200° C.:

$$2\,CuFeS_2 = Cu_2S + 2\,FeS + S.$$

As soon as the temperature rises above 540° C. the iron and copper sulphides melt, forming matte.

Pyrite, when heated to redness, is decomposed about as follows:

$$7\,FeS_2 = Fe_7S_8 + 6\,S.$$

The exact composition of the residual iron sulphide depends upon the temperature and the partial pressure of the sulphur vapor. For all practical purposes the reaction may be written

$$FeS_2 = FeS + S.$$

During the fusion stage the lead melts and reacts with any silver sulphide which may be present, as follows:

$$Ag_2S + Pb = 2\,Ag + PbS.$$

The metallic silver is immediately dissolved by the excess of molten lead.

SLAG FORMING REACTIONS.—According to the evidence of freezing-point diagrams a few simple combinations of silica and the various metallic oxides form compounds. So we are justified in writing reactions such as the following:

$$2\,PbO + SiO_2 = Pb_2SiO_4.$$

This may be termed a slag-forming reaction but, in general, slags, as far as we know, are igneous solutions of one constituent oxide in another. In the molten state they follow the laws of solutions and should be so considered.

Most chemical reactions cause either an evolution or an absorption of a considerable quantity of heat, but, from what little evidence we have, the heats of formation of silicates and borates from their component oxides is very small and it is doubtful whether these combinations should be termed reactions.

SIMPLE OXIDATION.—As soon as the air is admitted to the muffle, the lead begins to oxidize to PbO, and this oxidation continues through the whole scorification period.

ROASTING REACTIONS.—The sulphides in the ore are roasted as indicated by the following reactions:

$$\begin{aligned} FeS + 3O &= FeO + SO_2,\\ PbS + 3O &= PbO + SO_2,\\ 2PbS + 7O &= PbO + PbSO_4 + SO_2,\\ ZnS + 3O &= ZnO + SO_2,\\ Sb_2S_3 + 9O &= Sb_2O_3 + 3SO_2. \end{aligned}$$

Part of the Sb_2O_3 is volatilized, and part of it is oxidized to Sb_2O_5 and combines with litharge, forming lead antimonates, $xPbO.ySb_2O_5$. Arsenic behaves much like antimony.

The roasting reactions shown above are exothermic and, owing to the escape of the sulphur dioxide, proceed rapidly in a right-handed direction.

Reactions Between Sulphides and Oxides. — After enough PbO has been formed to slag the siliceous gangue, the litharge which is formed reacts on the partially decomposed sulphides, aiding in the elimination of sulphur, thus:

$$PbS + 2PbO = 3Pb + SO_2,$$
$$ZnS + 3PbO = 3Pb + ZnO + SO_2,$$
$$Ag_2S + 2PbO = 2Pb.Ag + SO_2,$$
$$As_2S_3 + 9PbO = As_2O_3 + 3SO_2 + 9Pb.$$

Lead sulphate also reacts with lead sulphide as indicated by the following reactions:

$$PbS + PbSO_4 = 2Pb + 2SO_2,$$
$$PbS + 2PbSO_4 = Pb + 2PbO + 3SO_2,$$
$$PbS + 3PbSO_4 = 4PbO + 4SO_2.$$

The double reactions shown above are endothermic, and hence are probably relatively unimportant in scorification.

If Cu_2S were present in the ore, part of it would be oxidized to CuO, and then the cuprous sulphide and the cupric oxide would tend to react as follows:

$$Cu_2S + 2CuO = 4Cu + SO_2.$$

A similar reaction between the litharge and the cuprous sulphide would probably take place as follows:

$$Cu_2S + 2PbO = 2CuPb + SO_2.$$

A prolonged scorification is required to remove the copper thus reduced and alloyed with the lead. The last two reactions are more pronounced at high temperatures, so that for the elimination of copper in the scorification assay it is evident that a low muffle temperature should be maintained.

Indications of Metals Present. — The color of the thin coating of slag on the scorifier is an indication of the amount and kind of metal originally present in the ore, and taken in connection with the mineralogical examination of the ore it gives a very good approximation as to its composition.

Copper gives a light or dark green, depending on the amount present. If there is much iron in the ore this color may be wholly or in part obscured by the black of the iron oxide. Practically all of the iron is removed in the first scorification, so that in assaying a copper matte the first scorifier may appear black while the second one will be green. The green color is said to be due to a mixture of blue cupric silicate and yellow lead silicate.

Iron. — A large amount of iron makes the scorifier black, from which the color ranges from a deep red through various shades of brown to a yellow brown.

Lead, in the absence of other metals, makes the scorifier lemon-yellow to a very pale yellow.

Cobalt gives a beautiful blue if other metals do not interfere.

Nickel colors the scorifier brown to black depending on the amount present. When much nickel is present the cupel becomes covered with a thick film of green nickel oxide.

Manganese colors the scorifier brownish-black to a beautiful wine-color.

Arsenic and antimony, if present in large amounts, will leave crusts on the inner surface of the scorifier even if much borax-glass is used. In the absence of other metals the scoria will be yellow in color.

If a scorifier is colored dark green, indicating much copper, dark blue, indicating much cobalt, or black with infusible scoria, indicating nickel, the button should be scorified again with more lead.

Rescorifying Buttons. — When it is necessary to rescorify buttons to remove copper or other impurities, or when bullion is assayed by scorification, a good plan is to place the scorifiers containing the right amount of test lead in a hot muffle. When the molten lead has ceased spitting, the button, or bullion, is dropped in. This precaution is suggested to prevent loss of bullion by spitting which occurs quite often in rescorifying, probably because of moisture in the scorifier. Another method is to place the scorifier in the muffle and heat for ten or fifteen minutes and then drop in the buttons and the proper amount of lead.

Buttons weighing over 35 grams should be scorified to 15 or 20 grams before being cupeled. If this is carefully done, the loss of silver should be less by the combined method than by direct cupellation.

Spitting of Scorifiers. — Occasionally small particles of lead are seen being projected out of the scorifier. This is due to decrepitation of the ore or to the action of some gas given off by the ore or scorifier itself. If the particles of lead do not all fall back into the scorifier a loss of precious metal will result. The direct cause may be found among the following and a proper remedy applied:

1. Dampness of scorifier.
2. Presence of carbonates in clay from which scorifier was made.
3. Imperfect mixing of charge, resulting in ore being left on the bottom of the scorifier and covered with lead.
4. Too high a temperature at the start, resulting in too rapid oxidation of sulphides, evolution of CO_2 or violent decrepitation.
5. Admittance of air into the muffle too soon, resulting in too rapid oxidation. (Especially to be avoided in the case of ores or products carrying zinc.)
6. Character of the ore itself. (Ores containing carbonates etc., are not suited for scorification.)

Assaying Granulated Lead. — Almost all assay reagents contain traces of gold and silver, but the lead and litharge are especially likely to contain these metals in appreciable amounts. Each new lot of granulated lead which is obtained should be sampled and assayed before it is used, and in case any silver or gold is found a strict account must be kept of the lead used in each assay and a correction for its precious metal contents made.

PROCEDURE. — Scorify 2 or 3 portions of 120 grams each in 3½ or 4 inch scorifiers. If necessary rescorify until the buttons are reduced to 15 or 20 grams. Cupel, weigh and part. This correction must be made even if extremely small, as any error thus introduced would be multiplied by 10 in reporting the results in ounces per ton.

Scorification Assay for Gold. — The silver in an ore can be determined with a sufficient degree of accuracy by taking 0.1 A. T. for each assay, since we may thus determine the contents of the ore to 0.1 of an ounce, or its value to 5 or 10 cents a ton. When, however, we determine gold to 0.1 ounce per ton by this same method, we have determined its value to only $2.00 per ton, which is not sufficiently accurate for any but very high-grade ores. For this reason the scorification assay is not usually chosen for gold ores unless they contain impurities which interfere seriously with the crucible assay.

SCORIFICATION ASSAY OF COPPER MATTE.

Procedure. — Take three portions of 0.1 A. T. of matte, mix with 45 grams of granulated lead and 1 gram powdered silica in a 3-inch Bartlett scorifier, and cover with 30 grams more of lead. Put half a gram of borax-glass and 1 gram of silica on top. Scorify hot at first and then at a low temperature to facilitate slagging the copper.

When the lead eye covers, pour as usual and separate the lead from the slag. Weigh each button and add sufficient granulated lead to bring the total weight to 60 grams and drop into three new scorifiers which have been heated in the muffle. Add about 1 gram of silica and scorify at a low temperature.

If necessary, repeat this second scorification until the cool scorifiers are light-green. Cupel as usual. The color of the cupel should be greenish and not black. The latter color indicates insufficient scorification.

Weigh the combined silver and gold and part, weighing the gold.

Notes: 1. For matte containing not more than 30 per cent of copper two scorifications are sufficient.

2. This method gives rather high slag and cupel losses and for exact work the slags and cupels are reassayed and a correction made for their silver and gold contents.

3. The final silver beads will often contain from 2 to 4 per cent of copper.

4. When accurate results in gold are desired, as many as 10 portions of 0.1 A. T. each of matte are scorified and the buttons combined for parting and weighing.

Losses in Scorification. — Losses in scorification may be due to "spitting," volatilization, oxidation and slagging as well as to shots of alloy lost in pouring. Some loss due to oxidation and slagging is unavoidable, but it should be low. If there is any decided loss by volatilization it shows that the process is unsuited to the ore.

The tendency of scorification assays to "spit" is one of the most serious objections to the process. Ores which decrepitate or contain volatile constituents such as CO_2, H_2O, etc., ($CaCO_3$, $CaSO_4.2H_2O$) are unsuited to the process and should be assayed by crucible methods. Very often a preliminary glazing of the scorifier with a mixture of sodium carbonate and borax-glass will prevent spitting. The scorifiers should always be kept in a warm, dry place.

Losses of alloy, due to failure of all the lead to collect in one piece, may be caused by careless pouring, in which case some of the lead may splash on the side of the mold and solidify there, or by a poor slag, or a cold pour, resulting in shots of alloy being left in the scorifier or scattered through the slag in the mold.

As scorification is an oxidizing process it is only reasonable to expect some loss due to oxidation of the precious metals, and this will naturally be greater the longer the scorification is continued and the more intense the oxidizing action. Silver is more easily oxidized than gold, therefore we should expect a much greater loss of silver than of gold. To keep this loss at a minimum let the liquefaction period be thorough. The molten lead tends to reduce and collect some of the silver previously slagged. Some assayers recommend sprinkling a small amount of charcoal over the slag in the scorifier just before closing the door of the muffle for the liquefaction period, with the idea of reducing some lead from the slag and thus collecting most of the oxidized silver by the rain of lead shot thus induced. English authorities almost invariably recommend this practice which they term "cleaning the slag."

Keller* gives average figures for corrected assays on anode mud known to contain 3750 ounces of silver per ton. Assays were by scorification and in one series scorifications and cupellations were run hot while in the other they were run cool. The results, each representing an average of twenty individual assays, are shown in the following table:

TABLE XVII.
ASSAYS OF COPPER ANODE RESIDUES.

Origin	Hot scorification and cupellation		Cool scorification and cupellation	
	Silver oz. per ton	Gold oz. per ton	Silver oz. per ton	Gold oz. per ton
In beads	3613.12	28.030	3688.85	27.815
In slag	55.38	0.010	56.44	0.020
In cupels	21.64	0.045	20.93	0.025
In decantation	....	0.075	....	0.225
Total	3690.14	28.160	3766.22	28.085

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* Trans. A.I.M.E., 60, p. 706.

The greatest difference between hot and cool assays is shown in the uncorrected assay results. The other figures agree surprisingly well. The loss of silver shown by these figures is very high, due to the repeated scorifications necessary and the effect of copper in increasing the loss. The loss of gold is extremely small and serves to illustrate the protective action of silver on gold.

The difference in temperature of hot and cool cupellations could not have been great, or else the cool scorification gave purer buttons for cupellation, as the cupel losses differ very little.

Because of the low results of the corrected assays, in the case of hot scorifications and cupellations, compared with the known silver content of 3750 ounces per ton, Keller concludes that there must have been a decided loss of silver by volatilization. This is a good argument for cool scorification in copper work as well as for cool cupellation.

The gold lost in decantation, in the case of beads resulting from cool work, is three times that for beads resulting from hot work. This difference he claims to be due to increased disintegration of the gold, because of the presence of added impurities retained in the beads resulting from cool cupellation.

Use of Large Ore Charges in Scorification. — While the usual charge for a scorification assay is 0.1 assay-ton, Simonds* claims to be able to obtain good results on practically all classes of sulphide ores using 0.5 assay-ton of ore, 75 grams of lead and 2.5 grams of borax-glass in a 3-inch shallow scorifier. This should certainly cause no difficulty with mixtures consisting only of galena and quartz.

Scorification Charges for Different Materials. — The following charges have been found generally satisfactory:

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* California Mines and Minerals, p. 226 (1899).

TABLE XVIII.

SCORIFICATION CHARGES.

Material	Charge				Scorifier Inches	Heat high at first then
	Ore Assay Tons	Granulated lead Grams	Borax-glass Grams	Silica Grams		
Galena	0.1	35	½–1	–	2¼	Low
Half galena, half silica	0.1	35	½–1	–	2¼	Low
Low grade galena	0.2	45	½–1	–	2½	Low
Pyrite	0.1	50	2–3	–	2¾	Medium
Half pyrite, half silica	0.1	45	1–2	–	2½	Medium
Stibnite	0.1	50–60	1–2	–	2¼–3	High
Sphalerite	0.1	60	3–5	1–2	3	High
Arsenical ore	0.1	45–60	1–2	–	2¾–3	High
Cobalt ore	0.1	60	3	–	3	High
Nickel ore	0.05–0.1	60	3	–	3	High
Chalcopyrite	0.1	60	1–2	1	3	Low
Tin ore	0.1	60–70	2–3	1	3–3½	High
Lead matte	0.1	50	½	–	2¾	Low
Copper matte	0.1	60	1	1	3	Low

FUSION PERIOD. — Place the scorifiers about midway in the muffle, close the door and allow the contents to become thoroughly fused.

ROASTING PERIOD. — When thoroughly fused, open the door to admit air to oxidize the ore and lead. If the ore contains sulphides these will now be seen floating on the top of the molten lead. The sulphur from these is burned going off as SO_2 and the base metals are oxidized and slagged. The precious metals remain unoxidized and are taken up by the lead bath. These patches of ore grow smaller and soon disappear, after which the surface of the melt becomes smooth, consisting of a bath of molten lead surrounded by a ring of slag.

The vapor rising from the assays will often indicate the character of the ore. Sulphur gives clear gray fumes, arsenic grayish-white and antimony reddish. Zinc vapor is blackish and the zinc itself may be seen burning with a bright white flame.

SCORIFICATION PERIOD. — The lead continues to oxidize and the ring of slag around the circumference of the scorifier becomes larger as more of the lead is oxidized. Finally the whole of the lead is covered with slag and the scorification is finished. The ore should be completely decomposed and practically all of the gold and silver should be alloyed with the metallic lead.

LIQUEFACTION PERIOD. — Close the door of the muffle and increase the heat for a few minutes to make the slag thoroughly liquid and to ensure a clean pour. Then pour the contents of the scorifiers into a dry, warm, scorifier mold which has been previously coated with chalk or iron oxide. Pour into the center of the mold, being careful to see that the lead does not spatter and that all of it comes together in one piece. The inside surface of the scorifiers should be smooth and glassy, showing no lumps of ore or undecomposed material.

When the slag is cold examine it and the sides of the mold carefully for shots of lead. These are most likely to occur at the contact of the slag with the mold, and if found should be saved and added to the main button. Next separate the main lead button from the slag, hammer it into the form of a cube and weigh to the nearest gram on the flux balance.

If the lead is soft and malleable, and the color of the scorifier does not indicate the presence of large amounts of copper, nickel or cobalt, the button is ready for cupellation. If it is hard or brittle it may contain impurities which must be removed by re-scorifying with an additional amount of granulated lead.

Finally cupel and weigh the resultant silver or doré beads. Report in your notes the weight of ore and reagents used, the weight of lead button obtained, as well as the weight and assay in ounces per ton of gold and silver. Note also the time of scorification and cupellation and describe the appearance of the scorifier and cupel.

Notes: 1. The ore must be so fine that a sample of 0.1 A. T. will truly represent the whole; 100-mesh may be fine enough for some ores, 170-mesh may be necessary for some others.

2. In weighing out the ore, spread the sample which has been thoroughly mixed, into a thin sheet on the glazed paper at one side of the pulp balance. Place the weight on the right-hand pan and the ore on the left-hand pan. With the spatula mark the ore off into squares 1 inch or so on a side, and then take a small portion from every square for the sample, being sure to take a section from top to bottom of the ore. During this first sampling the scale-pan should be held over the paper in one hand and the spatula in the other. When what is judged to be the right amount of ore is obtained the pan is put back on the balance and the hand with which it was held is used to turn the balance key.

The balance should be turned out of action each time ore is put on or taken off the scale-pan and the pointer need move only 1 or 2 divisions to indicate whether too much or too little ore is on the pan. To obtain the final balance, have a little too much ore in the pan, take off enough on the point of the spatula to reverse the condition of balance. With the balance key lift the beam only enough to allow the pointer to swing 1 or 2 divisions to the left of the center and then hold the key in this position. Hold the spatula over the pan and by tapping it gently with the first finger allow the ore to slide off onto the scale-pan a few grains at a time, until the balance is restored and the needle swings over to the center. By repeating this process, rejecting the ore retained on the spatula each time, an exact weight can soon be obtained.

3. The value of the results depends upon the care which is taken in mixing, sampling and weighing out the charges. Do not attempt to save time by slighting the mixing, for if a true sample is not obtained at this point no amount of subsequent care will avail to give reliable results.

4. Instead of being weighed, the granulated lead may be measured with sufficient accuracy by the use of a shot measure or small crucible. The borax-glass may also be measured.

5. The size of scorifier to be used depends upon the amount of ore, lead, borax-glass and silica used, and should be such as to give a button of approximately 15 to 18 grams. If a large scorifier is used with a small amount of lead the resulting lead button will be very small and a high loss of silver will result. Again, the larger the amount of borax-glass that is used the more slag there will be and the sooner the lead will be covered.

XLII.—TABLE OF ASSAY VALUATIONS

Values	One Part In	Per Cent.	Per Metric Ton			Per Long Ton of 2,240 Pounds					Per Short Ton of 2,000 Pounds	
			Troy Ounces	U. S. Dollars	Grams	Troy Ounces	Oz.	Dwt.	Gr.	U. S. Dollars	Troy Ounces	U. S. Dollars
One per cent.	100	1	321.50	$6,645.40^{6}$	10,000	326.666	326	13	8	6,752.20	291.666	6,028.75
One gram per metric ton = one part per million.	1,000,000	.0001	.03215	$.66^{45}$	1	.03266	......	......	15.68	$.67^{5}$	.029166	$.60^{29}$
One troy ounce per short ton.	29,166.66	.00342857 $= \frac{24}{7000}$	1.1023	22.78^{45}	34.2857	1.120	1	2	9.6	23.15	1	20.67
One troy ounce per long ton.	32,666.66	.0030612 $= \frac{3}{980}$	.9842	20.34^{34}	30.612	1	1	......	......	20.67	.892857	18.45^{8}
One troy ounce per metric ton	32,150	.0031104 $= \frac{2}{643}$	1	20.67	31.104	1.016	1	......	7.7	21.00	.90720	18.75^{2}
One dollar gold per short ton.	602,875	.00016587	.0533285	1.1023	1.6587	.054185	......	1	2	1.12	.048379	1
One zolotnik per 100 poods	384,000	.0002604	.083724	1.73^{06}	2.604	.08507	......	1	16.83	1.75^{8}	.075954	1.57
One loth per centner	3,200	.03125	10.046875	207.66	312.5	10.2183	10	4	9	211.21	9.11458	188.14
One oitavo per quintal	16,384	.00610	1.9623	40.53	61	1.9938	1	19	21	41.21^{18}	1.78654	36.80

CHAPTER VI

THE ASSAY OF COMPLEX ORES AND SPECIAL METHODS.

THE ASSAY OF ORES CONTAINING NICKEL AND COBALT.

Ores from the Cobalt district of Ontario present unusual difficulties for the assayer, as well as for the metallurgist. The high-grade ore, which carries several thousand ounces of silver per ton, is an intimate mixture of the arsenides and sulphides of cobalt, nickel and silver with a large amount of what appears to be native silver, but actually consists of an alloy of silver with arsenic, nickel and cobalt.

The question of determining the amount of silver in a shipment of such ore is actually more of a sampling than an assaying problem. The accepted method of sampling consists in crushing the entire lot of ore to a relatively small size and separating the metallic from the non-metallic portions. Each portion is then assayed separately and the results combined to give the average silver content of the ore. For a more detailed account of the sampling of such an ore the student is referred to Volume 11, pages 287 to 293 inclusive, of the Journal of the Canadian Mining Institute where the practice at the Copper Cliff smelter is described. A later paper describing the method used at the Cobalt sampler may be found in the Transactions of the Canadian Mining Institute, Volume 17, pages 199 to 251 inclusive.

For low-grade ores containing but little nickel, the crucible method of assaying will give satisfactory results. For details reference may be made to an article on this subject in the Engineering and Mining Journal, Volume 90, page 809.

For high-grade ores, a properly conducted combination method will yield higher and more concordant results than can be obtained by any "all-fire" method. The following method of A. M. Smoot is taken from his discussion* of this problem.

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* Trans. Can. Min. Inst. 17, pp. 244–250.

The Combination Assay. — Quarter- or half- assay-ton portions of the pulp are taken, the former weight if the sample contains over 2000 ounces per ton, the latter if the silver is less than this. The pulp is treated in beakers with strong nitric acid, added a little at a time until danger of frothing is past. About 75 c.c. of acid is required for 0.25 A. T. portions and 100 c.c. for 0.5 A. T. portions. The solutions are heated on a steam bath until red fumes cease to be generated and are then diluted with 200 c.c. of distilled water and allowed to stand until cold, preferably over night. It is very important that the solutions be allowed to stand before they are filtered, because with certain ores containing much arsenic together with some antimony and lime, a white crystalline coating appears on the bottoms and sides of the beakers and cannot be detached by washing or even scraping. This coating contains a little silver, and if it is not allowed to form in the original nitric acid solution it forms later on in the process and makes trouble. Insoluble residues are filtered off and washed thoroughly. If there is any coating on the sides and bottoms of the beakers which cannot be readily detached with a piece of filter paper, it is treated in the beaker with a hot solution of caustic soda which quickly disintegrates it. The caustic soda solution is acidulated with a little nitric acid and washed into the filter with the insoluble residue. Most of the silver is dissolved by the original nitric acid treatment and passes through the filters as silver nitrate, but a little remains with the insoluble residue. If the insoluble residues are large in amount they are dried and burned in crucibles, fused with sodium carbonate, borax-glass, litharge and a reducing agent. If they are small they are dried and burned in scorifiers and scorified with test lead and borax-glass. In either case, the lead buttons from the insolubles are reserved. Standard sodium chloride solution is added to the nitric acid solutions in amount sufficient to precipitate all of the silver as chloride, but any considerable excess of the precipitant is to be avoided. The silver chloride is stirred briskly until it agglomerates and is then allowed to stand for an hour until it settles and the supernatant liquid becomes clear. If it remains cloudy, rapid stirring is repeated and it is again allowed to settle. The clear solutions are filtered through double filter papers and the silver chloride precipitates transferred to the filters by a water jet and there washed slightly with water. The beakers are washed well with a wash-bottle jet and any traces of silver chloride remaining in them are wiped off with small pieces of filter paper which are placed in the filters. Filters containing the silver chloride are transferred to scorifiers which have been glazed on the inside by melting litharge in them and pouring away the excess. The glazing is done to prevent the porous scorifiers from absorbing moisture from the damp paper, and as a further protection, a small disc of pure sheet lead is placed beneath the filter papers. The scorifiers are transferred to a closed oven heated to about 250° – 300° C., where they are dried and the paper is slowly charred until it is practically all consumed. This method of burning the filter papers is an essential step, since it avoids losses of silver chloride which are apt to occur if the burning is done rapidly in a muffle. Fine test lead is sprinkled over the burned silver chloride residues and the lead buttons resulting from the crucible fusions or scorifications of the corresponding insoluble residues are added. Scorification is then conducted at a low temperature so as to obtain 15-gram lead buttons. These are cupeled at a low temperature, care being taken, in the case of large silver beads, to avoid "spitting" at the end of cupellation.

The combination method is acceptable to the smelters since it does not include slag and cupel corrections. Inasmuch as all impurities likely to effect variations in the volatilization and slag losses are removed prior to the fire work, the results of assays made on different days and in different muffles, under different conditions, are more uniform than when the untreated ores are assayed directly.

Small amounts of bismuth occurring in the Cobalt silver ores are a source of irregularity in "all-fire" methods because bismuth is retained to some extent by silver after cupellation. In the combination method, bismuth is eliminated before any fire work is done.

THE ASSAY OF TELLURIDE ORES.

The determination of the precious metals in ores containing tellurium has always been considered more than ordinarily difficult. Results obtained by different assayers and even duplicate assays by the same man have often been widely divergent. The literature of telluride ore assaying is extensive and none too satisfactory; however, it is safe to say that most of the reported differences between duplicates and between different assayers have been due more to difficulties in sampling than to the chemical interference of the element tellurium. When it is considered that most of the telluride ores which are mined contain less than 0.1 per cent of telluride mineral, it is apparent that more than ordinary care must be taken to ensure obtaining a fair proportion of this in the final assay portion. The telluride mineral itself may contain as much as 40 per cent of gold, so that one 100-mesh particle more or less in the assay portion may make a difference of several hundredths ounces of gold to the ton. To obviate, as far as possible, this lack of homogeneity, all telluride ores should be pulverized to at least 150- and preferably 200-mesh and then very thoroughly mixed before the assay portions are weighed out.

Effect of Tellurium. — Tellurium is a close associate of both gold and silver and is difficult to separate from these metals either in the crucible, scorification or cupellation processes. It is not, however, often found in abundance, and even in high-grade ores tellurium itself is found in comparatively small amounts. For instance, in two high-grade ores used by Hillebrand and Allen* in their experiments on the assay of telluride ores, containing respectively 15 and 19 ounces of gold per ton, there was tellurium amounting to 0.074 and 0.092 per cent respectively. It seems unreasonable to expect such small quantities of any element to influence seriously the results of a fire-assay.

In order to study the effects of tellurium in the gold and silver assay it is necessary to experiment with ores or alloys containing much more tellurium than those above mentioned. The following facts regarding the behavior of tellurium in cupellation and fusion are mostly due to the work of Holloway,† Pease† and Smith,‡ whom we have to thank for coördinating and elucidating much information which was hitherto much scattered and of doubtful value.

Effect of Tellurium in Cupellation. — The presence of tellurium in a lead button causes a weakening of the surface tension of the molten metal. The result is that the metal tends to "wet" the

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* Bull. 253, U. S. Geol. Survey.

† The assay of Telluride Ores, G. T. Holloway and L. E. B. Pease, Trans. I. M. M., **17**, p. 175.

‡ The Behavior of Tellurium in Assaying, Sydney W. Smith, Trans. I. M. M., **17**, p. 463.

surface of the cupel, and this allows some particles of alloy to pass into the cupel while others are left behind to cupel by themselves on its surface and form minute beads. In the case of a button containing 10 per cent or more of tellurium with an equal weight of gold or silver, complete absorption may take place. As the proportion of lead in the alloy is increased, the amount of absorption becomes less; when the lead amounts to eighty times the tellurium very little loss of precious metal occurs in a properly conducted cupellation.

Tellurium is removed comparatively slowly during cupellation, particularly in the early stages, as might be expected on comparing the heat of formation of its oxide with that of lead oxide. Rose* gives the following figures for the heat of combination of these metals with 16 grams of oxygen, —Pb to PbO 50,300 calories, Te to TeO_2 38,600 calories. To avoid danger of undue loss in cupellation of buttons from the assay of such ores, as much as possible of the tellurium should be removed before cupellation. It is also evident that the assayer should allow for large lead buttons in order that the ratio of lead to tellurium may be high.

Silver in the alloy protects gold from losses due to the presence of tellurium. It appears to act as a diluent for the gold and should always be added to every gold assay for this reason, if for no other.

In the case of imperfect cupellation, tellurium is retained by the bead and gives it a frosted appearance. In perfect cupellation the final condition of the tellurium is that of complete oxidation to TeO_2. Owing to its effect in reducing surface tension, as a result of which minute beads are often left behind, it would be well to use a cupel having a finer surface when cupeling buttons containing tellurium. Smith states that the loss due to subdivision and absorption in this case is much less when a "patent" (magnesia) cupel is used. Losses of gold and silver by volatilization, during properly conducted cupellation of lead buttons from ordinary telluride ores, is extremely small.

Effect of Tellurium in Fusions. — Tellurium was formerly believed to be oxidized to the dioxide during fusion and to go into the slag as a sodium or lead tellurate. Smith disagrees with this and argues that tellurates are decomposed at a red heat, and that lead tellurate is white, while he found the litharge slags obtained in the fusion of telluride compounds to be black. He believes that tellurium exists in the slag as the black monoxide, TeO.

The slag best suited to the oxidation and retention of tellurium in crucible assaying is a basic one containing a considerable excess of litharge. The temperature of fusion should be moderately low, as a high temperature prevents the satisfactory oxidation and slagging of the tellurium. Smith gives the following reaction for the oxidation of tellurium:

$$2PbO + Te = Pb_2O + TeO.$$

In support of this he claims to have found the black suboxide of lead in the slag.

Practically all authorities agree that the scorification process is not reliable for telluride ores. When a button from a crucible assay contains too much tellurium for direct cupellation Smith recommends fusing or "soaking" the button under an ample amount of litharge at a moderate temperature *i.e.*, 700–900° C.

Hillebrand and Allen used the following charge for ores containing from 15 to 19 ounces of gold and 0.074 to 0.092 per cent of tellurium.

Ore............	1. A. T.
Sodium carbonate	30 grams
Borax-glass......	10 "
Litharge........	180 "
Reducing agent..	for 25-gram buttons
Silver...........	2½ to 3 times gold

They find slag losses no higher than with ordinary gold ores and no serious cupellation losses. With ores containing much more tellurium than the above, the quantity taken should be reduced and the rest of the charge maintained as before.

THE ASSAY OF ORES AND PRODUCTS HIGH IN COPPER.

Crucible methods for the assay of matte and ores high in copper have largely supplanted the older scorification method. This is due to the fact that a larger amount of pulp may be used for

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* Trans. Inst. Min. Met., **14**, p. 384.

each individual assay, thus increasing the accuracy of the results. The copper is eliminated, as it is in the scorification assay, by the solution of its oxide in the basic lead oxide slag. The assay thus combines the advantages of the scorification with those of the crucible assay.

Perkins* has made a careful study of this process, and calls attention to the fact that the litharge used must be in proportion to the amount of copper and other impurities in the ore. The amounts he uses are very large, from 137 to 300 parts PbO to 1 part Cu, and make the method an expensive one. Others have reduced this amount considerably, and still manage to get buttons which will cupel.

The Slag. — The slag should be decidedly basic, for if the litharge is combined with large amounts of silica and borax, it will no longer retain its power of holding the copper in solution. A small amount of silica is necessary to prevent, to some extent, the action of the litharge upon the crucible. One part of silica to from 15 to 20 parts of litharge is generally allowed in the charge. Borax should be entirely omitted as it decreases the copper-holding capacity of the slag, and also causes boiling of the charge. Perkins states that the best results are obtained with a slag which exhibits, when cooled and broken, a somewhat glassy exterior gradually passing to litharge-like crystals towards the center. The amount of crystallization which takes place is, of course, a function of the rate of cooling and will depend among other things upon the size of the charge, the temperature of the charge when poured, and of the mold, so that too much weight should not be given to the above. The slag should, however, be crystalline and resemble litharge; a slag which is dull or glassy throughout indicates the presence of too much acid for a good elimination of copper.

Conduct of the Assay. — On account of the very corrosive action of the litharge slag it is especially necessary that the fusion be made rapidly. The muffle should be hot to start, 1000° to 1100° C., the hotter the better, and the fusion should be finished in from twenty to thirty minutes. This not only preserves the crucibles, but also, as a necessary sequel, prevents the slag from becoming charged with silica and thus forcing the copper into the button. The slag melts at a low temperature and a very high finishing temperature is not necessary. With a quick fusion there is less chance for oxidation of lead with the consequent reduction of too small a lead button.

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* The Litharge Method of Assaying Copper-Bearing Ores and Products, and the Method of Calculating Charges, W. G. Perkins, Trans. A.I.M.E., **31**, p. 913.

For the best work the hole in the back of the muffle should be closed and a reducing atmosphere maintained in the muffle. This may be accomplished by filling the mouth of the muffle with charcoal or coke, or by placing a few crucibles partly full of soft coal near the front of the muffle and using a tight-fitting door. If this precaution is not observed part of the silver will be oxidized and lost in the slag.

The following charges kindly furnished by the Boston and Montana Reduction Department of the Anaconda Copper Mining Company, Great Falls, Montana, are recommended for these ores.

TABLE XXV.

CHARGES FOR COPPER-BEARING MATERIAL.

Material	Approximate analysis		Charge for silver (In 20-gram crucible)		Charge for gold (In 30-gram crucible)	
Concentrates	Cu	9–15 per cent	Sample	½ A. T.	Sample	1 A. T.
	SiO_2	15–23 "	Soda	20 grams	Soda	30 grams
	FeO	33–40 "	Litharge	100 "	Litharge	150 "
	S	33–40 "	Silica	5 "	Silica	8 "
	Ag	3–5 ounces	Niter	15–25 "	Niter	40–60 "
	Au	0.015–0.025 ounces	Cover mixture		Cover mixture	
Matte	Cu	30–45 per cent	Sample	¼ A. T.	Sample	½ A. T.
	Fe	40–30 "	Soda	18 grams	Soda	25 grams
	S	30–27 "	Litharge	100 "	Litharge	200 "
	Ag	10–18 ounces	Silica	7 "	Silica	12 "
	Au	0.07–0.11 ounces	Niter	6 "	Niter	18 "
			Cover mixture		Cover mixture	
Matte	Cu	45–60 per cent	Sample	¼ A. T.	Sample	½ A. T.
	Fe	30–15 "	Soda	18 grams	Soda	25 grams
	S	27–24 "	Litharge	125 "	Litharge	240 "
	Ag	15–25 ounces	Silica	7 "	Silica	12 "
	Au	0.10–0.14 ounces	Niter	4 "	Niter	14 "
			Cover mixture		Cover mixture	

The cover consists of one-quarter inch of a mixture of 4 parts sodium carbonate, 2 parts borax and 1 part silica. Fusions in 20-gram crucibles require about thirty minutes, those in 30-gram is necessary to keep the antimony out of the lead button. The following charge is recommended by two English authorities:*

Ore........	0.5 A. T.
Na_2CO_3....	10–20 grams
Borax-glass.	5–10 "
Litharge....	100–120 grams
Niter......	19 "
Silica......	10 "

A preliminary assay to determine the reducing power is of course necessary. The above charge will be found to correspond almost exactly with our standard for sulphide ores, with litharge according to Lodge's rule.

George T. Holloway, in discussing this method, recommended the use of a much larger proportion of soda in the charge, *i.e.*, three times as much as stibnite, in order to aid in the retention of the antimony in the slag as a sodium antimonate.

ASSAY OF AURIFEROUS TINSTONE.

C. O. Bannister† finds a crucible assay with the following charge to be the most satisfactory method:

Ore..............25	grams
Sodium carbonate..40	"
Borax............10	"
Red lead..........60	"
Charcoal.......... 1.5	"

In this method the tin is converted into a fusible sodium stannate. The author found no tin reduced during the fusion, as shown by the fact that the button cupeled without difficulty. In all ores carrying over 1 ounce of gold per ton, the slags were cleaned by a second fusion with 10 grams of soda, 30 grams of red lead and 1.5 grams of charcoal.

Various other methods of assay were tested but none were as satisfactory as this.

CORRECTED ASSAYS.

In the assay of high-grade ores and bullion it is often desirable to make a correction for the inevitable slag and cupel losses.

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* William Kitto, Trans. Inst. Min. Met., **16**, p. 89.
William Smith, Trans. Inst. Min. Met., **9**, p. 332.

† Trans. Inst. Min. Met. (London) **15**, p. 513.

This is done in one of two ways: either by the use of a "check" or synthetic assay, or by assaying the slags and cupels resulting from the original or commercial assays.

In correcting by a "check" assay, a preliminary assay is first made and then an amount of proof silver or gold, or both, approximately equivalent to the amount present in the sample, is weighed out and made up to approximately the composition of the sample by the addition of base metal, etc. The check thus made is assayed in the same furnace, parallel with the real assay. Whatever loss the known amounts of precious metal in the check sustain is added to the weight of metal obtained from the sample as a correction, the sum being supposed to represent the actual metal present in the sample. This method of correction is always used in the assay of gold and other precious metal bullions, and is sometimes used in the assay of high-grade ores. A more detailed description of the method will be found in the chapter on the assay of bullion. This method, when properly applied, is the better and gives a very close approximation to the actual precious metal contents of a sample.

In the case of rich ores and furnace products other than bullion, a correction is usually made by assaying the slags and cupels resulting from the original assay. The weights of gold and silver thus recovered are added as corrections to the weights first obtained. This method, while approximating the actual contents of an ore, may occasionally give results a little too high, for although gold and silver lost by volatilization is not recovered and the corrections themselves must invariably suffer a second slag and cupel loss, yet on the other hand, the cupeled metal from both the first and second operations is not pure and may retain enough lead and occasionally other impurities from the ore and extra litharge used to more than offset the above small losses. The results of assays corrected by this method are evidently somewhat uncertain, but are nevertheless much nearer to the real silver content than are the results of the uncorrected or ordinary commercial assay.

Smelter contracts are almost invariably still written on the basis of the ordinary or uncorrected assay and when the corrected assay is made the basis of settlement, a deduction is made amounting to the average correction. This amounted to 1.1 per cent in the case of certain Cobalt ores.

Assay of Slags. — Assay slags are of such variable composition that no one method af analysis is universally applicable. Almost any plan of treatment whereby the slag is fused and a lead button reduced will result in the recovery of an additional amount of silver, but to make sure of obtaining practically all of the precious metals is quite another matter. Keller* states that to obtain a full recovery of the silver from slags it is necessary to reduce practically all of the lead from the charge and it is recommended that this procedure be followed.

In general, it is best to have the second slag differ materially from the original in order to ensure complete decomposition. It should be noted that the acid lead silicates are not decomposed by carbonaceous reducing agents, so that the slags resulting from Class 1 ores will have to be decomposed by means of metallic iron. Some additional borax may be required as a flux for the ferrous silicate resulting from the reaction of iron on lead silicate and if necessary an additional amount of sodium carbonate may be added.

In decomposing slags from niter assays by means of iron, it is advisable to carefully separate and reject the layer of fused sulphates which will be found on top of the cone of slag. If this is not done, the nails will be greatly corroded and even cut in two by the reaction with the fused sulphate; the formation of iron oxide and the production of an alkaline iron sulphide will result. The reaction is probably as follows:

$$Na_2SO_4 + 3Fe = Na_2S + Fe_3O_4.$$

If the lead button obtained is too large for cupellation, as will be the case in the decomposition of slags resulting from excess litharge fusions, it may be scorified to 20 or 25 grams.

Slags resulting from iron-nail assays should be fused with an excess of litharge, to ensure decomposing all of the sulphide with which the precious metals are combined. Borax and silica may be added, if necessary, to slag the resultant iron oxide as ferrous singulo-silicate. The slag resulting from an iron-nail assay of pure pyrite will probably contain about 3.5 grams of sulphide sulphur. This would reduce about 90 grams of lead from an excess of litharge. By limiting the amount of litharge it is possible to obtain a smaller lead button, which should, however, in this case, collect practically all of the gold and silver contained in the slag.

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* Trans. A.I.M.E., 46, p. 782.

CHAPTER VII

THE CRUCIBLE ASSAY.

Theory of the Crucible Assay. — The majority of ores are, by themselves infusible, or nearly so, but if pulverized and mixed in proper proportion with suitable reagents, the mixture will fuse at an easily attained temperature. The finer the ore is crushed, the better and more uniform are the results obtained. We assume in considering a crucible assay that there is such a thorough mixture of ore and fluxes that each particle of ore is in contact with one or more particles of litharge and reducing agent. As the temperature of the mass is gradually raised, part of the litharge is reduced to lead (commencing at 500° to 550° C.) by the carbon of the charge, and these reduced shots of lead, alloy and take up the gold and silver from the surrounding particles of ore, so far at least as the precious metals are free to alloy.

At about this same temperature, 560° C., the borax of the charge begins to melt and to form fusible compounds with some of the bases of the flux and ore charge. In the absence of borax or other fusible constituents, lead oxide and silica commence to combine at about 700° C., and from this point the slag begins to form rapidly. The conditions should be such that the slag remains viscous until the ore particles are thoroughly decomposed and every particle of gold and silver has been taken up by the adjacent suspended globules of lead. After this point has been passed, the temperature may be raised until the slag is thoroughly fluid, when the lead particles combine and, falling through the slag, form a button in the bottom of the crucible in which are concentrated practically all of the precious metals originally present in the ore.

To make an intelligent crucible assay it is necessary to know the mineral character of the ore, for a siliceous ore requires a different treatment from one which is mostly limestone and a sulphide requires to be treated differently from an oxide. For the purpose of the assayer, ores should be considered from two

Note

Experiments* on the size of lead buttons obtained in reducing power fusions, with varying amounts of silica in some instances, and borax-glass in others, give results approaching the theoretical values obtained above. They show that 10 grams of borax-glass has the same effect in preventing the reduction of lead from litharge as between 6 and 7 grams of silica.

Rose,† in a discussion of the refining of gold bullion with oxygen gas, made a number of experiments to determine the best proportions of borax, silica and metallic oxides. Borax alone was found to be unsatisfactory on account of the rapid corrosion of the crucible. Silica alone gave a pasty, very viscous, slag. The best slag found corresponded nearly to the formula $\frac{2}{3}$ (Na_2O, B_2O_3) + 3RO, $\frac{2}{3}B_2O_3$, $3SiO_2$. This is made up according to the following formula, $9RO + 2Na_2B_4O_7 + 9SiO_2$, where R = Ca, Mg, Pb, Zn, Cu, $\frac{2}{3}$Fe, $\frac{2}{3}$Ni. Leaving out of account the meta-borate of soda $Na_2B_2O_4$, it is a boro-silicate in which the relation of oxygen in acids to oxygen in bases is 2.66 to 1. This slag melts at a low temperature and is very fluid at between 1000° and 1100° C. It has only a slight corrosive action on clay crucibles. The flux contains 3 parts by weight of borax-glass to 4 parts of silica.

Charles E. Meyer‡ in fluxing zinc-box slime, made zinc into a bi-silicate with silica and added $Na_2B_4O_7$ for other bases. The other bases were all assumed to be Fe_2O_3 and borax-glass was added pound for pound, *i.e.*, 1 pound $Na_2B_4O_7$ for 1 pound Fe_2O_3.

Fluidity of Slags. — It is also necessary to distinguish between the melting-point and the fluidity of slags. Many slags of low melting and formation temperature are entirely unsuited for assay purposes on account of their viscous nature when melted. As a rule, the higher the temperature the more fluid a slag will become, but different slags vary much in this respect. All slags are viscous at their freezing-point, yet one slag will be thinly fluid 200° C. above its melting-point and another will be decidedly viscous at this degree of superheat. The viscosity of silicates increases with the percentage of silica above that required for the mono-silicate, and the same may be said for borates.

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* Lodge, Notes on Assaying, 2nd Ed. p.

† Inst. Min. and Met., **14**, p. 396, (1905).

‡ Jour. Chem. Met. and Min. Soc. of South Africa, **5**, p. 168, (1905).

Acidic and Basic Slags. — Slags more acid than the mono-silicate are generally termed acid, while those approaching a sub-silicate are called basic. The acid slags are all more or less viscous when molten and can be drawn out into long threads. They cool slowly and are usually glassy and brittle when cold. The basic slags are usually extremely fluid when molten; they pour like water, with no tendency to string out; in fact they may even be lumpy where the bases are in too great excess. They solidify rapidly and usually crystallize to some extent during solidification. Basic slags are dull and tough when cold. They are often of a dark color and on account of the large proportion of bases they contain they usually have a high specific gravity.

Mixed Silicates. — The mixture of two or more fusible compounds usually fuses at a lower temperature than either one taken alone, just as, for example, a mixture of potassium and sodium carbonate fuses at a lower temperature than either one of them alone. For this reason assayers always provide for the presence of a number of easily fusible substances, although their presence is not always necessary for the decomposition of the ore. For instance, even in the assay of pure limestone, which is a base, a certain amount of sodium carbonate, also a base, is always added.

Use of Fluxes. — For the sake of economy in material and time it is best to limit the amount of fluxes to the needs of the ore. The great saving to be made in this way may be illustrated as follows: If we use twice as much flux as necessary, we have to use twice as large a crucible which cuts down the furnace capacity very considerably. Besides this, the large charges require a longer time in the furnace to fuse and decompose the ore and this again reduces the furnace capacity.

The Lead Button. — In every gold and silver assay, a carefully regulated amount of the litharge is reduced. This results in the formation of a great number of minute globules of lead which serve to collect the gold and silver. When the charge becomes thoroughly liquid these collect in the bottom of the crucible forming the lead button. There is considerable difference of opinion as to the proper size for the lead button. Many assayers hold that it should be proportional to the total volume of charge; others vary the lead-fall according to the quantity of precious metals to be collected. Both of these ideas appear to have merit and agree in general with the experience of lead blast-furnace operators, who insist that the charge shall contain not less than 10 per cent of lead, all of which, of course, they attempt to reduce.

Miller* and Fulton, in experimenting on an ore containing 2260 ounces of silver per ton, found that the silver recovered from the lead button increased regularly with the increase in size of the lead button to a maximum of 28 grams. They concluded that the collecting power of a given weight of lead was independent of the amount of the charge.

In most cases a 28-gram lead button will collect all the gold and silver in the ordinary crucible charge, and the assayer is advised to figure for a button of this size unless some good reason for change is shown.

The Cover. — In practically all crucible assay work it was formerly customary to place a cover of some fusible substance on top of the mixed charge in the crucible. Different assayers advocate different materials, as salt, sodium sulphate, borax, borax-glass and soda, as well as different flux mixtures.

The idea which leads to the use of the cover is that, melting early, it makes a thick glaze on the sides of the crucible above the ore charge and that, if particles of ore or lead globules are left on the sides of the crucible by the boiling of the charge, the cover tends to prevent them from sticking there. As the fusion becomes quiet and the temperature rises, most of this glaze runs down to join the main charge and carries with it any small particles of ore or lead which may have stuck to it in the early part of the fusion.

The salt cover is thinly fluid when melted. It does not enter the slag but floats on top of it, thus serving to keep out the air and to prevent loss by ebullition.

The borax cover fuses before the rest of the charge. It is thick and viscous when melted and serves to prevent loss of fine ore by "dusting," as well as to stop loss by ebullition. It finally enters the slag and so ceases to be a cover after the fusion is well under way.

Some assayers object to the use of salt on the ground that it is likely to cause losses of gold and silver by volatilization. It is a well-known fact that gold chloride is volatile at a comparatively low temperature, commencing at 180° C. and that silver chloride is volatile in connection with the chlorides of arsenic, antimony, copper, iron, lead, etc. When an ore contains substances such as manganese oxide, basic iron sulphate etc., capable of generating chlorine upon being heated with salt, it would seem wise to omit the use of salt. If it is not desired to use salt a good cover may be made from a mixture of borax-glass and sodium carbonate in the proportion of 10 parts of the former to 15 parts of the latter.

The present tendency is to do away with the cover altogether. For muffle fusions, at any rate, a salt cover is entirely unnecessary and even objectionable, in that it fills the room with chloride fumes at the time of pouring. Salt assists in the volatilization of lead compounds and these are most injurious to health.

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* School of Mines Quarterly, **17**, pp. 160–170.

REDUCTION AND OXIDATION.

Reducing and oxidizing reactions are common in fire assaying as in other chemical work, and practically all fusions are either reducing or oxidizing in nature. For instance, the scorification assay is an oxidizing fusion in which atmospheric air is the oxidizing agent, while the crucible fusion of a siliceous ore is a reducing fusion in which argols, flour or charcoal act as the reducing agents.

By the term "reducing power," as used in fire assaying, is meant the amount of lead that 1 gram of the ore or substance will reduce when fused with an excess of litharge. For instance, if we use 5.00 grams of ore and obtain a lead button weighing 16.50 grams the reducing power of the ore is

$$\frac{16.50}{5.00} = 3.30.$$

By the term "oxidizing power" is meant the amount of lead which 1 gram of the ore or substance will oxidize in a fusion, or more exactly it is the lead equivalent of a certain amount of reducing agent or ore which is capable of being oxidized by 1 gram of the ore or substance.

Reducing Reactions. — The reduction of lead by charcoal is shown by the following reaction:

$$2PbO + C = 2Pb + CO_2,$$

from which it is seen that 1 gram of pure carbon should reduce $\frac{2 \times 207}{12} = 34.5$ grams of lead. However, as charcoal is never pure carbon the results actually obtained in the laboratory will be somewhat less, usually from 25 to 30. All carbonaceous materials have more or less reducing power. Those most commonly used as reducing agents in assaying are charcoal, R. P. ± 27.5; argols, R. P. 8 – 12; cream of tartar, R. P. 5.5; flour, R. P. 10 – 12.

Besides carbonaceous matter many other substances and elements are capable of reducing lead from its oxide. The most important of these are metallic iron, sulphur and the metallic sulphides. The reduction of lead by iron is shown by the following reaction:

$$PbO + Fe = Pb + FeO,$$

whence the reducing power of iron is $\frac{207}{56} = 3.70$.

The reducing power of sulphur and the metallic sulphides will vary according to the amount of alkaline carbonate present. For instance, the reduction of lead by sulphur in the absence of alkaline carbonates is shown by the following reaction:

$$2PbO + S = 2Pb + SO_2.$$

The reducing power of sulphur under these conditions would be

$$\frac{2 \times 207}{32} = 12.9.$$

In the presence of sufficient alkaline carbonates the sulphur is oxidized to sulphur trioxide which combines with the alkali to form sulphate. The reaction is as follows:

$$3PbO + S + Na_2CO_3 = 3Pb + Na_2SO_4 + CO_2,$$

from which we see that the reducing power of sulphur, under these conditions, should be

$$\frac{621}{32} = 19.4.$$

In the same way we find that the reducing power of the metallic sulphides varies according to the amount of available alkaline carbonate present. For instance, in the absence of alkaline carbonates and with a small amount of silica to slag the iron

oxide and to hold it in the ferrous condition, the following equation expresses the reaction between iron pyrite and litharge:

$$FeS_2 + 5PbO + SiO_2 = FeSiO_3 + 5Pb + 2SO_2.$$

This last statement is not strictly true, as in the entire absence of alkaline carbonate the reaction is not quite complete. Miller[*] found that under the above conditions the lead button and slag always contained sulphides and the actual results fell slightly below those called for by the above equation. According to this equation the reducing power would be

$$\frac{5Pb}{FeS_2} = \frac{1035}{120} = 8.6.$$

With an excess of sodium carbonate and in the absence of silica, the sulphur is oxidized to trioxide and the iron to the ferric condition, as shown by the following equation:

$$2FeS_2 + 15PbO + 4Na_2CO_3 = Fe_2O_3 + 15Pb + 4Na_2SO_4 + 4CO_2,$$

and this gives a reducing power of $\frac{3105}{240} = 12.9$.

With a small amount of silica present the iron may be left in the ferrous condition, which is much to be preferred. Then the reaction becomes:

$$2FeS_2 + 14PbO + 4Na_2CO_3 + SiO_2 = Fe_2SiO_4 + 14Pb + 4Na_2SO_4 + 4CO_2,$$

which gives a reducing power of 12.07.

All of the above reactions may take place simultaneously in the same fusion, and therefore it will be obvious that there may be obtained for pyrite any reducing power between 8.6 and 12.9, according to the amount of sodium carbonate, litharge and silica present. Unfortunately it is somewhat difficult to control the oxidation of the sulphur, and this makes it hard to obtain a lead button of the right size. What the assayer wants to know is the "working reducing power" of the ore, which always lies somewhere between the two extremes indicated, and this he determines by a preliminary fusion with a small quantity of ore, an excess of litharge and a carefully regulated amount of soda.

The accompanying table gives the reducing power of some of the common sulphides. The theoretical figures are computed

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[*] Trans. A.I.M.E., **34**, p. 395.

for sulphur oxidized to both SO_2 and SO_3. In the last column is given the reducing power of the pure minerals using the following charge Na_2CO_3 5 gms., PbO 80 gms., SiO_2 2 gms., ore to yield an approximate 25 gram button.

TABLE XX.

REDUCING POWER OF MINERALS.

Mineral	Formula	Computed		Actually determined
		S to SO_2	S to SO_3	
Galena	PbS	2.6	3.46	3.41
Chalcocite	Cu_2S	3.9	5.2	
Arsenopyrite	FeAsS	5.7	6.96	8.18[1]
Stibnite	Sb_2S_3	5.5	7.35	6.75
Chalcopyrite	$CuFeS_2$	6.2	8.44	7.85
Sphalerite	ZnS	6.37	8.5	7.87
Pyrrhotite	Fe_7S_8	7.35	9.9	10.00[1]
Pyrite	FeS_2	8.6	12.07	11.05

[1] The sample used probably contained pyrite.

As is the case with sulphur and the metallic sulphides the amount of lead reduced by the carbonaceous reducing agents also depends upon the nature of the charge, particularly upon the amount of silica present. Other things being equal, the more basic the charge, the greater the amount of lead which will be reduced by a unit quantity of the reducing agent. Thus, a certain sample of argols showed a reducing power of 11.04 when silica for a sub-silicate was added, 10.93 for a mono-silicate, 10.62 for a bi-silicate and only 9.26 for a tri-silicate. The rate of fusion and the final temperature both have a good deal to do with the amount of this reduction, for the reason that the silicates of lead more acid than the mono-silicate are but little reduced by carbon below 1000° C. With a limited amount of litharge present, part is bound to be converted into silicate before it can be reduced by carbon, and naturally the greater the proportion of silica, the larger the amount of litharge which will combine and thus be rendered unavailable for reduction by carbon.

Oxidizing Reactions. — Certain metals, notably iron, manganese, copper, cobalt, arsenic and antimony, are capable of existing

in two states of oxidation. When fused with a reducing agent the higher oxides of these metals are reduced to the lower state of oxidation at the expense of the reducing agent. Ores containing these higher oxides are said to have an oxidizing power on account of this property of using up reducing agent. For convenience this oxidizing power is measured in terms of lead, although the bulk of the oxidizing reaction in any assay fusion is probably accomplished against the reducing agent of the charge.

For instance if in an assay fusion containing silica we have ferric oxide, sufficient for a bi-silicate, and carbon, the following reaction takes place:

$$2Fe_2O_3 + C + 4SiO_2 = 4FeSiO_3 + CO_2,$$

from which we find that 1 gram of Fe_2O_3 requires 0.037 gram of carbon to reduce it to FeO. Expressed in terms of lead the relation would be as follows:

$$Fe_2O_3 + Pb = 2FeO + PbO.$$

That is to say the oxidizing power of Fe_2O_3 is $\frac{207}{160} = 1.31$. Similarly

$$MnO_2 + Pb = MnO + PbO.$$

The oxidizing power of MnO_2 is $\frac{207}{87} = 2.4$, which means that each gram of MnO_2 present in a fusion with litharge and a reducing agent will prevent the reduction of 2.4 grams of lead. It is easily seen, therefore, that this oxidizing power of ores must be taken account of in computing assay charges. The method of determining the oxidizing power of ores will be discussed later.

In the crucible assay of high sulphide ores it is frequently necessary to add some oxidizing agent to the charge to prevent the reduction of an inconveniently large lead button. A 28-gram lead button is usually sufficiently large to act as a collector of the precious metals, and were a larger button obtained, it would entail an extra loss due to scorification, or a prolonged cupellation, as well as consuming extra time in this treatment. When, therefore, the ore charge would of itself reduce more than 28 grams of lead we ordinarily add potassium nitrate or some other oxidizing agent. Niter is almost exclusively used in this country for oxidizing. Its action with carbon is shown by the following equation:

$$4KNO_3 + 5C = 2K_2O + 5CO_2 + 2N_2,$$

from which the theoretical oxidizing power of niter expressed in terms of lead is found to be 5.12. The theoretical oxidizing power may also be figured from its reactions with sulphur, or any of the metallic sulphides and will always give substantially the same result when the degree of oxidation of the sulphur is kept the same in the reducing and oxidizing reactions.

The actual oxidizing effect of niter is always found to be lower than this, partly because the niter ordinarily used for this purpose is not 100 per cent KNO_3 and partly because in the actual fusion some oxygen is likely to escape unused. This loss of oxygen increases as the acidity of the charge increases. The loss is also probably influenced by the depth of the charge, the rate of fusion and the temperature. In the case of actual assay fusions with sulphides, the oxidizing power will be found to vary between 3.7 and 4.7, the lower figure being approached when the charge contains considerable silica and borax-glass and but little litharge, the upper figure prevailing when no silica or borax is used and in the presence of an excess of sodium carbonate and litharge.

With both the reducing power of the sulphides and the oxidizing power of the niter varying with different proportions of sodium carbonate, litharge, borax and silica, as well as with variations of temperature, the problem of obtaining a lead button of the right size in niter assays is not a simple one. The only solution is so to control the conditions that the state of oxidation of the sulphur in the final assay shall be the same as that in the reducing power fusion. This is the first essential; the second is to decide on some slag of definite silicate degree and always use it; then the proportion of oxygen which escapes unused will be nearly constant and the oxidizing power of the niter, once determined, may be depended on to remain constant.

With the type of charge recommended in the latter part of the chapter, the oxidizing power of niter will be found to lie between 4.0 and 4.2 and with this minor variation but little trouble should be found in properly controlling the size of the button.

Just as we may obtain several reactions between any of the sulphides and litharge according to the degree of oxidation of the sulphur and occasionally also of other constituents of the mineral, so we may also obtain several different reactions between niter and the sulphides. For instance, in the absence of alkaline carbonates and in the presence of silica, the sulphur can be oxidized only to the dioxide, and the reaction between niter and pyrite would be as follows:

$$2KNO_3 + FeS_2 + SiO_2 = K_2O.FeO.SiO_2 + 2SO_2 + N_2.$$

In the presence of an excess of alkaline carbonate and litharge with little or no silica, both the iron and the sulphur would be oxidized as highly as possible and the following reaction would result:

$$6KNO_3 + 2FeS_2 + Na_2CO_3 = Fe_2O_3 + 3K_2SO_4 + Na_2SO_4 + 3N_2 + CO_2.$$

Ferric oxide is a most undesirable component of assay slags and its formation must be avoided. To prevent the iron from going to the ferric condition enough silica should be present to hold and slag it as ferrous singulo-silicate. If this is provided the reaction then becomes

$$28KNO_3 + 10FeS_2 + 6Na_2CO_3 + 5SiO_2 = 5Fe_2SiO_4 + 14K_2SO_4 + 6Na_2SO_4 + 14N_2 + 6CO_2.$$

A slight oxidizing effect may be obtained by using red lead in place of litharge, and this is sometimes done, especially in England and the British colonies. The oxidizing effect of red lead is shown by the following reaction:

$$Pb_3O_4 + Pb = 4PbO.$$

The oxidizing power in terms of lead is $\frac{207}{685} = 0.30$.

TESTING REAGENTS.

Each new lot of litharge and test lead should be assayed for silver and gold so that when any is found to be present a proper correction may be made. Different lots of argols, and flour are also found to vary in reducing power, and their reducing powers should also be determined.

The following procedure is designed, first, to allow the student to determine the reducing power of flour, charcoal or other reducing agents and at the same time to determine the silver correction for litharge, and, second, to familiarize him with the principal operations connected with the crucible method of assay.

Procedure. — Take two E or F pot-furnace crucibles, or 12 or 15 gram muffle crucibles.

Weigh into them, in the order given, the following:

No. 1		No. 2	
Sodium carbonate	5 grams	Sodium carbonate	5 grams
Silica	5 "	Silica	5 "
Litharge	60 "	Litharge	60 "
Flour	2.50 "	Charcoal	1.00 "

Weigh the flour and charcoal on the pulp balance as exactly as possible, the others on the flux balance. Mix thoroughly with the spatula by turning the crucible slowly with one hand while using the spatula with the other. When finished tap the crucible several times with the handle of the spatula to settle the charge and to shake down any material which may have lodged on the sides of the crucible above the charge. Finally put on a half-inch cover of salt.

Pot-Furnace Fusion. — Have a good bright fire in the pot-furnace which should not, however, be filled with coke more than halfway to the bottom of the flue. Place the crucibles so that their tops shall not be much above the bottom of the flue. Place a piece of cold coke directly under each crucible as it is put into the furnace. Cover the crucibles and pack coke around them, being careful to prevent the introduction of any coke or dust. Close the top of the furnace, open the draft if necessary and urge the fire until the charges begin to fuse. Then close the draft and continue the melting slowly enough to prevent the charges from boiling over. When the charges have finished boiling, note the time and open the draft if necessary, to get a yellow heat and continue heating for ten minutes.

Pour the fusions into the crucible mold, which has been previously coated with ruddle, thoroughly dried and warmed. When the material is cold, a matter of five or ten minutes for a small fusion, break the cone of lead from the slag and hammer it into a cube to thoroughly remove the slag. Weigh the buttons on the pulp balance to the nearest tenth of a gram and record the weights and reducing powers in the notebook.

Save the lead buttons and cupel them. The beads should contain all of the gold and silver in the 60 grams of litharge used. Weigh the beads and part to see if gold is present. Record the weights of the beads and compute the correction for silver in 30 grams of litharge.

Muffle Fusion. — If the fusions are to be made in the muffle have the muffle light red and the fire under such control that the muffle can be brought to a full yellow in the course of half an hour. Place a row of empty 30-gram crucibles in the front part of the muffle so as to close the space as completely as possible. These serve to keep the assays hot by reflection of heat and so prevent loss of heat by conduction through the door. See that the muffle door is tightly closed to prevent admission of air. Melt at sufficiently low temperature to avoid violent boiling and then when the sound of bubbling is no longer heard, raise the temperature and pour as in the case of the pot-furnace fusion.

Notes: 1. So-called silver-free litharge can now be purchased but even this often carries traces of gold and silver.

2. In assaying samples of litharge low in silver 120 to 240 grams may be required to give a bead of sufficient size to handle and weigh.

3. It is convenient to use litharge in multiples of 30 grams and therefore the silver correction is based on 30 grams of litharge.

4. The temperature which the muffle should have before the crucibles are introduced depends upon the number of charges which are to be put in at one time. If only one or two the temperature should be low to avoid danger of boiling over. However, if the muffle is to be filled with crucibles the initial temperature may be higher, as the crucibles can be depended upon to decidedly lower the temperature.

5. Pour the fusions carefully into the center of the molds and do not disturb until the lead has had time to solidify.

The following are the reducing powers of some of the common reducing agents:

Charcoal	25–30	Corn-starch	11.5–13
Argols	8–12	Sugar	14.5
Flour	10–12	Cream of tartar	4.5–6.5

ASSAY OF CLASS 1 ORES. GOLD OR SILVER.

This is the most common class of ores and as it is also the one which presents the fewest difficulties for the assayer, it is considered first. Actually, ores with no traces of sulphides are somewhat of a rarity, but the methods given below may be adapted to ores containing moderate amounts of sulphides by simply decreasing the amount of reducing agent used.

Slags for Class 1 Siliceous Ores. — To fuse a siliceous ore, basic fluxes must be added, the alkaline carbonates and litharge being the ones available. The bi-silicates of soda and lead are readily fusible and sufficiently fluid for the purpose; therefore, the basic fluxes may be limited to the amount necessary to form these silicates. Sodium carbonate and litharge combine with silica to form bi-silicates in proportions indicated in the following equations:

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2,$$
$$PbO + SiO_2 = PbSiO_3.$$

From a comparison of the molecular weights of the left-hand members of these equations, it may be determined that one assay-ton of pure silica will require either 51.2 grams of sodium carbonate, or 108 grams of litharge to form a bi-silicate.

As the mixed silicate of soda and lead is generally more satisfactory than either one alone, it is common to use both of these basic fluxes in every fusion, thus making a double, or bi-basic silicate. It is customary to use at least as much sodium carbonate as ore in every assay. On this basis it appears that approximately three-fifths of the silica is fluxed with soda, leaving two-fifths of it to be fluxed with litharge. Taking these proportions, then, there will be required for one assay-ton of pure silica exactly 30.7 grams of sodium carbonate and 43.2 grams of litharge.

In assaying an ore provision must also be made for a lead button to act as a collector of the precious metals. A 28-gram button is usually sufficient. To allow for this it will be necessary to add 30 grams more of litharge and also some reducing agent, say $2\frac{1}{3}$ grams of flour (R. P. 12).

The charge will now stand as follows:

Ore	1 A. T.
Sodium carbonate	30.7 grams
Litharge for slag 43 grams Litharge for button 30 grams	73 grams
Flour (R. P. 12)	$2\frac{1}{3}$ grams

The ore so far considered has been an ideal one, pure silica, which is rarely if ever found in practice. The ordinary siliceous ore almost invariably contains small amounts of iron oxide, various silicates of alumina, pyrite and other sulphides, as well as occasionally more or less calcite, all of which reduce the amount of silica for which basic fluxes must be supplied. It is obvious that for such an ore it is possible to make a bi-silicate slag with a somewhat smaller amount of basic reagents than those in the ideal charge shown above. It will be advisable also to use a small amount of borax in almost every fusion, as this helps both in fluxing silica and in slagging the basic oxides. So that, by rounding out the above charge and adding borax, the following practical bi-silicate charges for siliceous ores are obtained:

Ore	½ A. T.	1 A. T.	2 A. T.
Soda (Na_2CO_3)	15 grams	30 grams	60 grams
Borax	3–5 "	5–10 "	10–15 "
Litharge	50 "	70 "	110 "
Flour (R. P. 12)	$2\frac{1}{3}$ "	$2\frac{1}{3}$ "	$2\frac{1}{3}$ "

The larger the amount of ore used the more necessary it becomes to keep down the quantity of fluxes. The following charges, more acid than the bi-silicate, are regularly used by the author for the assay of siliceous tailings.

Ore	1 A. T.	2 A. T.	5 A. T.
Soda (Na_2CO_3)	30 grams	60 grams	150 grams
Borax	3 "	6 "	15 "
Litharge	60 "	90 "	180 "
Flour for a	28 gram	30 gram	35 gram lead button.

The results obtained with the last mentioned charges are good; the slags, of course, are more viscous than the bi-silicate slags but they pour well even when fusions are made in the muffle furnace. The crucibles are practically unattacked and if of good quality, can be used for many such fusions, especially if care is taken to cool them slowly.

The following table gives the amounts of the different common basic reagents required to form bi-silicates with pure silica. This will be found useful in calculating assay charges for various quantities of siliceous ores.

TABLE XXI.
BI-SILICATE SLAG FACTORS No. 1.

SiO_2	Quantity of bases required			
	PbO	Na_2CO_3	K_2CO_3	$NaHCO_3$
1 assay-ton	108. gm.	51.2 gm.	66.8 gm.	81.2 gm.
10 grams	37.0 gm.	17.6 gm.	22.9 gm.	27.9 gm.

One gram of FeO neutralizes 0.84 grams SiO_2 or requires 1.4 grams borax-glass. One gram of $CaCO_3$ neutralizes 0.60 gram SiO_2 or requires 1.0 gram borax-glass.

All assayers do not agree on the use of bi-silicate slags for siliceous ores, and even if they did agree they might prefer different proportions of sodium carbonate and litharge than those mentioned above. Many assayers consider it better to make the slag less acid than the bi-silicate; in fact there are certain advantages in making what is approximately a sesqui-silicate. The quantity of basic fluxes required for this silicate may be determined by increasing the figures found in the last table by one-third.

Where a large number of assays are to be made on ore of about the same character it is neither necessary nor desirable to weigh out each individual unit of flux, as this would take too much time. Instead, a flux mixture is made up and then a unit weight of this mixture is weighed out for each assay, or better still a measure is used which delivers the proper amount. There are innumerable formulas for such mixtures and even for the same ore many different mixtures are advocated. A good flux for the assay of siliceous ores consists of 3.5 parts of sodium carbonate, 0.5 parts of borax and 6 parts of litharge. If an assayer uses 100 grams of this mixture per assay-ton of quartz and reduces a 28-gram lead button he will have what is approximately a bi-silicate slag. If he prefers he may use 125 grams of flux which gives practically a sesqui-silicate. The latter proportion is somewhat more popular with assayers, and the student is advised to try both. It should be noted, however, that half of this quantity of flux will not give a sesqui-silicate with half an assay-ton of ore, unless at the same time the reducer is limited to the amount required for a 14-gram lead button. This latter procedure is not commonly followed, so that for half an assay-ton of ore approximately 75 grams of this flux should be used, if a sesqui-silicate and a button of reasonable size are to be obtained.

Slags for Class 1 Basic Ores. — In the assay of basic ores it is necessary to add acid fluxes, silica and borax to obtain a fusible slag. Also, on account of the fact that the silicates of iron, manganese, calcium and magnesium are by themselves infusible, or nearly so, at the temperature of the assay-furnace, it is customary to add some soda and excess litharge to the charge. These latter, combining with some of the silica and borax, form readily fusible compounds which help to take into solution the silicates of the basic oxides and by diluting them give more fusible and fluid slags. A weight of soda equal at least to that of the ore is generally taken as a starting point, and very often a quantity of litharge equal to that of the ore is also allowed for the slag.

The silicate-degree of the slag will depend on the character of the bases. For Class 1 ores, consisting principally of iron, manganese, calcium, or magnesium it has been found best to approximate a sesqui- or a bi-silicate slag.

If the silica and borax are cut down so as to make mono-silicates, the slags from limestone and dolomite will be lumpy when hot and full of lead shot when cold. Those from iron oxide will be lumpy when hot, and when they are poured the crucible will be left full of lead shot which refuse to collect. When cold, the slag will be found full of shots of lead and will be magnetic. This is due to the formation of the magnetic oxide of iron, which, being infusible, floats around in the lower part of the slag and interferes with the settling of the reduced lead.

The following table of bi-silicate slag factors will facilitate the calculation of charges for basic ores.

TABLE XXII.
BI-SILICATE SLAG FACTORS No. 2.

Quantity of bases	Quantity of acid required
1 A. T. FeO	24.5 grams SiO_2
1 A. T. $CaCO_3$	17.4 " "
1 A. T. $MgCO_3$	20.8 " "
10 gms. PbO	2.7 " "
30 " $NaHCO_3$	10.8 " "
30 " Na_2CO_3	17.0 " "
10 " K_2CO_3	4.4 " "

For sesqui-silicates use three-quarters of the above quantities of silica. When borax-glass is substituted for silica, 1 gram of borax-glass may be considered equivalent to 0.6 gram of silica.

The amount of silica which should be replaced by borax has not been determined, but on account of the greater fusibility and fluidity of boro-silicates it is well to replace at least a quarter to a third of the silica with its equivalent of borax or borax-glass. When the calculated amount of borax-glass falls below 5 grams, this quantity is generally used as a minimum.

The following example will illustrate the use of the table. Take 1 assay-ton of an ore consisting of 50 per cent $CaCO_3$ and 50 per cent SiO_2. Start with 30 grams of sodium carbonate and 60 grams of litharge, 30 for the slag and 30 for the lead button, and plan for a bi-silicate slag. Under these conditions the silica requirements of the different bases are as follows:

The $CaCO_3$ of the ore requires 0.5 × 17.4 =	8.7	grams SiO_2
30 grams of soda require	17.0	" "
30 grams of litharge require	8.1	" "
Total	33.8	" "
Deducting the silica of the ore, ½ A. T. =	14.6	
Silica or equivalent borax necessary	19.2	

If two-thirds of this is put in as silica, there remains 19.2 − 12.8 = 6.4 grams of silica, for which we must substitute the equivalent amount of borax-glass, which is $\frac{10}{6} \times 6.4 = 10.7$ grams.

The final charge stands

Ore	1	A. T.
Sodium carbonate	30	grams
Borax-glass	10.7	"
Litharge	60	"
Flour (R. P. 12)	$2\frac{1}{3}$	"
Silica	12.8	"

This charge contains 17.0 grams of $CaSiO_3$ and 34.6 grams of Na_2SiO_3, or about twice as much sodium bi-silicate as calcium bi-silicate. Figure 3 shows that such a combination will melt at a reasonably low temperature. The lead silicate and the borax-glass will, of course, reduce this melting temperature materially.

Following the procedure outlined above it may readily be determined that for pure calcium carbonate the charge shown below should be used:

Ore	1	A. T.
Sodium carbonate	30	grams
Borax-glass	23.6	"
Litharge	60	"
Flour	$2\frac{1}{3}$	"
Silica	28.3	"

This charge contains approximately equal amounts of the bi-silicates of sodium and calcium, as well as litharge and borax-glass. It fuses without difficulty and gives a glassy slag and a good separation of lead.

Figure 44 gives at a glance the quantity of reagents other than flour required to flux one assay-ton of any mixture of limestone and silica.

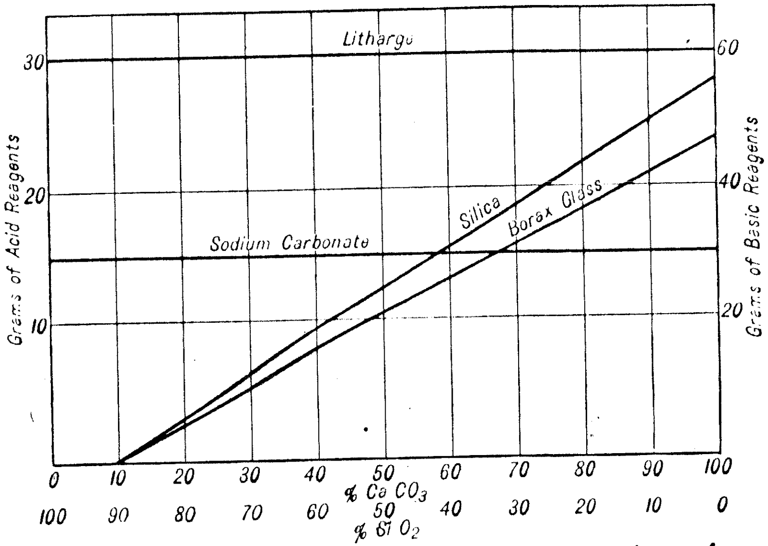

Fig. 44. — Quantity of fluxes required for 1 A.T. of any mixture of limestone and silica.

Magnesium silicates are somewhat more difficult to fuse than the corresponding calcium silicates; but the same method of procedure should be followed for ores containing magnesite or dolomite as for limestone. Precious metal ores containing large quantities of magnesium carbonate are not likely to be found; but the assayer may have to determine the quantity of silver contained in a magnesia cupel, and for this bi-silicate slags are the best.

Ores containing much calcium or magnesium carbonate cause considerable boiling in the crucible, due to their dissociation into oxide and carbon dioxide at a temperature about the same as that required to melt the charge. The assayer should bear this in mind in selecting a crucible for such an ore.

The charges for ores consisting mainly of iron or manganese oxides are figured in the same way as for those containing calcium carbonate. In assaying ores containing iron or manganese oxides, more than the ordinary amount of reducing agent must be added to counteract the oxidizing effect of these minerals.

Slags for Alumina. — Alumina is the most difficult to flux of any of the common metal oxides. Fortunately, pure alumina is never found associated with gold and silver, and the assayer is not likely to encounter anything worse than ores containing a good deal of alumina in the form of clay. Pure china-clay, or kaolinite, which has the following composition, $H_4Al_2Si_2O_9$, contains only 39.5 per cent of alumina. Ordinary clays contain more or less quartz and other minerals, so that even the above-mentioned content of alumina will not have to be dealt with. Small amounts of combined alumina are found in many ores but these cause no trouble in the fusion.

Metallurgists have never entirely agreed as to the behavior of alumina in slags. The work of Day, Shepherd, Rankin, Wright, Bowen and others has thrown much new light on the subject of the constitution and thermal properties of the ternary system $CaO - Al_2O_3 - SiO_2$. The melting-point curve of the $CaO - SiO_2$ series was shown in Chapter I. Figures 45 and 46 give the melting-point diagrams* of the $Al_2O_3 - SiO_2$ and the $CaO - Al_2O_3$ series respectively.

The $Al_2O_3 - SiO_2$ curve is almost a straight line between the melting-point of silica, 1625° C. and that of alumina, 2050°, the silicate of lowest melting-point being the eutectic containing 87 per cent of silica, which melts at 1610°. This curve is not at all like that of the $CaO - SiO_2$ series, as it might be expected to be if alumina were a base. It shows but one compound, $Al_2O_3.SiO_2$.

The $CaO - Al_2O_3$ curve, on the other hand, shows a number of compounds and, what is more important to the metallurgist, a very decided reduction of melting temperature at about the point where the components are of equal weight. The compound $5CaO.3Al_2O_3$, which contains 47.8 per cent of CaO, lies just between two eutectics, both of which melt at about 1400° C. It would seem from the above, that alumina behaves more like an acid than a base, and it is suggested that it be so treated.

Alumina makes slags viscous, no matter how it is treated, and

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* Am. Jour. Sci., **39**, pp. 9 and 11.

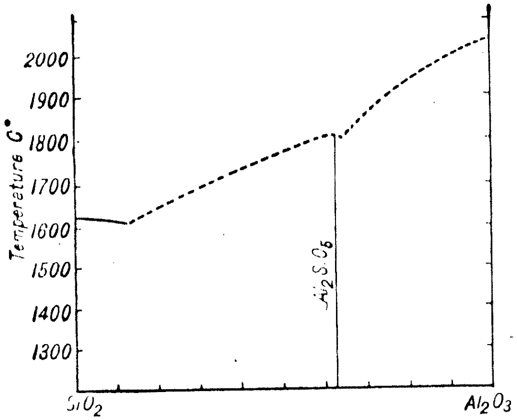

Fig. 45. — Melting points of the alumina-silica series.

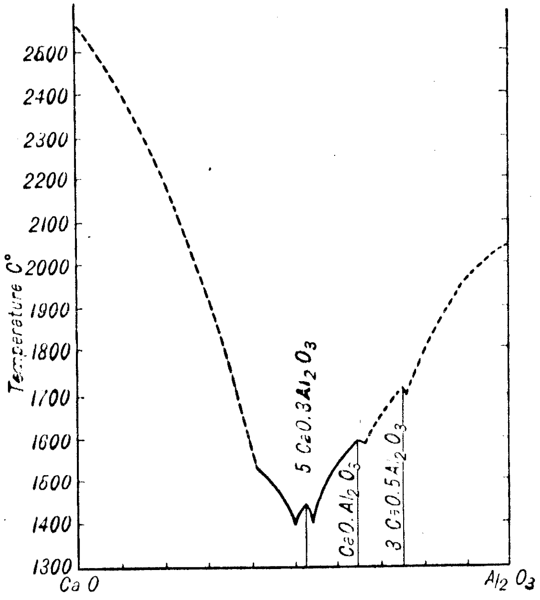

Fig. 46. — Melting points of the lime-alumina series.

it should not be allowed to exceed 10 or 15 per cent of the weight of the slag. Borax-glass should be increased as the alumina in a siliceous ore increases. The addition of lime has been found helpful in fluxing alumina, as might be expected from a study of the last curve. The following charge gives good results with pure china-clay:

Clay	⅓ A. T.
Lime (CaO)	6 grams
Sodium carbonate	20 "
Borax-glass	10 "
Litharge	45 "
Flour (R. P. 12)	2⅓ "
Silica	12 "

Cryolite is the best flux for alumina and dissolves it readily. Cryolite melts at about 1000° and dissolves more than 20 per cent of its weight of Al_2O_3. Either sodium fluoride or fluorite may be substituted if desired. The fluorides are all very liquid when fused and because of this property are particularly helpful as fluxes for ores containing alumina. The addition of 5 or 10 grams of any of the fluorides will be found beneficial with ores containing large quantities of alumina.

Procedure. — Carefully van some of the ore, estimate and record in the notebook the amount and character of each of the slag-forming constituents and also of any sulphides present. If the ore is mainly siliceous weigh out one of each of the following charges:

Charge (a)		Charge (b)	
Ore	0.5 A. T.	Ore	0.5 A. T.
Sodium carbonate	30 grams	Sodium carbonate	15 grams
Borax	5 "	Borax	5 "
Litharge	30 "	Litharge	50 "
Flour	*	Flour	*

Use F pot-furnace crucibles or if the work is to be done in the muffle 15- or 20-gram muffle crucibles.

Weigh out the fluxes and place in the crucible in the order given, adding the ore and flour last of all. Weigh the flour and ore on the pulp balance, the others on the flux balance. Mix thoroughly and if the fusion is to be made in the pot-furnace place a half-inch cover of salt or soda-borax mixture on top. Muffle fusions, except those for reducing power, do not require any covers.

Fuse at a moderate red heat to avoid danger of the charge boiling over and when quiet raise the heat to a bright yellow. In muffle fusions the assayer must depend upon the sound to tell when the bubbling has ceased. Allow fifteen minutes of quiet fusion. Pour as usual, tapping the crucible gently against the mold if necessary to make sure of getting out the last globules of lead.

When the material is cold, separate the lead buttons from the slag, keeping them in order (a) (b). Record in the notebook the character and appearance of the slags, the ease or difficulty of the separation of each from the lead buttons, the appearance of the lead buttons and their degree of malleability.

Weigh the lead buttons on the flux balance and cupel carefully to obtain feather crystals of litharge. Weigh the silver beads, correct for silver in the litharge used, part and weigh any gold found and finally report the value of the ore in ounces per ton.

Both of these charges should give good results on a siliceous ore. Charge (a) is a little less expensive, but charge (b) is more commonly used, as the slag contains two bases and the excess litharge will hold a moderate amount of impurities in solution. Charge (b) also gives a better separation of lead button and slag and has the further advantage that if the ore contains slightly more sulphide than was estimated the litharge will take care of it, giving a lead button free from matte. If in charge (a), there is more carbonaceous reducing agent plus sulphide mineral than the 30 grams of litharge can oxidize, some of the sulphur will combine with various metals of the charge, principally lead, and form a matte which will appear immediately above the lead button.

Approximately 30 grams of litharge from each charge will be reduced to give the 28-gram lead button and is therefore not available to combine with the silica. The active* fluxes are then in charge (a), 30 grams of soda, and 5 of borax, totaling approximately two and a half times the ore. In charge (b), the active fluxes are 15 grams of soda, 5 of borax and 20 grams of litharge,

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* Enough combined with the reducing material of the ore to give a 28-gram button.

* By an active flux is meant a flux which is to appear in the slag and therefore does not include the litharge which goes to form the lead button.

totaling approximately three times the ore. A very good rule to follow in making crucible charges is always to use at least two and a half times as much active flux as ore.

Borax in the charge should be increased as the bases increase. For an ore with 10 or 20 per cent of iron or manganese oxide, limestone or clay, add up to 10 or 15 grams of borax or 5 to 8 grams of borax-glass. For ores containing larger amounts of bases, work out a charge from the data given under the discussion of "slags for basic ores."

For high-grade ores and those containing considerable quantities of such common impurities as oxides of tellurium, copper, bismuth, arsenic, antimony, or nickel, the quantity of litharge must be increased in proportion to the amount of impurity present. Some idea as to the quantity of litharge required may be found in the chapter on Special Methods of Assay.

Notes: 1. Some assayers prefer to omit the borax from the charge and use a cover of crude borax or borax-glass in place of the salt. A borax cover may be used to advantage with ores which "dust" in the crucible, as the borax swells and melts early, tending to catch and hold down the fine particles of ore which are projected upward from the charge.

2. The crucible should never be more than two-thirds full when the charge is all in.

3. If a silver assay alone is asked for, it is customary to omit parting and report the combined precious metals as silver.

4. In assaying for gold alone, if sufficient silver for parting is not known to be present, a piece of proof silver should always be added to the crucible or to the lead button before cupeling. If the approximate amount of gold is known, about eight times its weight of silver should be allowed.

5. The slag should be fluid on pouring and should be free from lead shot. If it is pasty or lumpy, either the fusion has not been long enough to thoroughly decompose the ore, or the charge is too basic and more borax and silica should be added. The crucible should have a thin glaze of slag and should be but little corroded. It should show no particles of undecomposed ore or "shots" of lead. These latter can best be seen immediately after pouring, and the student should make it a point to examine his crucible immediately after every pour. Neither the cover nor the outside of the crucible should show any glazing, as this indicates that the fusion has boiled over. The cold slag should be homogeneous, as otherwise it indicates incomplete decomposition of the ore. Glassy slags are usually preferred by assayers but are not essential for all ores.

6. A brittle slag is to be preferred, particularly one which separates easily and completely from the lead button. If too acid, particularly if too much borax has been used, the slag is apt to be tough and to adhere tenaciously to the lead button so that when separated some of the lead comes off with the slag. This causes a great deal of annoyance and is bound to result in some loss of alloy. By setting the mold in cold water just after the red has disappeared from the slag, the latter may be made more brittle. The water must not be allowed to enter the mold, which must be handled carefully to avoid disturbing the still liquid lead.

7. If the button is hard or brittle or weighs more than 30 grams it should be scorified before cupeling. Hard buttons indicate the presence of copper, antimony, or nickel. Brittle buttons may be due to antimony, arsenic, zinc, sulphur, litharge or may be rich alloys of lead and the precious metals.

8. Examine carefully the line of separation of the slag and lead. The separation should be clean with no films of lead adhering to the slag. There should be no third substance between the slag and lead, nor should the surface of the lead show any disposition to crumble when hammered. Any lead-gray, brittle substance between the lead and slag or attached to the lead button is probably matte. This indicates incomplete decomposition of the ore, due to incorrect fluxing or too short a time of fusion. If the former is the cause, decreasing the silica and increasing the soda and litharge will usually prevent the formation of this substance in a subsequent fusion.

ASSAY OF CLASS 2 ORES.

Ores of this class containing only small amounts of sulphides are assayed in exactly the same manner as Class 1 ores but with lesser amounts of flour. However, when sulphides are present in such amounts as to reduce a lead button too large to cupel a different method of procedure must be followed. The most important methods for the assay of these ores follow:

1. Scorification. — This method has already been considered. It is not well suited for gold ores and fails for many silver ores.

2. Litharge-Niter Method. — The reducing power of the ore is first determined by means of a preliminary assay. Using the figure thus obtained, the assayer adds a certain amount of niter to the regular fusion to oxidize a part of the sulphur of the ore, thus preventing the reduction of too large a lead button. This is the most common method for the assay of sulphide ores. The sulphides are decomposed partly by litharge and partly by the niter.

3. Soda-Iron Method. — The litharge added to the charge is kept low so that the lead from it, plus that in the ore, will yield a button of suitable size for cupeling. The sulphide minerals of the ore are decomposed by means of the metallic iron. This is a good method for many ores and is commonly used.

4. Roasting Method — A carefully weighed portion of the ore is roasted to eliminate sulphur, arsenic, antimony etc., and the roasted ore is then assayed as a Class 1 ore.

5. Combination Wet-and-Fire Method. — The sulphides, etc. of the ore are oxidized with nitric acid, the silver is precipitated as chloride and combined with the insoluble residue containing the gold. This is filtered off and assayed either by scorification or crucible.

The Litharge-Niter Assay.

With half-assay-ton charges of ore in fusions containing an excess of litharge, there may be as much as 18 per cent of pyrite or proportionately larger amounts of other sulphides, depending on their reducing power, and lead buttons of the right size for cupellation may still be obtained by cutting down or entirely eliminating the flour or other reducing agent. With ores containing more than 18 per cent of pyrite the lead buttons obtained will be too large, unless some oxidizing agent is added to counteract this extra reducing effect. For this purpose potassium nitrate is commonly used. Figure 47 shows the quantity of flour; R. P. 12, or of niter, O. P. 4.2, which must be added to half an assay-ton of sulphide ore of any reducing power to obtain a 28-gram lead button.

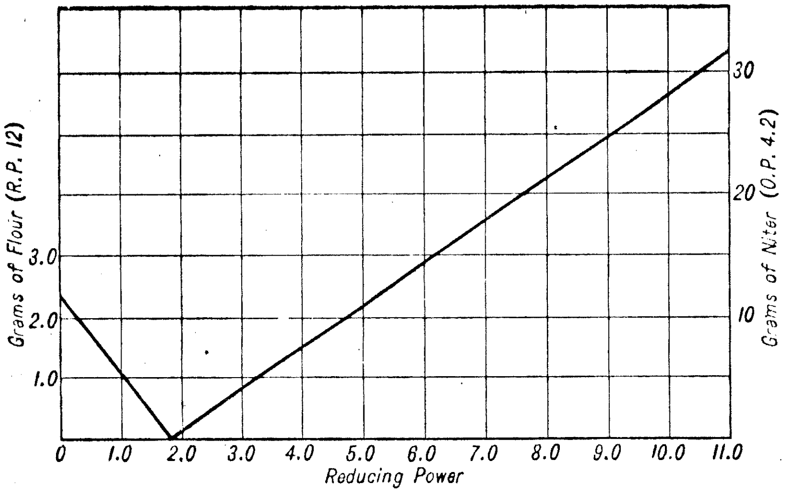

Fig. 47. — Quantity of flour or niter required per 0.5 A.T. of ore of any reducing power.

To perform an intelligent niter assay it is also necessary to know whether the ore is a simple sulphide of lead, iron, or zinc or whether it contains considerable amounts of metal impurities such as tellurium, copper, bismuth, arsenic, antimony, nickel or cobalt. In the latter case special measures have to be taken to eliminate these so-called " impurities." In the discussion of the process the simple case of the assay of " pure ores " will be taken first.

Slags for Pure Ores. — When an ore contains so large a proportion of sulphide minerals that it is necessary to add niter to prevent the reduction of too much lead, it will be found that the charges recommended for Class 1 ores will not allow a satisfactory decomposition of the ore. Instead of two products, slag and lead, a third intermediate product, matte, is often obtained as the result of the fusion. This amounts to an incomplete decomposition of the ore and as matte is a good collector of precious metals its presence is a sure indication of low results. A matte is much less likely to be formed, however, with a less acid charge and it has been found best, therefore, to make a slag approaching a monosilicate for all sulphide ores, as by this means more uniformly satisfactory results are obtained.

A moderate excess of litharge is always desirable in this method as it assists in the oxidation of the sulphides and also tends to keep the metal impurities out of the lead button. For this reason no less than 60 grams of litharge per half assay-ton should be used. Fifteen grams of sodium carbonate should be provided for the slag, as well as a small amount in addition, to combine with the SO_3 not taken care of by the K_2O of the niter.

In calculating a charge, the silica requirements of the various bases are determined, just as in the case of Class 1 basic ores, and the silica in the ore is deducted. A minimum of 5 grams of borax-glass is generally used; in the case of ores containing much zinc this should be increased to 10 grams. The silica equivalent of the borax-glass is deducted from the calculated amount of silica required.

Slags for Impure Ores. — When the ore consists mainly of sulphides or nickel, antimony, arsenic, bismuth, copper or tellurium the type of charge mentioned above does not contain enough uncombined litharge to keep the impurities out of the lead button. The remedy is to increase the litharge without increasing the silica, thus increasing the amount of uncombined litharge in the slag and thereby having it available for the solution of the base metal oxides. R. W. Lodge* recommends the use of from 15 to 25 per cent of litharge in excess of that called for by the reducing power of the ore and this yields satisfactory results with most impure ores. It calls for an increase in litharge as the reducing power of the ore increases. In the case of impure ores, this is equivalent to an increase of litharge with an increase of impurities. It is desirable in this case to figure for a sub-silicate slag. More detailed instructions for the assay of impure ores will be found in the following chapter.

Disadvantages of Excess Litharge. — Owing to its property of dissolving and forming easily fusible mixtures with oxides of the metals which are in themselves difficultly fusible, and particularly because of its property of keeping the impurities out of the lead button, litharge has become the assayers "cure-all." The student should have in mind, however, the possible disadvantages of the use of too much litharge. These include the extra cost of the added reagent and the more rapid destruction of crucibles, which most assayers prefer to use for a number of fusions. More important than the latter, is the damage which is done in case a crucible is eaten through, thus allowing this corrosive slag to run out on the muffle floor. It has long been recognized, also, that an increase of litharge increases very slightly the quantity of silver which is held in the slag, so that no more litharge than is necessary to ensure a pure lead button and proper decomposition of the sulphide should ever be used.

Conduct of the Fusion. — It was formerly believed that charges containing niter require very slow and careful heating to prevent loss due to boiling-over, and in some quarters this impression still prevails. This danger of loss due to boiling is a real one if fusions are made in coke pot-furnaces, as was formerly the custom; but to-day, in this country at least, practically all regular assay fusions are made in large muffles. In the coke-fired pot-furnace the charge is unevenly heated, the bottom melts while the top is still cold. Somewhere between the two is a zone of viscous semi-melted material which tends to be lifted bodily out of the crucible by the ascending gases. In the muffle, on the other hand, the crucibles are evenly heated from all sides and because of the heat-retarding effect of the bottom and sides of the crucible, fusion probably begins at the top and proceeds downward. This provides a fluid slag through which the gases may readily escape, so that the charge boils up only very little.

For the best results in niter fusions the crucibles should be introduced into a hot muffle and brought rapidly to fusion, the whole fusion process not taking more than ten or fifteen minutes. This method of procedure ensures a complete decomposition of the sulphide minerals of the ore and prevents the formation of a matte which is likely to result if the fusion takes a long time. The crucibles should be in the furnace not more than thirty, or at the most forty minutes. If a number of crucibles are to be charged at one time the furnace should be at a light yellow heat. The cold crucibles will lower the temperature materially and it need not be heated above a yellow heat, about 1000° C., to finish. In fact a higher finishing temperature, particularly if maintained for some time, will cause low silver results, probably due to volatilization.

To obtain good results, particularly when a large amount of litharge is used in the charge, the muffle door should be closed tightly and a reducing atmosphere maintained in the muffle. If coal-fired muffles are used for fusions, the holes in the back of the muffles should be closed and several crucibles containing bituminous coal placed in the front part. This latter precaution is unnecessary with gas, gasoline, or oil-fired furnaces as these ordinarily have a reducing atmosphere in the muffle or crucible chamber.

The quick fusion which occurs in properly conducted niter assays effects a rapid and apparently complete decomposition of the ore, but, except in the most skilful hands, the slag losses are higher than for Class 1 ores of corresponding grade. The rapid fusion and very liquid slag do not permit globules of lead to remain in suspension for more than a few moments and the high slag losses common with this method may be due partly to the less complete collection of the precious metals by the lead. For this reason it is essential to reduce a generous amount of lead in this assay, not less than 25 grams and even 35 grams in the case of large charges. The use of the large quantity of litharge and niter required in the assay of impure sulphide ores is thought to

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* Notes on Assaying, 2nd Ed., p. 105.

give high slag losses, due to oxidation of silver and its solution in the heavy litharge slag.

Perkins* finds that the excessive silver loss in this kind of slag may be largely prevented by maintaining a reducing atmosphere in the furnace throughout the fusion period.

Physical and Chemical Changes Taking Place in Niter Fusions. — When the crucibles are placed in the furnace the temperature of the charge immediately begins to rise, and soon any hydroscopic water contained in the reagents is driven off. When the temperature reaches 339° C., at which point niter melts, the charge begins to frit and some of the sulphides commence to react with the niter, although the action is slow at this temperature. At about 450°, silica begins to react on the niter with the evolution of oxygen, nitrogen and the formation of potassium silicate. The oxygen evolved reacts with some of the more readily oxidized sulphides, particularly pyrite which begins to oxidize readily at about this temperature.

Borax-glass begins to soften and combine with litharge at about 500°, and the fritting of the charge increases. At 530° niter begins to dissociate and the oxygen evolved helps to roast the still solid sulphides and probably converts some of the litharge into Pb_3O_4, thus making of it an oxygen carrier. Any pyrite remaining begins to decompose at 575° forming pyrrhotite and sulphur, but this reaction is slow until the temperature reaches 665°. Even in the absence of other fluxes, litharge and silica begin to combine at about 700° C. to 750° and at this temperature the charge becomes decidedly pasty, particularly in the presence of sodium carbonate and borax. If the temperature were to be held at this point the charge might boil over on account of its pasty consistency, but the properly conducted fusion is heated rapidly to 900° or 1000° C., and at this temperature it is entirely fluid and bubbles escape freely. The rate of oxidation of the sulphides increases rapidly as the temperature rises and these reactions evolve a large amount of heat.

At about 750° some of the metallic oxides and sulphates begin to react with the undecomposed sulphides and these reactions are endothermic. The following are examples:

$$PbS + PbSO_4 = 2Pb + 2SO_2 - 92{,}380 \text{ cal.},$$
$$PbS + 2PbO = 3Pb + SO_2 - 52{,}540 \text{ cal.}$$

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* Trans. A.I.M.E., **33**, p. 672.

The last reaction is only one of many similar ones, which might be written, showing the direct reduction of sulphides by litharge. In the presence of sufficient silica, any ferric oxide which is present will be reduced to the ferrous state by sulphides with the liberation of sulphur dioxide, as for example:

$$3Fe_2O_3 + FeS + xSiO_2 = 7FeO.xSiO_2 + SO_2 - 81{,}640 \text{ cal.}$$

This reaction is of importance above 900°.

In this assay the niter is limited to less than that required to entirely decompose the sulphides of ore, the amount of undecomposed sulphide left being just enough to react with litharge and give a lead button of the right size for cupellation. No one knows in just what order the reactions take place, but the net result is the same as if the niter continued to react until entirely consumed and then the remaining sulphide was oxidized by litharge.

It is noteworthy that all authorities recommend the use of an excess of litharge for the niter assay, although it may be recalled that it is possible to decompose the sulphides entirely by fusion with sodium carbonate and niter alone, as in the Fresenius method for the determination of sulphur in pyrite. This brings up the question, "Why, and how much, excess litharge is needed?" Beringer* answers the first half of the question by explaining, as is now well known to all assayers, that "when metallic sulphides are present in the ore, an excess of oxide of lead helps to keep the sulphur out of the button of metal," in other words, helps to prevent the formation of a matte. Lodge† calls for an excess above that required for the reducing power of the ore, but this is only necessary with impure ores when the litharge is required to hold these impurities in the slag.

It is obvious that every reagent has some influence on the result, but with enough litharge to provide a lead button and some small excess to help in making a fusible slag, the quantity of silica present and the rate of fusion have the greatest effect on the result. The presence of too much silica in proportion to the bases, or too slow a fusion, will result in the formation of a matte, and this means incomplete decomposition of the ore. The reason for this is not difficult to find. In the slow fusion at a low tem-

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* A Textbook of Assaying, 13th Ed., p. 93.

† Notes on Assaying, 2nd Ed., p. 105.

ore will be $\frac{3.40}{2} = 1.70$. Half an assay-ton of this ore would give a lead button weighing 24.8 grams without either flour or niter. If the galena had been estimated at 40 per cent, half a gram of flour (R. P. 12) would have been added and the result would have been a 30.8-gram button which could still be cupeled. In a similar manner, if the galena had been estimated at 60 per cent about 1 gram of niter would have been added and the resulting button of about 20.8 grams could also have been cupeled.

Again, in dealing with practically pure sulphides, as in the case of pyrite or galena concentrates, it is easy to estimate the reducing power and properly control the size of the lead button.

Determining the Oxidizing Power of Niter. — The oxidizing power of niter is found by fusing a weighed amount with an ore whose reducing power is known. To obtain comparative results the slags must be exactly like those used for the reducing-power fusion and, moreover, to give lead buttons of the proper size in the final assay, the slag that is made there must be similar as regards acidity, litharge excess, etc. to that made in the preliminary fusion.

The following example illustrates the method of finding the oxidizing power of niter:

Ore	5 grams	5 grams
Sodium carbonate	10 "	10 "
Litharge	60 "	60 "
Niter		4 "
Silica	5 "	5 "
Lead obtained	24.31 grams	6.61 grams

Reducing power of ore $\frac{24.31}{5} = 4.86$

Lead oxidized by 4 grams of niter $24.31 - 6.61 = 17.70$

Oxidizing power of niter $= \frac{17.70}{4} = 4.42$

Quantity of Sodium Carbonate Converted to Sulphate. — When the reducing power of the ore, its character and the oxidizing power of niter are known the charge for the regular assay can be made up. Assume that it is desired to make a slag containing 15 grams of sodium carbonate and 30 grams of litharge for 0.5 assay-ton of ore, and that enough silica should always be present to hold and slag the iron as ferrous singulo-silicate, thus preventing it from becoming converted to ferric oxide. With pure pyrite, the reducing power of which may be assumed to be 12, and with the further assumption that all of its sulphur is oxidized to SO_3, it is evident that if the soda in the slag is to be kept constant the soda which is added to the charge will have to be increased as the reducing power of the ore increases, because one of the products of the reaction of niter upon sulphides in the presence of soda is sulphate of soda, and because the soda thus used up no longer serves as a flux.

The reactions governing the decomposition of the pyrite under the assumed conditions are the following:

$$(a)\quad 2FeS_2 + 14PbO + 4Na_2CO_3 + SiO_2 = F_2SiO_4 + 14Pb + 4Na_2SO_4 + 4CO_2,$$

$$(b)\quad 10FeS_2 + 28KNO_3 + 6Na_2CO_3 + 5SiO_2 = 5Fe_2SiO_4 + 14K_2SO_4 + 6Na_2SO_4 + 14N_2 + 6CO_2.$$

When the ore has a reducing power of 12, $\frac{28}{12} = 2.33$ grams of pyrite react according to equation (*a*), yielding a 28-gram lead button. From the proportion

$$FeS_2 : 2Na_2CO_3 = 120 : 212 = 2.33 : 4.12,$$

it may be seen that this reaction results in the conversion of 4.12 grams of Na_2CO_3 into sulphate.

Reaction (*a*) is actually the last to take place, but was considered first to determine the quantity of pyrite in excess of that required to furnish the lead button, as this is the amount which must be oxidized by niter. There remains to be decomposed by niter under the conditions of equation (*b*) $14.58 - 2.33$ grams $= 12.25$ grams of pyrite. The sodium carbonate required to satisfy this reaction may be found from the proportion

$$5FeS_2 : 3Na_2CO_3 = 620 : 318 = 12.25 : y,$$

solving, y is found to be 6.28. Adding these two quantities, it will be seen that 0.5 assay-ton of pyrite, under these conditions, causes the removal of 10.4 grams of Na_2CO_3 from the slag.

It is possible to generalize from these figures and say that each gram of pyrite in the charge, up to 2.33 grams, requires the addition any lead shots have remained behind. Examine the button and line of separation between lead and slag, to be sure that lead buttons are free from matte. If matte or shotty lead is obtained, the assay should be repeated with such changes in manipulation of fire or of composition of charge as may be suggested.

An annoying situation occasionally encountered in assaying some sulphide ores, particularly those containing pyrrhotite and arsenical pyrite, is the behavior of the lead which refuses to collect and remains shotted throughout the slag. When the slag is poured, some clear slag comes first, then slag full of lead shot. The slag which is left in the crucible is also full of lead shot. This is usually due to too low a temperature of fusion or too little silica, but may also be caused by the oxidation of the iron to ferric oxide during the fusion. Ferric oxide is infusible at the temperature of the fusion and is insoluble in the ordinary slag at this temperature.

The best way of overcoming this difficulty is to increase the silica and run the new assay at a higher temperature. If sufficient silica is present to form bi-silicates with all of the bases, the iron will be held firmly in the ferrous condition and shots due to this cause are avoided. A high temperature favors the reduction of Fe_2O_3 to FeO or what amounts to the same thing, prevents the formation of Fe_2O_3 by the niter and litharge. This is in accordance with the well-known principle of physical chemistry, that "the change of heat energy into chemical energy takes place more readily at high than at low temperatures." According to data given by Richards* the thermal equations representing this type of reaction may be written as follows:

$$Fe_2O_3 + Pb = 2FeO + PbO - 13{,}400 \text{ cal.}$$
$$Fe_3O_4 + Pb = 3FeO + PbO - 22{,}900 \text{ cal.}$$

According to van't Hoff's law, when the temperature of such a system is raised, the equilibrium point is displaced in the direction which absorbs heat, that is to say, the above reactions will proceed in a right-handed direction.

Ferric oxide is soluble in an excess of litharge, and another way to avoid obtaining a slag containing lead shots is to use a large excess of litharge in the charge. This method of procedure is

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* Metallurgical Calculations.

open to the objection that the recovery of silver and gold is more or less incomplete when the slag contains ferric oxide.*

The following table of mono-silicate slag factors may be found useful in determining the quantity of silica required for any niter fusion.

TABLE XXIII.

MONO-SILICATE SLAG FACTORS.

Quantity of bases	Quantity of acids required	
	Silica	Borax-glass
8.65 grams FeO from ½ A. T. FeS_2 requires...	3.64	4.80
11.3 " FeO " ½ A. T. Fe_7S_8 "	4.75	6.38
12.17 " ZnO " ½ A. T. ZnS "	4.51	6.06
13.6 " PbO " ½ A. T. PbS "	1.84	2.44
15 grams Na_2CO_3 .... "	4.25	5.72
30 grams PbO .... "	4.06	5.46

To avoid low results due to oxidation by niter, it is often advantageous to reduce the quantity of ore used. When silver alone is being sought, the niter may be entirely done away with by reducing the ore charge to a quantity sufficient to give a lead button weighing not more than 30 grams. In gold assays, however, a charge less than 0.5 assay-ton is undesirable, as it fails to give a sufficiently close valuation of the ore.

The Soda-Iron Method.

The soda-iron, or iron-nail method of assaying sulphide ores is radically different from any of the other methods so far described. It consists of a reducing fusion of the ore with a large amount of sodium carbonate, as well as a limited amount of litharge and borax and occasionally a small amount of silica, together with an excess of metallic iron, usually in the form of nails or spikes. The principal difference between this and the other crucible methods consists in the use of metallic iron as a reducing and desulphurizing agent. As iron reduces lead from litharge, as well as from the common lead minerals,

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* Jour. Chem. Met. and Min. Soc. of South Africa, 2, p. 465.

least importance, and ruthenium at least is present in amounts of only a fraction of one per cent.

The material to be tested is dissolved by treatment with hot aqua regia and, if no large amount of gold or silver is present, is treated directly. If much gold or silver is present it may mask the reaction. The test is more sensitive if the excess acid has been removed by evaporation before the test is made.

A very thin piece of asbestos paper, held with tongs, is alternately dipped into the solution to be tested and heated in the Bunsen flame until about 0.2 c.c. has been absorbed, or better, the asbestos paper is placed on a light ring over a Tirrill burner and a drop or so at a time of the solution is placed on the center of the paper and heated to redness. The asbestos is finally heated to redness again, the gas is shut off and then quickly turned on again while the paper is still hot, but not visibly red. If any or all of the four metals enumerated above are present, the asbestos will glow where it has been moistened with the solution. The glow may last for some time and may be brought back after it has once died out by again heating the paper and holding it in the stream of gas. The burner should be adjusted to deliver a fairly rich mixture of gas in air, and the pressure should be kept low. For the greatest sensitiveness of the test the asbestos paper must be very thin, and the gas-air mixture should be warmed. For field testing, a lamp burning pure methyl alcohol, or other highly volatile liquid hydrocarbon, may be substituted for illuminating gas.

If the aqua regia solution is to be evaporated so as to concentrate the metallic contents, this should be done on the water bath, since heating in air at a high temperature will decompose all the platinum salts with the formation of the metals.

IDENTIFICATION.

Platinum. — Platinum forms two series of salts corresponding to the oxides PtO and PtO_2. The oxides themselves are very unstable and decompose into metal and oxygen when gently heated. Pure platinum is not oxidized on heating in air at any temperature.

Aqua regia dissolves platinum, converting it into chloroplatinic acid, H_2PtCl_6, a solution of which is yellowish orange and which may be crystallized, in which form it is colored orange-red. If solutions containing H_2PtCl_6 are evaporated to dryness and heated to a temperature higher than that of a water bath the chloroplatinic acid will be reduced to chloroplatinous acid and chlorine. Chloroplatinous acid, H_2PtCl_4, is known only in solution, in which condition it is dark brown. It is important to appreciate the readiness with which platinic chloride is reduced even on gentle heating, for in this condition it is not precipitated by ammonium chloride.

All platinum compounds, upon ignition, are reduced to the metallic state. From a solution containing fairly concentrated chloroplatinic acid, free from nitric acid and excess chlorine:

Ammonium Chloride precipitates* yellow $(NH_4)_2PtCl_6$, which is slightly soluble in water but practically insoluble in a dilute solution of ammonium chloride and in alcohol. The ammonium chloroplatinate may be dried and weighed as a salt or ignited and weighed as metallic platinum.

Potassium Chloride precipitates yellow K_2PtCl_6, which is difficultly soluble in solutions of potassium chloride and practically insoluble in alcohol.

Potassium Iodide may precipitate black platinic iodide, PtI_4, from highly concentrated solutions, but as this is readily soluble in dilute hydrochloric acid and excess of reagent it is more likely to yield a dark blood-red liquid, owing to the formation of the PtI_6 radical. This test is the one generally employed for the detection of platinum and is very sensitive. As little as 0.001 milligram may be detected.

It will be necessary to ensure the absence of copper salts before trying the test, as copper salts also give red colors.

Tellurium also gives a red color with potassium iodide in weakly acid solutions, but this turns yellow on boiling.

Hydrogen Sulphide precipitates black platinic disulphide, PtS_2, readily from a hot solution. The addition of magnesium chloride solution prevents the formation of colloidal PtS_2. The sulphide is soluble in alkaline polysulphides.

Ferrous Sulphate added to a solution neutralized with sodium carbonate and boiled, precipitates metallic platinum. It does not precipitate platinum in the presence of acid.

Stannous Chloride reduces H_2PtCl_6 to H_2PtCl_4 but not to metal. Small amounts of reagent with dilute platinum solutions give a golden yellow color.

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* See similar reaction of iridium.

sulphide reduces the Ir^{+4} to Ir^{+3} and then precipitates brown Ir_2S_3, which is readily soluble in ammonium sulphide.

Formic Acid precipitates black metallic iridium from hot solutions provided too much mineral acid be not present. To ensure complete reduction, ammonium acetate should be added.

Potassium Nitrite, added to hot solutions of iridium salts, yields a yellow precipitate insoluble in water. Compare rhodium.

Metallic Zinc in an acid solution precipitates the metal.

Ferrous Sulphate, oxalic acid, stannous chloride, and alcohol (hot) reduce the tetrachloride to the trichloride.

Hot Sulphuric Acid. — When an iridium salt containing as little as 0.001 milligram of iridium is heated with concentrated sulphuric acid and a small amount of silver nitrate is added, a beautiful blue color develops.

Rhodium. — Two oxides of rhodium have been fairly well identified, Rh_2O_3 and RhO_2. According to Carter,* rhodium begins to oxidize at 600° C., forming Rh_2O_3. At 1000° C. the action is appreciable and the metal begins to volatilize.

In the dense form, rhodium, like iridium, is practically insoluble in aqua regia. When precipitated from a solution of its chloride by means of formic acid or other reducing agents, it comes down in a very finely divided state. This precipitate, rhodium black, if not ignited, dissolves readily in boiling concentrated sulphuric acid and more readily in aqua regia. By treating the metal with chlorine in the presence of sodium chloride there is formed the soluble salt Na_3RhCl_6. This salt is the most important for the chemist. When a solution of sodium chlororhodite is concentrated and allowed to cool, dark red prisms of the hydrous salt crystallize out.

All rhodium compounds are converted to the metal by heating in an atmosphere of hydrogen.

From a solution containing sodium chlororhodite:

Hydrogen Sulphide precipitates from a hot solution brown Rh_2S_3, insoluble in alkaline sulphides, in which respect it differs from platinum and iridium.

Potassium Nitrite, from a warm solution, precipitates difficultly soluble, orange-yellow $K_3Rh(NO_2)_3$, soluble in hydrochloric acid. The corresponding sodium salt is soluble in water.

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* Notes on the Metals of the Platinum Group, Trans. Am. Electrochem. Soc., **43**, p. 329.

Potassium Iodide precipitates, from hot solution, a dark brown rhodium iodide, RhI_3.

Stannous Chloride, 40 per cent in 30 per cent hydrochloric acid added to a solution of a rhodium salt and heated to boiling, develops a brown color that changes to a raspberry shade on cooling. This test will detect less than 0.001 milligram of rhodium in 1 c.c. of solution.

Formic Acid, in the presence of ammonium acetate, precipitates metallic rhodium in the form of a fine black powder.

Metallic Zinc and magnesium in the presence of acid precipitates the metal.

For other reactions and identifying tests for these and the other metals of the platinum group the reader is referred to various authorities on chemistry, including particularly McAlpine and Soule's 1933 revision of Prescott and Johnson's "Qualitative Chemical Analysis," and to Vol. I of W. T. Hall's eighth English edition (1932) of Treadwell's "Analytical Chemistry."

TREATMENT OF ORES CONTAINING METALLIC GRAINS.

Platiniferous black sands always, and other materials occasionally, contain metallic grains, and these should preferably be removed before the sample is ground. The metallic grains and the finely ground ore are assayed separately, and the average assay of the lot is calculated from the known weights and assays. With large samples this may best be done by panning; with small samples weighing only a few hundred grams the grains may be separated by dry blowing.

For this purpose there is needed a set of testing sieves, a gold washing horn about 2 inches wide and 8 inches long, and a large working table. The dry material is weighed and closely sized, and then each size is treated separately by blowing. A suitable nest of sieves for this purpose might include a 10-, 20-, 35-, 65-, 100-, and 150-mesh screen. After spreading out a large piece of smooth paper to catch the rejections, one size of ore is placed in the horn, which is shaken longitudinally to cause a stratification of the particles, and then by blowing lightly and momentarily across the top of the sand toward the larger end, which is slightly elevated, some of the lighter grains are removed. The material is shaken again and the blowing repeated. This process is continued until finally, if proper skill is exercised, only gold and platinum with possibly some grains of metallic lead and iron are left. The reject which has been caught on the paper is reworked to ensure a complete recovery of the metallic grains. Each size is treated separately by this means, beginning preferably with the coarsest size and, of course, with a gradual reduction of the velocity of the air currents as the grain sizes become smaller. The metallic grains, which may first be weighed as a check, are combined and alloyed with silver by cupellation or with lead by fusion. The rejects are combined, finely ground, and fused in lots of one assay ton with appropriate reagents.

GENERAL REMARKS ON THE FIRE METHOD.

The fire method has the advantage that a relatively large amount of ore may be quickly and inexpensively decomposed with the collection of the platinum group of metals in the lead button, and the concurrent separation of most of the other constituents of the ore in the slag. A general knowledge of fire assaying chemistry and procedure as well as a knowledge of the following matters relating to the platinum metals are prerequisites to any attempt at analysis.

Fusion. — In a crucible fusion of material containing the platinum group of metals together with gold and silver, if the character of the material is such that the quantity of litharge may be held at a minimum and the conditions of fusion are strongly reducing, the lead button will collect practically all the gold, silver, rhodium, platinum, and palladium in the form of an alloy. The iridium, ruthenium, and osmium as well as any iridosmium, because of their greater specific gravity, high melting-point, and chemical inactivity, under these conditions will be collected and held in suspension in the lower part of the molten lead. On pouring, there is a danger that some of these unalloyed metals will remain behind in the crucible, but with a smooth crucible, a goodly quantity of lead, a hot, fluid, and slightly acid slag, the danger of a loss here is but slight.

In a crucible fusion where the conditions are strongly oxidizing, the osmium, ruthenium, and even the iridium may be expected to be wholly or partially oxidized and either volatilized or carried into the slag. The extent to which this oxidizing process will proceed will depend not only upon the conditions of the fusion, but also upon the state of division of the metals in the charge. In the compact form they will be much less readily attacked than if they are in the form of a finely divided precipitate or slime.

Cupellation. — In the cupellation of the lead buttons with sufficient silver so that the lead may be practically entirely eliminated, the final bead will contain, besides gold and silver, practically all the rhodium, platinum, and palladium in alloy form, and most of the iridium and iridosmium which was collected in the lead button, mechanically held. Most of the ruthenium and all the osmium will probably have been oxidized and lost.

Iridium and iridosmium if present, being very dense and not having alloyed with the lead or silver, will tend to sink to the bottom of the cupeling alloy and will be found in the lower part of the bead where they may be seen with the aid of a lens, in the form of black specks. Ruthenium and osmium, if present in sufficient amounts, will appear in the oxidized form as a black film on the surface of the driving lead. Some of this oxide will be left on the cupel, and some will remain as black crystalline spots on the surface of the bead.

The presence of the platinum group of metals raises the melting-point of the alloy constituting the final bead and necessitates a higher cupellation temperature to prevent freezing, and to remove as much of the lead as possible. When platinum alone is cupeled with lead about 40 per cent of lead is retained after cupellation. The residual platinum-lead alloy will have an irregular mossy appearance and will stick to the cupel. When platinum and silver are both present in about the same amount, lead equivalent to about 25 per cent of the platinum will be retained in the bead even when cupeling at a high temperature. Such a bead will fail to brighten but will flatten out and solidify, leaving a bead which is rough and dull gray when cold. As the ratio of silver to platinum increases, the amount of retained lead decreases, but even when the ratio of silver to platinum is greater than 4 to 1 and the temperature of cupellation is sufficient for gold assaying, lead will be retained in the bead. To ensure removal of all the lead, the ratio of silver to rare metals should be at least 10 to 1. Since the presence of copper aids in the removal of the last of the lead, it may be well, in some cases, to add a small amount, unless it is known to be present in the material being assayed. Care should be exercised when hammering the beads containing any of the platinum group, for the presence of even a small amount of lead renders them brittle.

Platinum and silver, though entirely miscible in the molten condition, are not entirely mutually soluble in the solid condition and therefore tend to separate during solidification. For this reason, silver-platinum beads should be allowed to remain in the muffle for five or ten minutes after solidification so that the platinum-rich crystals which solidify first may by diffusion be induced to give up some of their platinum to the adjacent alloy. Such an annealing process makes possible the satisfactory separation of silver in the sulphuric acid parting operation and the more complete dissolution of the silver in nitric acid parting.

THE ACTION OF ACIDS ON ALLOYS OF SILVER, GOLD, AND THE PLATINUM METALS.

The best-known and simplest method for the determination of platinum in ores depends upon the fact that when alloys of silver and platinum are subjected to treatment with hot, slightly diluted sulphuric acid, under the proper conditions, the silver is dissolved and the platinum is unattacked, whereas if nitric acid is used both silver and platinum are dissolved. When the material to be assayed contains gold, silver, and platinum, with no other metals of that group, the sulphuric acid method is well suited for the determination. Other metals of the platinum group interfere to some extent, but their presence does not necessarily entirely vitiate the results, if they are recognized and suitable precautions observed.

Sulphuric Acid. — To ensure complete removal of the silver, at least 10 times as much silver as platinum must be present. The sulphuric acid used must be free from nitrogen compounds and chlorides, as in the first case appreciable quantities of platinum will be dissolved, and in the second, both gold and platinum would go into solution to some extent. It is probable that a little silver will always remain undissolved, regardless of the ratio of silver used in the alloy, and for this and other reasons it is customary, where high accuracy is required, to run synthetic assays parallel to the samples under assay, and to correct the results accordingly.

Excessive boiling in concentrated sulphuric acid exerts a marked

solvent action upon the platinum in platinum-silver alloys. According to Steinmann,* this loss amounts to between 20 and 30 parts per 1000 parts of platinum, but may be as much as 50 parts. By using slightly diluted sulphuric acid and keeping the temperature below boiling, the silver may be extracted without material loss of platinum. Steinmann recommends heating for fifteen minutes with slightly diluted sulphuric acid at a temperature not exceeding 240° C. His procedure calls for acid made by diluting 100 volumes of concentrated acid with 22 volumes of water. This degree of dilution and the avoidance of boiling reduces to some extent the somewhat delicate and more or less objectionable manipulation and handling of boiling, concentrated sulphuric acid. The temperature recommended is nearly 100° below 338° C., the boiling-point of the concentrated acid. The treatment with acid should be repeated, after which the residue of platinum and gold is washed, dried and weighed.

With a ratio of 10 parts of silver to 1 of platinum in the absence of gold, the platinum is left in a finely divided state, and the subsequent separation by decantation is likely to result in some loss of platinum. For this reason it is best, when assaying materials which contain only platinum and silver, to reserve all the decanted solution and washings, and in case the solution contains finely divided particles to filter, on a small ashless filter, which is thoroughly washed and ignited. It should also be noted that when the platinum is left in a finely divided condition a relatively larger proportion of it is likely to dissolve in the sulphuric acid.

The presence of gold in sufficient amount is thought to reduce materially the quantity of platinum which is dissolved. When the sample being assayed contains gold the residue is not left in such a finely divided state, and filtering of the decanted solutions is not ordinarily required. In fact, it is customary to add such a ratio of gold as will retard or prevent the breaking up of the residue during parting. Very little work has been done to determine the best ratio of gold to use in parting ternary alloys. At least twice as much gold as platinum should be used, and some authorities prefer a very much higher ratio. Using a ratio of silver to gold plus platinum of 3 to 1, which is the ordinary commercial practice of bullion assayers designed to yield a cornet which

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* Schweiz. Woch. Chem. Pharm., **59**, p. 441 (1911), abs. J. Soc. Chem. Ind., **30**, p. 1216 (1911).

is indicated. Lodge* recommends a ratio of silver to platinum of 12 or 15 to 1, and reports that with this ratio separation is practically complete after three partings.

Since actually the platinum may never be entirely removed, and since there will be some loss of gold and platinum in the numerous cupellations involved, it is necessary, when high accuracy is required, to make a preliminary assay, and on the basis of the results to make up "checks" containing approximately the same proportions of gold, silver, and platinum as are contained in the sample under examination. These checks are put through the assay method parallel with the samples being assayed, and the gold and platinum results are corrected accordingly.

Platinum alloyed with copper, lead, zinc, and some other metals is also attacked and partly dissolved by nitric acid.

Palladium, which is much more readily soluble in nitric acid than is platinum, is entirely separated from gold by double parting, and in a single parting provided that silver is present in amount equal to ten or more times the combined gold, platinum, and palladium. Iridium and iridosmium, both of which are practically unaffected by cupellation with silver, are unacted upon by nitric acid and remain with the gold on parting. Rhodium, likewise, is practically unattacked by nitric acid. Consequently if iridium or rhodium are to be determined, or if the gold assay is to be corrected for these metals, special treatment of the residue is required.

But little elemental osmium or ruthenium is likely to have remained in the bead after cupellation. If present, osmium will be dissolved, but ruthenium will remain with the residue.

THE DETERMINATION OF PLATINUM, GOLD, AND SILVER BY THE SULPHURIC ACID PARTING METHOD.

This is the common commercial method for determining platinum, gold, and silver in the absence of the other metals of the platinum group, and yields satisfactory results when properly conducted; but, like all determinations of the platinum group metals, it requires much more time, manipulative skill, and knowledge of chemistry than are required for the determination of gold and silver by fire assay methods.

It is assumed in this description that no other metals of the platinum group are present. However, if iridium, iridosmium, and rhodium are present in small amounts, they may be estimated by a method to be described later. If palladium is present in small quantities, it may be determined by a supplemental step which will be described immediately after this procedure.

Epitome. — In this method the assay bead is parted in sulphuric acid, dissolving the silver and leaving the gold and platinum which are weighed together. Silver is then added by means of cupellation, and the bead is parted in nitric acid which dissolves the silver and platinum. When the gold is sufficiently purified by repeated inquartation and parting, it is annealed and weighed, and the platinum is found by difference.

Preliminary Assay. — Since rather definite proportions of gold to platinum, and of silver to gold plus platinum, are desirable if the assay is to be accomplished with the greatest accuracy and the least annoyance, a preliminary assay is usually required so that the approximate composition of the material to be assayed may be known in advance. For the highest accuracy the final assays are run with "checks" containing approximately the same proportions of platinum, gold, and silver as the sample, and these are put through the assay method parallel with the samples under assay, and for this reason, also, a preliminary assay is obviously a necessity.

As the materials which may be submitted for assay vary over so wide a range, it is impossible to lay down a definite procedure for the preliminary assay. The quantity of material to be taken may be as little as 0.1 to 0.2 gram in the case of an alloy, or as much as 5 or 10 assay tons for an ore. For rich sweeps, from 0.1 to 0.5 assay ton would be about right. The assay may begin with cupellation in the case of an alloy, or with scorification or crucible fusion in the case of sweeps, electrolytic slime, or ore.

The lead buttons, however obtained, are cupeled at a moderate temperature until about 5 grams of lead remains, then the heat is raised to that ordinarily employed for gold bullion assays. As has already been said, the cupellation requires a higher temperature as the proportion of platinum increases, and so in a preliminary assay the determination of the proper cupellation temperature is partly a matter of trial and error. If the bead is flat or otherwise unsatisfactory, or if the appearance of the cupel indicates that a large quantity of copper or other difficultly oxidiz-

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* "Notes on Assaying."

able impurities were present in the lead button, the bead should be recupeled with 5 or 10 grams more of lead. The final bead should be well rounded and free from lead. Its weight is accepted as that of the platinum, gold, and silver together. In the case of bullion, the difference between the weight taken and that of the bead gives the base metal present.

From the color and appearance of the bead, some idea of its composition is obtained. If it is not yellow, gold equal to 3 times its weight is carefully weighed and added to it, together with silver equal to 12 times its weight. The bead, with the added gold and silver, is wrapped in sheet lead, and cupeled so as to finish at such a temperature that the final metal will remain molten until after the brightening, so that, if possible, all the lead shall be removed. Finally, the bead is allowed to solidify and permitted to remain in the front of the muffle at a temperature of 800 to 850° C. for ten minutes.

The alloy thus obtained is flattened, annealed, rolled into a fillet, annealed again, and formed into a cornet. The cornet is parted in sulphuric acid in the manner recommended in the procedure for the final assay. The residue is washed, dried, annealed, and weighed, and considered to be platinum plus gold. After correction for added gold, the difference between this and the original cupellation bead is silver. The residue is inquartated by cupellation with from 3 to 10 times its weight of silver, which in this case does not have to be carefully weighed. The resulting bead is annealed as before, rolled out if a low ratio of silver to platinum plus gold has been adopted, and parted in nitric acid, and the residue is washed, dried, and annealed.

If the color of the cornet is that of pure gold, it is weighed; but if, on the other hand, it has a steel-gray color, it will be necessary to repeat the inquartation and parting so as to obtain a closer approximation of the amount of platinum present. The weight of the final cornet, corrected for the amount of gold added, represents the gold contents of the original bead. The difference between the weight of the final cornet and the residue after sulphuric acid parting gives the platinum.

Final Assay. — Take a quantity of the sample sufficient to yield an amount of platinum such that errors of weighing the final metal will not be excessive. With low-grade ores from 10 to 20 assay tons may be necessary. The ore should be fused in a number of portions, with a lead-fall of not less than 25 to 30 grams per assay ton, and the lead buttons combined by scorification to duplicate or triplicate portions each representing one-half or one-third of the original lot of ore. With high-grade material, care should be taken to see that the total weight of platinum in any assay does not exceed 100 milligrams.

From the results of the preliminary assay, enough gold and silver are added to the lead buttons to give a ratio of Pt:Au:Ag of 1:2:30 to 1:10:33, depending upon the amount of platinum present and the assay facilities available. If the latter ratio is used, the assay bead will have to be flattened and rolled into a cornet. For one who has not had considerable experience in this work, the writer recommends the use of an alloy containing a high ratio of silver so that the residue by breaking up during parting will give some indication that most of the silver has been dissolved.

The main part of the cupellation may be carried on at the ordinary temperature for gold bullion assaying, but at the end, the heat should be raised until the muffle temperature approaches a light yellow heat, 1050° C. After brightening, the muffle is cooled, or the cupels are drawn to the front so that the beads will solidify. They are then allowed to remain at a temperature of 800° to 850° C. for ten or fifteen minutes, after which they may be removed. After being allowed to cool, the beads are weighed and the weight is corrected for added gold and silver, and for accurate work, for cupel loss, applying the results obtained from check assays.

Sulphuric Acid Parting. — Sulphuric acid parting is best conducted in a 30-c.c. pear-shaped parting flask. The parting acid is made up by diluting 100 c.c. of concentrated sulphuric acid with 22 c.c. of water. Ten cubic centimeters of this dilute acid is placed in each flask, and these are then put on the asbestos-covered hot plate and heated not to exceed 240° C. If the low ratio of silver to platinum plus gold is used, the beads are flattened as in the gold bullion assay, annealed, and rolled in 2 or 3 passes, annealing after each pass to a fillet about 0.01 inch thick, and then formed into a cornet. The careful annealing of platiniferous cornets has a most important bearing on their subsequent behavior in parting acids.

The carefully cleaned beads or cornets are dropped into the acid before it gets too hot, otherwise the action may become too violent.

Heat at 240° C. until chemical action ceases and then for an additional ten minutes. The acid is then decanted and two additional acid treatments of ten and five minutes respectively are given, after which the residue is carefully washed. An orange-yellow solution at this point indicates palladium, in which case the procedure must be modified as described later. Great care must be taken in adding water to the hot sulphuric acid to avoid accidents. The solutions should be decanted over a piece of white paper so that the residue may be watched and prevented from passing over with the solution. The solutions and washings should be poured into clean white casseroles so that any loss of residue may be detected.

The next step after complete washing is to transfer the residue from the flask to a porcelain capsule or clay annealing-cup. To do this fill the flask, full to the edge, with distilled water, invert over it an annealing cup or porcelain capsule, and then turn the combination quickly through 180 degrees. Tap slightly, and rotate so that no residue remains on the sides of the flask, and when the residue is all in the cup, raise the flask gently and allow air to enter slowly so as to disturb the residue as little as possible. When the mouth of the flask is even with the top of the cup and the latter is full of water, slide the flask off quickly, invert it, and examine it carefully to be sure that no residue is left. Drain the water from the cup as completely as possible, dry carefully to avoid spattering, and anneal. Weigh the gold plus platinum.

Nitric Acid Treatment. — Add a quantity of silver equal to 3 to 10 times the residue, wrap in lead and cupel, finishing at a high temperature as before, and anneal ten minutes at 800 to 850° C. Clean the bead and part as in the gold assay. Wash, dry, anneal, and examine the residue. Continue the inquartation and parting until from the color it is ascertained that only gold remains. Three partings are usually sufficient for commercial work. Weigh the gold, apply corrections derived from the check if one has been run, and compute the platinum.

ESTIMATION OF PALLADIUM IN SOLUTIONS OBTAINED DURING THE SULPHURIC ACID PARTING METHOD.

Any one who has seen the distinct orange-yellow solution resulting from nitric acid parting of beads containing even very small amounts of palladium must have been struck by the thought that

the depth of this color might be made to serve as a means of determining the amount of palladium present. Particularly should this be true if he had experienced the difficulties and time-consuming manipulations necessary for the gravimetrical separation of platinum, palladium, and silver.

Frank C. Robinson* has described a colorimetric method evolved by himself for the estimation of small quantities of palladium in the sulphuric and nitric acids resulting from the parting of the beads in the assay as just described. The method consists essentially in comparing measured quantities of the colored parting acids with palladium solutions of known strengths. It has been found quick and simple in operation, and, as brought out in the discussion, it has stood the test of experience under various conditions and in different laboratories.

Since palladium has become such a common alloying element for the precious metals, most of the samples of scrap, sweeps, wastes, etc., which come to the assayer contain more or less of this element; and since the ordinary sulphuric acid parting method for the determination of silver, gold, and platinum is not reliable in the presence of palladium, the importance of this supplemental step will be obvious to all assayers. Since, when alloyed with silver, palladium dissolves both in the sulphuric and the nitric acid, both acids have to be tested and the silver and platinum results corrected accordingly. A summary of the method as described by Mr. Robinson and some items from the discussion follow.

Procedure. — It is necessary that the assay bead to be parted should contain gold, equal in amount to 10 times the platinum and palladium together, and silver about 3 times the combined weight of these three metals. If not in sufficient quantity as shown by a preliminary assay, known weights of gold and silver must be added to reach these proportions. The preliminary assay may also be utilized as a means of judging the amount of copper, nickel, and iron present in the sample so that suitable means may be taken to remove these completely before the bead is parted, since they all give colored solutions which might interfere with the determination. It should be noted that it is particularly difficult to get rid of copper in cupeling alloys containing these proportions of platinum, gold, and silver. The final cupellation should be

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* Trans. Inst. Mining Met., **35**, 423–425 (1926). Discussion, pp. 426–441.

light. Filter, and wash with water acidulated with nitric acid. If this precipitate is pink, it is certain that it contains palladium.

This separation of silver from platinum and palladium is the most unsatisfactory part of this method of procedure, for it always occasions considerable trouble and expenditure of time. The silver chloride is always contaminated with platinum and palladium, and for careful work it must be dissolved and reprecipitated at least twice. According to Smoot,* palladium is much more prone to come down with the silver chloride than is platinum. It probably comes down as the double silver salt of the metal, but, since both platinous and palladous nitrates are readily decomposed with the precipitation of basic nitrates, the contamination of the silver chloride may be in part due to this cause.

If the precipitated silver chloride is pink in color, or unless it is known to be free from palladium and platinum, test lead is sprinkled over the moist precipitate on the filter and the whole is transferred to a glazed scorifier containing the rest of the lead necessary for a scorification assay. The filter and precipitate are carefully dried on the hot plate, and the filter paper is smoked off at a temperature well below the melting-point of the lead. The smoking off and ignition may be done in front of the muffle if care is taken, but preferably in a special oven. Finally, the ignited silver chloride is scorified, and the buttons cupeled and parted. Precipitate the silver again, wash, and add the filtrate to that from the first precipitation. If much palladium was present in the material assayed, a third separation must be made. To test the completeness of the separation, the final silver chloride may be scorified and cupeled again, and the bead dissolved in a small quantity of nitric acid which will be colored orange if more than a few hundredths of a milligram of palladium are present.

Unite all filtrates from silver chloride precipitations, and evaporate to a small bulk, finishing the evaporation on the water bath. Take into solution with a little dilute HCl (1:3) and again evaporate to dryness to remove all HNO_3. Finally take up with 5 drops of dilute HCl and not more than 25 c.c. of water, and filter on a small paper in a 1½-inch funnel, catching the filtrate in a 100- or a 150-c.c. beaker. Wash fully, using a small wash bottle which will deliver a very fine stream of water.

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* Determination of Platinum, Palladium, and Gold, E. & M. J., **99**, p. 700 (1915).

Precipitation of Platinum and Palladium. — Make the filtrate slightly alkaline with sodium carbonate, add 10 c.c. of formic acid, and heat to boiling in a covered beaker. Boiling for about thirty minutes should precipitate all the platinum and palladium as metals, and cause them to coagulate so that they will filter readily. Filter on a 5-cm. ashless filter and wash with hot water, using a wash bottle which will deliver a very fine stream. Transfer the filter paper to porcelain crucibles or parting cups, dry, gradually raise the heat so as to smoke off the filter paper, and burn the residual carbon very slowly. If this operation is hastily conducted the platinum metals will adhere to the cup, but if properly done there will be no trouble. Finally ignite the residue for a few minutes in an atmosphere of hydrogen to reduce the palladium oxide to metal, discontinue the flow of hydrogen and heat for an instant only to drive off the occluded hydrogen, cool, transfer to the scale pan, and weigh platinum plus palladium.

An alternative to the ignition in hydrogen, when only small amounts of palladium are present, is to ignite moderately in air to ensure removal of all carbon, and then to reduce any palladium oxide which may have been formed; cool the residue, moisten it with formic acid, and heat on the hot plate long enough to evaporate the excess of formic acid, then cool and weigh.

An alternative to the precipitation of platinum and palladium by boiling with formic acid is to add 5 c.c. of HCl, dilute to 100 c.c. with hot water, heat to 70° C., and pass in a rapid current of H_2S for some time. Filter and wash the platinum and palladium sulphides with hot H_2S water containing a little HCl. Dry on the hot plate, smoke off the filter paper, and burn off the carbon and sulphur with a plentiful supply of oxygen very slowly and carefully to avoid fusing the sulphides of palladium. When oxidation is complete, ignite in an atmosphere of hydrogen or treat with formic acid to reduce palladium oxide.

Precipitation of Palladium. — After the combined platinum and palladium are weighed they are dissolved in a little aqua regia and evaporated just to dryness on the water bath. The residue is again moistened with a few drops of HCl, diluted to 50 c.c. or less, dependent upon the amount of palladium present, and cooled to room temperature; then a 1 per cent solution of dimethylglyoxime in 95 per cent ethyl alcohol is added drop by drop, with constant stirring until there is no further precipitation. Palladium is precipitated as canary-yellow dimethylglyoxime containing, after drying at 105° C., 0.3167 per cent of metallic palladium. There should be added 25 milligrams of the solid reagent for every 10 milligrams of palladium. If the palladium content is low, say less than 0.5 milligram, it is advisable to keep the volume of solution of chlorides very small, and to add but a few drops of the dimethylglyoxime solution. The palladium precipitates more readily in concentrated solution, and the precipitate is more easily filtered.

Allow to stand at room temperature for a few moments, then filter and wash with distilled water, first cold and then hot. The precipitate, if clear yellow, may be considered free from platinum, but if much platinum is known to be present in the solution, and for greatest precision, a second precipitation may be advisable. If platinum comes down, owing to heating or other cause, the precipitate is colored bronze-green. The precipitate may be filtered, dried at 105° C., and weighed in a Gooch crucible or on tared filter papers if large in amount, but if small it may be dried, then slowly and carefully ignited in a porcelain crucible. If it is ignited, the final residue should be treated with a drop of formic acid to reduce the palladium oxide. The metallic palladium is then weighed. If the precipitate is to be weighed without ignition, it should be washed first with alcohol, since the precipitant is substantially insoluble in water.

The platinum may be found by difference, or it may be recovered and weighed. To recover the platinum, the filtrate from the palladium precipitate is evaporated almost to dryness in a small porcelain dish, then a little nitric acid is added and the evaporation completed. The residue is heated almost to redness to remove all organic matter which, if allowed to remain, would interfere with the precipitation of platinum. The residue is extracted with a little aqua regia, evaporated just to dryness on the water bath, taken up with a drop of dilute HCl, and diluted with a little distilled water. The solution is made alkaline with Na_2CO_3 and then boiled with formic acid to precipitate the platinum, which is filtered off, washed, ignited, and weighed.

In certain instances some saving in time might be possible by estimating the palladium in the combined nitric acid solutions colorimetrically after the separation of platinum from gold, then proceeding as described until the combined platinum and palladium sponge has been weighed, and finding the platinum by difference.

THE DIRECT DETERMINATION OF VERY SMALL AMOUNTS OF PLATINUM.

The assayer is frequently called upon to test or assay for platinum in ores of gold, silver, or other metals in which the quantity of platinum, if it is present at all, is so small that it may readily escape detection in the regular gold and silver assay. The sulphuric acid parting method, if applied to such ores, would give residues the difference in weight of which would be so slight as to yield inconclusive evidence either as to the presence or absence of platinum. In many cases, reports of platinum discoveries which have been the cause of considerable excitement and unjustifiable mining exploitation have no basis in fact other than errors made by inexperienced assayers. Many of these would have been avoided, even by an inexperienced assayer, if he had made his assay by the method to be described here:

Frederick P. Dewey,* formerly Chief Assayer of the United States Mint, devised a method of testing for, and determination of, very small amounts of platinum which avoids the disadvantages and defects of the "difference" method and is worthy of the consideration of all assayers. The method depends upon the selective precipitation of platinum, in the presence of a very large excess of silver salts, by hydrogen sulphide. It has the advantage common to all direct determinations, that the metallic platinum itself is weighed free from gold or silver, after which it may be subjected to suitable tests to determine that it really is platinum, and to reveal the presence of other members of the platinum group.

Epitome. — The gold and silver beads thought or suspected to contain platinum are annealed after cupellation and parted in nitric acid in the regular manner, all the solutions and washings being carefully saved. Any small amount of platinum which is present will be readily and practically entirely dissolved provided sufficient silver is present. If care has been taken to use only a small amount of nitric acid, the solution is diluted and a limited quantity of very dilute hydrogen sulphide water is added. This precipitates practically all the platinum together with a small fraction of the silver. The precipitate is allowed to settle over night and is then filtered off, dried, and ignited in a porcelain crucible. The sponge is wrapped in a small piece of lead foil and

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* Trans. A.I.M.E., 43, pp. 578–581 (1912).

cupeled. The bead is parted in sulphuric acid, and the platinum residue is washed, dried, annealed, and weighed. The final metal is examined qualitatively.

Procedure. — Take such a quantity of ore as will yield either a weighable amount of platinum or, in the absence of a weighable residue from sulphuric acid parting, will clearly justify a negative report. Fuse with suitable reagents, scorify the resultant lead buttons if necessary to eliminate copper, and cupel and anneal the beads as in all platinum assays. Part in as small an amount of nitric acid as possible, and wash. If an excess of nitric acid has been used for any reason, evaporate to remove excess acid and dilute considerably. Add slowly and with constant stirring a limited quantity of very dilute hydrogen sulphide water. One part of strong hydrogen sulphide water diluted with 10 to 20 parts of water is recommended. The solution is at once darkened, but there should be no immediate separation of a visible precipitate. The solution should be stirred occasionally and warmed if necessary; in about two hours, flocks of precipitate should appear. It may be filtered in three to four hours, but it is a good plan to let it stand over night.

The amount of hydrogen sulphide required depends, of course, on the amount of platinum present. If this should be roughly known or suspected, the amount used should be enough to precipitate the platinum and from 3 to 5 times as much silver. On an entirely unknown ore; it is recommended to use at first 1 c.c. of strong hydrogen sulphide water, diluted to 15 c.c., and to reserve the filtrate from the sulphides for re-treatment, if necessary.

After filtering off the precipitate, which is usually sufficiently washed by the operations necessary to transfer it to the filter, the moist filter is transferred to a porcelain crucible, carefully dried, and then smoked off at a low heat and the carbon burned by gentle ignition. The residue, now in the form of a metallic sponge, is carefully transferred to a piece of lead foil, wrapped up, and cupeled. The resultant bead is parted in sulphuric acid in the ordinary manner. The platinum will be left as a dark residue usually collected in sponge form, even when minute in quantity. This sponge is suitably washed by decantation, annealed, and weighed.

The final metal usually speaks for itself as being platinum, but if there should be any doubt, it may be dissolved in a drop or two of aqua regia and gently evaporated. The solution obtained may be tested with potassium iodide or with stannous chloride. Most of the palladium which may have been in the bead should have been dissolved in the sulphuric acid and its presence clearly indicated by the color of the solution. If the amount of final metal is considerable, the platinum may be separated as ammonium platinic chloride, carefully ignited, and weighed as metal. Any decided difference would indicate the presence of other members of the platinum group, for which direct tests may be made.

It may happen that the final metal shows the yellow color of gold, by reason of the fact that exceedingly fine float-gold passed over in decanting the solution of silver nitrate from the gold. In such a case, the metal must be re-alloyed with silver and the treatment repeated, followed by a filtration before the hydrogen sulphide treatment. When the proportion of gold to silver in the metal being parted is so small that the gold separates in a very finely divided state, it will often save trouble to filter the silver nitrate solution to separate any float-gold, before adding the hydrogen sulphide.

If the material contains a considerable amount of platinum, not all of it may dissolve in a single nitric acid treatment. In this case, the residue from the first parting in nitric acid must be alloyed with silver and parted a second time in nitric acid before proceeding to precipitate the platinum with hydrogen sulphide.

Dewey reports having found this method satisfactory for determining very small amounts of gold and platinum in various silver products such as fine silver. It is comparatively easy to gather the gold from very large samples of silver, up to 100 grams or more in, say, 100 milligrams of silver, and then part in nitric acid as usual. Even electrolytically refined silver will be found to yield minute amounts of gold when assayed by this method. In assaying bullion a little more than the theoretical amount of nitric acid, well diluted, is allowed to act on the samples which have preferably been granulated, or rolled out and cut in small pieces. When the silver is entirely dissolved or the acid is exhausted, it is poured off and any small amount of residual silver is dissolved in a small amount of fresh acid. The combined solutions are evaporated nearly to dryness and then diluted to 250 c.c., and 5 c.c. of strong hydrogen sulphide solution, diluted to 50 c.c., is poured in with constant stirring, and the assay is completed as usual.

Properly burned sheep bones will yield an ash containing about 90 per cent calcium phosphate, 5.65 per cent calcium oxide, 1.0 per cent magnesium oxide, and 3.1 per cent calcium fluoride. Ordinary commercial bone-ash also contains more or less silica and unoxidized carbon. If more than a fraction of a per cent of silica is found in bone-ash, it is evidence that sufficient care has not been taken in cleaning the bones, and cupels made from such bone-ash are more likely than others to crack during cupellation, often resulting in the loss of small beads. If the bone-ash shows black specks it is an indication of insufficient oxidation and the assayer should allow the cupels to stand for some time in the hot muffle, with the door open, before using. Carbon is an undesirable constituent of cupels as it reacts with the lead oxide formed giving off CO and CO_2 which may cause a loss of the molten alloy due to spitting.

Bone-ash for cupels should be finely ground to pass at least a 40-mesh screen and the pulverized material should consist of such a natural mixture of sizes as will give a solid cupel with enough fine material to fill interstices between coarser particles. Opinions differ as to the best size of crushing for bone-ash and this will depend no doubt upon the character of the material. The bone-ash represented by the following screen analysis has, however, yielded particularly good cupels.

TABLE VIII.

Size of Bone-Ash.

Size mesh	Size mm.	Per cent weight
On 40	0.380	9
Through 40 " 60	0.244	14
" 60 " 100	0.145	17
" 100 " 150	0.098	10
" 150		50

With cupels made from this bone-ash it was possible to reduce losses to 1.60 per cent, using 100 mg. of silver and 25 grams of lead, while with some other lots of bone-ash containing smaller proportions of −150-mesh material it was found impossible to keep the losses below 2.0 per cent.

Making Cupels. — Cupels are made by moistening the bone-ash with from 8 to 20 per cent of water and compressing in a mold. The bone-ash and water should be thoroughly mixed by kneading, and the mixture should finally be sifted through a 10- or 12-mesh sieve to break up the lumps. Some authorities recommend adding a little potassium carbonate, molasses or flour to the mixture, but with good bone-ash nothing but pure water need be added. The mixture should be sufficiently moist to cohere when strongly squeezed in the hands, but not so wet as to adhere to the fingers or to the cupel mold. Twelve per cent of water by weight is about right; but the amount used will depend somewhat on the bone-ash and on the pressure used in forming the cupels. The greater the pressure the smaller the amount of water which is required. It is better to err on the side of making the mixture a little too dry than too wet.

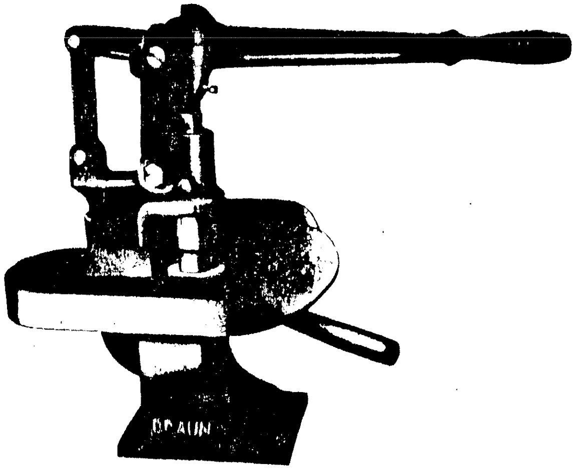

Fig. 39. — Cupel machine.

The cupels may be molded either by hand or by machine. The hand outfit consists of a ring and a die. The ring is placed on the anvil and filled with the moist bone-ash, the die is inserted and pressed down firmly. It is then struck one or more blows with a heavy hammer or mallet, and turned after each blow; finally the cupel is ejected. The cupels are placed on a board and dried slowly in a warm place. The amount of compression is a matter of experience and no exact rule for it can be given;

but it may be approximated by making the cupels so hard that when removed from the mold they are scratched only with difficulty by the finger nail. One man can make about 100 cupels an hour, using the hand mold and die.

Several types of cupel machines are on the market and one of the best is shown in Fig. 39. This machine, has a compound lever arrangement which gives a pressure on the cupel equal to twenty times that applied to the hand lever. By adjusting, different degrees of compression may be obtained. These machines have interchangeable dies and rings so that different sizes of cupels may be made. The rated capacity of this machine is two hundred cupels an hour. Another machine made by the same company has an automatic charging arrangement. This machine is claimed to have a capacity of six hundred cupels an hour. Cupels should be uniform in hardness, and it would seem that with a properly designed machine a more uniform pressure could be obtained than by the use of hammer and die. Some assayers, however, still prefer hand-made cupels.

Cupels should be air-dried for several days, at least, before use. Most assayers make them up several months in advance so as to insure complete drying. They should not be kept where fumes from parting can be absorbed by them as, if this occurs, the CaO present will be converted into $Ca(NO_3)_2$. This compound is decomposed at the temperature of cupellation and may cause spitting of the lead button.

Cupels should not crack when heated in the muffle and should be so strong that they will not break when handled with the tongs. Good cupels give a slight metallic ring when struck together after air-drying. It is best to heat cupels slowly in the muffle as this lessens the chance of their cracking.

A good cupel should be perfectly smooth on the inside, and of the right porosity. If it is too dense, the time of cupellation is prolonged and the temperature of cupellation has to be higher, thus increasing the loss of silver. If the cupel is too porous it is said that there is danger of a greater loss, due to the ease with which small particles of alloy can pass into the cupel. The bowl of the cupel should be made to hold a weight of lead equal to the weight of the cupel.

The shape of the cupel seems to influence the loss of precious metals. A flat, shallow one exposes a greater surface to oxidation and allows of faster cupellation; it also gives a greater surface of contact between alloy and cupel, and as far as losses are due to direct absorption of alloy, it will of course increase these. The writer, using the same bone-ash and cupel machine, and changing only the shape of the cupel, has found shallow cupels to give a much higher loss of silver. In doing this work it was found harder to obtain crystals of litharge with the shallow cupel without freezing, and it was very evident that a higher cupellation temperature was required for the shallow cupel. The reason for this is that in the case of the shallow cupel the molten alloy is more directly exposed to the current of air passing through the muffle, and consequently a higher muffle temperature has to be maintained to prevent freezing. T. K. Rose* also prefers deep cupels on account of smaller losses. French found shallow cupels less satisfactory on account of sprouting.

A satisfactory size of cupel for general assay work is $1\frac{3}{8}$ inches in diameter and 1 inch high with a maximum depth of bowl of $\frac{11}{32}$ inch. A bone-ash cupel of these dimensions weighs slightly more than 40 grams and will hold the litharge from a 30-gram button with but little leakage. If necessary a 40-gram button may be cupeled in it, but if it is so used the bottom of the muffle should be well covered with bone-ash. A bone-ash cupel will absorb about its own weight of litharge.

Cupellation. — The muffle is heated to a light red, and the cupels, weighing about one-third more than the buttons which are to go into them, are carefully introduced and allowed to remain for at least ten minutes, in order to expel all moisture and organic matter. During this preliminary heating the door to the muffle is ordinarily kept closed, but if the cupels contain organic matter it is left open at first and then closed for five minutes or so before the buttons are introduced.

When all is ready the buttons are placed carefully in the cupels and the muffle door again closed. If the cupels are thoroughly heated, the lead will melt at once and become covered with a dark scum. If the temperature of the muffle is correct this will disappear in the course of a minute or two when the molten lead will become bright. The assays are then said to have opened up or "uncovered." This signifies that the lead has begun to oxidize rapidly, raising the temperature

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* Eng. and Min. Jour. 80, p. 934.

of the molten alloy considerably above that of its surroundings, whence it appears bright. It assumes a convex surface, and molten patches of litharge passing down over this surface give it a lustrous appearance. It is then said to "drive."

When the assays have uncovered, the door of the muffle is opened to admit a plentiful supply of air to promote oxidation of the lead, while at the same time the temperature of the muffle should be reduced. According to Fulton*, if the buttons are practically pure lead the temperature of uncovering is about 850° C. However, if antimony, cobalt, nickel etc., are present, the temperature of uncovering and also that required for cupellation will be higher.

The greater part of the lead oxide formed remains liquid and flows down over the convex surface of the molten alloy. If the temperature of the cupel is high enough this molten litharge is absorbed. A small part of the lead oxide is vaporized and appears as fume rising from the cupel.

After cupeling has proceeded for a few minutes, a ring, caused by the absorbed litharge, may be seen around the cupel just above the surface of the metal. If the temperature is right for cupeling this will be very dull red, almost black. If it is bright red, the temperature is too high. The color of the alloy itself will be much brighter than that of the absorbed litharge, as it is in fact much hotter than the cupel or surrounding air, on account of the heat generated by the rapid oxidation of the lead. Next to the formation of abundant litharge crystals, the appearance of the absorbed litharge is the best indication of proper cupellation temperature.

If the temperature is exactly right feather-like crystals of litharge form on the sides of the cupel above the lead. This is due to sublimation of some of the volatilized lead oxide. In cupeling for silver the temperature should be such that these crystals are obtained on at least the front-half of the cupel, and as the button grows smaller they should follow it down the side of the cupel, leaving, however, a slight clear space around it. If the temperature becomes too low for the cupel to absorb the litharge, the crystals begin to form all around and close to the lead in the cupel, and soon a pool of molten litharge is seen forming all around the annular space between the lead and the cupel.

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* Western Chemist and Metallurgist, **4**, p. 31. (Feb. 1908.)

If the temperature of the cupel is not quickly raised, this pool increases in size and soon entirely covers the lead and then solidifies. When this occurs the button is said to have "frozen," although the lead itself may be liquid underneath. Frozen assays should be rejected as the results obtained from them, by again bringing to a driving temperature, are usually low. If the freezing is noticed at the start, it may be arrested by quickly raising the temperature of the cupel in some way, i. e., by taking away the coolers, closing the door to the muffle, opening the draft, putting a hot piece of coke in front of the cupel, etc.

Beginners have difficulty in noting the first symptoms of freezing, but all should be able to see the pool of litharge starting. This gives the appearance and effect of oil; if the cupel is moved the button slides around as if it were greased.

Toward the end of the cupellation process the temperature must be raised again, because the alloy becomes more difficultly fusible as the proportion of silver in it increases, and in order to drive off the last of the lead a temperature of about 900° C. should be reached. The temperature should not be raised so high as to melt the crystals of litharge, for if this is done too great a loss of silver results.

As the alloy becomes richer in silver it becomes more and more rounded in shape and shining drops of litharge appear and move about on its surface. As the last of the lead goes off, these drops disappear, the fused litharge covering becomes very thin and, being of variable thickness, gives an effect of interference of light, so that the bead appears to revolve and presents a succession of rainbow colors. This phenomenon is termed the "play of colors." The colors disappear shortly, the bead becomes dull and after a few seconds appears bright and silvery. This last change is called the "brightening."

After brightening, the cupels should be left in the furnace for a few minutes to ensure removal of the last of the lead, and then moved gradually to the front of the muffle before they are taken out, so that cooling may be slow.

As the bead solidifies it will "flash" or "blick," i. e., suddenly emit a flash of light due to the release of the latent heat of fusion, which raises the temperature very much for a short time.

Cupels containing large silver beads should be drawn to the front of the muffle until they chill. Just as the bead is about to seen forming at least on the front half of the cupel. Then continue the cupellation at this temperature. Finally finish the assay at a somewhat higher heat, increasing the temperature by starting up the fire, removing the coolers or by shutting off some of the cold air supply by partly closing the door to the muffle. If the cupels are running very cold it will be necessary to start raising the temperature some five minutes before the end. The fire should be under good control at all times. As soon as the cupellation is finished remove the assay carefully from the muffle to avoid sprouting. All assayers agree that the best results are obtained by having a hot start, a cold drive, and a higher heat again at the finish.

Notes: 1. When a number of cupellations are carried on at one time, the buttons should be charged in the order of their size, i.e., largest first, so that all may start driving together.

A skilful assayer, with a large muffle, can run as many as fifty cupellations at one time and obtain feather crystals on all.

2. When a number of cupellations are carried on at one time, the cupels are not moved about after the lead is put in, but the temperature is regulated by means of the draft and firing and by the use of coolers, (cold scorifiers, cupels, crucible covers, etc.) which are put in toward the back of the furnace and replaced as soon as they become heated.

3. Bear in mind that although the temperature of the muffle may be as low as 650° or 700° C., the cupel itself should be slightly above the freezing point of litharge, to allow of its being absorbed. It has been found best, therefore, to protect the body of the cupel itself from the draft through the muffle, by placing an extra row of cupels or a low piece of fire-brick in front of the first row of cupels.

4. Buttons containing copper may be cupeled at a lower temperature than those consisting of pure lead and silver, owing to the fact that cupric oxide lowers the freezing point of litharge.

5. After the cupellation is finished, the cupel should be left in the muffle one or two minutes, depending on the size of the bead, to remove the last traces of lead. After this it should be withdrawn; otherwise a loss of silver ensues.

6. When the finishing temperature is too low, the beads will solidify without brightening. They retain lead and have a dull appearance and sometimes show flakes of litharge on the surface. Under certain conditions they flatten out, leaving a gray, mossy bead.

7. When the button contains only gold, a higher finishing temperature is required than when working for silver.

8. When gold is present in considerable amounts the bead will not sprout even if taken directly out of the muffle.

9. Besides gold and silver, the bead may contain platinum, palladium, rhodium, iridium, ruthenium, osmium, and iridosmium.

10. If the upper surface of the bead appears to be frosted this indicates the presence of tellurium or some member of the platinum group.

11. Buttons which contain a large amount of platinum flatten out and will not blick. They have a steel-gray color and a dull surface.

SECOND EXERCISE. CUPELLATION ASSAY OF LEAD BULLION.

Procedure. — Weigh out carefully three portions of bullion of $\frac{1}{2}$ A. T. each. Wrap each in 10 to 15 grams of silver-free lead foil so that the whole is very compact, having each piece of lead foil of the same size and weight.

Have a good fire so that the lead will melt, and start to drive without delay. Use cupels which weigh 35 grams or more and have them all in a row with an extra row in front. Drop the assays in as quickly as possible and close the door. As soon as the lead starts to drive, close the drafts and cool as soon as possible so that feather crystals of litharge form on at least the front half of the cupel. Finally open the draft and otherwise increase the temperature for the last minute or two of cupellation to drive off the last traces of lead. Have some hot cupels in the muffle and, as soon as the beads brighten, pull them forward in the muffle to chill and then put a hot cupel over them and withdraw both slowly from the muffle. All danger of sprouting is over when the inside of the cupel reaches a dull red or when the bead has become solid throughout. Remove from the furnace to the cupel tray and allow to cool. When the bead is cold, detach it from the cupel with the pliers and brush with a stiff brush to remove bone-ash, or place it on its side on a clean anvil and slightly flatten with a hammer. When the bead is free from bone-ash, weigh it, recording in the notebook the weight of gold and silver. Then part and weigh the gold; finally report the amount of gold and silver in ounces per ton.

Notes: 1. Have a sheet of clean white paper at hand and when transferring the bullion from the scale-pan to the lead foil do it over this so that in case any is spilled it will be seen and recovered. Do all of the wrapping and compressing over this paper for the same reason.

2. If the assay is not compact, it may overflow the cupel while melting, or else leave small particles on the sides of the cupel, which will not come down into the main button.

Loss of Silver in Cupeling. — There is always some loss in cupellation, the amount depending on many factors such as the nature and shape of the cupel, the temperature of cupellation, the proportion of lead to silver, the amount and character of impurities, the draft through the muffle, etc. Losses may be due to spurting, absorption of bullion by the cupel, oxidation and absorption of silver with litharge, and volatilization of silver either alone or accompanied by other metals.

The cupel surface may be regarded as a membrane permeable to molten litharge and impermeable to lead. The more nearly the material of the cupel surface approaches this condition the lower the losses may be made. Some cupels, particularly some of magnesite, present spots of material which are permeable to lead and consequently give a high loss of silver.

The most important factor relative to cupel loss, however, is the temperature. The higher the temperature, the higher the loss, is an invariable rule. The increased loss due to higher temperature seems to be due mostly to an increased oxidation of the silver and a consequent greater absorption loss. The volatilization loss is also increased by an increase of temperature. A loss of 1 per cent silver is allowable and the loss may usually be kept close to this figure by taking pains to cupel with abundant crystals of litharge. If this matter is overlooked a loss of 4 or 5 per cent may readily be obtained and this, of course, is entirely inadmissable.

The following table, taken from Lodge's "Assaying," illustrates this point and shows the importance of cupeling at the correct temperature. The temperature was taken with a Le Chatelier pyrometer, the junction being held about one-quarter inch above the button.

TABLE IX.

Effect of Temperature on Loss of Silver in Cupellation.

Silver milligrams	Lead grams	Temperature degrees centigrade	Silver loss per cent[*]	Remarks
200	10	700	1.02	Crystals of PbO all around button.
200	10	775	1.30	Crystals of PbO on cooler side of cupel.
200	10	850	1.73	No crystals.
200	10	925	3.65	" "
200	10	1000	4.88	" "

[*] Average figures.

The amount of lead and silver present in any button has a marked effect on the percentage loss of silver in cupellation. Rose,[*] in speaking of cupellation says, "The losses of silver at first are small, so long as large quantites of base metals protect it from oxidation. .... Later, when the percentage of silver is high it is freely oxidized .... and the oxidation is at its maximum when the silver is practically pure."

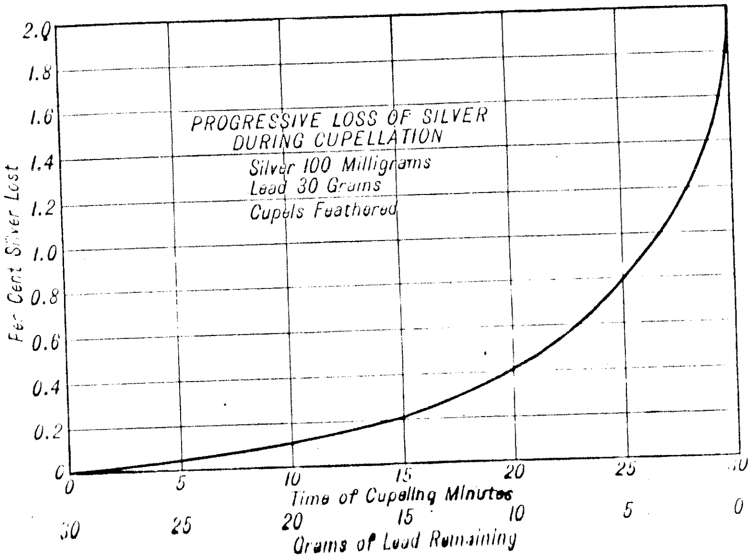

Fig. 40. — Curve showing cumulative loss of silver in cupellation.

This is well illustrated by the curve shown in Fig. 40 in which is plotted the cumulative, minute-to-minute, loss of silver in cupeling a 30-gram button containing 100 milligrams of silver. This is the result of considerable careful experimental work done in the fire assay laboratory of the Massachusetts Institute of Technology, several years ago.

Keeping the amount of silver constant and varying the lead, Lodge obtains the results shown in the following table:

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[*] Trans. Inst. Min. Met., 14, p. 420.

TABLE X.

EFFECT OF LEAD ON LOSS OF SILVER IN CUPELLATION.

Silver milligrams	Lead grams	Temperature degrees centigrade	Silver loss per cent[1]
200	10	685	1.39
200	15	685	1.38
200	20	685	1.52
200	25	685	1.85

[1] Average of two nearest together.

When the quantity of lead remains constant and the silver is varied the percentage loss of silver is found to increase as the silver is reduced. The following representative figures taken from Godshall's paper on "Silver Losses in Cupellation"* show this very clearly.

TABLE XI.

EFFECT OF VARYING SILVER ON CUPELLATION LOSSES.

Weight of Lead	1/2 A. T.	1/2 A. T.	1/2 A. T.	1/2 A. T.	1/2 A. T.	1/2 A. T.	1/2 A. T.
Weight of Silver	200 mg.	100 mg.	50 mg.	20 mg.	10 mg.	5 mg.	2 mg.
Silver Loss	1.73%	2.03%	2.65%	2.82%	3.44%	4.46%	6.90%

Loss of Gold in Cupeling. — There is always some loss of gold in cupeling, but owing to the greater resistance of this metal to oxidation this loss is smaller than the corresponding silver loss. The following table, taken from Lodge, shows the relation between the loss of gold and the temperature of cupellation.

TABLE XII.

EFFECT OF TEMPERATURE ON LOSS OF GOLD IN CUPELLATION.

Gold used milligrams	Lead grams	Temperature degrees centigrade	Gold loss per cent[1]	Remarks
200	10	700		Button froze.
200	10	775	0.155	
200	10	850	0.385	
200	10	925	0.460	
200	10	1000	1.435	
200	10	1075	2.990	

[1] Mean of two results nearest together.

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* Trans. A I.M.E. 26, pp. 473–484 inc.

In the case of the gold with temperatures of 1000 degrees and above, the higher losses seem to be due in part to a lessening of the surface tension owing to the increased temperature, for when the cupels were examined with the microscope a large number of minute beads were found all over the inner surface. It would appear that small particles of the alloy were left behind to cupel by themselves.

As in the case of silver, the percentage loss of gold is found to increase as the quantity is reduced. Hillebrand and Allen* show that, contrary to the usual opinion, the loss of gold in cupeling is not negligible, and is greatly influenced by slight changes in temperature. They found that the most exact results were obtained when feather crystals of litharge were obtained on the cupels.

Effect of Silver on the Loss of Gold in Cupeling. — Lodge, in his "Notes on Assaying," states that the addition of silver in excess lessens the loss of gold, but gives no figures. Hillebrand and Allen† state that the loss of gold in cupeling is greater with pure gold and alloys poor in silver than with alloys rich in silver. Smith‡ gives the following figures showing the protective action exercised by silver on gold during cupellation:

	Per cent of total gold recovered.	
	Tellurium added.	Without tellurium.
Without silver	94.9	98.2
With silver	97.0	99.5

In order to obtain more light upon this subject, Mr. A. B. Sanger, a student at the Massachusetts Institute of Technology, made a large number of careful experiments, using proof gold and C. P. silver. The work was done in a gas furnace and the temperature was measured by a thermo-electric pyrometer, the junction of which was placed in the center of a blank cupel in line with the cupels which were being used. Mr. Sanger used 10 milligrams of gold and various amounts of silver with 25 grams of lead, and with four different temperatures. His results § are shown in Fig. 41. The gold losses include any solution losses there may have been in parting, but these are extremely small, or nil. The results show a very decided protective effect of sil-

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* Bull. No. 253 U. S. Geol. Survey. p. 20 et seq.

† Op. cit.

‡ The Behavior of Tellurium in Assaying. Trans. Inst. Min. Met. 17, p. 472.

§ Thesis No. 492, M.I.T. Mining Department.

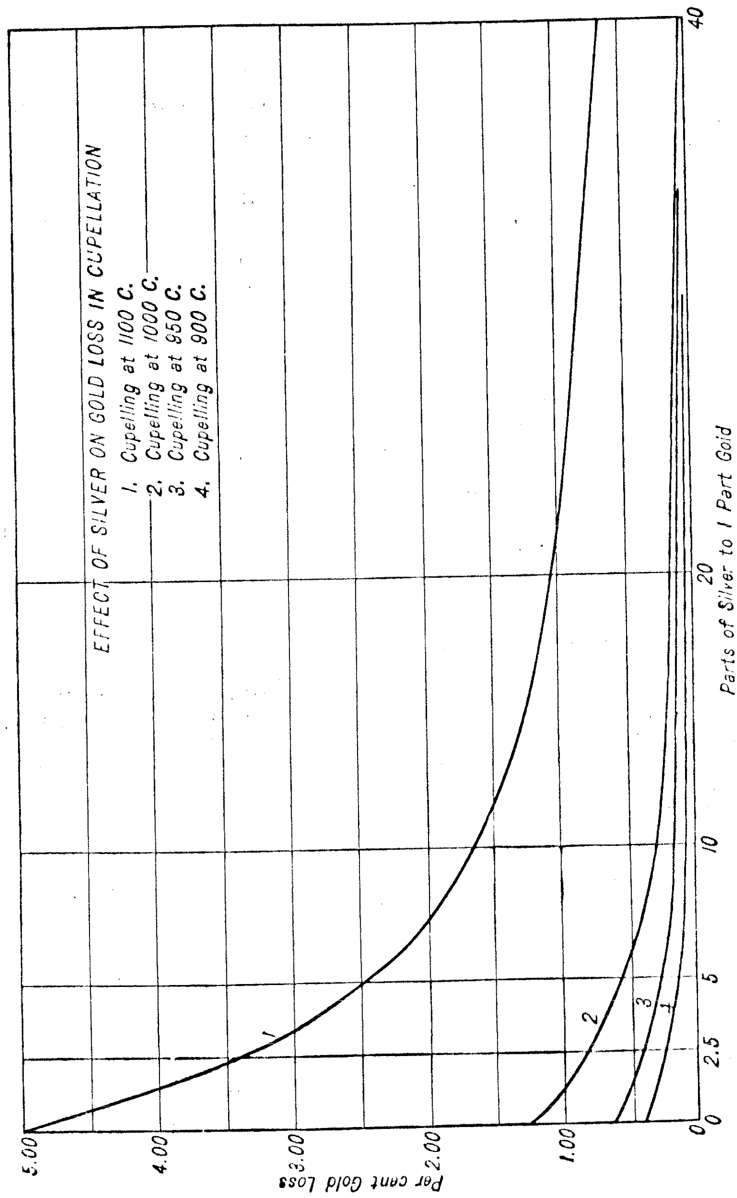

FIG. 41. — Curve showing protective effect of silver on gold in cupellation.

ver and confirm the statements of Lodge and others. A glance at the curves shows how important it is to run gold assays at a temperature close to that at which feather crystals are obtained. With smaller amounts of gold the percentage losses will be correspondingly greater.

Influence of Impurities on the Loss of Precious Metals during Cupellation. — According to Rose,* tellurium, selenium, thallium, bismuth, molybdenum, manganese, copper, vanadium, zinc, arsenic, antimony, cadmium, iron and tin, all induce extra losses of gold and silver in cupellation and should be removed before this stage is reached.

The behavior of tellurium in cupellation will be mentioned in the discussion of the assay of telluride ores. Copper is perhaps the most common impurity, and on account of the difficulty of removing it completely in scorification or crucible fusions, a knowledge of its behavior in cupeling is particularly important. Eager and Welch† give the following table showing the effect of copper on the loss of silver in cupellation.

TABLE XIII.

EFFECT OF COPPER ON SILVER LOSSES IN CUPELLATION.

No.	Silver used grams	Lead grams	Temperature degrees centigrade	Copper per cent of the silver	Per cent silver lost		Ratio of lead to copper
					Individual	Mean	
1	.20382	10	775	5	1.00		1000 to 1
2	.20256	"	"	"	1.15		"
3	.20036	"	"	"	0.93	1.03	"
4	.20618	"	"	10	1.19		500 to 1
5	.20193	"	"	"	1.00		"
6	.20118	"	"	"	1.06	1.11	"
7	.20140	"	"	15	1.35		333 to 1
8	.20138	"	"	"	1.27		"
9	.20432	"	"	"	[1]1.15	1.31	"
10	.20282	"	"	20	[1]1.15		250 to 1
11	.20100	"	"	"	1.45		"
12	.20338	"	"	"	1.46	1.46	"
13	.20224	"	"	25	1.05		200 to 1
14	.20496	"	"	"	0.95		"
15	.20420	"	"	"	1.07	1.02	"

[1] Disregarded.

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* Jour. Chem. Met. and Min. Soc. of South Africa, **5**, p. 167.

† Thesis No. 225, M.I.T. Mining Department.

When the results shown in this table are compared with those in Table IX, it appears that the presence of a small amount of copper, not more than 1 part to 500 of lead, and not more than 1 part to 10 parts of silver, reduces the loss of silver below that which results when no copper is used. This may be due to the protective action which copper is known to exert upon silver.*

With a ratio of 1 part of copper to 333 parts of lead and with 6.67 parts of silver, the loss is about the same as in the absence of copper.

With an increase in the amount of copper to 1 part to 250 of lead and 5 parts of silver the loss is greater than when no copper is used.

With a ratio of 1 part of copper to 200 parts of lead and 4 parts of silver the loss apparently becomes less, but this was found to be due to the retention of copper in the silver bead.

TABLE XIV.

Effect of Copper on Gold Losses in Cupellation.

No.	Gold used grams	Lead grams	Temperature degrees centigrade	Copper per cent of the gold	Per cent gold lost		Ratio of lead to copper
					Individual	Mean	
1	.20181	10	775	None	0.15		
2	.20104	"	"	"	0.16	0.16	
3	.20288	"	"	5	0.18		1000 to 1
4	.20110	"	"	"	0.20		"
5	.20318	"	"	"	0.10		"
(In the following the beads show a gain in weight.)							
6	.20102	"	"	10	-0.03		500 to 1
7	.20142	"	"	"	-0.03		"
8	.20138	"	"	"	-0.02	-0.03	"
9	.20024	"	"	15	-0.11		333 to 1
10	.20060	"	"	"	-0.26		"
11	.20048	"	"	"	-0.18	-0.18	"
12	.20100	"	"	20	-0.13		250 to 1
13	.20101	"	"	"	-0.56[1]		"
14	.20161	"	"	"	-0.20	-0.17	"
15	.20422	"	"	25	-0.29		200 to 1
16	.20296	"	"	"	-0.21		"
17	.20284	"	"	"	-0.32	-0.27	"

[1] Disregarded.

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* Rose, Trans. Inst. Min. Met. **14**, p. 422.

When the amounts of lead and copper in 10, 11 and 12 above are compared, it is found that the ratio of lead to copper should be at least 250 to 1 to ensure the removal of the copper, and at least 333 to 1 if the apparent loss of silver is not to be noticeably increased.

The effect of copper on the loss of gold is shown in the preceding table.

It appears that 5 per cent of copper with this lead ratio has no effect on the loss of gold. The gain in the weight of the gold beads with 10 per cent and over of copper shows clearly that copper is retained by the gold under these conditions. This was also indicated by the color of the gold beads. With a higher cupellation temperature the amount of copper retained would doubtless be smaller. It is interesting to note that with 10 per cent of copper the amount retained by the bead approximately neutralizes the loss of the gold itself. Apparently the ratio of lead to copper should not be less than 500 to 1 if the copper is to be completely removed.

Rule Governing Cupellation Losses. — As is well recognized in large-scale cupeling operations, the concentration of precious metal in the litharge increases as the concentration in the lead increases. W. J. Sharwood* after examining a large number of experimental results enunciated the following empirical rule connecting the actual or percentage loss with the weight of the bead: "When a given amount of silver (or of gold) is cupeled with a given amount of lead, under a fixed set of conditions as to temperature, etc., the apparent loss of weight sustained by the precious metal is directly proportional to the surface of the bead of fine metal remaining."

If the above is true the following are also true.

(1) "The loss of weight varies as the $\frac{2}{3}$ power of the weight, or as the square of the diameter of the bead."

(2) "The percentage loss varies inversely as the diameter of the bead, or inversely as the cube root of the weight."

As Sharwood points out it might be better to base the calculations on the original weight of metal taken, but in every day practice this is not known and we have to depend on the weight of the bead.

Inasmuch as small variations in the amount of lead have but

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* T.A.I.M.E. **52**, p. 180.

as well as occasional rare metals, many of which may exert considerable influence on the results of the assay if provision is not made for them. It is always important to determine the nature of the constituents of the material which is being assayed; and the behavior of the cupeling lead and the appearance of the cupel and bead during and after cupellation will often give much valuable information concerning the elements present. When the character of the constituents is ascertained, the skilful assayer will know exactly what to do, and when he again comes to the cupellation stage everything will go smoothly. All that is known about qualitative analysis is not found in books devoted to that subject, as assayers well know; and in the case of certain rare elements at least, the fire assayer has a decided advantage over the ordinary chemist.

As soon as the button melts any slag which may not have been removed in cleaning it, together with sulphides or arsenides of some of the base metals, if present, will come to the surface of the alloy as a dark-colored pasty dross. If not too great in amount this will go to the side of the cupel and cupellation may be continued. If zinc, tin, iron, nickel, cobalt, antimony or arsenic are present these will oxidize and come off in the order named. The oxides of zinc, tin, iron, nickel and cobalt are but slightly soluble in molten litharge and, if present in any considerable amount, give infusible scoria which float on top of the lead and interfere with cupellation.

Zinc if present will burn with a brilliant greenish-white flame and emit dense white fumes. A considerable part of the oxide condenses on the cupel and may cover over the lead thus preventing cupellation.

Tin if present in the button, is quickly oxidized, forming SnO_2, which, if present in sufficient quantity, covers the lead with infusible yellow scoria and stops cupellation.

Iron gives brown or black scoria if present in large amounts, as do also cobalt and manganese. Small amounts of iron oxide dissolve in the litharge and stain the cupel dark red.

Nickel in small quantities gives dark green scoria and greenish stains. Larger amounts cause the button to freeze.

Antimony is readily soluble in lead in almost all proportions, and for this reason the button may contain a large amount of it. It comes off in the first stages of cupellation, giving dense fumes of Sb_2O_3 and yellow scoria of antimonate of lead around the cupel. This scoria appears when 2 per cent or more of antimony is present. It solidifies almost as soon as formed and expands in so doing. If much antimony is present the cupel will be split open by this action, allowing the lead to run out into the muffle. If present in smaller amounts it may simply crack the cupel and leave a characteristic ridge of yellow scoria.

Arsenic acts much like antimony but is not so often carried into the lead button. The scoria from arsenical lead is light yellow and the fumes are less noticeable.

Bismuth is less readily oxidized than lead and thus tends to remain with the silver until most of the lead has gone. It is finally oxidized and absorbed by the cupel and leaves a ring of orange-yellow around the silver bead. For purposes of comparison it should be noted that pure lead gives a brown-yellow cupel. Bismuth is the only other metal which behaves like lead in cupeling; this, however, makes it possible to cupel argentiferous bismuth directly.

Copper, like bismuth, is less readily oxidized than lead, but it differs from bismuth in that its oxide alone is not liquid at the temperature of cupellation. Cuprous oxide, however, is readily soluble in molten litharge and the mixed oxides are absorbed in the cupel, giving a stain which ranges from dirty green almost to black according to the amount present. The intensity of the green coloration may be taken as an indication of the amount of copper present in the button. Even very small amounts may be detected in this way. Owing to the relative difficulty with which it oxidizes, copper tends to concentrate in the button and if too large in amount causes it to freeze. Sometimes it will go down to a small amount and then flatten out, leaving a copper-colored bead.

Tellurium gives the surface of the cupel a pinkish color most of which fades away upon cooling. If much tellurium is present it gives a frosted appearance to the bead. In an experiment with 200 milligrams of silver and 10 grams of lead, the frosting made its appearance when 40 milligrams of tellurium were added. Tellurium reduces the surface tension of the lead alloy and thus increases the loss of the precious metals, and, as it is less readily oxidized than lead, most of it remains with the precious metals until a large part of the lead is removed.

In attempting to determine the presence of various elements in the lead by the color of the cupel it must be remembered that one constituent, particularly if it has an intense coloring power and more particularly if the color produced is dark, will tend to mask other constituents producing lighter and less intense colors.

Indications of Rare Metals. — The members of the platinum group of metals practically all yield evidence of their presence either in the appearance of the surface of the finished bead or, in some cases, during the later stages of the cupellation process. We are indebted mostly to Lodge[*] and to Bannister[†] for information relative to the appearance of the surface of the finished bead. Lodge worked with relatively large amounts of rare metals and small amounts of silver, and depended on the unaided eye for his observations. Bannister worked with very much smaller quantities of rare metals and large amounts of silver and gold and used a low-power microscope. These indications, which should be recognized by all skilful assayers, may be made an important contribution to our knowledge of the qualitative analysis of these metals. At least they should serve to put the assayer on his guard and cause him to suspect the presence of rare metals in samples of ores and bullion submitted without request for their determination. In general, where the presence of any of these metals is suspected, the cupels should be finished at a reasonably high temperature and the beads allowed to cool slowly in order to fully develop their crystalline structure.

Platinum. — As little as 1.6 per cent of platinum gives a characteristic frosted appearance to a silver bead which is visible to the naked eye. Under a low-power microscope as little as 0.4 per cent may be detected in beads weighing only 0.1 gram. The effect of platinum on gold beads is not so marked as in the case of silver. The presence of 8 per cent of platinum seems to give a maximum amount of roughness and frosting to the silver bead. Buttons which contain a large amount of platinum flatten out when near the finishing point and refuse to drive, leaving a gray, mossy-appearing bead which sticks to the cupel. Such beads usually retain considerable lead. The only other metal of this group which gives a structure approaching that of platinum is palladium, the effect of which is dealt with later.

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[*] Notes on Assaying, 1907.

[†] Trans. Inst. Min. Met. **23**, pp. 163–173.

Iridium. — Iridium is but slightly soluble in silver or gold at the temperature of cupellation, and most of it sinks to the bottom of the bead, where it will appear as black specks. These specks are more readily distinguished after the bead has been rolled into a cornet for parting. On the surface, crystal boundaries are clearly visible, the roughness being, according to Lodge, of finer texture than that produced by platinum. Bannister notes that beads containing iridium were more nearly spherical than normal beads. Under the microscope, the crystal faces were strongly marked with lines, crossing one another after the manner of slip-bands. This strained appearance seemed to be caused by internal stresses.

Rhodium. — The presence of mere traces of rhodium may be detected. As little as 0.004 per cent in silver beads was found to cause a distinct crystallization, visible to the naked eye. The facets of the crystals give the appearance of a cut gem.

With 0.01 per cent of rhodium this appearance is more distinct. The presence of 0.03 per cent of rhodium in silver causes the bead to sprout and spit in spite of all precautions. With this and larger amounts, the surface of the bead assumes a bluish-gray color.

Ruthenium. — The presence of ruthenium is always indicated by a black, crystalline deposit firmly attached to the bead, usually on the bottom edge. This is distinctly visible to the naked eye even with as little as 0.004 per cent. Under the microscope the surface shows a distinct herringbone structure.

Osmium. — Osmium is partly oxidized and volatilized during cupellation. According to Lodge, if the osmium is not completely volatilized, small black spots appear on the silver bead when nearly finished. These flash off and on, but finally disappear when the bead brightens. Bannister found no specific indications of the presence of osmium in his tests.

Palladium. — According to Lodge, palladium gives the surface a raised and embossed appearance. According to Bannister, it is much like platinum. Fortunately its presence is indicated by a coloration of the solution in the parting operation.

Molten gold beads have a beautiful green color and when pure may be cooled considerably below the true freezing-point and still remain liquid. On solidification they "flash" as do silver beads and in solidifying they emit an apple-green light. Acnot crack, and they absorb nearly their own weight of litharge. The silver loss due to absorption is greater than for bone-ash.

J. W. Merritt* compared the results obtained with bone-ash and cement cupels and found two essential points of difference: 1st, Beads from a bone-ash cupel were well rounded and stood on a small base, while those from Portland cement cupels were flatter and stood on a base as wide as the broadest diameter of the bead; 2nd, The cement sticks tenaciously to the beads from Portland cement cupels but hardly at all to those from bone-ash cupels.

Mann and Clayton,† in a study of cupellation losses, found cement cupels to give very high silver losses even under the most favorable conditions. They also found it very hard to clean the bottom of the bead without danger of loss.

Cement cupels are very much cheaper and more durable than bone-ash, but on account of the above disadvantages should not be used for careful, uncorrected silver assays. One disadvantage of cement cupels for gold assays is the extra care which must be taken in cleaning the bead. This is necessary because, in parting, a considerable amount of the cement would remain insoluble as gelatinous silica and would be weighed as gold. Bone-ash, on the other hand, is practically entirely dissolved.

Magnesia cupels are very hard, which is an advantage in that they do not suffer so much breakage in shipment. They are always factory-made and are decidedly more expensive than bone-ash cupels, which may be home-made. Certain brands of magnesia cupels give an apparently lower loss of silver in cupeling than can be obtained with bone-ash cupels but it is a question how much of this is real and how much due to an increase in the amount of impurities retained in the silver beads.

Magnesia cupels behave quite differently from ordinary bone-ash cupels, and the assayer who is accustomed to bone-ash cupels will have to learn cupeling over again when he starts using those made of magnesite. This difference in behavior is due mainly to the different thermal properties of the two materials. Both the specific heat and the conductivity of magnesite are decidedly greater than those of bone-ash, so that with cupels of both kinds running side by side, the lead on the magnesia cupel is comparatively dull while that on bone-ash is very bright.

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* Min. and Sci. Press. **100**, p. 649.

† Technical Bulletin, Vol. II, No. 3, Missouri School of Mines, p. 33.