A TEXTBOOK OF
FIRE ASSAYING

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OF
FIRE ASSAYING

BY

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PREFACE TO THE THIRD EDITION

In the preparation of the third edition, the text has been thoroughly revised and very largely rewritten. Some sections have been removed but much new material has been added. The resulting fifteen per cent increase in the text has not made the book unwieldy since it has been completely reset in a slightly larger page size.

Among the new items are some hitherto unpublished results of research in the author's laboratory. These include a study of the influence of copper on the loss of silver in cupellation, revision of the rule governing cupellation losses, and new matter relating to the assay of black sands and similar material. Other additions which it is hoped will prove of value to the graduate deal with the assay of cyanide mill slime pulp and tailing. A new method for the determination of small amounts of platinum in cupellation beads, depending upon micro-titration, very much simplifies this difficult problem.

An entirely new chapter dealing with the special problems of plant or commercial assaying and entitled "Practical Assaying" has been added, although the viewpoint set forth in the preface to the first edition — "avoidance of cookbook style" — has been maintained. This was designed to be of help to the advanced student as well as to the graduate.

To both old and new friends and teachers who have offered constructive criticism, who have supplied information, or who have provided illustrations, the writer extends sincere thanks. He is again indebted to Mr. Rufus C. Reed for careful reading of much of the manuscript.

EDWARD E. BUGBEE

August, 1940

PREFACE TO THE FIRST EDITION

This book is the outgrowth of a set of mimeograph notes prepared in 1911 and intended for use in the course in fire assaying at the Massachusetts Institute of Technology. The mimeograph notes were succeeded by a book of 150 pages published by the author in 1915. The present volume has been revised and enlarged and is offered as a small contribution toward the scientific explanation of the ancient art of fire assaying. It contains some hitherto unpublished results of research, as well as considerable new data derived from a careful search of all the available literature, none of which have previously appeared in book form.

Although intended primarily as a college textbook, it is not entirely elementary in character and it is hoped that it will be found sufficiently complete and fundamental to be of service to the more mature student of the science. Every effort has been made to avoid the old " cook-book " method of presentation so common in books of this kind and to give the underlying scientific reasons for the many phenomena which occur, as well as the rationale of each process and detail of manipulation.

The object of instruction in fire assaying should not be merely the training of students to obtain results of a certain degree of precision by blindly following some set procedure, as is unfortunately too often the case. On the contrary, their attention should be focussed on the physical and chemical principles which govern the various operations. If they truly understand the reasons for the use of each of the reagents and for the various details of technique, they will not have to hunt over the pages of a receipt book when confronted by an ore of unfamiliar constitution, but will be able to make up their own assay charges and outline their own details of manipulation.

The author believes that a course in fire assaying is the logical place to introduce the study of metallurgy. The study of general metallurgy, which is abstract and uninteresting by itself, is made concrete and intensely interesting if the various processes of fire assaying are used to illustrate its principles. Most of the principles of metallurgy are utilized in one stage or another of the fire assay and if taught in this connection, the student's interest is awakened, the principles are understood and the study of this branch of metallurgy becomes a pleasure and not a burden. With this end in view, emphasis has been laid on those metallurgical principles which are of importance in fire assaying, for example, the thermochemistry of the metals and of their oxide and sulphide compounds, the nature and physical constants of slags, the characteristics of refractories and fuels, the principles of ore sampling, the behavior of metallic alloys on cooling and the chemical reactions of oxidation and reduction.

In the short time allowed for instruction in fire assaying in the crowded curricula of our technical schools, the time factor is an important consideration. With large classes and a limited number of laboratory instructors, the author's experience leads him to the conclusion that it is inadvisable to rely too much on verbal instruction in the classroom and laboratory, particularly during the first few weeks when so much that is entirely new has to be mastered before any real progress can be made. Explicit directions are given, therefore, for the first analyses; thus saving the student's time and conserving his efforts by making it possible for him to attack the subject intelligently and without any unnecessary delay. As the work progresses, less stress is laid upon detailed procedure and the student is placed more upon his own resources and encouraged to work out his own assay charges from his knowledge of fundamental principles, aided by a study of typical examples

The order of arrangement of laboratory work is the logical one beginning with cupellation, first in the qualitative and then in the quantitative way. The assay of lead bullion leads naturally to parting for the determination of the gold, after which either scorification or crucible assaying may be undertaken.

When available, the source of what may be termed " new information " has been acknowledged, but this has not always been possible and the author trusts he may be pardoned for any serious omissions in this particular. Although it is hoped that in the present book all of the errors which occurred in the author's edition have been eliminated, some new ones may have crept in and the author will esteem it a favor to have these called to his attention. He would also be pleased to receive any suggestions and criticisms which might be embodied in a subsequent edition, if such should be required.

To the many friends who have supplied material or helped in other ways the writer wishes to express his gratitude. The officials of the Anaconda Copper Mining Company and of the United States Smelting, Refining and Mining Company have been especially helpful in this way. The author is particularly indebted to Mr. Rufus C. Reed for many helpful suggestions and for reading the type script. He wishes also to express his appreciation of the courtesy of the Allis-Chalmers Mfg. Co., the Braun Corporation, the Denver Fire Clay Co., the Thompson Balance Co., and the United States Bureau of Mines for furnishing photographs and electrotypes.

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A TEXTBOOK OF FIRE ASSAYING

CHAPTER I

ASSAY REAGENTS AND FUSION PRODUCTS

Assaying is 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 a branch of quantitative chemical analysis in which metals are determined in ores and metallurgical products with the aid of heat and dry reagents. The method is applied today principally to the determination of silver, gold, and some members of the platinum group although lead, tin, copper, and mercury in ores are also in some instances determined by fire-assay methods.

The fire assay for silver and gold depends mainly upon:

1. The very great degree of solubility of these metals in molten metallic lead and their almost complete insolubility in slags of suitable composition.
2. The decided difference in specific gravity between the two liquids, lead and slag, which permits the completion of the separation of the precious metal-bearing alloy from the slag.
3. The fact that lead may be practically completely removed from the precious metals by a carefully controlled oxidizing fusion, involving differential filtration, in a porous vessel known as a cupel.
4. The ready solubility of silver and the complete insolubility of gold in dilute nitric acid.

The slags and cupels are usually discarded, but in certain determinations where very high precision is required they are saved and re-assayed to recover the small fraction of precious metals which they contain. The assay beads resulting from the cupellation process are weighed and then treated with nitric acid to remove the silver. The residual gold is weighed, and, by subtracting its weight from that of the corresponding bead, the silver is determined by difference.

No description of the methods for the determination of the base metals is attempted in this work. With this explanation and a reference to the preceding paragraphs it may be seen that precious-metal assays which depend solely upon dry chemistry must be for silver alone or for gold in the exceedingly rare instance of its occurrence unaccompanied by silver. Actually, practically all gold determinations involve the wet operation of parting. When the assay includes the determinations of members of the platinum group a more involved wet process follows the fusion and cupellation.

In the assay of ores and metallurgical products which contain considerable amounts of certain difficultly oxidizable metallic impurities for which metallic lead has considerable affinity, better results are often obtained by first treating the material with acids to effect a preliminary separation of the impurities. The residue is later treated by the regular fire procedure. Various other combinations of dry and wet chemistry are employed in the determination of gold, silver, and the metals of the platinum group, and such of these as are considered of importance are described.

The advantage of the fire assay over wet methods of analysis of ores for gold and silver and in some instances for members of the platinum group is dependent primarily on the cheap and quick elimination of practically all of the associated mineral substances in a simple crucible fusion requiring less than one hour and using a substantial quantity of ore. The identity and purity of the metals obtained can be verified by ocular examination and further confirmed by appropriate chemical tests. The chemical tests are seldom necessary. On a quantity basis, gold and silver ore assays cost but a fraction of a dollar per sample, and results may be had within three hours of receipt of the sample. To obtain similar precision by wet chemical methods would require the expenditure of some tens of dollars per sample and at least two or three days' time.

Strictly speaking, an **ore** is a natural mineral substance from which a metal, alloy, or metallic compound may be extracted at a profit. The term is loosely used to include almost any inorganic substance that occurs in nature as, for example, pyrite, an ore of sulphur. From the metallurgical standpoint ores consist of two parts, the metalliferous or valuable portion, and the " gangue " or valueless portion. According to their chemical composition the gangue minerals may be acidic, basic, or a combination of the two. Silica is an acid gangue mineral; lime, magnesia, and the lower oxides of iron, manganese, sodium, and potassium are some of the common basic constituents of ores. A complete quantitative analysis of almost any gold or silver ore would list some twelve or fifteen constituents, and the ore would be considered to be acidic, basic, or perhaps neutral according to the preponderance of one or the other group of slag-forming constituents. If the acid and basic constituents occurred in the right proportion to form a slag of the desired silicate degree the ore would be considered to be self-fluxing.

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.

Acids and Bases. The acids and bases of fire chemistry differ from the more familiar acids and bases of wet chemistry in that they are anhydrous and most of them are insoluble in water; consequently they do not respond to the ordinary tests familiar to the chemist. How then may we distinguish them? Indicators of the wet chemist are of no avail, a study of their behavior during electrolysis is ruled out, and no one has to be told that silica, our strongest acid, does not taste sour. The common chemical definition of an acid does not fit, since the acids of fire chemistry contain no hydrogen.

One property which does seem to hold, in part at least, is that acids react with bases to form salts. The reaction involved in neutralizing sodium carbonate with sulphuric acid:

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O$$

has a close analogy in the reaction taking place when sodium carbonate is fused with silica:

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2,$$

the only difference being that no water is evolved. The silica is just as truly an acid in its behavior as is the sulphuric acid. The products are almost identical; carbon dioxide is evolved and escapes as a gas in both reactions. The resulting compounds are very similar, the sodium carbonate being known as a salt, the sodium silicate as a slag. By slow cooling we may persuade the latter to crystallize and then we recognize that it too is a salt. The best we can say about chemical action at high temperatures is that the substance which acts as a base in aqueous solution tends to act as a base at high temperatures and similarly the acid in aqueous solution acts as an acid at high temperatures.

The bases of fire chemistry are all fundamentally oxides of the metallic elements, although certain reagents such as sodium carbonate and some gangue minerals as calcite containing both basic and acid constituents are classed as bases since when they are heated the acid radical CO_2 is driven off.

The acids of fire chemistry may be either oxides of metals or of non-metallic elements. By far the most important of these is silica, SiO_2; then come B_2O_3, P_2O_5, As_2O_5, Sb_2O_5, WO_3, V_2O_3, SO_3, and TiO_2. Only the non-volatile or difficultly volatile acid anhydrides are of importance in fire chemistry.

The oxides of aluminum, zinc, lead, bismuth, tin, and a number of other heavy metals are amphoteric, that is, they possess the properties of both acids and bases. For example, we have the mineral kaolinite $Al_2O_3 \cdot 2SiO_2$, in which alumina is certainly a base, and again spinel, $MgO \cdot Al_2O_3$, in which alumina plays the part of an acid.

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, whereas 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 a substance 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 1750°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 bisilicate, corresponding to the formula $CaSiO_3$, which fuses at 1512°C. A second compound, corresponding to the formula Ca_2SiO_4, the calcium singulosilicate, melts at 2080°C. A

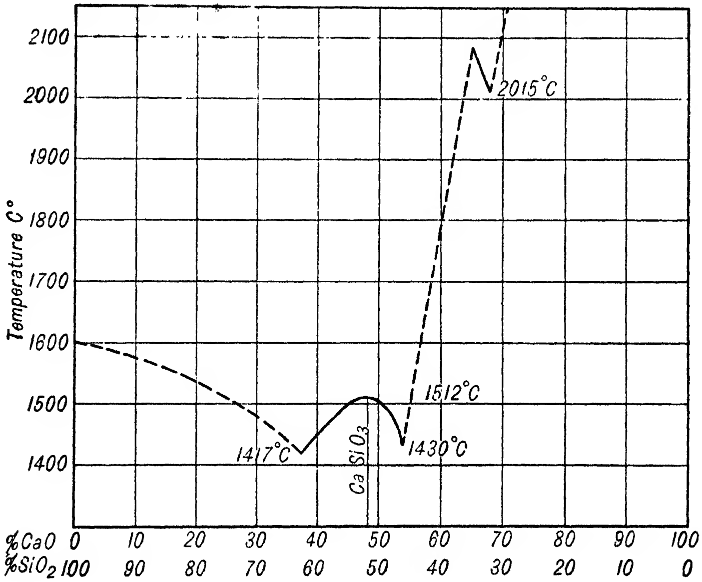

FIG. 1. Freezing-point curve of lime-silica series.

cursory glance at this curve will be sufficient to suggest the desirability of trying to make approximately a bisilicate slag when assaying ores which contain considerable lime.

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, $Na_2B_4O_7 \cdot 10H_2O$, 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. In small amounts, however, it lowers the temperature of slag formation and promotes a quiet and orderly fusion.

Borax is often used as a cover for crucible fusions. When properly used it is believed to prevent the mechanical loss of fine ore which frequently results when a large volume of gas escapes rapidly at a temperature below that of incipient fusion. Borax, containing, as it does, 47 per cent of water, loses approximately half of its weight by fusion, and consequently when used as an acid flux, approximately twice as much borax as borax glass is required.

Borax Glass, $Na_2B_4O_7$, is made by fusing borax to drive off its water of crystallization and then cooling and crushing the solidified glassy residue. It is usually purchased in the powdered form and should be kept in air-tight containers, as the fine material takes on moisture from the air and tends to cake. Under ordinary conditions it behaves like a true glass, having no definite freezing or melting point. If, however, it is subjected to rapid vibration when cooling it may be induced to solidify in the crystalline form at a definite temperature. This crystallized borax glass melts at 742°C. If not subjected to vibration it remains a viscous fluid even below a visible red. Finely divided amorphous borax glass begins to sinter at about 500°C. It is extremely viscous when melted, even when heated well above its melting temperature.

Its rational formula, $Na_2O \cdot 2B_2O_3$, indicates an excess of acid, and experiment proves this to be present. At a red heat it becomes a strong acid and dissolves and fluxes practically all the metallic oxides, both acid and basic. It is one of the best fluxes for alumina.

Five borates of alkalies and alkaline earths are recognized, the chemical classification being as follows:

TABLE I
CLASSIFICATION OF BORATES

Name	Oxygen Ratio Acid to Base	Formula R = Bivalent Base
Orthoborate	1 to 1	$3RO \cdot B_2O_3$
Pyroborate	1½ to 1	$2RO \cdot B_2O_3$
Sesquiborate	2 to 1	$3RO \cdot 2B_2O_3$
Metaborate	3 to 1	$RO \cdot B_2O_3$
Biborate	6 to 1	$RO \cdot 2B_2O_3$

According to the metallurgical classification, *i.e.*, the ratio of oxygen in acid to oxygen in base, the first of these would be neutral and the others acid. The writer's experiments with alkaline borates show that the metaborate is decidedly viscous when fused but that at the same time it shows a strong tendency to crystallize during cooling. The pyroborate, when fused, was decidedly fluid, being comparable to the subsilicate of soda. It would seem proper, therefore, to regard the sesquiborate as the neutral one when considered from this standpoint.

Fusing as it does at a low temperature, borax helps to facilitate the slagging of the ore, and in the hydrous or anhydrous condition it is used in almost every crucible assay. In general, it may be said to lower very appreciably the fusing point of all slags, and this, in addition to the fact that it is such an excellent solvent for the metallic oxides, accounts for its almost universal use in fire assaying. The borates of lead and the alkalies are more viscous than the corresponding silicates. This viscous effect persists far below the apparent solidification point unless the slag is decidedly basic.

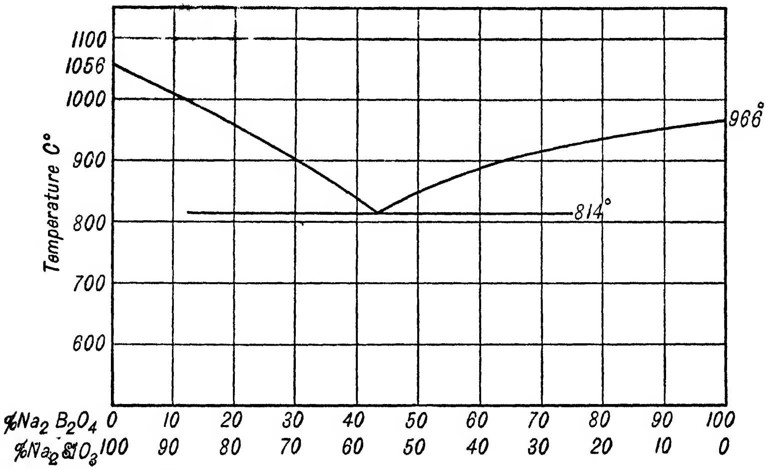

FIG. 2. Freezing-point curve of sodium metaborate-sodium bisilicate series.

If too much borax is used in the assay of siliceous ores there 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 metaborate-sodium bisilicate series, is shown in Fig. 2. The melting point of sodium bisilicate 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 decomposed, however, 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 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.

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 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 mole of SiO_2 for each mole of Na_2O must be added. Combinations less acid than the bisilicate retain CO_2 indefinitely. The bisilicate melts at about 1018°C.

The fluxing effect of sodium carbonate is shown in the accompanying freezing-point curve of the calcium bisilicate-sodium bisilicate series.

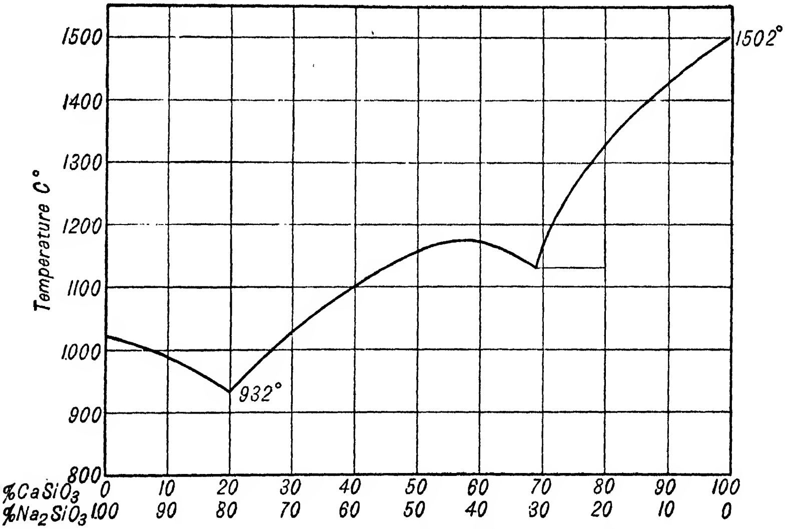

FIG. 3. Freezing-point curve of calcium bisilicate sodium-bisilicate series.

Between the melting point of sodium bisilicate, 1018°C., and that of calcium bisilicate, 1502°C., is 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 moles of Na_2CO_3 for each mole of $CaCO_3$, or roughly 60 grams of Na_2CO_3 for $\frac{1}{2}$ assay ton of pure $CaCO_3$, together with sufficient silica for a bisilicate. The addition of borax will materially reduce the melting temperature of the mixture.

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* *J. Am. Chem. Soc.* **35**, 1693–1727.

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 moles of SiO_2 to 1 mole 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:

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

Like 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.

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

The freezing-point curve of part of the $PbO\text{-}SiO_2$ system is shown in Fig. 4. The melting points of compounds shown do not agree exactly with those of Mostowitch. Compared with sodium bisilicate, which melts at 1018°, the corresponding lead silicate is decidedly more fusible. This explains why it is customary to provide for the presence of litharge in almost all assay slags.

Litharge has such a strong affinity for silica that, if the crucible charge does not contain enough silica, the acid material of the crucible itself will be attacked. If left long enough, a hole may be eaten through it.

Litharge readily gives up its oxygen if heated with carbon, hydrogen, sulphur, metallic sulphides, iron, etc. It thus acts as an oxidizing and, in the presence of sulphur, as a desulphurizing agent. Examples of these reactions are shown below:

$2PbO + C = CO_2 + 2Pb$ (oxidizing),
$3PbO + ZnS = ZnO + SO_2 + 3Pb$ (desulphurizing and oxidizing).

The liberated lead is then available for the collection of the gold and silver.

The reaction with carbon begins below 500°C., and is rapid at 600°. Reduction by CO starts below 200°.

Litharge begins to volatilize at 800°C., which is considerably below its melting point.

Lead silicates do not readily give up their lead to carbonaceous and sulphurous reducing agents. The higher the proportion of silica, the less readily is the silicate broken up. In order that all the lead may be extracted it must first be set free by the use of a stronger basic flux. Hofman* says, " Metallic iron decomposes all fusible lead silicates at a bright red heat, provided enough is added to form a singulosilicate."

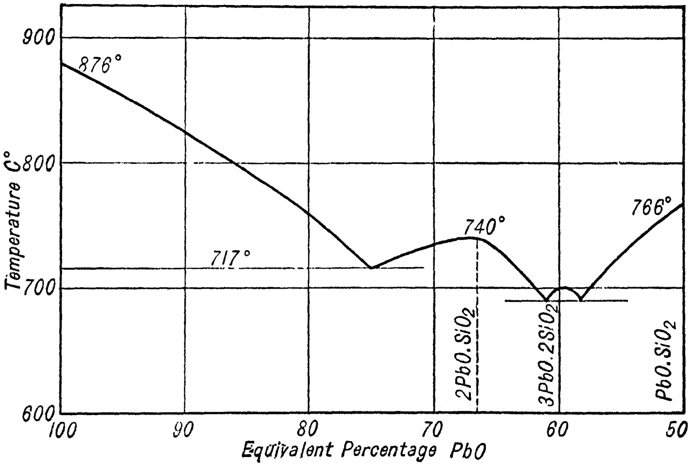

Fig. 4. Freezing-point curve — litharge-silica series.

Ordinarily commercial litharge contains a small amount of silver, varying from 0.2 ounce to 1.0 ounce or more per ton. A practically silver-free variety is made from Missouri lead by giving a zinc treatment, as for the Parkes process, and then cupeling. It is never safe to assume, however, that litharge is silver-free until it has been proved so by assay.

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* "Metallurgy of Lead," p. 38, 1918.

Each new lot received should therefore be carefully mixed to make it uniform, and assayed.

Assay litharge should be free from bismuth, as this will be reduced during the fusion and, owing to its slow rate of oxidation, will concentrate in the lead during cupellation, finally giving irregular silver results.

Lead in the granulated form, test lead, is used in the scorification assay as a collector of the precious metals and as a flux. When oxidized by the air of the muffle it becomes a basic flux. Ordinary test lead may contain more or less silver, and every new lot should be assayed before being used.

Test lead may be made by pouring molten lead, just above its freezing point, into a wooden box and shaking it violently in a horizontal direction just as it becomes pasty and continuing until it becomes solid. The fine material is sifted out; the coarse is remelted.

Lead in the form of foil is used in the fire assay of gold, silver, and lead bullion. Lead melts at 326°C. Like litharge it should be free from bismuth.

Argol is a reducing agent and basic flux. It is a crude bitartrate of potassium obtained from wine barrels, and is one of the best reducing agents.

Cream of tartar, $KHC_4H_4O_6$, is refined bitartrate of potassium. Being free from sulphur it is used as a reducing agent in the copper assay. Both argol and cream of tartar break up on heating with silica and excess litharge as follows:

$$2KHC_4H_4O_6 + \text{heat} = K_2O + 5H_2O + 6CO + 2C.$$

The K_2O thus liberated is available as a flux.

Flour, sugar, starch, etc., are all reducing agents because of the carbon that they contain. Flour is very commonly used in flux mixtures and is satisfactory in most respects.

Charcoal is usually accorded first place as a reducing agent by most of the older authorities on fire assaying. For ordinary use it should be very finely pulverized to accord with assay theory. Charcoal of good quality contains about 93 per cent carbon, 3 per cent ash, and the balance oxygen and hydrogen. It has the highest reducing effect per gram of any reducing agent, and this is somewhat of a disadvantage mainly because in excess litharge charges it is difficult to scoop a sufficiently exact amount. In certain instances carbon is to be preferred to argol, flour, or other organic reducing agents. These latter all undergo destructive distillation at a low temperature, liberating carbon monoxide and other reducing gases all of which react with and reduce litharge at about 300°C. Pure carbon, on the other hand, does not become an active reducing agent until a temperature of 500° to 600°C. has been reached, at which time the average charge will have begun to melt. If we can prevent the reduction of the litharge by reagents during the earlier part of the crucible assay it is available for other purposes, as for example the decomposition of sulphides. Later the carbon of charcoal may be called upon to decompose an additional amount of litharge or to reduce certain oxides from a higher to a lower state.

Sulphur in powdered form is occasionally used as a means of holding copper in the slag both in the crucible assay of copper bullion and in the assay of completely oxidized ores, either for their precious-metal or their lead content. It acts as a reducing agent for litharge, and hence the quantity used must be carefully regulated.

Iron is a desulphurizing and reducing agent. When it is heated with the sulphides of lead, silver, mercury, bismuth, and antimony the sulphides are decomposed, yielding a more or less pure metal and iron sulphide. Copper, nickel, and cobalt sulphides are partly reduced by iron, as would be expected from a study of their heats of formation.

Iron also reduces most of these metals and some others from their oxide combinations, as for example:

$$PbO + Fe = Pb + FeO.$$

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

$$xPbO{\cdot}SiO_2 + xFe = xFeO{\cdot}SiO_2 + xPb.$$

It should therefore always be used in the lead assay.

It is used in the form of spikes, hoop iron, 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 400°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.

Silver in some form is added to the crucible charge in gold-ore assaying and also when platinum is being sought. It serves to reduce the loss of gold during cupellation and is essential in the subsequent parting operation. Some authorities believe that it is of some benefit as a collector in the crucible or scorification fusion.

In some mine assay office practice a definite quantity of silver chloride or silver nitrate is added to the assay flux mixture. Silver in the form of foil is used in other laboratories, and some even run silver nitrate solution from a buret into each crucible after the charge has been stirred. Silver discs of definite and substantial weight are used in most government mints and assay offices.

As silver foil is likely to carry more or less gold, it is important to test all new lots of this material. For details of such tests see page 133.

Red lead, Pb_3O_4, is occasionally recommended as a substitute for litharge as a source both of metallic lead and of PbO, to which form it is converted on heating. The commercial grade of red lead, however, is somewhat more expensive than the corresponding grade of litharge. Since when heated it parts with one-fourth of its oxygen, it has a slight oxidizing effect, and this is occasionally of advantage in that with it replacing litharge the use of niter may sometimes be avoided. When used in connection with sulphide ores the oxygen from 60 grams of red lead should prevent the reduction of 18 grams of lead.

Hematite, Fe_2O_3, is occasionally used as a combined basic flux and oxidizing agent as a substitute for part of the litharge. The most logical application of this reagent would be in the assay of class 1 siliceous ores of moderate reducing power, that is, ores which yield lead buttons somewhat larger than necessary. Each gram of pure hematite added to a really acid non-sulphide charge should prevent the reduction of approximately 1.3 grams of lead.

Lime in some form, caustic (CaO), hydroxide (CaOH), or carbonate ($CaCO_3$), is recommended as a flux by some assayers for ores which contain little or none of this substance. It is basic in character, and cheap, and it tends to lower the density of the slag. To a certain extent it aids in overcoming the very annoying sticking of the lead button to the slag. It is probable that in very acid assay slags the addition of lime may increase fluidity, and under these circumstances it may properly be termed a flux.

The individual assayer's ideas as to whether the additional agitation of the melt by the carbon dioxide evolved from calcite at about 900°C. is beneficial or not will determine whether this or some other form of lime should be used. It is still an open question.

Fluorspar, CaF_2, is occasionally used as a flux in fire assaying since like borax it increases the fluidity of almost any charge. How it does this is somewhat of a mystery since its melting point, 1380°C., is far above the normal fire-assay fusion temperature. Most authorities state that it is inert and does not enter to any extent into combination with the other constituents of the charge.

When fluorspar is used as a flux in the assay of cupels according to a formula developed in the writer's laboratory the crucibles show distinct evidence of attack in the form of a ring just above the level occupied by the molten lead. This fact tends both to confirm and refute the last-mentioned idea as to its chemical behavior since if it combined readily with the other constituents of the charge the area of attack should be more general. As it is, the type of slag made in this work contains no litharge and its specific gravity is less than that of fluorspar, 3.2. If fluorspar does not combine with the other slag-forming constituents and is heavier than this particular type of slag, it is logical to find it concentrated in a layer just above the lead. The fact that the crucible is attacked at this level suggests that fluorspar is not inactive as most writers would have us believe. It is possible that in the presence of alkaline carbonate, which may assist in some way, the following reaction is of importance:

$$2CaF_2 + 2SiO_2 = SiF_4 + Ca_2SiO_4,$$

in which both components of the fluorite attack the silica of the crucible.

Other authorities* confirm the fact that calcium fluoride exerts a marked deleterious effect on assay crucibles. Rand assayers, particu-

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* Watson, Toombs, White, and Martyn, *Chem. Met. Mining Soc. S. Africa*, **18,** 220, 222, 234; **19,** 19.

larly, have tried to substitute fluorspar for borax for reasons of economy, and since it costs only a small fraction as much as borax glass this is natural. When both borax and fluorspar are used in the same charge, it is reported to cause the charge to froth up and even to boil over. H. A. White believes that these two fluxes should not both be used in the same fusion. He calls attention to the probability of the formation of boron fluoride from the reaction of these two substances. The reaction is as follows:

$$Na_2B_4O_7 + 6CaF_2 = Na_2O + 6CaO + 4BF.$$

Boron fluoride is a gas and in the method of melting formerly used in Rand assay offices would naturally cause difficulty due to foaming. Martyn reports that by the use of fluorspar he can cut down the quantity of flux by about 10 per cent which is a worthwhile saving in quantity assay work.

Fluorspar has been used in the writer's laboratory for a long time, both in experimental work and in routine assaying. It is of material benefit in facilitating the separation of lead button and slag, and it very definitely increases the fluidity of the slag. In experimental work, where either pure silica or silica and kaolinite were used in place of ore, all the lead buttons exhibited a dull blue-gray surface when fluorspar was added in contrast with the bright metallic lead surface obtained in its absence.

Experimental fusions, made with 27.5 grams silica, 30 grams sodium carbonate, 60 grams litharge, 10 and 15 grams respectively of fluorspar and reducing agent sufficient for a 30-gram lead button yielding slags of approximate bisilicate ratio if the lime of the fluorspar is disregarded, resulted in slags which were somewhat milky in appearance when cold. The same charges with the addition of 15 grams of boric acid invariably yielded clear, glassy slags. In the absence of the boric acid radical the limit of solid solubility of fluorspar in the above type of slag was somewhere between 5 and 10 grams since the fusion carrying 5 grams of fluorspar yielded a clear glassy slag. Obviously boric anhydride increased the solid solubility of the fluorspar.

The fact that a slag is milky or white when solid is not evidence that some constituent is insoluble in the liquid state since it may have crystallized out during solidification. A case in point is the assay of cupels according to the procedure recommended in a later chapter. For a normal cupel this charge contains 30 grams of bone ash and 15 grams of fluorspar. The resulting slag is a white enamel-like glass when cold. One well-known authority believes that neither bone ash nor fluorspar combines with the fluxes to form a slag but simply remains suspended in the fusion. This does not appear reasonable since the lead collects into a button without difficulty and the slag pours perfectly, and it is hard to conceive how this could be with about 45 per cent of the nonmetallic components of the melt in solid suspension. Experience proves that the presence of a very much smaller amount of a truly solid suspension in an otherwise satisfactory type of slag results in a slag literally full of lead shot which refuse to collect and, in fact, in considerable part, do not even leave the crucible.

Cryolite, $AlNa_3F_6$, is a powerful flux, commonly used in the manufacture of enamels and occasionally in the melting of bullion. It melts at 995°C. and in a two-component melt will dissolve up to 25 per cent

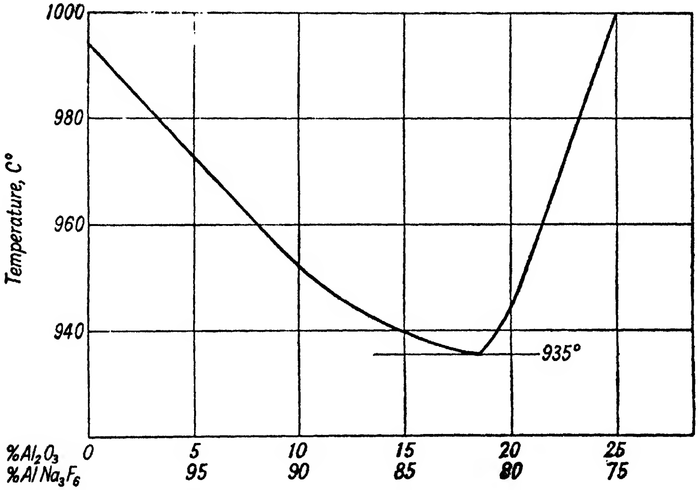

FIG. 5. Freezing-point curve of cryolite-alumina series, partial.

of alumina at temperatures below 1000°C., as a glance at the freezing-point curve, Fig. 5, will indicate. With the addition of sodium oxide, lead oxide, and boric oxide in proper proportions much lower melting temperatures are attained.

Boric acid, H_3BO_3, may be used as a source of boric anhydride in place of borax or borax-glass if desired. On heating it loses water, and in an assay fusion it may be considered to break up as follows:

$$2H_3BO_3 = B_2O_3 + 3H_2O.$$

One gram of boric acid contains more than 1.5 times as much of the acid radical B_2O_3 as does ordinary borax and about 0.8 times as much as 1 gram of fused borax. Boric acid is supplied in crystals, powder, and fused. It is readily obtained in a state of purity and has the advantage of being entirely acidic in character, whereas borax is an acid salt. This is somewhat of an advantage in research connected with crucible fusions since it simplifies computations. In assay fusions containing boric acid and soda the same desirable viscous conditions occur as when equivalent quantities of borax and soda are used.

TABLE II

ASSAY REAGENTS

Name	Formula	Properties in order of their importance
Silica	SiO_2	Acid flux
Glass	$xNa_2O \cdot yCaO \cdot zSiO_2$	Acid flux
Borax	$Na_2B_4O_7 \cdot 10H_2O$	Acid flux
Borax-glass	$Na_2B_4O_7$	Acid flux
Boric acid	H_3BO_3	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
Red lead	Pb_3O_4	Basic flux, oxidizing
Lime	CaO	Basic flux
Hematite	Fe_2O_3	Basic flux, oxidizing
Potassium nitrate	KNO_3	Oxidizing, desulphurizing
Argol	$KHC_4H_4O_6 + C$	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

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 634.5°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.

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. With salt, this third product is almost entirely sodium chloride; with niter, 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 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 and borates of the metallic oxides contained in the ore and fluxes used. Slags in the molten state are usually solutions, but in rare instances they may be chemical compounds. In the solid state they are usually either solid solutions or eutectic mixtures; occasionally they may be chemical compounds.

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 threads in pouring. If too basic, it will be lumpy and break off short in pouring. When cold, the neutral or acid slag is glassy; the basic one is dull and stony-looking.

COVER LAYER. Although under some circumstances fused salts of various kinds are referred to as slags, it is preferable in fire assaying to consider them under a separate category. For want of a better name, sodium chloride which some assayers still use as a cover and the sulphates of the alkalies which are formed in some of the reactions of the crucible assay, since they tend to float on top of the slag, may be termed the cover layer.

With the ordinary type of assay slag which contains a fair proportion of litharge there is a sharp plane of division between fused salts and slag, which fact taken in connection with the almost white color of the solid cover layer indicates an absence of solubility of slag-forming constituents in the fused salts. With slags containing little or no litharge the conditions are quite different. Not only is there no sharp plane of division between salt layer and slag, but the salt layer is likely to be highly colored; often it is nearly black. The inference is that there is a considerable degree of mutual solubility between the alkaline borosilicate slags and the fused salts of the alkalies. This behavior is explained by the fact that the unsaturated alkaline borosilicates as well as the fused salts are good solvents for both alkaline and base metal sulphides. Unsaturated litharge-bearing slags, on the other hand, react to decompose the sulphides.

Attention is called to the reaction between metallic iron and fused sulphates to be found in the directions for the assay of slags.

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 it 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; 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

FURNACES AND FURNACE-ROOM SUPPLIES

Furnaces for assaying may be divided into the two following classes:

1. Crucible or Pot Furnaces. These are furnaces used solely for melting purposes, in which the crucible is in direct contact with the fuel or flame and the contents, therefore, more or less subject to the action of the products of combustion.

Pot furnaces have the advantage of size, so that in dealing with low-grade ores, for instance, a larger charge and crucible may be used than in muffle furnaces of the ordinary size. A higher temperature may be obtained in pot furnaces than in muffles, and this, occasionally, is an advantage of the pot furnace.

2. Muffle Furnaces. These are furnaces in which the charge to be heated is in a chamber, the muffle, apart from the fuel or products of combustion. The muffle is a semi-cylindrical receptacle of fire clay or other refractory material, set horizontally and so arranged that the fuel or products of combustion pass around and under it. Thus, the material to be heated is entirely separated from the products of combustion.

As muffle furnaces may be used for melting purposes as well as for scorification and cupellation, many assayers in America use this type of furnace exclusively, especially in connection with soft-coal fuel. The advantages of muffle furnaces for melting are the greater ease and saving of time in charging and pouring, the better control of temperature, and the better distribution of heat for melting purposes. Crucibles also seem to stand more heats in a muffle furnace than they will in pot furnaces, probably on account of the slower and more uniform heating.

The furnaces themselves are made of fire brick or fire clay tile and may be set in an iron jacket or surrounded by common red brick. Fire brick is best laid in a mortar made from a mixture of 2 parts ground fire brick and 1 part fire clay. Sometimes a small amount of Portland cement is added. In any event the brick and tiles should be thoroughly wet before the mortar is applied. Finally, as little mortar as possible should be used, since the bricks are much harder than the solidified mortar.

SOURCES OF HEAT

Assay furnaces may be heated by electricity or by the combustion of practically any kind of gaseous, liquid, or solid fuel. The choice of method of heating is governed principally by the availability and cost of the different sources of heat energy.

Electricity is the cleanest source of heat energy for assay furnaces. The absence of noise is in its favor, and with properly designed equipment the heat control is satisfactory. The original installation cost is higher than for any of the many types of furnaces dependent on the direct combustion of fuel, but when electric power is cheap the initial expense may be justified by the several advantages obtained in operation. It is not fool-proof and has to be operated with care if heating-element replacement costs are to be held to a low figure.

Gas is the most easily controlled, most efficient in combustion, and, except in the case of a natural supply, the most expensive fuel.

Oil is nearly as clean and as convenient to use as gas, the efficiency of combustion is high, and in localities near the oil fields it may be very cheaply obtained. The calorific power of the hydrocarbon fuel oils is high, about 50 per cent more than the best coals, which makes them particularly suited for use in isolated localities where freight charges are high. Gasoline is forced under pressure through a heated burner where it is vaporized, and the gas injected into the furnace carries with it a sufficient supply of air for combustion. Fuel oil requires steam or air under pressure to aid in atomizing the oil, preliminary to proper combustion. Gasoline and kerosene both have a heating value of about 21,000 B.t.u. per pound; crude petroleum, about 18,500.

Solid fuels are usually the cheapest and are therefore more extensively used than any of the others. In isolated districts where coal or coke is not available, wood is occasionally burned as fuel in assay furnaces. For this purpose the wood should be felled in winter and thoroughly air-dried for at least six months or longer, according to the climate. The air-dried wood still retains from 20 to 25 per cent of water and in this condition has a heating value of about 6000 B.t.u. per pound. Charcoal is seldom used in this country for assay purposes on account of the abundance of other fuels.

Bituminous coal is the most satisfactory solid fuel for muffle-furnace firing and coke for pot furnaces. Good soft coal has a calorific power of about 14,500 B.t.u. per pound. It should be low in sulphur, and the ash must not be too readily fusible. Coke should be hard, strong, and low in sulphur, and the ash should be infusible at the temperature of the furnace. That is to say, it should be high in silica and alumina and low in iron, calcium, magnesium, and the alkalies, to prevent clinkering of the walls of the furnace.

Gas and Oil vs. Solid Fuel. Gaseous and liquid fuels have many advantages over solid fuels for assay purposes. Some of these advantages are:

1. The fire is kindled in an instant, and the furnace may be quickly heated to the desired temperature for work.

2. The temperature is readily controlled and may be quickly varied to suit the requirements of the work.

3. A high efficiency of combustion is possible in properly designed furnaces, and as soon as the work is completed the fuel supply may be shut off and fuel consumption stopped.

4. The avoidance of labor in firing gives the assayer more time for other duties.

5. The cleanliness in operation, due to absence of solid fuel and ash, is obviously a great advantage in any analytical laboratory.

On account of the expense, however, coal is much more generally used than either oil or gas. It is easy to make a comparison of the costs of any of the fuels by considering the heat units. For instance, with soft coal at $10 per ton and gasoline at 25 cents per gallon, 1 cent invested in soft coal may be said to buy $2 \times 14{,}500 = 29{,}000$ B.t.u. and the same amount invested in gasoline to buy approximately $\frac{1}{25} \times 6.0 \times 21{,}000 = 5040$ B.t.u. That is to say, the gasoline is more than six times as expensive as the coal on the basis of heat units, and for steady running this may be taken to be approximately correct. However, for a small amount of work, a gasoline furnace may be cheaper to run even with the cost of fuel as above assumed, for the small furnace is quickly heated and as soon as the work is completed the oil supply may be shut off and the expense stopped, while a coal furnace takes much longer to heat and then must be allowed to burn out after the work is completed.

Coal Furnaces. This type of furnace is used in many of the large custom and smelter assay offices in this country.

The furnace may be built either with a tile or fire-brick lining. The tile lining is more easily set up, but whether or not it is as durable as a properly constructed fire-brick lining is open to question. The outside of the furnace is usually laid up with common hard-burned red brick. If the furnace is to be lined with fire brick several rows of " headers " should be left to hold the lining securely in place. The furnace is held together with angle irons, stays, and tie rods.

A great improvement in the construction of these furnaces may be made by introducing a single course of insulating brick between the fire brick and the red brick. The use of these brick permits a quicker heating of the furnace, affords a considerable economy in fuel, and provides a much more comfortable working place, because of a large reduction in the heat losses due to radiation.

In Figs. 6, 7, and 8 are shown front elevation and longitudinal and transverse sections of twin double-muffle soft-coal furnaces using NN muffles. In Fig. 6 is also shown an iron-topped pouring table with slagging anvils made of sections of steel rails. The operator stands between the table and the furnace when working at the furnace, and on the other side of the table when hammering out his lead buttons. Insulating brick is used in the construction of these furnaces, and the system of bonding the wall with " headers " is shown in the sections.

FIG. 6. Twin double-muffle soft-coal furnace.

In the furnace, as ordinarily constructed, the muffles are supported by " jamb " bricks projecting from the sides. When these are used, it is well to leave a hole or loose brick on the outside of the furnace, to facilitate the removal of the stubs when these bricks become broken off and the ends slagged in. Fulton recommends using long tiles which meet in the center, thus giving better support for the muffle. He claims a prolonged life for the muffle with this arrangement. The writer has found the Scotch Gartcraig brick to outlast 3 or 4 best American fire

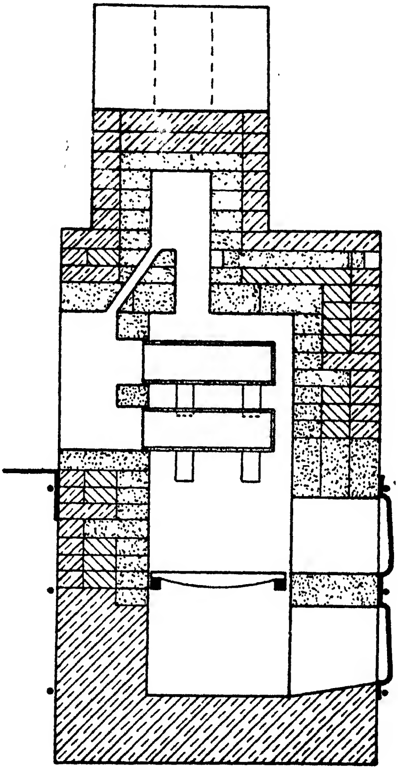

Fig. 7. Longitudinal section of double-muffle soft-coal furnace.

brick for muffle supports. Another method of supporting muffles in furnaces of this type is by means of iron pipes or castings which extend directly across the furnace and through which cooling water is circulated.

These furnaces occupy a floor space of approximately 3½ by 4 feet. They are built in a variety of sizes; those taking NN, QQ, and UU muffles are the sizes most commonly used. The NN muffle is 10¼ by 19 by 6½ inches outside, the QQ is 12½ by 19 by 7¾ and the UU is 14 by 19 by 7½ inches outside.

Each NN muffle will hold twelve 20-gram, or eight 30-gram crucibles, allowing in each case for a row of empty crucibles in front to act as warmers, while the QQ muffle will hold fifteen 20-gram, or twelve 30-gram crucibles, also allowing for a row of empty crucibles in front.

The furnaces are best arranged to be fired from the rear, although they may be arranged to be fired from the front or sides. The flue makes off from near the front of the furnace, thus tending to heat the muffle uniformly throughout its entire length. It should be from one-sixth to one-eighth the grate area.

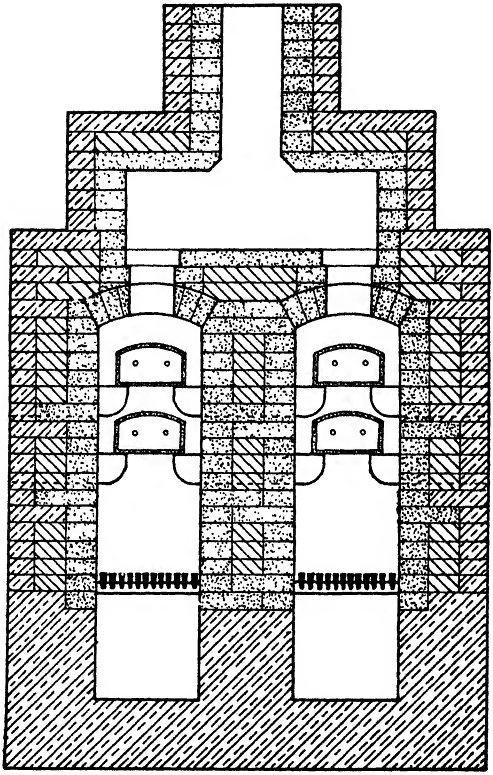

Fig. 8. Transverse section of double-muffle soft-coal furnace.

The stack for one of the furnaces will need to be at least 20 feet high and possibly higher, depending largely on the kind of coal. It should not be built directly on the furnace but may be placed directly over the furnace if supported by arches and cast-iron columns, or it may be put to one side of the furnace and extend down to the ground. When the stack is supported independently of the furnace it allows the furnace to expand and contract with less danger of cracking and also permits of tearing down and rebuilding the furnace without interfering with the stack.

With long-flame coal these furnaces are best fired with a rather thin bed of fuel, say 6 inches. The sequence of firing consists, first, of running the slice bar along the entire length of the grate in one or two places and lifting up the fire to break up any large cakes and thus allow free passage of air through the fire; second, of pushing the well-coked coal forward with the hoe; and, third, of adding 1 or 2 shovels of fresh coal near the firing door. As this coal is heated it begins to coke; the gas given off passes over the white-hot coal of the fire and is there mixed with heated air. This results in a free draft and good volume of hot flame. If instead of being added near the firing door the fresh coal is spread all over the fire it will quickly cake and tend to smother the fire by shutting off the draft.

It is not necessary to use the slice bar every time, but only when the fire is tightly caked or after a long run when the grate is covered with clinkers.

The temperature of the muffle may be regulated at will by manipulating the draft and firing doors. For instance, after a batch of cupels has started, the draft may be closed and the firing door opened, to admit cold air above the fire and quickly cool the muffles to any required degree.

Soft-coal furnaces have the advantage of simplicity and low initial cost. They burn from 40 to 50 pounds of good bituminous coal an hour.

Wood Furnaces. Wood-burning furnaces are made with single and double muffles and are much like the soft-coal furnaces except that fire box and grate are larger. Wood is usually sawed in 2-foot lengths, and with dry wood the muffle may be easily heated sufficiently for assaying. Hard wood is much to be preferred as it does not burn out as rapidly, but almost any kind of dry wood may be used.

The large fire box and the grate, which is set about 8 inches below the bottom of the fire door, are the principal distinguishing characteristics of a wood-burning assay furnace.

Coke Furnaces. Coke is still burned to some extent in pot furnaces, but for muffle-furnace fuel it has fallen into disuse.

The great advantage of the coke pot furnace is the very high temperature which may be obtained and the fact that, even though the crucibles boil over or eat through, no harm is done to the furnace. Coke furnaces should be supplied with fuel of an especially good quality. If the ash tends to melt, the walls quickly become covered with clinkers and are bound to be more or less damaged when these are removed.

Gasoline Furnaces. A gasoline-furnace outfit consists of a furnace, which may be either a muffle, a crucible, or a combination of the two, a burner with piping, etc., and a gasoline tank with pump. The tank for a small assay office is an ordinary tinned-steel pressure tank equipped with a hand pump, pressure gage, and the necessary piping connections. Tanks range from 2 to 15 gallons capacity.

A complete gasoline-furnace outfit is shown in Fig. 9. This is a combination crucible and muffle furnace made in several sizes ranging in capacity from 6F or 4G crucibles to 10F or 6G crucibles. In the illustration the crucible compartment is shown open although, of course, when actually in use, it is closed with special fire-clay covers. The muffle is situated directly above the crucible chamber. The advantage of this type of furnace is that fusions may be started within fifteen minutes after the heat is turned on, and while the fusions are in progress the muffle is heating. At the end of two rounds of fusions, the muffle is hot enough for cupellation.

FIG. 9. Gasoline-furnace outfit.

The burners are usually constructed of special bronze alloys capable of withstanding oxidation at high temperatures. They consist of a filtering chamber for purifying the gasoline, a generating chamber where the gasoline is vaporized, a generating pan and valve for the initial heating of the burner, a spraying nozzle and valve through which the gasoline vapor is injected into the furnace, and a mixing chamber where the proper amount of air for combustion is mixed with the gas. From the filter the gasoline passes around the interior of the burner face, the generating chamber, where it is heated by the heat radiated from the furnace and vaporized, so that once the furnace is under way the generating burner may be shut off. Gasoline is supplied to the burner under a pressure of 20 to 50 pounds per square inch.

The great object to be sought and one of the hardest to attain in any gasoline furnace is an even distribution of heat. Another objectionable feature in many gas and gasoline furnaces is the poor draft through the muffle. Owing to the fact that the pressure inside the furnace is slightly greater than that of the atmosphere there is a great tendency for the products of combustion to work back through the hole in the rear of the muffle, thus to a large extent excluding the air and unduly prolonging cupellation or scorification.

In operating a gasoline burner care should be taken to see that combustion occurs only in the furnace. All burners have more or less tendency to back-fire, that is, for the flame to jump back and remain in the mixing chamber. If this is allowed to continue, the burner gets so hot that the metal oxidizes and then it is only a short time before it is entirely destroyed. Every furnace should be provided with a shut-off valve between the burner and the gasoline tank. When it is desired to shut off the furnace, close this valve, letting the burner continue as long as any pressure is left, and never entirely close the burner valves. The valve stem or needle is of steel and the seat is of bronze; owing to the different rates of expansion of these metals, the valve is injured if these are left in close contact when the burner is cooling. This precaution is especially to be observed when the burner is provided with the ordinary needle valve, as when this opening is once enlarged the efficiency of the burner is destroyed.

Gas Furnaces. Gas furnaces are used in some assay offices, especially where a natural gas supply is available. Where artificial gas has to be burned this type of furnace proves decidedly expensive, if run for any considerable amount of work. As the gas is not ordinarily under sufficient pressure to carry in its own supply of air for combustion, these furnaces are customarily supplied with air from a blower, which adds to the expense and difficulty of the furnace operation.

In many of the western mining states the larger cities are connected with natural-gas lines and the gas companies supply gas at high pressure from what they term their industrial lines. When such gas is available the burner may be of the inspirator type, thus doing away with the blower.

Fuel-Oil Furnaces. When a cheap oil supply is available, oil is an ideal fuel for assay furnaces. Fuel oil and kerosene cannot be vaporized in the burner as they deposit carbon when heated and thus clog the passages. Consequently, to insure complete combustion, the oil must be thrown into the furnace in as fine a state of mechanical subdivision as possible. This is accomplished by atomizing the oil with a jet of air or steam.

The air for atomizing the oil may be supplied: (1) by a high-speed motor-driven fan giving a large volume of air at a pressure of 6 to 14 ounces; (2) by a positive pressure blower giving a pressure of 1 to 5 pounds; or (3) directly from a compressor. Air supplied by a compressor is reduced to any desired pressure by a suitable regulating valve.

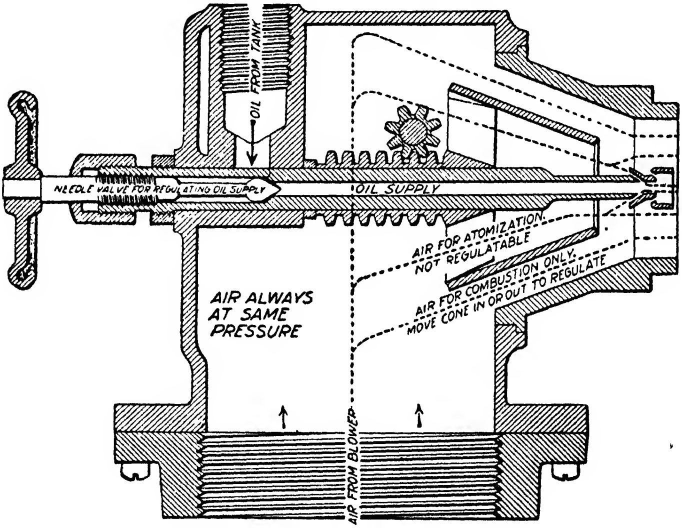

FIG. 10. Low-pressure oil burner, sectional view.

The burner must be designed to operate properly with air at the available pressure. Therefore, there are low-, medium-, and high-pressure burners. The high-pressure systems are noisy and therefore objectionable from this standpoint as well as because of the large amount of power required. The low-pressure burner, operating usually at 6 or 8 ounces air pressure, makes very little noise and requires a comparatively small amount of power. It is said, moreover, to take less oil and to cause less damage to the furnace, and is therefore most common. A section of a low-pressure oil burner is shown in Fig. 10. This burner is adjustable for oil and air so that a wide range of temperature variation is available. The oil is introduced through the central channel, the quantity admitted being regulated by a needle valve. The oil channel terminates in an enlarged orifice through which the oil is discharged in a thin, circular film. It is caught by a rotating air blast and discharged from the nozzle as a fine mist. Air for atomizing passes through the cone and is given a whirling motion by fins which project from it. Extra air for combustion passes in around the outside of the cone, which is operated from the side by means of a rack and pinion, and may be completely shut off by moving the cone out as far as it will go.

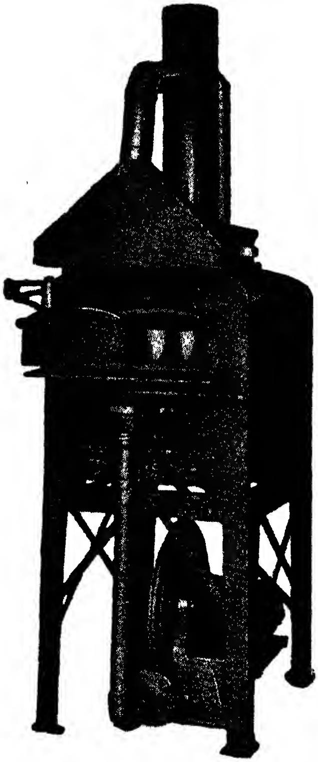

Fig. 11. Oil-fired assay furnace with motor blower.

Any fuel oil lighter than 28° Baumé at 60°F. may be used in these burners with gravity feed and only a few feet of head. A heavier oil may be used if heated, although then a pressure feed may be desirable. The oil consumption for assay furnaces runs from $1\frac{1}{2}$ to $2\frac{1}{2}$ gallons per hour, dependent on the size of furnace and grade of oil.

The muffle type of furnace is commonly used both for fusions and for cupellations. The furnace proper may be considered to consist of three parts: a combustion chamber where the oil is ignited, a muffle chamber which contains the muffle and where combustion is completed, and the damper block which contains the dampers for controlling the atmosphere in the muffle and the flow of gases through the furnace. The combustion chamber serves to protect the muffle from the intense direct heat of the flame and is lined with removable tiles. Between it and the muffle is a heavy fire-clay plate which serves as a support for the muffle and protects it from the flame. By adjusting the dampers, either an oxidizing or reducing atmosphere may be obtained in the muffle.

In Fig. 11 is shown an oil-fired assay furnace with motor blower. One of the dampers is to be seen just to the right of the lower part of the hood. The muffle door is conveniently hung on a double-crane hinge, thus permitting it to be set at any position.

Electrically Heated Muffle Furnaces. Where electric power is cheap as compared with coal or oil, electrically heated muffle furnaces have found favor. Many of the gold-mining companies of northern Ontario and Quebec are using this type of furnace exclusively. They have batteries of four to six furnaces with muffles 12 to 16 inches wide, 18 to 25 inches deep, and 8 inches high, each run from a separate transformer. The temperature may be manually controlled by multiple switches which vary the voltage delivered to the furnace terminals, or it may be automatically controlled by means of a somewhat more expensive mechanism. The muffles hold from twenty to thirty-five 20-gram or fifteen to twenty-four 30-gram crucibles and are run on a 24-hour schedule.

The heating elements are return-bend coils of heavy-gage nickel-chromium or other resistance wire held in grooves in replaceable units of high-grade refractory material which when assembled constitute a chamber enclosing the muffle on sides, top, and bottom. The units should be easily removable so that damaged coils may be replaced or repaired by electric welding. The elements gradually corrode, and hence the heating capacity of the furnace diminishes and the melting time increases as the coils grow older. For this reason it is customary to use those furnaces containing the newer heating units for fusions and the older ones for cupellation.

For the removal of fumes, each furnace is fitted with a metal housing above the door suitably connected with an exhaust fan. A separate vent pipe of about 2.5-inch diameter provided with a regulating valve should be suitably connected with the opening at the back of each muffle, and these pipes in turn must be connected either with an exhaust fan or with a stack having positive draft.

To preserve the bottom units and to protect them against seepage of litharge through the floor of the muffle and against spills of metal and slag, many assayers use trays of suitable heat-resisting alloys as false bottoms on which crucibles or cupels are placed.

The installation cost of one of the pioneer* applications of electrical heating for large-scale fire assaying was of the order of $1000 per furnace. The muffles 13 by 24 by 8 inches each hold twenty-four 20-gram crucibles or 96 cupels. During heating and when fusing, each furnace requires about 11.0 kilowatts. During cupellation somewhat less power is required.

By the use of resistors of heavy cross section operating on low-voltage alternating current, the life of the unit is increased and the moderate change in cross section due to oxidation does not seriously alter their heating characteristics.

With nickel-chromium resistors, care must be taken not to overheat the elements since they deteriorate rapidly if heated much above 1100°C. Fusion temperatures should not exceed 1000°C., and with some types of ore this is somewhat of a disadvantage. With this as a top limit, heating elements in continuous service last for an average of 6 or 8 months. At the above-mentioned installation electrically heated muffles were considered more economical, more efficient, and simpler to regulate than the oil furnaces which they replaced. The absence of dirt and noise is also in their favor.

Recently several new resistance alloys, with decidedly higher heat ranges than nickel-chromium alloys, have been developed. In general these retain chromium but substitute various proportions of aluminum, cobalt, and iron for the nickel. The best of these alloys have a resistivity from 25 to 35 per cent higher than pure nickel-chromium alloys and a lower specific gravity. The safe operating temperature of the element itself is 1350°C., giving a better margin of safety and a high resistance to oxidation together with a higher working temperature for assay work.

The alloy is more expensive than nickel-chromium alloys, and, though soft and ductile as supplied, it becomes decidedly brittle after heating to a high temperature. For this reason elements must be well supported and protected from shock. Bricks and cements in contact with these new alloys should not contain free silica or iron oxide, but with refractories containing silicates such as materials high in alumina the silica content is not so important.

In Fig. 12 is shown an electrically heated open-type furnace with door in position for changing the upper row of heating elements. In normal

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* W.R. Dodge, *Trans. Can. Inst. Mining Met.* **34**, 239 (March, 1931).

pouring and cupeling position the door is lowered rather than raised, and the opening in the door coincides with that of the furnace. A shelf attached to the door serves to aid in handling of crucibles, cupels, etc.

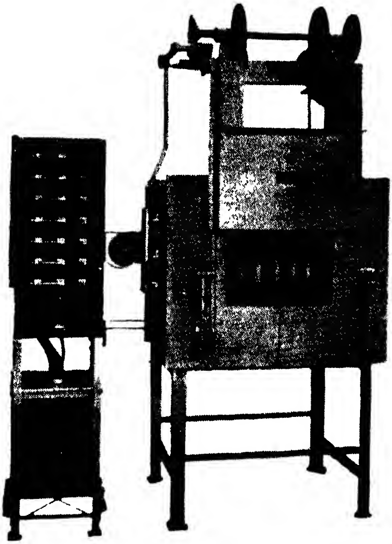

FIG. 12. Open-type electrically heated assay furnace.

Care of Muffles. Muffles are expensive, and care should be taken to make them last as long as possible. They are subject to injury by corrosion due to basic reagents, principally litharge, and by cracking, due to sudden changes of temperature. Care should be taken, particularly in oil furnaces, to bring the heat up slowly so that all parts of the furnace may become heated gradually. To prevent injury by corrosion try to avoid accidental spilling, and so proportion the size of crucibles to the charges that boiling over is impossible. Cupels should weigh 20 per cent more than the button to be cupeled in order to prevent litharge from seeping through and onto the muffle floor. Cracking due to changes of temperature is much more rapid when the inside of the muffle is glazed. This is due to the different rates of expansion of the glazed and unglazed parts.

When any lead or slag is spilled in the muffle, or a fusion is found to have eaten through its container, the muffle must be quickly scraped out and the spot well covered with bone ash. The bone ash absorbs the litharge and forms a thick paste with the slag so that it can easily be cleaned out with a scraper. It is well to keep a thin layer of bone ash in the muffle at all times.

When the furnace is not in use the drafts and muffle doors should be kept closed, and at the end of the day it should be allowed to cool down slowly.

Furnace Repairs. Fire clay usually forms the basis of mortars used in furnace construction and repairs, as lime mortar and hydraulic cement are not suitable for use with masonry exposed to high temperatures. Fire clay is a clay containing only very small amounts of iron, lime, magnesia, and the alkali oxides. It forms a more or less plastic and sticky mortar; on heating it loses its moisture and plasticity and the mortar hardens.

All clays shrink more or less on drying and burning, and to prevent this as far as possible, as well as to make the mortar strong, a certain amount of crushed fire brick or sand should be added. Crushed fire brick is better than sand owing to its porous and irregular shaped grains, which give a better mixture with the clay and a stronger cement.

A good mortar for general use around assay furnaces is made with a mixture of 2 parts fire brick ground through 12-mesh and 1 part fire clay. A small amount of Portland cement or molding clay, say not over $\frac{1}{3}$ part, will cause the mixture to adhere better and make the mortar harder when set. For work at very high temperatures the Portland cement must be omitted as it acts as a flux for the other materials and causes the whole to melt.

All mortars should be made up dry and thoroughly mixed before the required amount of water is added. The water should be thoroughly mixed in, and the mortar should be sticky and of the right consistency. It is well to mix the mortar several hours before using. When bricks are being laid or repairs made about a furnace, the bricks and brickwork should be thoroughly wet before the mortar is applied, as otherwise the bricks absorb so much water that the mortar does not form a good bond with them.

In laying fire bricks, as little mortar as possible should be used as the bricks are always harder than even the best of mortar. The mortar should be made to fill every crevice. The best way to attain this is to put an extra amount of fairly thin mortar on the wet brick and then drive or force it firmly into place, allowing the excess mortar to squeeze out.

The ash from many coals is quite readily fusible and results in the formation of clinkers and accretions on the sides of the furnace, especially just above the grate. When the furnace is cold these adhere very tenaciously to the walls of the furnace, and when they are broken off, pieces of the brick are removed with them. To remove these accretions with the least possible damage to the furnace cut them off with a chisel bar just after a hot fire has been drawn.

In putting in a new muffle, first remove the old one with the mortar that held it, also any clinkers which would interfere with the working of the furnace. Patch the lining of the furnace if necessary and see that the bricks or other supports for the muffle are in place and in good condition. After trying the muffle to see that it rests properly on the supports, remove it, sponge over the brickwork where the mortar is to come in contact with it, place some rather thick mortar on each of the supports and replace the muffle. See that it rests evenly on the different supports and on the front wall of the furnace. The muffle should be level or slope slightly toward the front end. Fill up the space between the muffle and the front wall of the furnace with some rather thick mortar, working from both inside and outside of the furnace. This outside joint should be finished up neatly with the aid of a trowel. It is best to allow the furnace to dry for a day or two if possible, but if necessary it may be used as soon as finished by heating up slowly.

For patching the linings of furnaces use the mixture recommended for general use or try the following which is recommended by Lodge. Fire brick through 12-mesh 7 parts; Portland cement 2 parts, fire clay 1 part. Put this on as dry as possible and it will make a patch almost as hard as the original brick.

Cracked and broken muffles may be made to last much longer if patched with one of the above-mentioned mixtures.

METALLURGICAL CLAY GOODS

Under the caption, "Metallurgical Clay Goods," are included muffles, crucibles, scorifiers, roasting dishes, annealing cups, etc. These embrace many of the most important utensils of the assayer, and upon their good properties much of his success depends. Fire clay is the only material which answers the double purpose of satisfactory service and inexpensive construction. Refractory clay or fire clay, as it is commonly called, is a clay which will stand exposure to a high temperature without melting or becoming, in a sensible degree, soft or plastic.

All clays contract both upon drying and upon burning, and this leads to more or less warping and cracking of the finished product. To prevent this shrinkage as far as possible and also to add strength to the finished article it is customary to add a certain amount of sand or well-burned clay to the mixture. Burned clay is usually preferred to sand for this purpose, not only because its rough porous grains give a better bond with the fire clay and make a stronger cement, but also because it makes an article which is less readily corroded by assay slags and fusion products. The intermixture of coarse grains of burned clay also helps in that it makes a product better able to withstand sudden changes in temperature.

The exact proportions of raw and burned clay used by any manufacturer are carefully guarded trade secrets and depend, of course, very much on the clay used as well as on the article to be manufactured. The larger the article the more care must be taken to prevent warping and cracking. Usually however, the proportion of raw to burned clay will lie between the limits of 1 to 1 and 1 to 2.

Muffles. Muffles for fire-assay purposes are made either of fire clay or of clay-bonded silicon carbide. They are made in a great variety of sizes and shapes. However, when crucible fusions are to be made in the muffle, a nearly rectangular cross section is preferred, as this gives a muffle of almost uniform height without any appreciable waste space.

The largest muffles used in fire assaying known to the writer are those in use at the East Helena plant of the A. S. & R. Co. These measure 19.5 by 25 by 8.5 inches inside. They hold thirty 30-gram crucibles in six rows of five each.

Muffles, as well as other fire-clay ware, should be stored in a warm, dry place and should be heated and cooled slowly and uniformly. The life of a muffle is also much influenced by the way it is supported.

Silicon Carbide Muffles. Muffles made from silicon carbide bonded with clay are sold under a great variety of trade names and when properly made and suitably supported give remarkable service in assay furnaces. Silicon carbide does not decompose and oxidizes only very slowly at any temperature attained in fire assaying. Muffles made from it have a thermal conductivity about 10 times as great as fire-clay muffles, and a very low coefficient of expansion, both of which properties make it highly resistant to spalling and cracking due to sudden changes of temperature. The high thermal conductivity makes for quick heating, uniform distribution of heat, and economy in fuel or electric consumption. Besides this, silicon carbide muffles have exceptional mechanical strength, which assures their ability to carry a heavy load of crucibles without deformation or other damage. Except for the clay used in bonding, these muffles are highly resistant to attack by the reagents which may come in contact with them from inside the muffle or by the alkalies and iron oxide from the coal ash which, in the event of coal firing, may tend to accumulate on their outside surfaces. To overcome the effect of spills and litharge seepage through cupels, some laboratories use a floor covering or hearth of some high-melting oxygen-resistant alloy, which may be removed at will for cleaning or straightening.

These muffles list at about four times the price of fire-clay muffles, but most users consider them well worth the difference because of the long life and saving of time and inconvenience of frequent changing. When these muffles are suitably protected from the effect of spills some laboratories have obtained a life of more than a year from them in continuous 24-hour service.

Crucibles. Assay crucibles are made either of a mixture of raw and burned clay or of a mixture of sand and clay, the first being known as clay or fluxing crucibles and the second as sand crucibles. The raw clay is finely ground, mixed with the right proportion of coarser particles of sand or burned clay and water, and the whole well kneaded and compressed in molds of the proper shape. They are then very slowly dried and baked.

Good crucibles should have the following properties:

1. Ability to withstand a high temperature without softening.
2. Strength to stand handling and shipping without breaking.
3. Ability to stand sudden changes of temperature without cracking.
4. Ability to withstand the chemical action of the substances fused in them.
5. Impermeability to the substances fused in them and to the products of combustion.

Of course it is impossible to get any one crucible which will possess all the above good properties to a high degree. For instance, if a crucible is desired as nearly impermeable as possible, it will be made of very fine-grained material and tightly compressed. Such a crucible, however, will not stand handling or sudden changes of temperature as well as one made with a skeleton of coarser material. Furthermore, the manner and temperature of burning have much to do with the ability of crucibles to stand handling and shipping. A fairly hard-burned crucible will be stronger and less likely to be broken in handling, but on the other hand it will not stand sudden changes of temperature as well as a soft-burned crucible. Crucibles made of clay containing little uncombined silica and of burned clay of the same nature will stand a high temperature and chemical corrosion much better than those made of sand and clay or of clay containing much free silica.

Crucibles are tested for resistance to chemical corrosion by actual service and also by fusing litharge in them and noting the time it takes to eat through. To make a test of this sort which is of any value, care must be taken to see that the temperature, the quantity of litharge, and all other conditions are the same for the crucibles being tested. A crucible may be tested for its permeability to liquids by filling it with water and noting the time it takes before it becomes moist on the outside.

Crucibles come in a great variety of shapes and sizes. Those most commonly used for assaying may be classified into two groups as follows:

Pot-Furnace Crucibles. These are comparatively slim, heavy-walled crucibles with practically no limit as to height. The base is small, so that they may be forced down into the fuel, and for this reason they are easily tipped over and are not suitable for muffle work. The sizes most used are the E, F, G, H, J, and K. Crucibles of the same designation but made by different manufacturers vary considerably in capacity. The approximate capacity of some of the pot-furnace crucibles is shown in the following table:

TABLE III

CAPACITIES OF POT-FURNACE CRUCIBLES

Crucible Designation	E	F	G	H	I	J	K
Battersea[1].....	180 ml.	210 ml.	300 ml.	420 ml.	... ml.	600 ml.	750 ml.
Denver[2].......	180 ml.	240 ml.	400 ml.	......	530 ml.	685 ml.	950 ml.

[1] Made by the Morgan Crucible Co., London, England.
[2] Made by the Denver Fire Clay Co., Denver, Colorado.

Muffle Crucibles. These are made with a broader base so that they may stand securely on the floor of the muffle, and are usually not more than 4 inches high. Muffle crucibles are designated by gram capacity, the 10-, 15-, 20-, and 30-gram sizes being most frequently used. The numbers are intended to indicate the grams of ore charge which the crucibles will take. They are usually generously proportioned, so that often an assay ton of ore (29.166 grams) may be treated in a 20-gram crucible. The approximate capacity of the more important muffle crucibles is shown in the following table:

TABLE IV

CAPACITY OF MUFFLE-FURNACE CRUCIBLES

Crucible Designation	10-gm.	12-gm.	15-gm.	20-gm.	25-gm.	30-gm.
Denver..........	98 ml.	131 ml.	142 ml.	177 ml.	195 ml.	231 ml.
Battersea........	100 ml.	......	135 ml.	190 ml.	......	260 ml.
Utah............	100 ml.	130 ml.	140 ml.	180 ml.	230 ml.	280 ml.

Scorifiers. These are shallow fire-clay dishes used in the scorification assay of gold and silver ores. They should be smooth on the inside, dense and impermeable to lead and slag, and so composed as to withstand, as much as possible, the corrosive action of litharge. Scorifiers are designated by their outside diameters. Of the large number of sizes made, the following are the most commonly used: $2\frac{1}{4}$, $2\frac{1}{2}$, $2\frac{3}{4}$, 3, and $3\frac{1}{2}$ inches. The Bartlett scorifier is shallower than the regular one and was designed for the treatment of heavy sulphide ores containing considerable metallic impurities. Scorifiers should be made of clay containing a minimum of uncombined silica, as the scorifier slags are usually very basic. Particularly when they contain copper, they attack the silica of a scorifier with avidity, and one with a siliceous skeleton may become perforated and allow its contents to escape to the floor of the muffle, thus spoiling the assay and injuring the muffle.

FURNACE TOOLS

The more important furnace tools consist of crucible, scorifier, cupel and annealing cup tongs, cupel rakes and shovels, muffle scrapers and spatulas, and the various pouring molds, cupel and annealing cup trays, hammers, slagging forceps, anvils, etc.

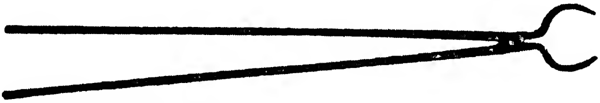

FIG. 13. Crucible tongs for use in muffle.

FIG. 14. Crucible tongs for use in coke pot-furnace.

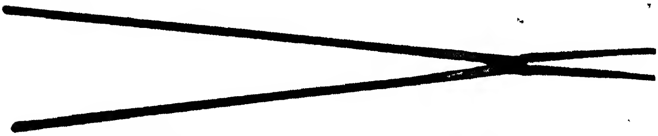

FIG. 15. Crucible tongs for use in gasoline melting-furnace.

Crucible Tongs. Two types of crucible tongs are in common use, those which grasp the body of the crucible and those which grip the top edge of the crucible inside and out. In Fig. 13 is shown a pair of crucible tongs of the first type, suited for use in a laboratory where the fusions are made in the muffle. Thirty inches is a convenient length for these tongs. Figure 14 illustrates a good strong pair of the second type of tongs, especially suited for coke pot-furnace work. These may be made somewhat shorter, say 26 inches long. Figure 15 shows a lighter construction of the second type for use in gasoline melting furnaces and in muffle work. These should be about 30 inches long. A combination of these two types of tongs is listed by most supply houses, but is of little practical use as it cannot be used in a muffle full of crucibles to grasp the body of the crucible, owing to its shape, and neither is it as satisfactory as the one illustrated in Fig. 15 for use in gasoline melting furnaces. Another convenient tool for crucible furnace work, shown in Fig. 16, is known as a charging fork. It consists of a fork-shaped piece of steel, which fits the crucible about midway, mounted on the end of a long rod. This is used principally for charging and occasionally for pouring; 46 to 48 inches is a convenient length.


Fig. 16. Charging fork.


Fig. 17. Scorifier tongs.

Scorifier Tongs. Several different designs of scorifier tongs are employed, the first and oldest being shown in Fig. 17. The curved fork fits the bottom of the scorifier while the long arm extends across the top. These tongs are preferably made of ¾- by ⅛-inch steel and should be about 30 inches long. They may be flattened enough at the bend to give the right degree of spring. Several different sizes should be supplied to handle the different sizes of scorifiers, although a pair made with a space of 1⅝ inches between the two members of the fork will handle 2½-, 2¾-, and 3-inch scorifiers perfectly. The form of crucible tongs illustrated in Fig. 15 is also occasionally used for handling scorifiers. With these, scorifiers may be lifted from the rear of the muffle without disturbing those in front. They are convenient in that one pair of tongs will fit any size of scorifier.

Cupel Tongs. A good form of cupel tongs is illustrated in Fig. 18. It may be made of ½-inch half-round stock and should be about 30 inches long. It is best to curve the points of these tongs to conform to the cupel, so that if the operator happens to grasp a cupel below its center of gravity it cannot turn over and spill the contents. For handling a large number of cupels at one time, a cupel shovel of light-weight iron is often used. This may be made of any convenient width and from 24 to 30 inches long. The cupels are moved on or off the shovel with a rake or rabble of the same width.

Fig. 18. Cupel tongs.

Fig. 19. Annealing cup tongs.

Annealing and Parting Cup Tongs. A pair of tongs arranged to handle annealing cups is shown in Fig. 19. They should be made so that when closed they fit the cup somewhat above its center. When a large number of annealings are to be done at one time the cups may be placed in some form of clay dish and all put in the muffle together.

Muffle Scrapers and Spatulas. The muffle scraper, as its name implies, is a tool intended for the prompt removal of anything spilled upon the floor of the muffle. A muffle spatula is a long rod of, say, ¼-inch iron, flattened at the end. It is useful in spreading bone ash over a slagged spot in the muffle, as well as in adding reagents, etc., to crucibles and scorifiers already in the muffle. In Figs. 20 and 21 are shown a muffle scraper and spatula.

Fig. 20. Muffle scraper.

Fig. 21. Muffle spatula.

Molds. Various forms of molds to receive the molten charge are in use. They are usually made of cast iron and should be machined on the inner surface. For crucible fusions, the writer prefers one having a fairly sharp (50°) conical cavity holding about 60 milliliters and with a slightly rounded bottom. In Fig. 22 is shown a four-hole mold of this description. This leaves the lead button in good shape for pounding and permits a good separation of lead and slag. Some assayers prefer a

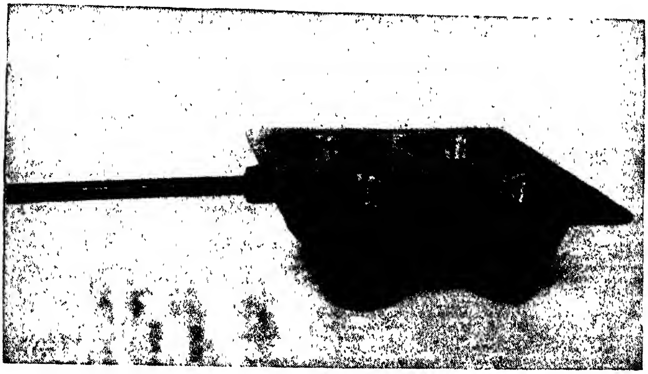

FIG. 22. Four-hole crucible mold.

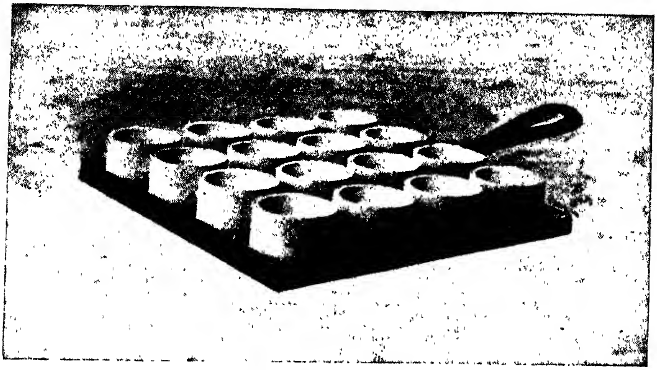

FIG. 23. Cupel tray holding 16 cupels.

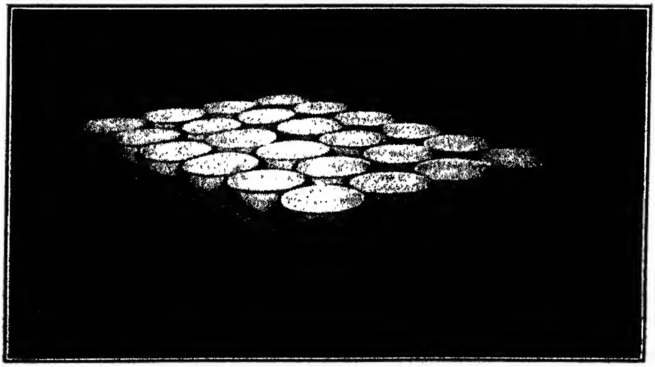

FIG. 24. Clay dish holding 24 annealing cups.

solid block mold with a conical cavity, claiming that the fusions cool more rapidly. A mold of this type, however, is heavier to handle and more expensive. If a muffle full of crucibles is poured at one time, it will be found that those first poured are ready for slagging almost immediately, even if the lighter molds are used.

For scorification fusions, molds with smaller cavities are used. They are made with spherical or with flatly coned cavities, and both types are satisfactory. A convenient form of mold is one in which the number of cavities equals the number of scorifiers which the muffle will hold

Cupel Trays, etc. A convenient cupel tray is illustrated in Fig. 23. A clay dish for annealing is shown in Fig. 24. Any form of hammer will serve for slagging the buttons, but one with a round section is preferable. Ten-inch forceps are satisfactory both for holding buttons while slagging and for removing the nails from iron-nail fusions.

CHAPTER III

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 expressions correct sample, representative sample, and 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. Careful sampling and assaying cannot be disregarded and, in fact, 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 deals 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. 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 for large lots it would entail too much labor and would usually unfit the ore for future treatment. The method generally adopted is a compromise, consisting 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, the process being repeated until finally the assay sample is obtained. From the business standpoint the problem is to get a representative portion from a large mass with the least possible amount of labor and expense.

The care 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, depend 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 copper contents of a car of copper ore worth $50 a ton. Therefore, it may be seen that it will pay the seller or buyer of the copper ore to go to more pains and expense in the sampling of the ore than if he were dealing with the less valuable iron ore.

The commercial conditions are met when the ultimate sample obtained comes within an allowable limit of error, usually 1 per cent, of the ideal or true figure, provided also that it has been obtained without undue delay and at a reasonable cost.

PRINCIPLES OF SAMPLING

Varying Relation of Size of Sample to Maximum Particle. Every ore-sampling operation is in effect a laboratory experiment in probability, and the variation of any portion or sample of a lot from the average composition of the whole may be considered to be due to the excess or deficit of one or more particles of the ore.

The effect upon the results will be greatest when the piece or pieces which are in excess or deficit are of the largest size, greatest specific gravity, and greatest variation in quality from the average.

Disregarding for the moment the last two of these factors and supposing the ore particles to be approximately uniform in size, it is evident that the sample must contain so many particles that one additional particle of the richest mineral would cause practically no variation in the value. This means that the sample of the ordinary ore must contain a very large number of particles 500,000 in some cases, 5,000,000 in others.

Having determined how many particles of the ore it is necessary to include in the sample, and assuming the different minerals to be entirely detached from one another, it would be fair to take such a weight of ore after each reduction as would contain this established number of particles. Or, as the weight of a lump is proportional to the cube of its diameter, the weight of ore taken for the sample should be proportional to the cube of the diameter of the largest particle of the ore.

In the ordinary ore, however, the different minerals are not entirely detached from one another, but approach this condition more and more closely as the size of the ore is reduced. Hence a fixed number of the particles of the fine ore is less likely to be a true average of the whole than the same number of pieces of the 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.

This table, which has been widely copied, is subject to one criticism, namely, the use of the words " grade " and " uniform " as synonymous; actually they are not at all so. An ore may be very low grade and at the same time very spotty.

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 to low-grade lead, zinc, and copper ores and even to low-grade pyritic gold ores, without native gold, where the pyrite is evenly distributed through the ore.

Columns 3 and 4 apply to ores in which the valuable minerals are less uniformly distributed. Columns 5 and 6 apply to ore containing fine particles of native gold or silver, also to telluride and other "spotty ores."

It should be remembered that the above-mentioned rules for sampling will not hold for ore containing large pieces of malleable minerals such as native gold, silver, silver sulphide, chloride, etc. These roll out and do not crush and must be treated by special methods. See "Sampling Ores Containing Malleable Minerals."

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	0.85
200.000	20.70	11.40	7.60	5.10	3.20	0.54
100.000	14.70	8.00	5.40	3.60	2.20	0.38
50.000	10.70	5.70	3.80	2.50	1.60	0.27
20.000	6.60	3.60	2.40	1.60	1.00	0.17
10.000	4.60	2.50	1.70	1.10	0.71	0.12
5.000	3.30	1.80	1.20	0.80	0.50	
2.000	2.10	1.10	0.76	0.51	0.32	
1.000	1.50	0.80	0.54	0.36	0.22	
0.500	1.00	0.57	0.38	0.25	0.16	
0.200	0.66	0.36	0.24	0.16	0.10	
0.100	0.46	0.25	0.17	0.11		
0.050	0.33	0.18	0.12			
0.020	0.21	0.11				
0.010	0.15					
0.005	0.10					

In using the table, it is not necessary to crush successively to all the sizes shown in any of the columns. The ore may be crushed to any convenient fineness, and then a sample of the weight shown in the table may be taken. In sampling-mill practice it is customary to reduce the diameter of the coarsest particles one-half at each stage or crushing, thus reducing the volume to one-eighth or 12.5 per cent. It is also customary in practice to take a 20 per cent sample at each stage; consequently the ratio between the weight of sample and of maximum size particle is constantly increasing throughout the sampling process, thereby meeting theoretical conditions previously discussed.

Relation of Size of Sample to Grade of Ore and Effect of Specific Gravity of Richest Mineral. Although it had long been appreciated that the size of the sample would have to be greater as the ratio of the grade of the richest mineral to the average grade increased, it remained for Brunton* to develop a formula by which the proper ratio between these could be scientifically controlled. According to him, each of the following factors must be included in any formula to be used for the control of sampling operations.

W = weight of sample in pounds.
k = grade of richest mineral in ounces per ton.
c = average grade of ore in ounces per ton.
s = specific gravity of richest mineral.
n = number of maximum-sized particles of richest mineral in excess or deficit in sample.
f = a factor expressing the ratio of the actual weight of the largest particle of richest mineral which will pass a screen of a given size to the weight of the largest cube of the same mineral which will pass the screen.
p = allowable percentage error in sample.
D = diameter in inches of the holes in the screen, or other normal diameter to which the ore is crushed.

From these Brunton found

$$D = 0.65\sqrt[3]{\frac{Wcp}{fsn(k-c)}}.$$

Making p, the allowable percentage error, = 1, the formula becomes

$$D = 0.65\sqrt[3]{\frac{Wc}{fsn(k-c)}}.$$

To determine a value to use for n, Brunton made a number of assays on two different lots of high-grade ore crushed to pass a certain limiting screen. The average deviation from the mean = p was substituted in the formula, and results of 2.64 and 3.14 respectively were found

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* *Trans. A.I.M.E.* **25**, 826 (1895).

for n. Assuming that 3 is a safe value for n and cubing each side we find

$$D^3 = \frac{Wc}{10.8fs(k - c)},$$

or

$$W = \frac{10.8fsD^3(k - c)}{c},$$

from which may be found the safe weight in pounds for a sample of any ore whose largest particle is D inches.

Table VI was compiled after the style of the table first shown in Hofman's "Metallurgy of Lead," four examples being taken, pyrite, galena, native silver, and native gold, as the richest minerals, and different values for D, k, c, and f being assumed. The values for f used for the fine sizes were those determined by Brunton's experiments, *i.e.*, 4 for pyrite and galena and 6 for native silver and native gold. This value of f is reduced gradually, until for 1-inch diameter it is made equal to 1, this variation therefore tending to compensate for the greater uniformity of value of the particles as they become larger.

Table VI 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 throughout the gangue, a much smaller sample than that given in the table may be taken for the coarse sizes, although for the fine sizes the full quantities shown in the table should be taken. Another ore, with perhaps the same ratio of value of the richest mineral to average grade, having the rich mineral in larger crystals or masses, will have to be sampled as carefully as indicated by the table throughout the entire operation. To sum it all up it may be be said that sound theory together with experience and good judgment are the prerequisites for obtaining correct samples.

It should be noted also that, except with native metals, the richest minerals are usually more finely divided by crushing than the gangue; therefore the extreme case provided for by the formula is seldom met in practice.

In the case of ores containing metallic gold, ratios of grade of richest mineral divided by average grade are necessary, different from those for pyrite, galena, and native silver, if the table is to be of real use. This accounts for the line of figures within rulings, separating the last group of figures from the three preceding ones.

TABLE VI

WEIGHTS TO BE TAKEN IN SAMPLING ORE

Specific Gravity of Richest Mineral	Size of Particles		Grade of Richest Mineral Divided by Average Grade					
	Mesh	Diam., inch	10	50	200	600	1500	2500
			Safe Weight in Pounds When Largest Particles Are of Size Given in Second Column					
5.0	120	0.0043			0.003	0.010	0.025	0.043
	100	0.0055	0.0003	0.0018	0.007	0.021	0.053	0.089
	50	0.0100	0.0017	0.0095	0.039	0.116	0.291	0.485
	14	0.0364	0.0585	0.319	1.29	3.90	9.76	16.3
	4	0.145	2.96	16.1	65.5	195.	494.	823.
	2	0.338	30.0	163.	664.	2,000.	5,000.	8,340.
		0.5	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	0.0043			0.005	0.015	0.038	0.064
	100	0.0055	0.0005	0.0027	0.011	0.032	0.080	0.134
	50	0.0100	0.0026	0.0143	0.058	0.174	0.437	0.727
	14	0.0364	0.0878	0.479	1.94	5.85	14.6	24.5
	4	0.145	4.44	24.2	98.3	293.	740.	1,230.
	2	0.338	45.0	245.	996.	3,000.	7,500.	12,500.
		0.5	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	0.0043	0.0005	0.0027	0.011	0.032	0.081	0.135
	100	0.0055	0.0010	0.0055	0.022	0.068	0.170	0.283
	50	0.0100	0.0041	0.0222	0.090	0.272	0.679	1.13
	14	0.0364	.148	0.804	3.26	9.83	24.6	41.0
	4	0.145	7.78	42.4	172.	518.	1,300.	2,160.
	2	0.338	78.8	429.	1,740.	5,250.	13,100.	21,900.
		0.5	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	0.0036	0.0798	0.159	0.319	0.798	1.59	3.19
	120	0.0043	0.136	0.272	0.544	1.36	2.72	5.40
	100	0.0055	0.284	0.569	1.14	2.84	5.69	11.4
	50	0.0100	1.14	2.28	4.56	11.4	22.8	45.6
	14	0.0364	41.2	82.5	165.	412.	825.	1,650.
	4	0.145	2,170.	4,350.	8,690.	21,700.	43,500.	86,900.
	2	0.338	22,000.	44,000.	88,100.	220,000.	440,000.	881,000.

SAMPLING PRACTICE

RECORDING. Every lot of ore coming into an assay office, laboratory, custom mill, or smelter should be given a lot number which should never be repeated. The lot should be immediately labeled with this number. A record book, kept for this purpose, should show the number of the sample; date of receipt; name of mine, company, or individual from whom received; the gross and net weight; as well as notes on the general mineral character, etc.

Weighing. Large lots of ore are first weighed and then often sampled for moisture. Small lots may be first dried and then weighed.

Crushing. All the ore, unless already fine enough, is broken or crushed to pass a screen of some limiting size. This size depends upon the value and uniformity of the ore and the precision desired. If the ore is to be smelted, most of it should be left in the coarse state, as fine ore is undesirable. If it is to be roasted or leached, on the other hand, fine ore is not objectionable, and the first crushing may be carried further. As a rule, however, the aim is to minimize the crushing, thus saving in cost and keeping down the dust.

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 overcareful 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, though occasionally used, are being replaced whenever possible 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, 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.

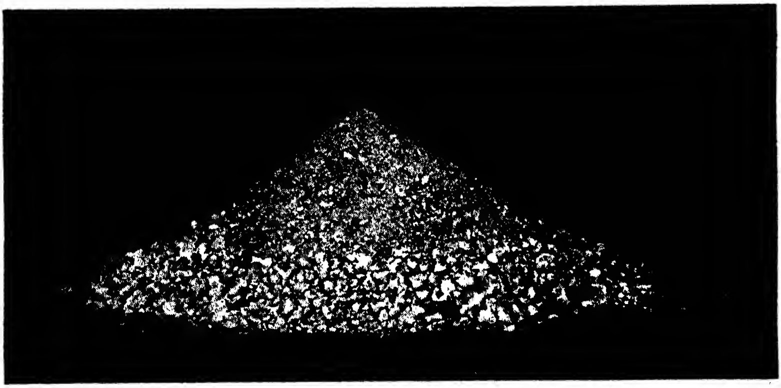

Fig. 25. Cone of crushed ore.

Figure 25,* 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 quart-

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* From *U. S. Bureau of Mines Technical Paper* 86, "Ore Sampling Conditions in the West."

erer. These quarters should, of course, radiate from the position of the center of the original cone. Two opposite quarters are removed 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 it may be crushed, coned, and quartered as the case may require.

FIG. 26. Partly flattened cone.

FIG. 27. Truncated cone from which reject quarters have been removed.

Figure 26* shows a partly flattened cone and Fig. 27* a cake from which the reject quarters have been removed.

When properly carried out, this method may be made to yield fairly accurate results, but at best it is a slow and tedious process, requiring

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* From *U. S. Bureau of Mines Technical Paper* 86.

the most conscientious work on the part of the laborers to insure correct results. It is open to the objection that it affords opportunity for manipulation of the sample by dishonest operators.

Coning and quartering is the old Cornish method of ore sampling. It is still used to some extent as a finishing method at sampling works and by engineers in the field where no machinery is available.

Bench System of Coning. The tendency to segregate, which is the principal objection to coning, can be largely overcome by what is known as the bench system of coning. Under this system all the ore is not piled in a single cone; a part of it is coned first, and this small cone is worked out into a layer of considerable diameter and but little thickness. Another part of the ore is then coned on top of this and the cone truncated. This is repeated until all the ore is used. This method is said to give much more satisfactory results than those obtained by the regular system.

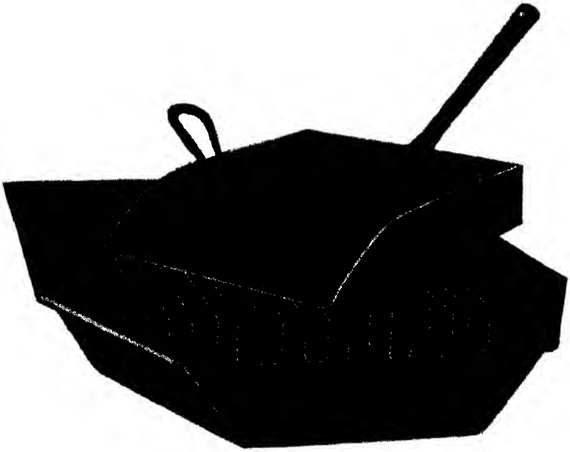

Fig. 28. Split shovel and pans.

Riffle Cutting. Riffle cutting or splitting is the most accurate laboratory method available. The riffle, splitter, or split shovel consists of a number of parallel troughs with open spaces between them, the spaces usually being of the same width as the troughs. These troughs are rigidly fastened together and either provided with a handle, making a split shovel, or set up at an angle of about 45° making an inclined riffle. Figure 28 shows a split shovel with pan and shovel. These may be made in different sizes but are useful only for small scale work.

The ore is taken up on a flat shovel or special pan and spread over the troughs, care being taken not to heap the ore above the troughs.

Either the ore which falls in the troughs or that which falls between them may be taken as the sample. The cutting may be repeated as many times as is deemed desirable.

Flat-bottomed riffle samplers should be used only on such small quantities that there is no possibility of overloading. With overloading, an excess of coarse material runs off between the closed troughs and a corresponding surplus of fine material remains. The more irregular in size, specific gravity, and value the minerals are, the greater is the care which should be taken in this particular. The sample should be mixed before recutting.

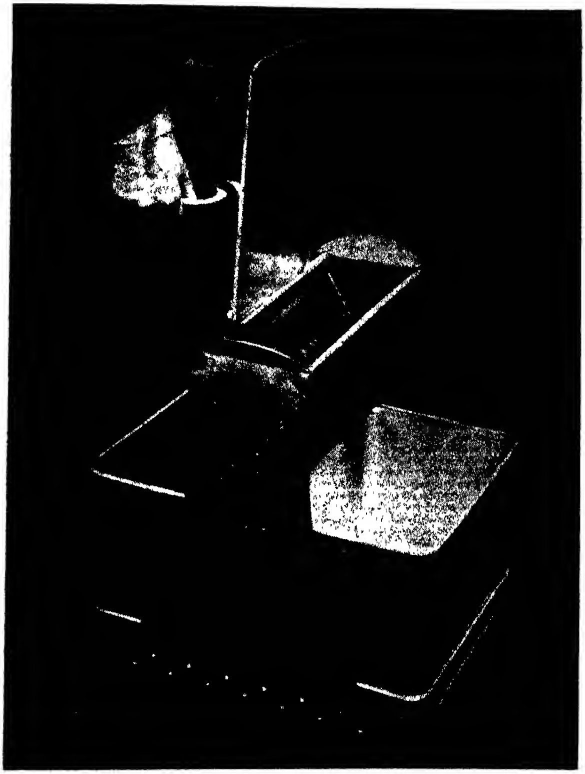

FIG. 29. Brunton splitter.

The shovel or pan used in feeding ore to riffle samplers should be flat-bottomed, straight-edged, with right-angled sides and of a width equal to some even number of riffles.

Self-discharging riffle type samplers, originally known as Jones samplers, are the most convenient form for finishing work and are least subject to errors of manipulation due to carelessness or stupidity. This type is a riffle sampler in which the bottoms of the riffles are steeply inclined, first in one direction and then in the other. The ore is spread over the riffles in the Jones sampler exactly as over the split shovel, and is caught in two pans placed underneath.

The Jones splitter and those similar to it have one decided advantage over the flat type shown in Fig. 28, in that the riffles cannot be overloaded, a very common fault of the shovel type. In Fig. 29 is shown a very substantial form known as the Brunton riffle, the operation of which is self-evident.

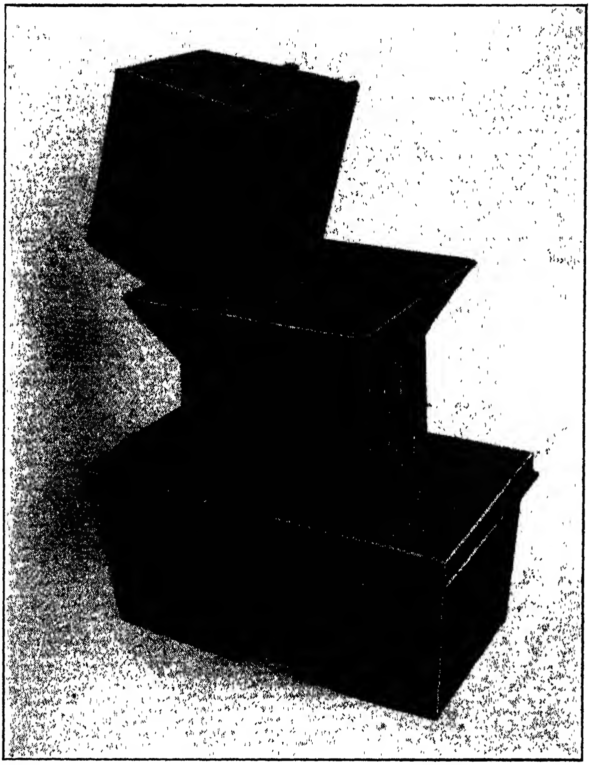

Fig. 30. Closed-type splitter.

One objection to the Jones sampler and similar models is the possibility of the loss of considerable fine ore dust, due to the greater length of fall of the ore before coming to rest. One way to obviate this would be to moisten slightly the thoroughly mixed ore before cutting. A better way is to close the bottom of the sampler and set it directly on the pans. This type of splitter is shown in Fig. 30.

In selecting a split shovel or riffle cutter for any particular sampling operation, care should be taken that the distance between the riffles be at least four times the diameter of the maximum particle of ore. It is found that a slight bridging action may occur if this precaution is not observed. Riffle cutting is the most rapid method of hand sampling and is also the most accurate.

Machine Cutting. A large number of machines have been devised to take the place of the slow, laborious methods of hand sampling. All these machines depend on taking the sample from a stream of falling ore. They may be classified as continuous and intermittent samplers. The continuous samplers take part of the stream all the time, by placing a partition in the falling stream of ore to separate sample from reject. The intermittent samplers, as the name implies, deflect the entire stream at intervals to make the sample. This is accomplished by passing a sample cutter directly across the stream.

The continuous method of sampling is open to the objection that it is impossible to get a stream of falling ore containing coarse and fine particles which is uniform across its entire section. This is because the ore on its way from the preceding crusher, bin, or elevator practically always passes through a sloping chute in which the large lumps roll away from the small ones and the heavy minerals become more or less separated from the lighter ones. Therefore, any continuously taken sample will be either richer or poorer than the average. Because of these conditions this type of sampler will not ordinarily give reliable results.

The intermittent method of sampling gives better results. The machine should be so designed that it takes equal portions across the stream at frequent and regular intervals. In one mill the first time sampler cuts 24 and the last one 76 sections per minute.

Although it is not possible to produce a stream of ore which is uniform in value throughout its entire length, and no single cut would be likely to give an exact representation of the lot, yet if a large number of small samples be taken entirely across the stream, the composite thus obtained will, according to the theory of probability, approach very near to the composition of the entire lot. It is essential that the percentage of sample taken from all parts of the delivery pipe be the same, in other words, that the vertical sample section, taken in a direction parallel to the motion of the intake-spout, should be a rhomboid.

Three machines of this type have come into general use: the Brunton, the Vezin, and the Snyder.

Figure 31 is a line drawing of the Brunton sampler. It consists of an oscillating divider swinging back and forth, in a vertical plane, beneath the end of the feed spout. It is suspended on a horizontal shaft and swings through an arc of 120°. It receives its motion through a train of gears, a disc crank, and rocker arm, and by a change of gears any proportion of the stream, from 5 to 20 per cent, may be taken.

The sample cutter, which has horizontal edges not shown in the figure, deflects the sample forward into a hopper. The rest of the ore is deflected in the opposite direction into a chute leading to the reject bin. It is essential that the sample cutter move entirely out of the stream in each direction and that its velocity be uniform while any part of it is underneath the falling stream. Otherwise, it would take too much from one part of the stream and not enough from other parts.

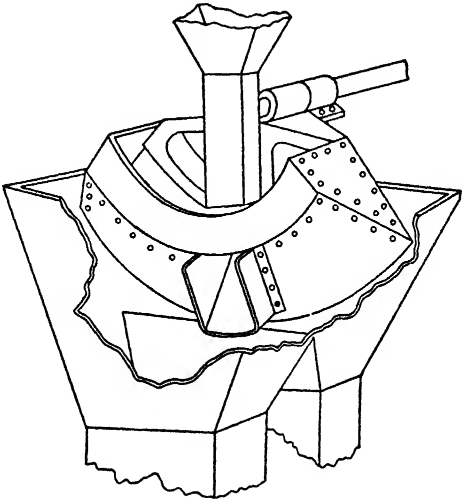

FIG. 31. Brunton time sampler.

This type of sampler requires less headroom than any of the others and thus, by reducing the necessary height of building, saves in the cost of mill construction. Its rocking motion helps to dislodge any rags or strings which may have fallen on the cutting edges, and its short cutting edges render accidental distortion impossible. A further advantage claimed for the Brunton machine is that centrifugal force assists in the discharge of ore from the sampler and the machine can, therefore, be run at a much higher rate of speed than any of the sector machines.

The Vezin sampler, shown in Fig. 32, is probably the best-known automatic sampler. Various modifications in shape are possible, but generally speaking, it consists of one or two sample cutters which rotate about a vertical shaft and pass through a falling stream of ore, taking out a part of it and conveying this part through a central spout to a sample hopper. The theory of sampler design requires that the horizontal cutting edges be radii of the axis of revolution. This is necessary in order to insure taking the same amount of ore from every part of the stream. The entire mechanism is supported in a frame, the bottom of which forms a hopper to collect the reject.

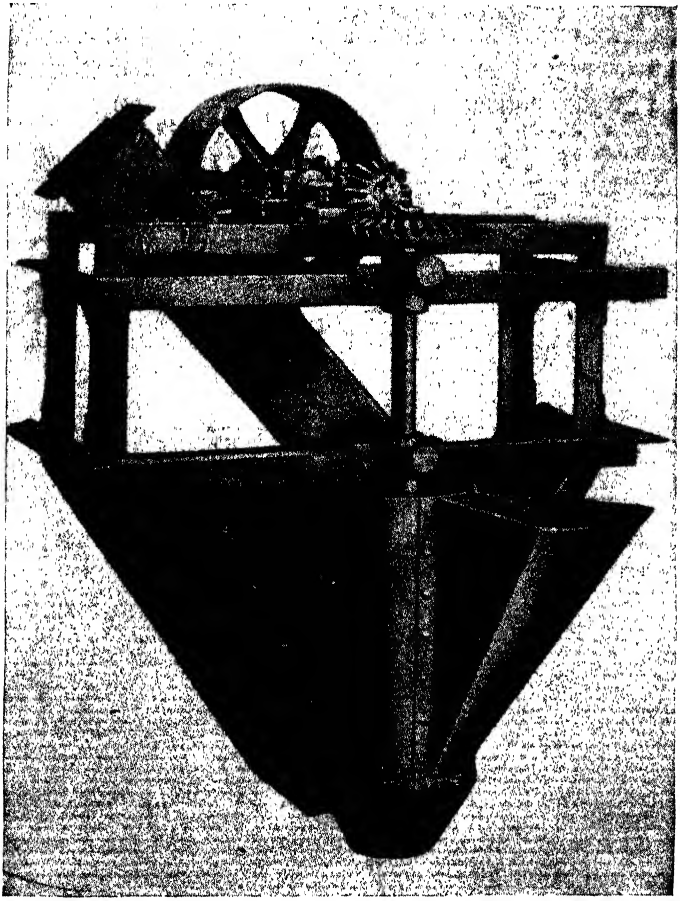

Fig. 32. Vezin sampler.

Particularly for coarse ore, this sampler requires more headroom than the Brunton and its long cutting edges are likely to be distorted. It is designed to take a definite proportion, usually one-fifth of the stream, and this proportion cannot be altered after the machine is made.

The Snyder sampler, shown in Fig. 33, is the simplest of all. It consists of a circular casting much the shape of miner's gold-pan, mounted on the end of a horizontal shaft. One or more holes are made in its sloping flange, and the edges of these project both front and back of the flange. The sampler revolves from ten to thirty times a minute, and the material to be sampled comes to it by way of a sloping chute, not shown in the cut. The ore stream falls on the inside of the sloping flange and either passes through the opening into a suitable sample hopper or slides off the flange into a hopper leading to the reject chute.

The sides of the sample spout should lie in planes passing through the axis of revolution. Such a sampler, 60 inches in diameter, will take material 3½ inches in diameter.

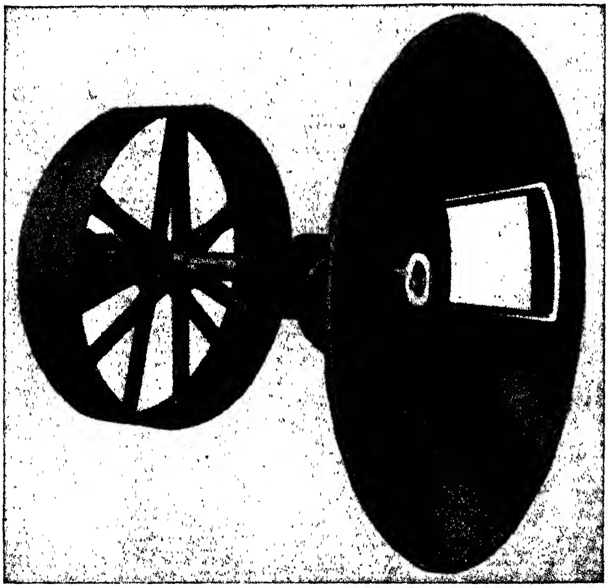

FIG. 33. Snyder sampler.

Figure 34 is a section through a sampling mill showing how a number of crushers and samplers are combined in an automatic plant. To simplify the drawing, the roll feeders have been omitted. Such a plant will treat a 50-ton carload in less than an hour. It is cleaned by brushing with the aid of compressed air.

Hand and Machine Sampling Compared. In comparing hand and machine sampling it may be said that machine sampling is generally cheaper and, with a properly designed machine, is more accurate than coning or fractional shoveling. Perhaps the most important advantage of all is that, being strictly mechanical in operation, it affords less opportunity for manipulation of the sample.

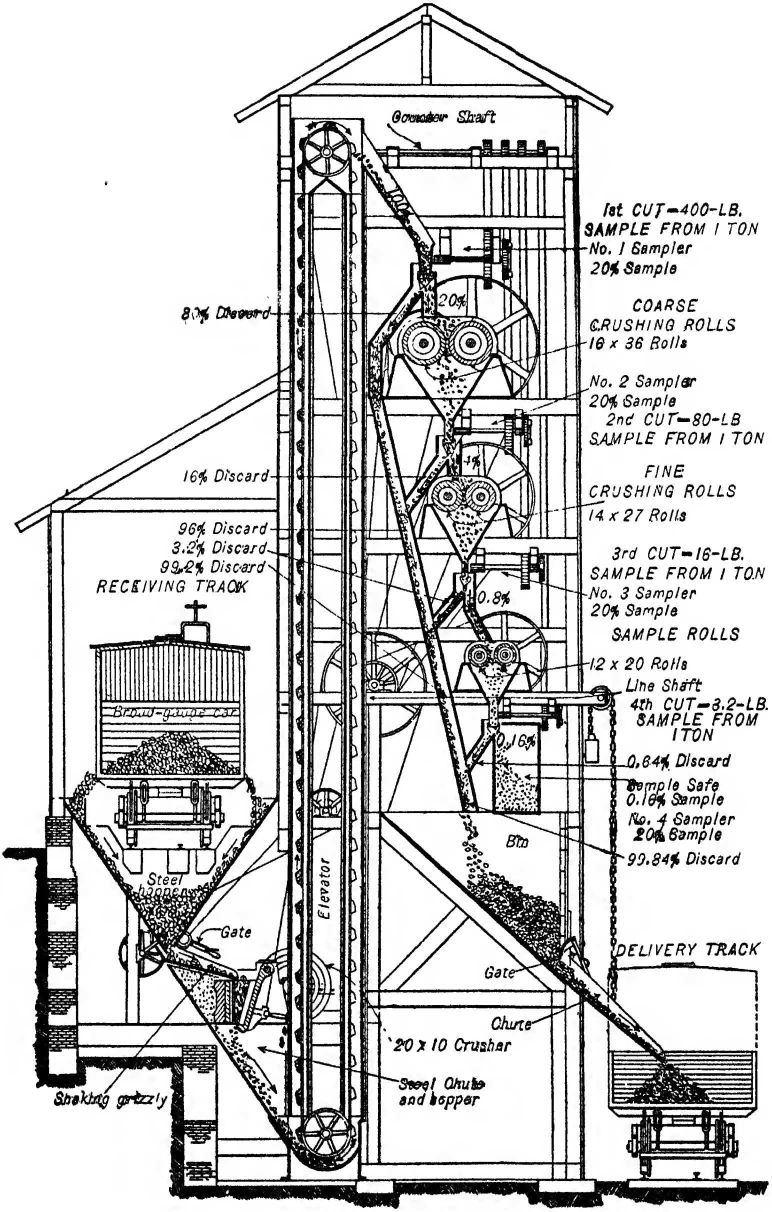

Fig. 34. Taylor and Brunton sampling system.

Precaution to Be Observed. Besides the danger of "salting" from crushing machines, elevators, sampling machines, etc., special attention must be paid to the disposition of the fine ore dust. As a rule the rich minerals in the ore are more brittle than the gangue, with the result that the dust is far higher in grade than the average of the ore, hence is seen the necessity of preserving all the dust and of taking pains to see that the sample contains its proper proportion of it.

Grab Sampling. This is a rapid method for sampling large quantities of low-grade and uniform material, such as iron or coal. It may also be used to obtain rough samples of the less homogeneous ores containing copper, lead, zinc, gold, and silver. The methods of sampling iron ore and coal are fairly well standardized. They consist in taking small shovelfuls from definite points in the car or vessel as the material is being unloaded, and combining and working them down by some of the standard finishing methods.

The method is obviously both rapid and inexpensive, but is so unscientific that no one considers it suitable for obtaining a sample from which the amount of gold, silver, copper, or lead contained in an ore is to be determined. Unfortunately, however, some smelters still continue to use the grab sample to determine the amount of moisture in custom ores.

Moisture Sample. Assays and chemical determinations are always made on dry samples, and the value of a lot of ore is always figured on the moisture-free basis. Unless the entire lot be dried, it is necessary to take a sample from which to determine the moisture. This sample must be taken as quickly as possible after the ore is weighed. If, as still too often happens, a grab sample serves as the basis for a moisture determination, much of the careful work of obtaining the sample for the determination of the other constituents may be nullified. Inasmuch as fines will ordinarily contain very much more moisture than lump ore, and as the grab sample is small in amount, it is clear that any sample of mine-run ore thus taken will tend to carry more than its due share of moisture. Such a result leads to an undervaluation of the ore, because the net weight reported is too small. In this connection it should not be forgotten that this so-called sample is taken by an interested party, an employee of the smelting company, who may be entirely honest but who certainly will not purposely lean over backwards in his efforts to be fair to the shipper. At any event, it is safe to say that samples for the determination of moisture should be taken with the same amount of care as samples for the determination of metallic contents, and that apparently the simplest and only scientific way of obtaining them from shipments of mine-run ore is to take them from the sample safe or reject from the last mechanical sampler.

Since the ore is weighed on the cars before it is sampled, and since in dry climates there is obviously some loss of moisture by evaporation from the ore in its passage through the crushing, elevating, and sampling machinery, it is customary to make a correction to the moisture figure, as determined by the last-described method, to compensate for this loss. This correction usually consists of the addition of an arbitrary percentage to the moisture reported by the chemist. Brunton* finds 10 per cent in summer and 7 per cent in winter a fair average figure. For instance, if the sample showed 5 per cent moisture for a lot of ore shipped during the summer months a fair figure for the actual moisture content would be 5.5 per cent.

This addition of a more or less arbitrary correction is not entirely satisfactory partly because the reason for it is not always understood by the shippers, but nevertheless this corrected method of arriving at the moisture content of an ore is far superior to that which depends on the grab sample, and with its use there are fewer disputes and less ill-feeling between seller and buyer.

Moisture determinations are made in duplicate on samples weighing from 2 to 5 pounds. These are weighed out into porcelain or enameled-iron dishes and dried at 105°C., the loss of weight being called moisture.

The moisture figure, either because of the method of taking the sample or the amount of the compensating correction applied, still continues to be a frequent source of dissatisfaction on the part of sellers of ore. The practice of taking one or more grab samples from each car of ore is the most unscientific part of the whole ore-purchasing business. This practice is unfortunately still common even when the ore is of such a nature that it must be passed through a mechanical sampling plant to obtain the sample used for determining the metallic contents. In this latter case, grab sampling has nothing to recommend it, unless it be the opportunity for manipulation or error, and it should be abandoned. If the ore is of such a nature that a satisfactory sample for the determination of metallic contents can be obtained without mechanical sampling, the same method may ordinarily be applied to obtain a moisture sample.

Duplicate Sampling. To check the accuracy of the sampling operations, we may resort to the process of duplicate sampling or to resampling. Duplicate sampling in the laboratory should consist in first cutting the entire lot into two portions and then sampling each one separately. As a general rule, the results should check within 1 per cent. Failure to do so indicates either poor mixing and cutting or a too rapid reduction of sample.

Some sampling mills are arranged to allow for taking duplicate samples,

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* *Trans. A.I.M.E.* **40,** 567 (1909).

so that they have constant checks on the accuracy of their sampling operations. The following results of assays made on original and resampled lots are taken from D. K. Brunton's paper, " Modern Practice of Ore-Sampling,"* and show how closely such work is made to check.

TABLE VII

RESULTS OF RESAMPLING

Lot No.	Sample Ounces Gold per Ton	Resample Ounces Gold per Ton
3192	3.62	3.64
3198	5.04	5.015
3219	2.70	2.67
3235	3.18	3.16
3310	1.17	1.17
3324	6.52 .	6.51
3340	0.71	0.78
3388	1.70	1.84
3424	9.24	9.20
3471	30.64	30.52

FINISHING THE SAMPLE

The 12- or 14-mesh ore cut by the last sampler is further reduced in size by means of sample grinders, and its weight is reduced by coning and quartering or by riffle cutting. The principles of sampling laid down in the first part of the chapter should be followed throughout, even to the final portion which is weighed out for assay determination.

As the sample grows smaller, more and more care has to be taken to prevent contamination or " salting." A few particles of rich ore, which if introduced into the original lot would have had no material effect on the average, might seriously alter the result if allowed to enter the final sample.

Before the final pulverizing is begun, the sample should be thoroughly dried by heating to 100° or 110°C. No greater degree of heat than this should be used, as there is danger of roasting the sulphides or otherwise altering the composition of the ore.

Mixing. In addition to coning, the following methods of mixing are common in some stage of the finishing treatment of ore.

1. ROLLING. For lots of 100 pounds or less the method of mixing, whereby the ore is rolled on canvas, rubber sheeting, or paper, is often used. When the ore particles are fairly uniform in size and specific gravity, this method is satisfactory, but for ordinary ores in the coarse state it should be avoided. For ore crushed so fine that it has little or no

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* *Trans. A.I.M.E.* **40,** 567 (1909).

tendency to stratify, as for example the assay pulp ground to 100- or 120-mesh, the method is found satisfactory when the operation is properly performed. This method is almost universally used by assayers for mixing the final lot of pulverized ore, just before taking out the assay portion.

2. POURING. For small samples the method of pouring from one pan into another is sometimes employed, especially as a preliminary to riffle cutting. Like the one above, it is imperfect when performed on an ordinary mixture of coarse and fine ore.

3. SIFTING. For mixing small lots of ore or fluxes, the method of sifting is particularly good. The apertures in the sieve should be two or three times as large as the largest particles. The ore should be placed on the sieve a little at a time and allowed to fall undisturbed into a flat receiving pan, until all the ore has passed the sieve. Two or three siftings are equivalent to 100 rollings. Sifting has the further advantage over the other methods that all lumps are broken up and the ore composing them distributed. It should be noted that sifting with a screen, the apertures of which are smaller than the coarsest particles of ore, will tend to separate hard and tough minerals which resist grinding, from soft and brittle ones which tend to become very finely pulverized.

Grinding. Two kinds of grinders are used for finishing work, the cone grinders and the disc pulverizers. They should be so constructed that they may be easily and thoroughly cleaned. Many excellent pulverizers are unsuited for sampling work on account of the labor and difficulty involved in cleaning them effectively.

Figure 35 shows a thoroughly reliable and efficient disc pulverizer which takes $\frac{1}{4}$-inch ore and reduces it in one operation to 100-mesh or finer. It is as nearly dust-tight as possible, and the grinding plates are renewable. It is shown open for cleaning in Fig. 36.

The bucking board is now but little used for grinding ores except for very small samples weighing less than 100 grams where, because of ease of cleaning and small dust loss, it may still be used. It is also used to regrind the last oversize resulting from screening.

One of the best methods of cleaning the bucking board or sample grinder is to brush it out, then grind a quantity of some barren material, such as sand or crushed fire brick, and follow this by a second brushing.

Screening. It is customary in careful work to screen all final samples of assay pulps. Although a good pulverizer, properly adjusted, will grind practically everything fine enough to pass 100- or 120-mesh in one pass, the exact adjustment is difficult to get and to maintain on account of wear and expansion due to heating. Besides, there is always a small amount of ore remaining in the feed chute, which has not been

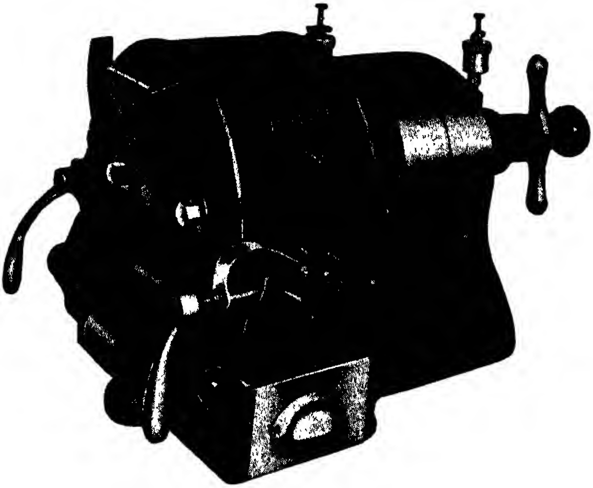

FIG. 35. Disc pulverizer closed.

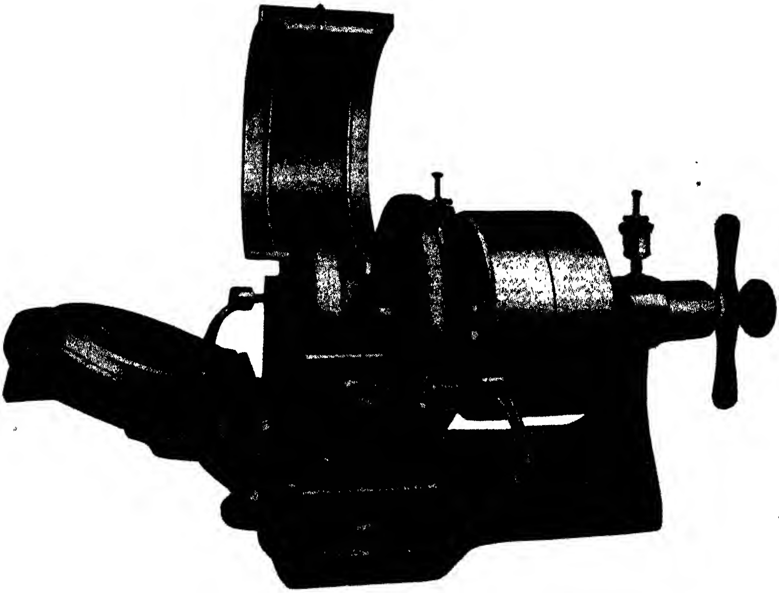

FIG. 36. Disc pulverizer open for cleaning.

ground and which in itself necessitates screening of the pulp. The screens should be at least 9 inches in diameter to give satisfactory capacity, and the screen wire should be of uniform grade. The screen itself consists of a suitable frame in which the screen wire is stretched, fitting into a pan that holds the sifted ore. Both should be free from crevices that might provide lodging places for ore, which would be given up later to enrich a subsequent sample.

The operation of screening consists of a combination of shaking in a horizontal plane and tapping of the screen against the tabletop or workbench to keep the meshes clean. Usually it is neither necessary nor desirable to use washers or a brush to assist in screening. Both tend to force oversize particles through the screen. Screens should be carefully brushed out after sifting each sample, and after a high-grade ore has been screened some of the barren material put through to clean the grinder should be sifted and then thrown away.

The sifted ore should be thoroughly mixed before sampling, as screening under these conditions favors a certain amount of segregation. For this reason, too, if the equipment or ore is of such nature that a sufficiently fine grind cannot be obtained in a single stage, the pan under the screen should not be emptied when the oversize is returned to the grinder, and in addition a particularly careful mixing should follow the completion of grinding to overcome such segregation as is certain to result from stage grinding.

When any portion of ore has been selected as a sample and is to be passed through a sieve, it is essential that the whole sample be made to pass. The harder portions which resist crushing the longest are almost invariably of a different composition from the remainder and if rejected render the whole sample worthless.

Size of Assay Pulp. For assay purposes, all ore should be reduced to at least 100-mesh and rich spotty ores should be pulverized to 140-mesh or finer to insure a fair sample for the final crucible or scorification assay. For a crucible assay using 1 assay ton, an ore may be left coarser than for a scorification assay where only 0.1 assay ton charge is used. If the assayer has difficulty in obtaining results checking within 0.5 per cent he may well look for the difficulty in the size of the assay pulp. Very often regrinding to a finer size will overcome the difficulty.

Grinding to too fine a size should be avoided. From 100- to 200-mesh is probably the best range. The heat generated in too intensive grinding may result in loss of water of combination from minerals such as gypsum or may cause oxidation and volatilization of sulphur or other constituents. This precaution is of importance only in the assay of extremely rich materials. Since too fine grinding of the gangue minerals of certain ores leaves them in a very light and fluffy condition and since the density of gold is so much greater than that of the remainder of the ore, it is believed that segregation may occur with some types of ores if the grinding is too fine.

ORES CONTAINING MALLEABLE MINERALS

In the crushing of ores containing native gold, silver, and copper, also chloride, bromide, iodide, or sulphide of silver, as well as other malleable minerals, more or less of these will be left on the sieve as flat scales, cylinders, or spheres. When an ore that might be expected to contain such minerals is being sampled great care should be observed, first, in watching for the metallics and seeing that they are saved, as the inexperienced operator is likely not to appreciate their value and to throw them away, and second, so to conduct the grinding that they may be removed at every opportunity. The coarser these particles are, the more difficult it becomes to obtain an accurate sample, both from the standpoint of sampling theory and from the fact that a larger amount of highly intelligent and painstaking labor is necessary throughout each stage of the sampling and assaying process.

Two mistakes are common. The first is to throw away a small amount of residue resting on the screen without carefully examining it to insure the absence of any valuable constituent. The second arises from the practice, occasionally noticed, of putting the metallics back on the bucking board or into the grinding machine with a small amount of the pulverized ore and continuing the grinding until everything passes the sieve. This practice is fully as objectionable as the first, both on account of the impossibility of obtaining an even distribution of the metallic particles in the final sample of assay pulp weighed into the crucible and because of the loss resulting from the smearing of the metallics on the working surfaces of the grinding machines. Another disadvantage of the second practice is the danger of salting the next sample from the metal remaining on the grinding surfaces, particularly if the sample is of low grade. Lodge gives an example of this kind to illustrate the necessity of a thorough cleaning of machines and bucking boards after rich ore has been ground. In this case sand carrying 0.04 ounce per ton in gold, after grinding in a "salted" machine, was found to assay 0.78 ounce per ton.

When an ore containing metallics is being sampled the original sample must be carefully weighed, the particles found on each sieve must be separately preserved and weighed, and the pulp resulting from each sampling and sifting must also be weighed. This not only gives the data from which to calculate the true or " metallic " assay of the sample submitted but also acts as a check on any carelessness in the whole sampling operation. If the pellets are gold or silver they are wrapped in lead foil, cupeled, weighed, and parted. If of copper, the weight of the metallic contents is otherwise established, perhaps by cleaning in hydrochloric acid and direct weighing, or by making a fusion as in the Lake Superior fire assay. Other cases may arise; for instance, in the sampling of molybdenum ores flat scales of molybdenite left on the screen will require special attention. Various metallurgical products, for instance, slag, matte, furnace or cupel bottom, dross, litharge, precipitate, etc., very often contain metallics and must be handled in this way.

Calculation of Results. Various writers give rules and formulas both for assaying and calculating results of this sort. No simple formula can cover all cases, and no rule or formula can take the place of the experience and common sense of the practical assayer, so that each example should be made an individual problem with its proper assumptions based on actual knowledge of conditions and occurrences during the sampling. The following example obtained in the assay or an ore from Cobalt, Ontario, will illustrate some of the problems which have to be taken into consideration.

DATA. Dry weight of sample received 129.6 grams. Size 16-mesh. This was crushed to pass a 120-mesh screen and yielded metallics on the screen 5.60 grams and pulp through the screen 121.6 grams. The pellets were scorified and cupeled, giving 3.823 grams of silver. The pulp assayed 1992 ounces per ton silver.

SOLUTION. It is at once seen that the sum of the weight of the pellets and pulp do not equal the weight of the original sample, the difference or loss being 2.4 grams. The assayer must decide what to do with this loss before proceeding to calculate the assay. However, it should first be pointed out that some loss is inevitable, the dust in any grinding room being sufficient evidence of this. The assayer does not know how much metal value this lost ore actually carries, but he knows that it does carry some and for that reason he cannot neglect it. It is obvious, however, that he should observe every precaution to keep the loss at a minimum to reduce this uncertain factor. In the example cited it was believed that all the loss was in dust, which was assumed to assay the same as the fine ore pulp. The amount of silver in 129.6 − 5.6 = 124.0 grams of pulp, assaying 1992 ounces per ton, is then calculated and added to the silver from the pellets. This gives the total silver contained in the original sample of 129.6 grams.

Silver in metallics		3.823 grams
Silver in 124.0 grams of pulp	$\frac{124.0 \times 1.992}{29.166}$	= 8.469 “
Total silver in sample		12.292 “

The average amount of silver in 1 assay ton of the original sample would then be found from the following proportion:

$$129.6 : 12.29 = 29.166 : x.$$

When this is solved x is found to be 2.765 grams, whence the “ metallic ” assay of the ore is 2765 ounces silver per ton.

In order to show the method clearly, the above calculation has been worked out with more precision than is ordinarily necessary. Whether the sample of 129.6 grams of 16-mesh ore is a reliable one is open to question, but it is obviously the duty of the assayer to analyze the material submitted to him to the best of his ability, regardless of the above consideration.

There may be a shorter method of calculating the “ metallic ” assay in the simple problem shown above, but in more complicated cases, where metallics are found on several screens in the reduction of a sample of considerable size, it is best to follow the general method illustrated as being less likely to lead to confusion and error. One additional assumption has to be made when a lot of ore reduced by stages yields metallics on different screens: in any sampling the reject contains the same proportionate weight and value in pellets as the sample. It need hardly be mentioned that, if the proper ratio between size of sample and maximum grain has been maintained, the above assumption will be borne out in practice.

The following example illustrates the more complicated case:

CALCULATION OF ASSAY WHEN ORE CONTAINS COARSE PARTICLES OF NATIVE GOLD

Data

A sample of 23.75 kilograms or 23,750 grams was crushed to pass a 40-mesh sieve.

On sieve 25 grams. This yielded 6.2750 grams of gold.

Through sieve 23,600 grams (loss 125 grams).

A sample from this of 5825 grams was crushed to pass a 120-mesh sieve.

On sieve 3 grams. This yielded 1.6720 grams of gold.

Through sieve 5802 grams (loss 20 grams).

The fine ore assays 1.21 ounces gold per ton.

Calculations	Weight Gold
Total pellets from 23,750 grams of ore on 40-mesh	6.275 grams
Total 40-mesh ore assuming loss to be same as the rest, *i.e.*, sample now 23,725 grams.	

Total pellets from 23,725 grams on 120-mesh

$$= \frac{23{,}725}{5825} \times 1.6720 = \qquad 6.810 \text{ grams}$$

Assuming all ore to be crushed through 120-mesh and no loss, there would be $23{,}725 - \frac{23{,}725}{5825} \times 3 = 23{,}713$ grams fine ore (assaying 1.21 ounces)

$$\text{Total gold in this} = \frac{23{,}713 \times 0.00121}{29.166} = \qquad 0.981 \text{ ''}$$

$$\text{Total gold in original lot} \qquad \overline{14.066} \text{ ''}$$

$29.166 : x = 23{,}750 : 14.066$

$x = 0.01727 =$ gold from 1 assay ton

Ore assays 17.27 ounces per ton.

If the metallics are mainly iron or other barren material the metallic assay may be lower rather than higher than the assay of the fine pulp.

CHAPTER IV

BALANCES AND WEIGHTS

The reliability of every assay or other quantitative determination is directly dependent upon the accuracy of the weighing, both of the ore charge and more especially of the resultant product, for example, the silver bead or the parted gold. Any error made in the weighing will, of course, invalidate all the rest of the work, regardless of the care which may have been given it. The operator should, therefore, familiarize himself with the construction, sensitivity, and operation of his balance before attempting to do any accurate assaying.

A good assay balance, used carefully and intelligently, is capable of weighing to 0.01 milligram or 0.00001 gram. For the most delicate assay balances an accuracy of 0.000002 gram is claimed. The necessity of weighing to this degree of accuracy may be understood when it is considered that, if 1 assay ton, about an ounce, of ore is used and the resultant gold weighed to the nearest 0.01 milligram, the value of the ore is determined only to within 35 cents per ton. This is usually sufficiently close, but any lower degree of accuracy would not be so considered.

At least three grades of balances are necessary for the fire-assay laboratory. These are known as flux, pulp, and button or assay balances. In large assay laboratories, there are also usually found bullion and chemical balances as well as separate assay balances for gold and for silver.

Flux Balance. The flux balance, for the weighing of fluxes, reagents, etc., should be an even balance scale, provided with a removable scoop-shaped pan, capable of weighing 2 kilograms and sensitive to 0.1 gram. Figure 37 shows a most satisfactory flux balance made with agate bearings and side beam graduated from 0.1 to 5.0 grams. With this balance no weight smaller than 5 grams is required.

Pulp Balance. The pulp balance for weighing the ore or pulp for assay and the buttons from lead assays, etc., should be an even balance scale. The pans should be made removable, and each should have a capacity of at least 2 ounces of sand. The pulp balance should be enclosed in a glass case and should be sensitive to half a milligram. Such balances are sometimes listed in the manufacturers' catalogue as prescription balances. If more than one pulp balance is to be obtained, it is well to get one or more having a pan capacity of 4 or 5 ounces of sand. For ½ and 1 assay ton charges the 2-ounce pan is to be preferred, as it is easier to transfer ore from it to the crucible than from a larger pan. Figure 38 shows a good type of pulp balance made with steel edges and agate bearings.

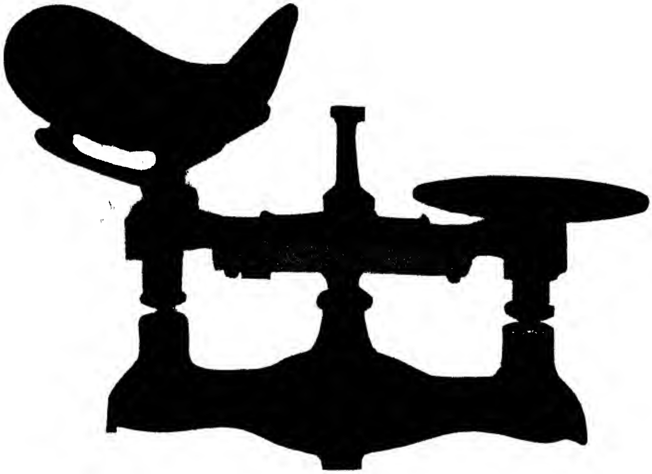

FIG. 37. Flux balance.

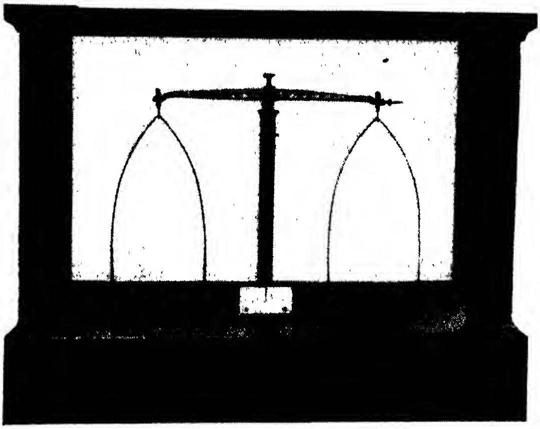

FIG. 38. Pulp balance.

Assay Balance. The button or assay balance is the most sensitive balance made. It should be capable of weighing to at least 0.005 milligram, should be rapid in action, making a complete oscillation in

10 to 15 seconds, and should have stability of poise; that is to say, it should be so made that its adjustments will not change sensibly from day to day as the result of slight changes of temperature and atmospheric conditions. The capacity of the assay balance need not be large, 0.5 gram maximum being sufficient, but the beam should be rigid at this load.

Such a delicate piece of apparatus must be handled with great care if good service is expected of it. It should be as far as possible from any laboratory or part of the plant where corrosive fumes are being evolved, and should be covered when not in use, to keep out the dust.

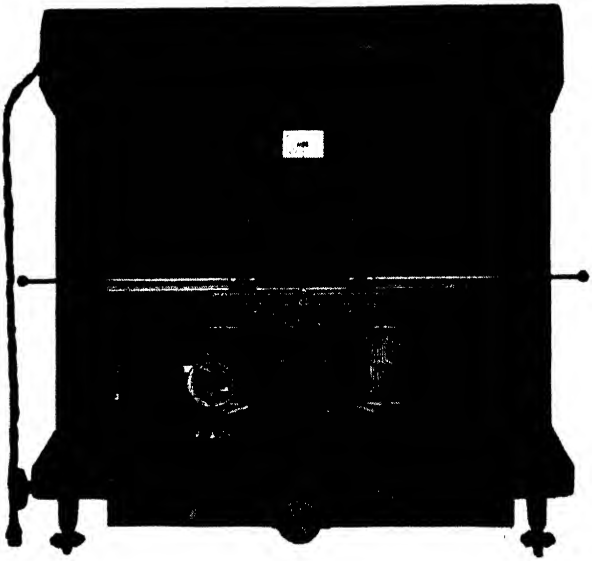

FIG. 39. Gold assay balance.

The balance beam should be as light as it can be made without sacrificing the necessary rigidity. For this reason the truss frame construction is usually adopted, giving the maximum strength with the minimum weight. The construction should be such that the two balance arms are of equal weight and length, and all three knife-edges should lie in the same plane. For obvious reasons the material of the beam should be non-magnetic and should have a small coefficient of expansion. The knife-edges and bearings should be of agate, ground, polished, and mounted so as to have equal angles on each side. The knife-edges should be so sharp that a strong pocket lens will show no flatness on the bearing edge, and the agate bearings should appear perfectly smooth. All the metal work of the balance should be protected from attack by chemical fumes, by some such means as gold plating or lacquering. Lacquering seems to resist chemical fumes rather better than the ordinary gold plating. The construction of the balance should be such that the rider may be placed on the zero graduation and used from the zero point to the end of the beam.

The balance must be mounted in such a way that it will be free from vibration. Such a support may be obtained by placing the shelf on which the balance rests on one or more posts which are set in the ground and which come up through the floor without touching it.

There are a number of good assay balances, many of them provided with reading glasses and other special attachments. Figure 39 shows one of the inverted type, the principal advantage of which is that, when the pointer is inverted, the ivory scale is on a level with the eye. This construction necessitates the offsetting of the zero graduation on the beam.

Theory of the Balance. The balance is essentially a light trussed beam, supported at its center by a knife-edge. At each end of the beam is hung a scale pan. The two pans should be of equal weight.

Let the three knife-edges A, B, and C be in the same straight line. Let $AB = BC = l$. Let G be the center of gravity of the beam, whose weight is W. Let the distance of the center of gravity below the point of support, $BG = l'$.

With a load of M in each pan there will be equilibrium. Now if a small weight (m) is added to the right-hand pan, the balance will swing through a small angle θ and the beam will again come to equilibrium in a new position $A'BC'$. The condition for equilibrium will be obtained by taking the moments of the three forces, M, $M + m$, and W, about the axis B. This gives the relation

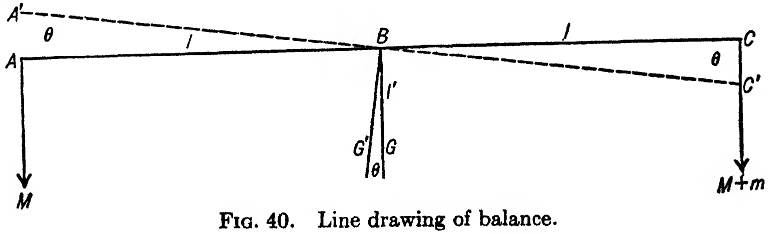

FIG. 40. Line drawing of balance.

$$Ml \cos \theta + l' \sin \theta \, W = (M + m) \, l \cos \theta$$

or

$$\frac{\sin \theta}{\cos \theta} = \tan \theta = \frac{lm}{Wl'}.$$

The sensitivity of a balance is usually denoted by the angle through which the beam will swing when a small weight, usually 1 milligram (for assay balance 0.1 milligram), is added to one pan. For small angles the tangent and its angle may be taken as equal, and therefore the expression deduced for tangent θ above may be taken as a measure of the sensitivity of the balance.

The equation for tangent shows that the sensitivity of a balance varies:

(*a*) Directly as the length of the balance arms.
(*b*) Inversely as the weight of the beam.
(*c*) Inversely as the distance of the center of gravity below the point of support. (Distance BG.)

The sensitivity is seen to be independent of the load if all three knife-edges are in the same plane, and most balance makers attempt to approach this condition in their assay balances. When B is above AC the sensitivity is decreased with the load; when B is below AC it is increased up to a certain limit, beyond which the equilibrium becomes unstable.

The condition of increased sensitivity with long beam and small weight (*a*) and (*b*) conflict, as the longer the beam is made the heavier it must be. The length of the arm is also limited by the time of swing of the balance, which may be considered to be a compound pendulum, and, as such, a long-arm balance swings too slowly for twentieth-century assayers. Formerly the long-arm balances were common, but at present the makers are restricting the length of the beam to 5 inches.

By bringing the center of gravity nearer to the center of support the sensitivity is increased. As the center of gravity nears the center of support, the stability of poise decreases. If the two should coincide there would be no point of rest and the balance would be unstable or "cranky." The most difficult thing to obtain is a balance with great stability and extreme sensitivity. It is obtained by making the beam as light as possible and then keeping the center of gravity sufficiently below the center knife-edge to give the necessary stability. Most high-grade balances are provided with a screw ball or sliding weight so that the center of gravity may be adjusted. If the balance lacks stability, *i.e.*, is cranky and oversensitive, both conditions may be remedied by lowering this weight and thus lowering the center of gravity of the system.

In the above discussion the assumption has been that the arms of the balance were equal. Modern high-grade balances usually approach this condition very closely. The process of "double weighing," however, serves to eliminate any error that may be due to inequality of the arms. Call the observed weight of the body as weighed in pan A, W', and that in pan C, W''. Then W, the true weight, is found as follows:

$$W = \sqrt{W'W''}$$

when W' and W'' are nearly equal $W = \frac{W' + W''}{2}$.

General Directions for Weighing. Brush off the pans and if necessary clean the front plate of the balance. See that the weighing rider is on the zero graduation or on the carrier, as the balance may require. Adjust, if necessary, to make the point of rest coincide with the center graduation on the ivory scale, and try the adjustment every time you have any weighing to do, as it is never safe to assume that the balance will stay in equilibrium. Note the maximum load the balance will carry and do not exceed this.

Put the balance into action by gently lowering the beam onto the knife-edges. It may then start swinging slightly of its own accord. If it does not, set it swinging by blowing gently on one pan with a device such as a medicine dropper. Have the amplitude of swing not more than one or two divisions each side of the center.

In reading the position of the pointer on the ivory scale, arrange always to have the reading eye in the same position relative to the ivory scale, that is, in a plane perpendicular to the scale and passing through the center graduation. A mark may be made on the glass door opposite the center division of the ivory scale by which to line up the eye before each reading. The final reading must be made with the door closed.

Arrest the swinging of the balance when the pointer is at the center of the scale. This prevents any undue jarring of the beam, which is very likely to get the balance out of adjustment. Always turn the balance out of action before adding weights to the pan or taking them from it. When the balance is not in use, raise the beam from the knife-edges and leave the rider on the beam.

Do not allow the direct rays of the sun to strike the balance, and never attempt to do close weighing unless the temperature of the room and balance can be maintained virtually constant.

Each silver bead should be placed on its side on a small anvil, hammered, and then brushed before it is weighed.

To transfer gold from the parting cup to the scale pan, lift the scale pan with the forceps and place on the front part of the glass mounting base. Gradually invert the parting cup over it, tapping it gently. All the gold should slide into the pan. Any particles adhering to the cup may be detached by touching gently with the point of the forceps or by means of a small feather trimmed to a point.

Before weighing the gold, examine it carefully to see whether it is clean, and remove any foreign matter present.

To remove gold from the scale pan after weighing, pick up pan in the forceps and invert it over the parting cup, brushing off lightly at the same time.

Weights should be placed only in the box or on the scale pan and should be handled only with ivory-tipped forceps. Record the weight of the substance, first, by noting the weights which are absent from the box, second, by checking off each weight as it is put back in the box. Record all weights in the notebook and not on scraps of paper.

For ordinarily accurate commercial work the weighing of the gold and silver is done by the " method of equal swings," using the rider for the final weighing. For extreme accuracy, as for instance in the calibration of weights, the weighing is done by " deflection," also called the " method of swings."

Weighing by " Equal Swings." First of all, the balance is adjusted by the star wheel or preferably by the adjusting rider, if one is provided, until the needle swings exactly the same distance on each side of the center, reading always in the same order, say from left to right. For accurate gold weighing it will be necessary to estimate tenths of divisions on the ivory scale.

Put the substance to be weighed on the left-hand pan and add weights to the right-hand pan until their weight is within a fraction of a milligram of the weight of the substance. Apply the weights in a systematic manner, starting with one which is estimated to be too large. If too large, remove it and try the next smaller weight, always working from larger to smaller weights until within 1 milligram of the true weight.

In trying any weight have the beam off the knife-edges, put the weight in the pan, and gently turn the balance key until the pointer inclines slightly to one side or the other. This swing of only one or two divisions should indicate immediately whether the weight on the pan is too much or too little. Again turn the balance out of action before making any change of weight.

When within a fraction of a milligram of the correct weight, shift the right-hand or weighing rider about, until, when the balance is put into action, the needle does not move very decidedly in one or the other direction. Then set the beam swinging one or two divisions each side of the center. If it does not swing evenly, arrest the swing, change the position of the rider, and try again. Repeat until the needle swings exactly as when adjusted. After one has become familiar with the balance only two or three trials of the rider will be necessary.

The weight of the substance is found from the sum of the weights on the pan plus the fractional part of a milligram indicated by the position of the rider on the beam.

Weighing by "Method of Swings." First, determine the point of rest under zero load by noting the position of the pointer at the extreme swing on each side, taking three, five, or a greater odd number of consecutive readings. Call the center division zero, and count divisions and estimate tenths to each side, calling those to the left of the center −, and to the right +.

Average the readings for each extreme, add the two algebraically, and divide the sum by 2; the result is the point of rest. The method is illustrated in the following example.

Left	Right
−3.9	3.6
−3.7	$\underline{3.4}$
$\underline{-3.5}$	$2\,\big|\,\underline{7.0}$
$3\,\big|\,\underline{-11.1}$	3.5
−3.7	
$\underline{+3.5}$	
$2\,\big|\,\underline{-0.2}$	
−0.1 = point of rest.	

Or the point of rest would be 0.1 division to the left of the center.

Call the point of rest under zero load r. Place the object to be weighed on the left-hand pan and weights on the right-hand pan until equilibrium is nearly established. With the rider determine the weight to the next smaller 0.1 milligram. Set the beam swinging as before, and find the position of rest for the pointer. Call it r'. Shift the rider to the right, one whole division (= 0.1 milligram) so as to bring the point of rest on the opposite side of r, find the position of rest again, and call it r''. The fraction of a milligram to be added to the weights and rider reading when r' was found is then

$$\frac{r' - r}{r' - r''} \times 0.10.$$

For instance, let the weights and rider reading be 27.4 milligrams, and let $r' = -1.4$ and $r'' = +1.6$. Then

$$\frac{r' - r}{r' - r''} = \frac{-1.4 + 0.1}{-1.4 - 1.6} = \frac{-1.3}{-3.0} = +0.43,$$

and the true weight would be $27.4 + (0.43 \times 0.1) = 27.44$ milligrams.

Weighing by Deflection. Weighing by "deflection" requires a knowledge of the sensitivity of the balance. Suppose that a weight of 0.10 milligram will cause a deflection of the point of rest of 2.0 divisions on the ivory scale. Adjust the balance so that the point of rest with no load corresponds to the zero of the ivory scale. Place the substance to be weighed in the left-hand pan, and again determine the point of rest. Suppose the deflection to be 1.2 divisions. Then the weight of the substance is 0.06 milligram. With a good balance this is a rapid and accurate method for small amounts of gold, but it is not commonly used.

Weighing by No Deflection. A fourth method of weighing, called weighing by "no deflection," is sometimes employed for rough work. It consists in applying the necessary weights and then shifting the rider until the needle shows no deflection when the balance is lowered gently onto the knife-edges. This method disregards friction and inertia and is not so accurate as the three methods previously described.

Weighing by Substitution. This method of weighing is usually adopted for the standardization or adjustment of weights, as it avoids any possibility of error due to inequality of arms. It consists simply in placing the substance to be weighed on one pan, counterbalancing it with weights placed on the other pan, and then removing the substance and adding standard weights until the balance is again in equilibrium. The weight of the substance is obtained from the substituted weights.

Check Weighing. Students are advised to check all gold weighings in the following manner: Weigh and record weight of each lot of parted gold resulting from duplicate or triplicate assays; then place all on one scale pan and obtain the total weight. Compare this with the sum of the weights obtained in the separate weighings. The figures should check within 0.01 or at most 0.02 milligram. If they do not, some of the weighings are at fault, some of the weights are in error, or the zero point has changed. By weighing the combined gold from two or three assays and reducing to milligrams per assay ton, the accuracy of the assay is correspondingly increased. This practice is followed by all good assayers.

Accumulative Weighing. A modification of the above method of check weighing is to weigh the gold accumulatively. For instance, suppose that an assayer has fifty lots of gold to weigh, each one of them perhaps less than 1 milligram. He can save time by weighing one after the other, without bothering to remove the previous lot, until all fifty are on the scale pan at one time. He records, of course, after the first weighing, the difference of weight caused by each increment of gold.

Besides saving time, this method of weighing reduces to a negligible amount any constant error, such as change of adjustment, as instead of occurring in each one of the fifty weighings, the full amount of this error occurs only once in all, and but one-fiftieth of it applies to any one weighing.

ADJUSTING AND TESTING AN ASSAY BALANCE

Leveling. Level the balance by adjusting the footscrews and by observing the plumb bob or level. Be sure that it rests firmly on the table or other support so that it will not be moved during the test. See that the beam, scale pans, and hangers are in their proper places and have not been forced out of normal position by previous careless usage.

Equilibrium. Lower the beam carefully until the agate knife-edges rest on the agate supports. This motion and the reverse one must be gentle to prevent injury to the knife-edges and also to prevent a shock or jar, which would tend to change the adjustments. Adjust the balance so that the pointer swings equally on each side of the center. A star wheel, a small projecting piece of metal or "flag," revolving on a vertical axis at the middle of the beam, or preferably an extra rider, constitutes the attachment for this adjustment. If this adjustment cannot be made and the balance on starting to one side or the other continues to swing in that direction with increasing velocity, it is in unstable equilibrium, and the center of gravity must be lowered until the proper equilibrium is obtained.

Time of Oscillation. Set the balance in motion and note the time of one complete oscillation, *i.e.*, swing from one extreme to the other and back again. For the modern 5-inch-beam assay balance this should be from 12 to 15 seconds. If much faster than this the balance will probably not be very sensitive; if much slower, the balance may lack stability and each weighing will take a correspondingly longer time.

Lowering the center of gravity of the beam results in decreasing the time of oscillation.

Stability. By "stability" of a balance is meant its property of remaining in adjustment during use and in spite of moderate changes of room temperature. It is a common error of assayers to neglect testing for stability when selecting a fine balance, and yet stability is fully as important as a high degree of sensitivity.

After each of the tests the beam should be lowered and the adjustment of the balance noted. If it no longer swings equally on each side of the center, due care having been taken to avoid disturbing any of the settings, it lacks stability. This may be due to excessive sensitivity, which can be overcome by lowering the center of gravity of the system by means of the screw ball, or it may be due to a defect in construction, arms of unequal length, etc., in which event it cannot be remedied.

Resistance. If the knife-edges are dull or the supporting surfaces rough the frictional resistance to swinging will be considerable and the diminution in the amplitude of swing will be rapid. Note the position of the pointer on the scale at the extremes of several successive swings. The difference between successive readings on the same side will show the diminution in amplitude due to friction and to resistance of the air. In a good assay balance this should not exceed 0.1 division when the amplitude of swing is 1 division. The horizontal section of the beam and the area of the pans and other projecting parts should be as small as possible, to reduce the air resistance.

Let the balance swing until it comes to rest; read the position of the pointer, lift the beam from the knife-edges, and repeat several times. The positions should not differ by more than 0.05 division. A greater difference than this indicates flatness of the knife-edges or roughness of the supporting surfaces. If the beam is exceedingly slow in coming to rest this test is unnecessary.

Sensitivity. The sensitivity of a balance is defined by physicists as the angle through which the beam moves when 1 milligram excess weight is added to one pan. If the scale graduations are laid out on the arc of a circle whose radius is the distance from the center knife-edge to the scale, the number of scale divisions passed over are proportional to the angle of deflection and, in any given balance, may be taken as a measure of the sensitivity. Unfortunately, however, there is as yet no standard distance between scale graduations and no uniformity of length of pointer, so that the number of scale divisions passed over cannot be used directly as a means of comparing the sensitivities of balances of different makes.

From a practical point of view, the sensitivity is the smallest difference in weight which the balance will indicate. Thus, when we say that a balance is sensitive to 0.01 milligram we mean that 0.01 milligram added to one pan will cause a noticeable difference in the swing or in the position of the point of rest.

Comparative Sensitivity. With a distance between scale graduations of 0.05 inch it is easily possible to estimate the position of the pointer at each extreme of a swing to the nearest 0.2 division or to within 0.01 inch. Pointers on a number of the better American assay balances range from 5.5 to 6.75 inches in length and average about 6 inches. With the usual length of pointer, the position of the point of rest should be shifted at least 0.01 inch when an unbalanced weight of 0.01 milligram is placed in one pan, if the balance is to be termed sensitive to 0.01 milligram. With this as a basis anyone may work out his own method of comparing the sensitivities of different balances by taking into account the distance between graduations and the length of the pointer.

To Test Equality of Arms. Adjust balance to swing evenly with no load, and then place equal weights on each pan, equivalent to the full load of the balance. If the pointer does not now swing evenly the arms are of unequal length.

To Determine Whether All Knife-Edges Are in Same Horizontal Plane. Adjust balance and determine sensitivity with no load. Then place full load on each pan and again determine sensitivity. When the three knife-edges are in the same plane there should be no change of sensitivity with any weight up to the full load of the balance. When the full load of the balance is not known the sensitivity should be determined for gradually increasing loads and a curve of sensitivity drawn. If the three knife-edges are in the same plane this curve should be a straight line up to the point where the beam begins to be deflected by an overload.

WEIGHTS

For the three balances above described we require four sets of weights, as follows:

For the flux balance we should have a block containing weights from 1 kilogram to 1 gram. These weights need not be extremely accurate.

For the pulp balance two sets are necessary, gram and assay-ton weights: gram weights, from 20 grams to 10 milligrams for weighing flour and ore for lead, copper, and tin assays, as well as the buttons from the same; assay-ton weights, 2 assay tons to $\frac{1}{20}$ assay ton for weighing ore, matte, speiss, and lead bullion for the gold and silver assay.

For the button balance a set of milligram weights of the utmost accuracy is required, from 1 milligram up to 500 milligrams. These are preferably made of platinum, as an absolutely non-corrosive weight is imperative. Riders are used for determining fractions of a milligram. Riders are of fine aluminum wire and are usually made to weigh 0.50 or 1.00 milligram. The balance beam is usually divided into 100 spaces on each side of the center, and when a 1-milligram rider is used each space represents 0.01 milligram.

For many balances, a rider with a diamond-shaped loop, known as the Thompson rider, is to be preferred. Its principal advantage is due to its property of always hanging in a vertical position when on the rider arm. Even if it falls over to one side when on the beam it will slip back to the vertical position when lifted by the rider arm. The diamond-shaped loop prevents it from swinging or twisting around on the rider carrier and permits the rider to be placed squarely on the beam.

Multiple-Rider Attachment. Most balance makers supply, on demand, what is called a multiple-rider attachment, designed to do away with the use of the smaller weights. It consists of a carrier supplied with a number of riders of different weights, for instance, 1, 2, 3, 5, 10, 20, 30 milligrams, so arranged that any or all may be placed on a support provided for the purpose. This is equivalent to placing flat weights of the same value in the pan.

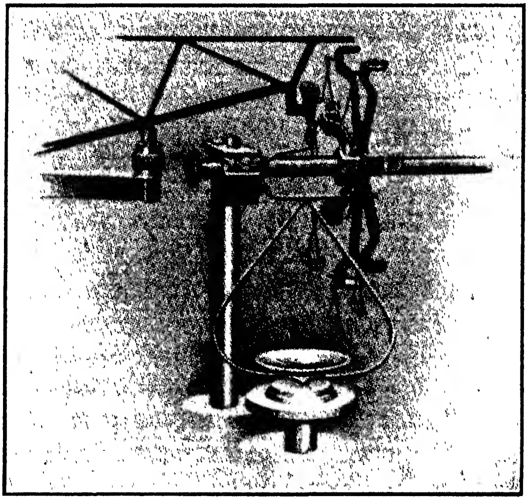

FIG. 41. Thompson multiple-rider attachment.

In Fig. 41 is shown a multiple-rider attachment, the horizontal arm of which extends through the glass side of the balance and terminates in a milled head. The different riders are distinguished from each other by differently formed ends. An advantage claimed for this device is a saving in the wear and tear of weights, as the small flat weights, frequently handled by forceps, become broken and inaccurate, whereas the riders, on which there is practically no wear, maintain their original weight almost indefinitely. A second advantage claimed is a saving in time, as with this attachment the riders can be manipulated much more quickly than the flat weights, which must be handled with forceps. It is not necessary to open the door of the balance in weighing any bead under 40 or 50 milligrams, and this alone is a saving of some time and also allows all air currents to subside before the final reading is made.

Multiple-Weight Attachment. The multiple-weight like the multiple-rider attachment is designed to save time and wear on weights due to handling. The weights, in the form of perforated discs, when not in use, are carried on nine conically tipped vertical staffs which in turn are controlled by a keyboard on the front of the balance. By depressing any one of the keys the corresponding weight is deposited in one of nine corresponding recesses in a perforated grid which is made a part of the right-hand hanger yoke. The weights may be applied independently or in any desired combination. They total 221 milligrams so that all but the very largest assay beads may be weighed without the necessity of opening the balance door. The general details of construction may be seen by reference to Fig. 42.

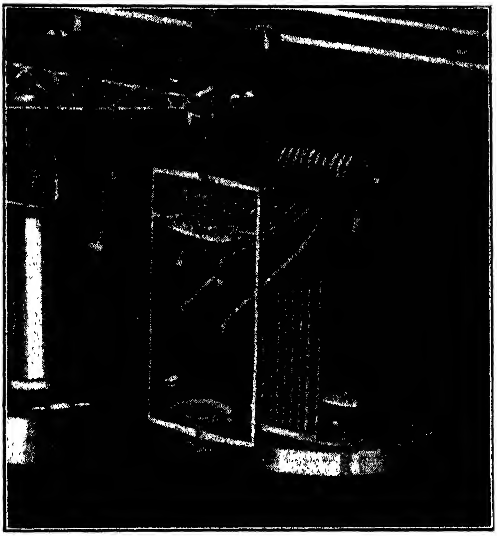

FIG. 42. Keyboard operated multiple-weight attachment.

Mechanical Pan Extractor. Wilfrid Heusser has developed a cleverly designed device by means of which the assay beads or parted gold to be weighed are introduced and removed from the balance case without the necessity of opening the door. This not only saves time in quantity weighing but also helps to maintain a constant temperature inside the case. Its use results in less disturbance of weighing due to air currents and protects the balance against dust.

As may be seen by referring to the cut, Fig. 43, the left-hand balance pan is supported in the middle of the hanger frame by means of a claw and light column. In weighing position the ring-shaped mechanical hand is within the balance directly beneath the pan which is free to swing because of the column type of pan support. A circular hole in the balance door, which during weighing is covered with a spring-actuated glass shutter, serves to permit the passage of the extractor hand and pan in the process of transferring beads. The device is actuated by means of a knob located on the left-hand side of the balance base which when turned results in lifting the pan from the claw support and brings it opposite the center of the shutter. Pushing back the knob now results in swinging forward the extractor carrying the pan, the hand pushes open the shutter and brings the pan outside of the casing.

FIG. 43. Heusser mechanical pan extractor.

The door may be raised or lowered in the ordinary manner when the pan extractor is not in use. All motions are limited by stops, and the possibility of upsetting the pan or of disarranging the hanger from its supporting knife-edge is eliminated by means of suitable locking devices.

When this device is used in connection with a multiple-weight attachment one may weigh for days at a time without opening the balance door, and the time of weighing is materially reduced. Without either of these attachments a skillful operator can weigh and record about 30 golds per hour; with the aid of the attachment, some 60 or more.

Assay-Ton Weights. The assay-ton system of weights was devised to facilitate the calculation of the results of gold and silver assays. In the United States and Canada the results of such assays are reported in troy ounces of gold and silver per 2000 pound avoirdupois ton of ore. With the ordinary system of weights a tedious calculation would have to be made for each assay with the possibility of mathematical errors.

The basis of the assay-ton system is the number of troy ounces (29,166. +) in one ton of 2000 pounds avoirdupois. The assay ton is made to weigh 29.166 grams. Then

1 ton avoirdupois : 1 ounce troy : : 1 assay ton : 1 milligram.

Therefore, with 1 assay ton of ore, the weight of the silver or gold in milligrams gives the assay directly in ounces per ton.

In England and Australia the long ton of 2240 pounds is used, and the assay ton weighs 32.666 grams.

In Mexico, as ores are bought and sold in metric tons of 1000 kilograms, and assays are reported in grams of gold and grams or kilograms of silver per metric ton, it is convenient to weigh out the ore in grams.

Calibration of Weights. The weights supplied by the makers cannot always be relied upon, and even originally perfect ones are subject to changes of weight due to wear or accumulation of dirt. Therefore it behooves the assayer to check his weights occasionally and to determine the correction to be applied to the marked value. This necessitates a standardized weight which should be carefully preserved and used for this purpose only.

The method of swings should be followed, and the weighing done by deflection after the sensitivity of the balance has been determined. First determine the position of rest and the sensitivity with no load and with 100, 250, and 500 milligram loads, respectively. The sensitivity should not vary much throughout this range. The method to be followed can be understood from the following example.

CALIBRATION OF A SET OF ASSAY WEIGHTS

Designate each weight by its marked value in the parenthesis, and when there are several of the same value note some peculiarity by which each may be designated. The weights in the set, marked in milligrams, are:

$$(500) = a, \quad (200) = b, \quad (100) = c, \quad (100') = d, \quad (50) = e, \quad (20) = f,$$
$$(10) = g, \quad (10') = h, \quad (10'') = (5) + (2) + (2') + (1) = i.$$

The weight (100) is compared with the standard 100-milligram weight, and the weights are then compared among themselves by the method of swings. The letters represent the true values.

In calibrating the weights from 100 milligrams to 10 milligrams, observations should be made on the following combinations:

Left-hand Pan	Right-hand Pan
(100)	100-mg. standard
(100)	(50) + (20) + (10) + (10′) + (5) + (2) + (2′) + (1)
(50)	(20) + (10) + (10′) + (5) + (2) + (2′) + (1)
(20)	(10) + (10′)

The recorded observations are as follows:

$$\begin{array}{lll} 100\text{ mg.} & = c & -\ 0.020\text{ mg.} \\ c & = e + f + g + h + i & +\ 0.190 \\ e & = f + g + h + i & +\ 0.020 \\ f & = g + h & +\ 0.040 \\ g & = h & +\ 0.015 \\ h & = i & +\ 0.040 \end{array}$$

Solving these equations,

$$\begin{aligned} i &= i \\ h &= i + 0.040 \\ g &= i + 0.055 \\ f &= 2i + 0.135 \\ e &= 5i + 0.250 \\ c &= 10i + 0.670 \\ c &= 100.020\text{ mg.} \end{aligned}$$

From the last two values of

$$\begin{aligned} 10i &= 99.350\text{ mg.} \\ i &= 9.935\text{ mg.} \end{aligned}$$

Substituting this value for i in the above equations, we find the following values for the other weights of the set:

Designation	Actual Weight	Correction* to Marked Value
c	100.020	+ 0.020 mg.
e	49.925	− 0.075 "
f	20.005	+ 0.005 "
g	9.990	− 0.010 "
h	9.975	− 0.025 "
i	9.935	− 0.065 "

* A + correction means that the weight is heavier than the normal value.

The smaller weights in i may be calibrated in a similar manner. The large weights (100), (200), and (500) may be standardized by a simple modification of the above.

The process is made much simpler by having a complete set of standard weights which are very carefully handled and kept solely for standardizing purposes, and these the larger assay offices usually have.

Testing Riders. Every new rider should be tested before use, as riders often vary 0.01 or 0.02 milligram from their supposed value. If a rider is too heavy, a little bit at a time may be cut off with a pair of scissors until it comes down to the standard.

CHAPTER V

CUPELLATION

In every assay of an ore for gold and silver, we endeavor to use such fluxes and to have such conditions as will give us as a resultant two products:

1. An alloy of lead, with practically all the gold and silver of the ore and as small amounts of other elements as possible.
2. A readily fusible slag containing the balance of the ore and fluxes.

The lead button is separated from the slag and then treated by a process called cupellation to separate the gold and silver from the lead. This consists of an oxidizing fusion in a porous vessel called a cupel. If the proper temperature is maintained the lead oxidizes rapidly to PbO, which is partly (98.5 per cent) absorbed by the cupel and partly (1.5 per cent) volatilized. When this process has been carried to completion the gold and silver are left on the cupel in the form of a bead.

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 cause a high loss of silver.

The cupel is a shallow, porous dish made of bone ash, Portland cement, magnesia, or other refractory and non-corrosive material. The early assayers used cupels of wood ashes from which the soluble constituents had been leached. Agricola, writing about the year 1550, mentions the use of ashes from burned bones. Ashes from deers' horns he pronounces best of all; but the use of these was becoming obsolete in his time, and he states that assayers of his day generally made the cupels from the ashes of beechwood.

Today it is thought that the bones of sheep are the best for cupels. The bones should be cleaned before burning and as little silica as possible introduced with them. It is important not to burn the bones at too high a temperature as this makes the ash harder and less absorbent. It is also advisable to boil the bones in water before burning them as this dissolves a great part of the organic matter, which if burned with the bones yields sulphates and carbonates of the alkalies.

Properly burned sheep bones 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 being used. 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 for bone ash; no doubt the nature of the material is an influential factor. The bone ash represented by the following screen analysis has 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 milligrams of silver and 25 grams of lead; 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 10 to 14 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 depends somewhat on the bone ash and on the pressure exerted in forming the cupels. The greater the pressure the smaller the amount of water required. It is better to err on the side of making the mixture a little too dry than too wet.

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; 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, with the hand mold and die.

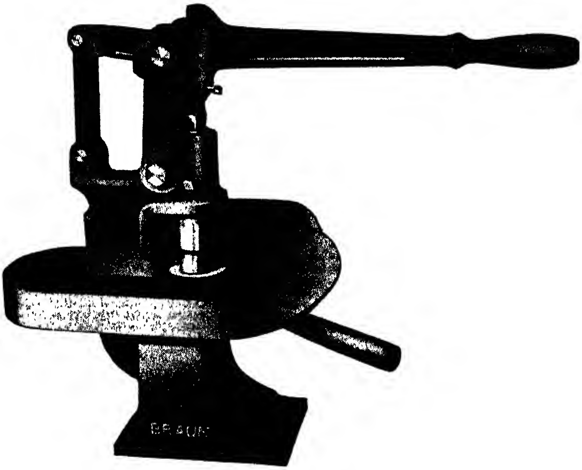

Fig. 44. Cupel machine.

Several types of cupel machines are on the market, one of the best of which is shown in Fig. 44. 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 adjustments, 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 200 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 with 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.

Cupels should not crack when heated in the muffle and should be so strong that they will not break when handled with the tongs. To obtain this strength with bone-ash cupels a fairly high pressure, as great as 800 to 1200 pounds per square inch is recommended. The high pressure gives a cupel of greater density which when properly manipulated permits of cupellation with lower losses.

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, owing 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 with 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.

Testing Cupels for Absorption of Silver. An occasional test of cupels and especially of each new lot of bone ash is desirable. Select some standard amount of lead and silver, and always use the same amounts so that results may be comparable. Convenient quantities are 100 milligrams of silver and 25 grams of lead.

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 10 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 5 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 of the alloy considerably above that of its surroundings, so that 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.

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

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, featherlike 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 all sides of the cupel cup, and as the button grows smaller they should follow it down the cupel, leaving, however, a slight clear space around the bead. 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 ring of molten litharge is seen forming all around the annular space between the lead and the cupel. If the temperature of the cupel is not quickly raised, this ring increases in size, soon entirely covering 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, *e.g.*, by taking away the coolers, closing the door to the muffle, opening the draft, or putting a hot piece of coke in front of the cupel.

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

Toward the end of the cupellation process the temperature must be raised, since the amount of heat supplied by the oxidation of the lead is constantly decreasing and because the alloy becomes more difficultly fusible as the proportion of silver in it increases. In order to drive off the last of the lead a temperature of about 900°C. should finally 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." When conditions are such that brightening is clearly defined from the subsequent phenomena one sees a bright liquid globule of noble metal free from any oxide coating. It will reflect a poker or other dark object held over it.

If the muffle temperature is above the melting point of the alloy, it should now be allowed to cool until the bead solidifies. 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 watched carefully after brightening; just as the silver begins to solidify, very hot cupels may be placed over them and allowed to stand for several minutes, after which they are slowly withdrawn from the muffle. The hot cupel melts the outside crust of solid silver and causes solidification to go on from below. If this precaution is not taken, the beads may " sprout " or " spit." This action is caused by the sudden escape of oxygen which is dissolved in the molten silver and expelled when the bead solidifies. If the bead is allowed to solidify rapidly, a crust of solid silver forms on the outside, and as the central part solidifies this crust is violently ruptured by the expelled oxygen, giving a cauliflowerlike growth on the bead and causing particles of silver to be thrown off. As a consequence the results obtained from sprouted beads are unreliable. Beads containing one-third or more of gold will not sprout even if rapidly withdrawn from the muffle. Sprouting is said to be an indication of the purity of the silver.

The silver bead should appear smooth and brilliant on the upper surface, and should be silver-white in color and spherical or hemispherical in shape, according to its size. It should adhere slightly to the cupel and appear frosted on the under surface. If the bead is smooth on the bottom and does not adhere to the cupel, it is an indication of too low a finishing temperature. Such a bead always contains lead. If it has rootlets which extend into cracks of the cupel the results are also to be taken as unreliable, as some of the silver may be lost in the cupel.

Lead buttons very rich in gold and silver have a peculiar mottled appearance after cupeling begins. Oily drops of litharge appear and move about on the surface of the alloy; finally they run down the side of the convex surface and are absorbed by the cupel. This appearance is characteristic and once seen is easily recognized again. It may be observed toward the end of cupellation with any alloy containing much precious metal and is an indication of the approach of the end and a reminder that the temperature should be raised to insure driving off the last of the lead.

The minimum temperature at which cupellation will proceed has been a more or less disputed point, owing largely to different conceptions of the process and involved conditions. At least three methods of measuring the temperature have been proposed. One experimenter held his pyrometer junction ¼ inch above the alloy in the cupel, another placed the junction inside the cupel, while a third measured the temperature of the alloy itself. According to Fulton* the alloy itself must be between 800 and 850°C. Litharge melts at 884° (Mostowitch), 906° (Bradford), but passes through a pasty stage before becoming liquid. It would seem that the cupel itself must be maintained above the melting point of litharge in order to allow of absorption. At any event the cupel is much hotter than the space around it partly because of the heat generated by the oxidation of the lead and partly because the cupel rests on the floor of the muffle and its interior portion becomes heated by conduction through the muffle floor on which it stands. Bradford† found 906°C. to be the minimum cupel temperature which would permit of absorption of litharge. Lodge found that for silver cupellation, with a moderate draft, the muffle temperature (taken ¼ inch above the cupels) should be between 650° and 700°C.

FIRST EXERCISE. PRACTICE IN CUPELLATION

Procedure. Wrap from 0.10 to 0.20 gram of silver in 25 to 30 grams of sheet lead. Prepare two or three of these portions, and cupel one at a time in order to become familiar with the operation and with the correct temperature. To study the end phenomena " play of colors," " brightening," " blick," etc., the same or a larger amount of silver may be used with a smaller amount of lead, say 10 grams.

Have the muffle at a bright red; be sure that the cupels are dry, and then heat gradually until they are red. Allow at least 10 minutes for this. Be sure that the cupels weigh more than the lead, and that the bowl is sufficiently large to contain the melted alloy. Have a row of extra cupels in front of those which are to be used, and keep them there throughout the process. Keep the door to the muffle closed, and when

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* *Loc. cit.*

† *J. Ind. Eng. Chem.* 1, 181.

the cupel is red throughout and heated to about 900°C. place the packet of lead and silver carefully in the cupel and close the door to the muffle so that the lead will fuse as quickly as possible. As soon as the assay begins to " drive," note the time, open the door of the muffle, and lower the temperature of the cupel by checking the fire and by placing cold scorifiers, etc., around it. Continue to reduce the temperature until feather crystals of litharge form on all sides 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 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 5 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 may be charged in the order of their size, *i.e.*, largest first, so that all may start driving together.

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

2. All cupels should be of the same height and should be placed close together, with their tops level.

3. 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.

4. 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.

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

6. When the finishing temperature is too low, the beads will solidify without brightening. They retain lead, 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 if 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. A frosted appearance of the upper surface of the bead 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. DETERMINATION OF SILVER LOSSES IN CUPELLATION

Procedure. Weigh two portions of c.p. silver foil of 100 ± 1 milligram exactly to the nearest 0.01 milligram on the assay balance. Wrap each in 25 grams of sheet lead, being careful to keep the two portions separate. Cupel one with abundant feather crystals of litharge and the other at the highest temperature of the muffle. Each is to be protected from the incoming air by having a cupel immediately in front of it. Detach, clean, and weigh the silver beads; determine the percentage loss of silver in each portion, and show the results to an instructor for approval.

This exercise should not be attempted until some facility has been gained in cupellation and the student feels that he is competent to cupel with abundant crystals.

THIRD EXERCISE. CUPELLATION ASSAY OF LEAD BULLION

Procedure. Weigh out carefully three portions of bullion of ½ assay ton 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. Select cupels which weigh 35 grams or more, and arrange 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 the feather crystals of litharge form on all sides of the cupels. Finally open the draft and otherwise increase the temperature for the last few minutes of cupellation to drive off the last traces of lead. Do not disturb the cupels, but allow them to cool slowly, taking suitable precautions to prevent sprouting. All danger of sprouting is over when the inside of the cupels reaches a dull red or when the beads have become solid throughout. Remove from the furnace to the cupel tray and allow to cool. When the beads are cold, detach from the cupels with the pliers and brush with a stiff brush to remove bone ash, or place on their sides on a clean anvil and slightly flatten with a hammer. When the beads are free from bone ash, weigh and record 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 transfer the bullion from the scale pan to the lead foil over this so that if any is spilled it will be seen and recovered. Do all 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.

After a student has begun to practice cupellation and has had the misfortune to freeze a number of assays he is inclined to go to the other extreme and to run the succeeding assays too hot, which is equally disastrous as far as results are concerned. At about this time he begins to wonder why he is not provided with a pyrometrically controlled furnace which will automatically relieve him of the onerous and perspiration-provoking job of controlling heat input and of manipulating coolers. This is a perfectly normal reaction and such a foolproof robot would appeal to many older assayers as well. Though a beginner might get some help from such a device, the behavior of cupels of different characteristics and the influence of various metallic impurities on the cupeling operation itself are such that it would still be necessary for a competent operator to give careful personal attention to each lot if good results were to be obtained. For this reason, the student is urged to master the art of cupeling at this stage of the educational process and he may rest assured that it will stand him in good stead in all subsequent work.

Essentials for Good Cupellation. Besides having cupels of the right composition, density, shape, etc., it is also essential to have all cupels used in any operation of the same height. Moreover, the floor of the muffle must be smooth and level so that the tops of the cupels are truly level. The air supply should be uniform across the entire width of the muffle and should continue so beyond the back row of cupels since an irregular air supply gives irregular losses. The direction of fumes is a good guide as to this condition. The velocity of the air should be moderate, or otherwise the opening of a door or window somewhere may suddenly chill a muffle full of cupels. An air supply which gives an oxidation rate of about 1 gram of lead a minute has been found satisfactory. The heat supplied to the muffle should be so regulated that the temperature throughout the muffle is constant. This requires that more heat be supplied toward the front than toward the back of the muffle. The cupels should be placed close together, and the front row should be protected from undue cooling by a solid row of cupels of uniform height or preferably by a special bar of refractory material the same height as the cupels and as long as the inside width of the muffle.

LOSS OF PRECIOUS METALS DURING CUPELLATION

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

With good cupels and properly conducted cupellation the loss of precious metals is thought to be due mainly to oxidation and absorption of the oxides together with litharge. A small proportion of the loss is due to volatilization If it is remembered that silver is more readily oxidized than gold, the fact that the alloy which is recovered in the assay of cupels is always higher in percentage of silver than that which formed the assay bead is an indication that the loss is of a chemical nature rather than purely mechanical.

In regard to volatilization, King* found that when cupeling at a muffle temperature of 920°C., which is much higher than normal for silver work, the volatilization loss of silver was only about 0.5 per cent of the total loss.

The most important single factor relative to cupel loss is the temperature. The higher the temperature, the higher the loss, is an invariable rule; hence cupellation should be conducted at the lowest practicable temperature.

Apparent and True Loss. In any consideration of the loss of precious metals in cupeling the student must take pains to distinguish between apparent and true loss. When pure silver or pure gold is cupeled alone and the resultant bead weighed, the difference in weight is ordinarily termed loss. This is the case for example, in Tables IX, X, and XI. Actually, since the bead probably always retains some lead and sometimes other base metals, the true loss is really greater than that indicated by the difference in weight, and to distinguish between them this loss due to difference is here termed " apparent " loss. For practical purposes, in gold-assay work involving parting, provided that sufficient silver is used, no such distinction need be made.

The determination of true loss is somewhat of a task, but the most direct method would require the development of a quantitative microchemical method for the analysis of the assay beads. An approximate measure of the true loss could be obtained by means of carefully corrected assays of the original cupel supplemented, if warranted, by the

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* "The Influence of Cupels on Silver Loss," *Bull.* 147, University of Toronto Press, p. 36, 1934.

addition of some factor for secondary slag and cupellation as well as for volatilization loss.

Feathering of Cupels. The most important single factor relative to cupel loss is the temperature, by which is meant the temperature at the surface of the cupeling alloy — the reacting surface. With a normal air supply which gives an oxidation rate of about 1 gram of lead a minute and other conditions which experienced assayers recognize as essential, the securing of a good crop of feather litharge is, with the exception of acceptable results from a " check " assay, the best available measure of suitable cupellation conditions. A descriptive classification of feathered cupels with the significance of the same is useful for student and experienced assayer alike, both for purposes of evaluation of results and for record and reference with respect to each assay. The following designations have long been in use in the writer's laboratory.

FULL FEATHERED. The cupel has been carried for all but the last few minutes at a temperature which permits the formation of litharge crystals all around and just above the receding circle of contact of the cupeling alloy and the cupel surface. There is no better measure of ideal cupellation than this if it is at the same time accompanied by the general and well-known indications of a properly finished bead.

HALF RING. Feathers are found from top to bottom on one-half of the cupel surface, the cooler side. This indicates that the heat distribution was imperfect, and the losses will be higher than for a " full-feathered " cupel.

HIGH RING. The feathers form a ring near the top of the cupel but do not follow down the cupel cup. This indicates that the temperature was correct near the beginning of the cupeling process but increased as the process progressed. Losses will be unduly high under these conditions.

LOW RING. A good ring of feathers lies slightly above the finished bead but none near the top of the cupel. This is a clear indication that the temperature was too high during the early stages of the process but had been reduced to a suitable point toward the end of the operation. The loss should be less than for the high ring, since the temperature was proper when the silver concentration was high, at which time suitable temperature conditions are most essential.

Loss of Silver. The literature relating to the losses of silver in cupellation is voluminous, but most of the quantitative data are of little value owing to the omission of essential details or because of inadequate control of important conditions. Such statements as " approximate temperature of air in muffle 750°C.," for example, does not help very much in regard to the temperature of cupellation.

"Cupeled at a low temperature" leaves much to the imagination. Many of the writers have not fully appreciated the great complexity of the process and the interactions of the many variables, hence their conclusions should be critically studied before they are accepted.

The effect of temperature on the loss of silver in cupellation is shown in the following table adapted from work by Eager and Welch.* The temperature was taken with a Le Chatelier pyrometer, the junction of which was held about ¼ inch above the lead.

TABLE IX

EFFECT OF TEMPERATURE ON LOSS OF SILVER IN CUPELLATION

Silver, mg.	Lead, grams	Temperature, °C.	Silver Loss, per cent[1]	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	" "

[1] Average figures.

Everything else being the same, the loss of silver increases as the quantity of lead increases, as is shown in Table X, also from Eager and Welch.

TABLE X

EFFECT OF LEAD ON LOSS OF SILVER IN CUPELLATION

Silver, mg.	Lead, grams	Temperature, °C.	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.

It goes without saying that when the quantity of lead remains constant and the silver is increased the loss of silver also increases. It is important to note, however, that, although the actual silver loss increases as the quantity of silver cupeled increases, the percentage loss decreases.

In any single cupeling operation the rate of loss is slow in the early stages and increases with the concentration of silver in the alloy. This

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* Thesis 225, M.I.T., Mining Department.

is well illustrated by the curve shown in Fig. 45, in which is plotted the cumulative, minute-to-minute loss of silver in cupeling a 30-gram button containing 100 milligrams of silver.

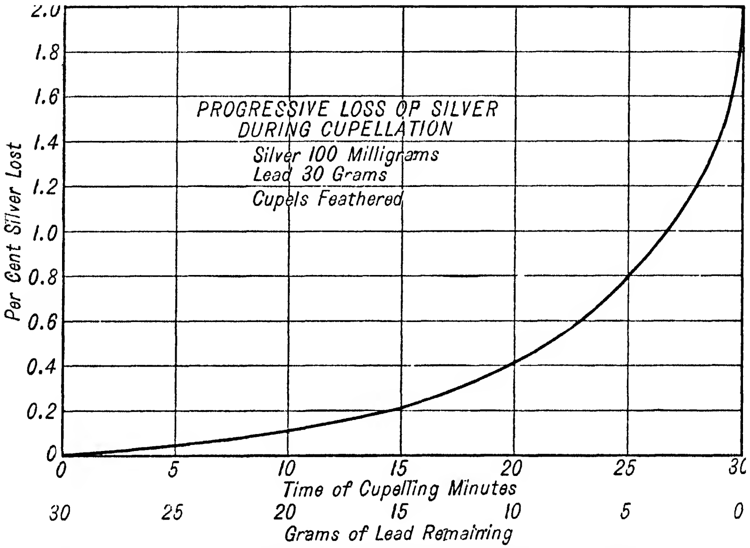

FIG. 45. Curve showing cumulative loss of silver in cupellation.

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 Eager and Welch, shows the relation between the loss of gold and the temperature of cupellation.

TABLE XI

EFFECT OF TEMPERATURE ON LOSS OF GOLD IN CUPELLATION

Gold Used, mg.	Lead, grams	Temperature, °C.	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.

In cupellation at temperatures of 1000° and above, the higher losses of gold seem to be due in part to a lessening of the surface tension caused by the increased temperature, for when the cupels were examined with a 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 with silver, the percentage loss of gold is found to increase as the quantity is reduced. Hillebrand and Allen* showed 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:

	Percentage of Total Gold Recovered	
	Tellurium added	Without tellurium
Without silver	94.9	98.2
With silver	97.0	99.5

In order to throw more light upon this subject, a large number of careful experiments‡ were made using proof gold and c.p. silver in varying proportions. The work was done in a gas furnace under carefully controlled temperature conditions. The temperature was measured and controlled by means of a thermoelectric pyrometer, the junction of which was placed in the center of a blank cupel in line with the cupels which were being used. Ten milligrams of gold was used in each case with 25, 50, 100, 200, and 400 milligrams of silver, respectively, together with 25 grams of lead. Four series of tests were made at different temperatures, namely, 900°, 950°, 1000°, and 1100°C. The results are shown in Fig. 46. The gold losses include any solution losses which may have occurred in parting, but these are extremely small or nil. The results show a very decided protective effect of silver, confirming 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.

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* *Bull.* 253 U. S. Geol. Survey, p. 20 et seq.

† "The Behavior of Tellurium in Assaying," *Trans. Inst. Min. Met.* **17**, 472.

‡ A. B. Sanger, Thesis 492, M.I.T. Mining Department.

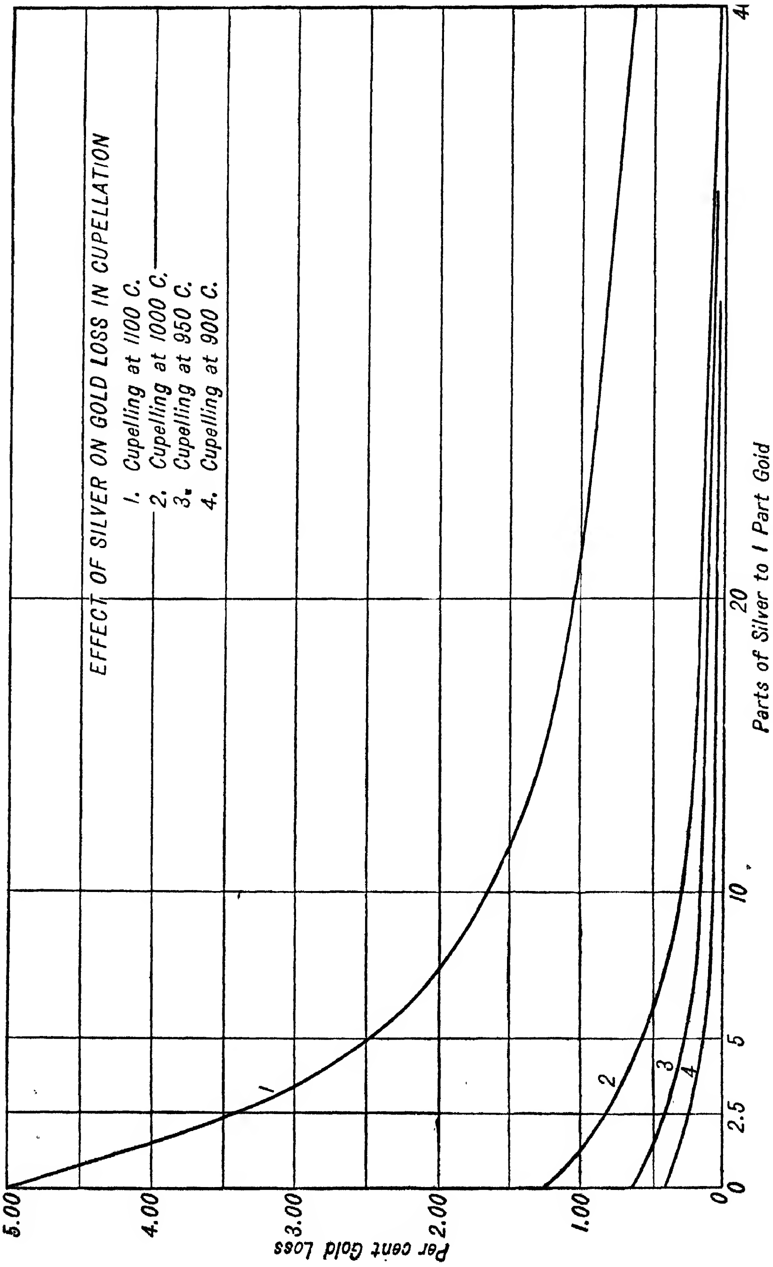

FIG. 46. Curve showing protective effect of silver on gold in cupellation.

Influence of Impurities on the Losses of Precious Metals During Cupellation. By "impurities" is meant such base metals or non-metallic elements as may occur in ores or other material submitted for assay which tend to follow the precious metals into the lead button.

The only impurities which are likely to be found in lead buttons from crucible or scorifier fusions are arsenic, antimony, bismuth, copper, nickel, tellurium, thallium, and selenium, and some of these are so rare that many assayers know them by reputation only. Some of these elements do undoubtedly, in some instances, exert considerable influence on the assay results, but by and large their deleterious effects are rather overstressed. Too often quantitative data based on a single experiment, or on experiments under uncontrolled or loosely controlled conditions, have been given undue prominence in books on the subject.

As Beringer recorded more than fifty years ago, "It will not do to place too much reliance on any set of figures," and so but few exact data are here cited with respect to the effect of impurities. What follows is intended to be restricted to well-recognized fact or well-supported original data.

Arsenic and Antimony. Neither of these metals interferes unless present in amounts greater than 2 per cent. When they exceed this amount they should be previously removed by scorification.

Bismuth in small amounts is a fairly common associate of lead in ores and is also found in the bullion resulting from the smelting of lead ores. It follows the lead into the assay button, and during cupellation it not only increases the absorption loss but is also in part retained to contaminate the silver bead. Some assay beads are found to contain as much as 2 per cent of bismuth. In causing undue silver loss, bismuth seems to reduce the surface tension of the molten alloy as does tellurium.

Tellurium. The behavior of tellurium will be described in the discussion of the assay of telluride ores, to which the interested reader is referred.

Selenium is in many ways similar to tellurium but is a less common associate of the precious metals. It is believed to behave much like tellurium in cupellation.

Nickel. The behavior of nickel in cupellation is discussed in the chapter on scorification and will not be repeated here.

Copper. Because of its frequent association with gold and silver in nature and, furthermore, on account of the impossibility of completely removing it in crucible and scorification fusions, a knowledge of the influence of copper on gold and silver losses in cupellation is particularly important to the assayer. It is generally, but not universally, believed that copper, in common with many other so-called impurities, induces extra losses of silver and gold in cupellation. The evidence for copper is somewhat contradictory. Hofman, referring to cupeling on a commercial scale, states that cupriferous lead is cupeled more quickly and with less loss in lead and silver than if the lead were free from copper. By way of explanation he states that the presence of copper oxide reduces the melting point of litharge so that it flows at a lower temperature than it would otherwise. It may be noted in this connection that the eutectic in this oxide system freezes at 698°C. Note that the reason for this low loss is the low temperature at which the cupellation is carried on.

On the other hand, mint assayers, who invariably run their cupellations at a high temperature to insure complete removal of lead, are agreed that copper, when present in important amounts, causes increased losses of both silver and gold. For example, Percy, in discussing the surcharge in gold bullion assaying, states that when a large quantity of copper is present the surcharge " becomes negative in consequence of absorption of gold by the cupel." In view of the stupendous number of carefully controlled assays of bullion which have been made in mints all over the world, there can be little doubt but that the unanimous conclusions of these operators as to the effect of copper on cupellation losses *at high cupellation temperatures* is correct. It does not necessarily follow, however, that the same is true for cupellations conducted at low temperatures.

In an effort to obtain more light on this situation a series of carefully controlled cupellation assays were made by the staff of the writer's laboratory some years ago, of which this is the first published record. Assays were made in a gas-fired muffle furnace provided with suitable pyrometer temperature control. As a further check on temperature and other factors which influence silver loss, a single row only was cupelled at one time, and each row carried three checks consisting only of silver and lead alternating with four assays similar in all respects except that these last carried a given quantity of copper. For each assay 100 milligrams of silver and 25 grams of lead were used, with varying quantities of copper. Beginning with 25 milligrams the quantity of copper used was increased by increments of 25 to 100 milligrams, then by 50 to 200 milligrams, then by jumps of 100 to 1000 milligrams, and finally by increments of 250 milligrams to an extreme quantity of 2000 milligrams of copper per assay. The quantity of copper used was purposely carried beyond the amount which could be eliminated with 25 grams of lead.

All told, including preliminary and calibrating runs, some 325 cupellations were made. Good litharge crystals were obtained on practically all the cupels, and this served as an additional confirmation of the uniformity of conditions of cupellation which was primarily governed by the loss of silver in the checks. For a series of 11 runs last made, the average silver loss in the 33 checks was 1.85 per cent, with extremes ranging from a low of 1.65 per cent in one case to a high of 1.95 per cent. The variation in loss of the three checks in the row for any given run was much less than this. Consequently, it is felt that any differences between copper-bearing and copper-free assays can fairly be attributed to the influence of the copper.

Without going into great details it may be said that the beads from the cupels which contained copper were almost identical in weight with the corresponding check assays which contained no copper. The beads from cupels containing copper and cupels containing no copper were practically identical in appearance until a quantity of 700 milligrams of copper was added. At this point a slight flattening of the beads from the copper-bearing assays was observed, and as the quantity of copper increased the flattening increased in proportion; at 1000 milligrams of copper they became slightly irregular in shape. Obviously those beads which resulted from cupeling assays carrying 700 milligrams and more of copper retained copper, but even here the difference in weight between assays and checks was only of the order of 0.15 milligram or 0.15 per cent.

By comparing the percentage losses of silver with and without copper up to 700 milligrams of copper the average results gave an apparent loss of silver of 0.05 per cent less for copper-bearing assays than for the corresponding checks. This small difference might easily be attributed to experimental error. Unfortunately, there was no precise method for determining the actual quantity of copper in the beads, but the experimenters were satisfied that it was little if any greater than the amount of lead retained in the beads resulting from cupeling the checks.

One noteworthy difference in behavior in this series is that out of 33 checks no beads sprouted, but 29 out of 44 of the assays carrying copper and identically treated did sprout. This difference may be explained by the well-known oxygen-carrying capacity of the copper.

As a result of all this work the writer feels safe in saying that, in cupeling at a temperature yielding abundant crystals as is essential for all uncorrected silver assays, with 1 part silver and 250 parts of lead, copper up to 7 parts causes no appreciable additional apparent loss of silver. Furthermore, this conclusion has been confirmed and amplified by a careful study of about 750 corrected assays made in this laboratory. For the purpose of this study these were divided into two groups, one copper-bearing, the other copper-free. Comparison of silver losses, based on actual assays of cupels, for ores of approximately the same silver contents showed practically no difference, which warrents us in leaving out the word " apparent " in the first sentence of this paragraph, making it read: " causes no appreciable additional loss of silver."

To conclude, so long as the silver beads are well rounded and otherwise normal in appearance, or so long as the above ratio of copper to lead in the button is not exceeded, no purchaser of copper-bearing ore need be alarmed that he is paying for copper as silver, since the cupellation loss from copper-bearing or copper-free buttons is, for all practical purposes, identical.

The effect of copper on the apparent loss of gold in cupellation is shown in Table XII, which is condensed from the work of Eager and Welch.

TABLE XII

EFFECT OF COPPER ON GOLD LOSSES IN CUPELLATION
TEMPERATURE, 775°C

Gold, mg.	Lead, grams	Copper, mg.	Gold Loss, percentage (apparent)	Ratio of Copper to Gold	Ratio of Lead to Copper
201	10	None	0.155	0 to 100	1000 to 0
202	10	10	0.19	5 to 100	1000 to 1
201	10	20	-0.03[1]	10 to 100	500 to 1
200	10	30	-0.18[1]	15 to 100	333 to 1
201	10	40	-0.17[1]	20 to 100	250 to 1
203	10	50	-0.27[1]	25 to 100	200 to 1

[1] Note that these figures represent gains in weight over the gold originally taken.

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 more 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 apparent loss of the gold itself. Evidently the ratio of lead to copper should not be less than 500 to 1 if the copper is to be completely removed at this low cupellation temperature.

The actual effect of copper upon the loss of gold in cupellation can best be obtained by means of an assay involving parting, since then no confusion can result from the retention of unknown amounts of copper and lead in the assay bead.

It is a generally accepted fact that, in the presence of silver, an increase in the quantity of copper results in an increase in the loss of gold. The loss also increases with the amount of lead used, and decreases as the amount of silver is increased, as has already been shown. According to Rose, the loss of gold in the assay of standard gold is about 0.3 to 0.4 part per 1000. According to W. F. Lowe,* who based his statements upon the assay of cupels, the loss of gold in cupeling the standard alloy is 0.7 part per 1000 parts of alloy.

Rule Governing Cupellation Losses. Two accepted methods of establishing corrections for the loss of precious metals in cupellations are described elsewhere in this book. These depend either on the re-assay of the cupel or on the use of " checks " as in the standard method for the assay of gold bullion. The first method is unduly expensive; the second requires that the check assay contain approximately the same amount of precious metal as the assay which is to be corrected. If we knew the exact relationship between the weight of precious metal in any assay and the loss or percentage loss in cupeling, then by keeping all other conditions constant the loss from a check of any weight could be used for determining the loss for all the assays in a row even though the content of precious metal was entirely different from that in the check.

Working on the assumption that the loss was purely a function of the surface of exposed metal of the cupeling alloy and basing his theory on the mathematical relationship between surface and volume, 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 everyday 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 little effect on the cupellation loss, and as temperature conditions in a given row across a muffle are nearly uniform, he proposed to apply this rule to determine the proper correction for a bead of any weight by a cal-

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* *J. Soc. Chem. Ind.* **8**, 687.

† *Trans. A.I.M.E.* **52**, 180.

culation applied to the loss observed in a proof of an entirely different weight, but cupeled at the same time under the same conditions.

Reference to Sharwood's paper indicates that in the main he has supported his thesis by comparison with the published results of a number of writers, most of whose papers when examined are not entirely convincing as to the closeness of control of temperature and other conditions from run to run. Without the most careful duplication of temperature conditions for succeeding runs it is very easy to obtain data which are decidedly misleading. Since it seemed desirable to test the validity of this " rule " by a series of cupellations made under closely controlled conditions a series of assays* was recently made in this laboratory and the results were conclusive enough and sufficiently at variance with Sharwood's empirical rule to warrant recording.

The same pyrometrically equipped gas furnace was used as had been used in other cupellation studies in this laboratory, and the same general assay procedure was followed. This involved the cupellation of but one row at a time with all cupels " full feathered." Each run carried a check assay of 100 milligrams of silver, and not only did the cupels have to be well feathered but the loss as shown by the check had to be in accord with losses from other runs before the results were accepted. As a measure of the uniformity of the cupels themselves and the uniformity of cupeling conditions in the row, a row of five assays of 100 milligrams of silver and 30 grams of lead was made; results are shown below:

No. of Cupel	Weight of Silver, mg.	Weight of Bead, mg.	Silver Loss, mg.	Deviation, mg.
1	100.04	98.455	1.585	+0.042
2	100.16	98.550	1.610	+0.067
3	100.04	98.565	1.457	−0.068
4	100.14	98.615	1.525	−0.018
5	100.01	98.490	1.520	−0.023
		Mean or total	1.543	0.218

$$\text{Average deviation } \frac{0.218}{5} = 0.0436.$$

Average deviation, percentage of average loss 2.8.

Though these losses are not so uniform as might be desired, they are perhaps close enough, considering how difficult it is to get exactly the same conditions between different runs.

All told, 210 cupellations were made in two series, one using 25 grams,

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* " A Study of Sharwood's Rule Relating to Cupellation Losses," J. C. Rene Martin, M.I.T. Dept. of Mining Engineering, master's thesis, 1939.

the other 30 grams, of lead. The quantities of silver taken began with 1 milligram, then 2 milligrams, and increased according to a progression based on the addition of the last two quantities taken. Thus the series became, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144, and 233 milligrams, respectively. Added to these were the 100-milligram checks in each row.

Data from a typical run as arranged in the furnace are shown below:

Run 38	30 Grams of Lead				
Weight of silver, mg....	89.14	55.09	100.05	233.06	144.04
Weight of bead, mg. ...	87.65	54.12	98.55	229.84	141.91
Loss, mg.............	1.49	0.97	1.50	3.22	2.13
Loss, per cent.........	1.67	1.76	1.50	1.38	1.48

Cupels full feathered, beads well attached.

No less than three well-cupeled assays were obtained for each quantity in the series, and for the smaller quantities a much larger number of assays were made in order to endeavor to eliminate the greater irregularities which are found to occur at that end of the series. Thus for the 25-gram lead series eight assays on 1 milligram of silver and five on 2 milligrams were averaged to arrive at the final figure.

When the average loss for each of the quantities in the progression was plotted on logarithmic paper against the amount of silver cupeled, one series of figures for 25 grams of lead and another for 30 grams of lead, there resulted two parallel straight lines but of different slope from one drawn according to Sharwood's equation. The equations for these lines were determined to be:

$$y_{30} = 0.04x^{0.80},$$
$$y_{25} = 0.034x^{0.80},$$

where y_{30} is the loss of silver in milligrams when x milligrams of silver is cupeled with 30 grams of lead, and y_{25} the same when cupeled with 25 grams of lead.

A logarithmic plot of an equation of the form $y = cx^n$ is a straight line. When the horizontal and vertical scales are equal, the tangent of the angle made by the line and the x axis is the exponent n.

Because of the care with which this work was done, and its confirmation by the parallelism of the two curves, it is believed that the general equation of the form

$$y = cx^n$$

with an exponent 0.80 gives a closer approach to the loss-quantity relationship of cupellation than does the equation with the exponent $\frac{2}{3}$.

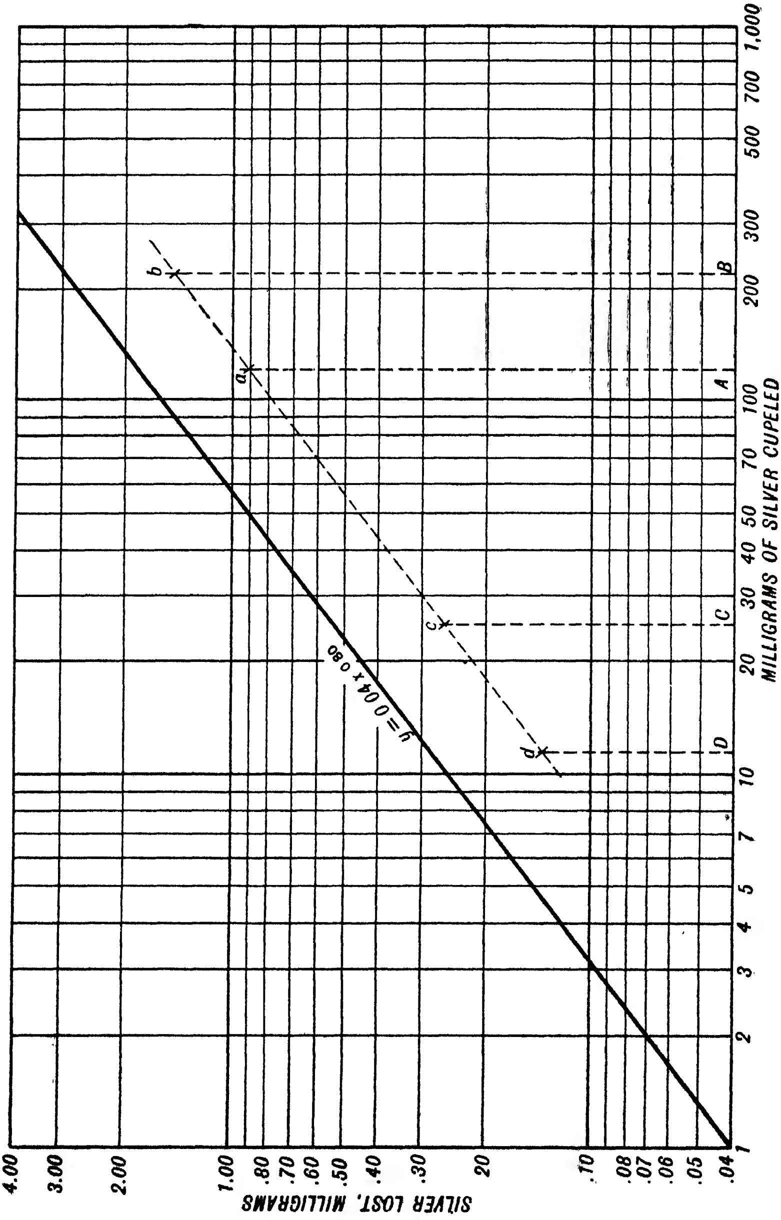

Fig. 47. Curve of the equation $y = 0.04x^{0.80}$

If this is true it follows either that the reaction which is responsible for the loss is not entirely of a surface nature but is in part, at least, related to mass as well as to surface, or that, owing to the continued oxidation of lead at and near the surface, the surface layer of alloy is higher in silver than the average for the entire alloy and thus yields the observed results.

In Fig. 47 is plotted the equation $y = 0.04x^{0.80}$ when the abscissa x equals the milligrams of silver cupeled and the ordinate y equals the silver loss in milligrams. To find a correction, run one proof, as near the expected weight as possible, in each row, plot the corresponding point (a) on the diagram, and draw through it a line parallel to the guide line $y = 0.04x^{0.80}$. Note the points on the line corresponding to the weights B, C, and D of other beads weighed, and read the correction for each from the scale.

Dewey warns against placing too much reliance on Sharwood's rule, because, as he says, " It is so easy to say ' if all other conditions remain the same ' but it is so extremely difficult, and in practical work impossible, to actually maintain equal conditions."

Indications of Metals Present. The lead buttons obtained from the assay of ores ordinarily give but little trouble in cupellation, but occasionally the ore may contain some unsuspected impurity which makes its appearance during the cupellation process. In addition to all sorts of ores the assayer often has submitted to him various kinds of bullion, numerous by-products of the mining and metallurgical industries, as well as such material as jeweler's sweeps, dental alloys, etc. All these may and do usually contain considerable amounts of base-metal impurities 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; the behavior of the cupeling lead as well as 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 skillful 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 respect to 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. Zinc, tin, iron, nickel, cobalt, antimony, or arsenic if present will be oxidized, 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, leaving an orange-yellow ring 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. Copper 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 imparts a pinkish color to the surface of the cupel 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.

GOLD AND SILVER. In cupeling pure gold or silver with pure lead it is found that the part of the cupel occupied by the bead as the last of the lead was going off will be stained green. The higher the temperature and consequently the higher the loss of precious metals, the larger this green area becomes. Certain brands of patent cupels give a large amount of this green stain, and whenever this happens a serious loss of silver is found to have occurred.

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 if in commercially important amounts all yield evidence of their presence either in the appearance of the finished bead or, in some cases, during the later stages of the cupellation process. All assayers should be on the watch for evidence here or elsewhere that some unusual element is present. The manifestations are many and varied, as will be indicated in the following paragraphs.

Perhaps the assay may fail to finish even though carried at a temperature known to be satisfactory for silver and gold. This will be true when the platinum or palladium metals exceed, say, 5 to 10 per cent of the total noble-metal contents. This is due to the high freezing temperature of these silver-soluble metals.

Assuming that the cupellation has gone to completion, the surface structure of the beads may differ from that of pure silver or silver-gold beads which are generally thought of as reasonably smooth and regular in conformation but, actually, under slow cooling conditions show evidences of crystal growth, in that the surface is likely to be made up of striated polygonal-sided planes, differing in orientation and in level. When platinum metals are present: (*a*) the bead may be irregular in shape; (*b*) it may have a rough, pitted surface without much evidence of crystalline growth; (*c*) it may appear to be embossed, owing perhaps to growth of dendrites; (*d*) it may be broken into a multitude of plane-surfaced crystals — a surface appearance which is ordinarily termed "frosting"; or (*e*) while still remaining entirely metallic in composition, it may have a color differing from that of pure silver. Beside the above, all of which have entirely metallic appearing surfaces, it may (*f*) carry patches or be entirely covered with specks or crystals of some non-metallic substance usually brilliant blue or jet black in color.

Although these surface effects can hardly be made to yield quantitative results, they do have some partial qualitative value and at least should serve to put the assayer on his guard and cause him to suspect the presence of rare metals. 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 cooled slowly in order to develop their crystalline structure. During solidification they should be closely watched for flashing, which also yields evidence relating to rare-metal content. The following surface effects are believed to be reasonably characteristic of the individual rare metals in binary combinations with silver.

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 that 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.

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 is 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 0.04 per cent and larger amounts, the surface of the bead assumes a bluish gray color which becomes deeper as the amount is increased until the beads become blue-black.

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, if not masked, 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. Palladium yields a bead with a surface appearance similar to that of platinum except that rather more palladium must be present before marked indications are noticeable. One specific difference observed in the writer's laboratory but not elsewhere confirmed is that when cupellation has been conducted at a moderate temperature the surface of the bead is likely to show a very definite rose color. This color has been observed in beads containing from 2 to 24 per cent of palladium.

It should be obvious that, even with binary alloys of the same composition and yielding beads of the same size, different cupellation temperatures and slightly differing cooling rates will exert markedly different effects on the chemical reactions during cupellation and the crystal growth during solidification, and these in turn will cause notable variations in the surface appearance of the beads. In polycomponent systems there are obviously so many possible variations that definite conclusions as to specific rare-metal contents is, in the light of present knowledge, practically impossible.

Gold. 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. According to Reimsdijk,* copper promotes the surfusion of gold. He also points out the curious fact that gold fused on a cupel without the addition of lead is not subject to surfusion and sets gradually without flashing.

Very small quantities of iridium, rhodium, osmium, ruthenium, and iridosmium prevent this flashing in gold beads and probably also in silver beads. This gives us another indication of the presence of the more uncommon metals of the platinum group. It should be noted in this connection that small amounts of platinum and palladium do not hinder flashing. Over 6 per cent of platinum, however, does prevent it.

Retention of Base Metals. It has already been mentioned that a plus error may be incurred because of the retention of lead in the silver bead. If the bead contains much lead, it will appear dull or slightly yellow, being thinly coated with litharge; the part resting against the cupel will be smooth, and it will not blick. Occasionally a bead will show the play of colors and even flash, and still retain as much as 1 or 2 per cent of lead. Sprouting, however, is considered proof of the absence of all but traces of impurities. When the alloy contains copper, the silver beads may retain from 1 to 2 per cent of copper without showing any unusual symptoms.

All gold and silver beads cupeled in the absence of copper probably retain small amounts of other impurities, and in beads cupeled in the presence of copper there is probably always some copper left. Hillebrand and Allen† found gold beads retaining from 0.30 to 0.37 per cent of lead. Keller‡ reports the results of analysis of 30 grams of beads resulting from scorification assays. This showed 0.16 per cent of lead and 0.15 per cent of bismuth, the bismuth having been concentrated from the granulated lead used for scorification, which at the time contained approximately 0.02 per cent of that metal. Another series of tests by Keller§ showed total impurities averaging 0.45 per cent. It also appears from Keller's work that large beads are of slightly lower fineness than small ones.

The persistency with which a small amount of copper is retained by gold and silver beads is utilized in the gold-bullion assay to toughen the beads so that they can be rolled thin without cracking. A small amount of lead, which is invariably retained in the absence of copper, causes the fillet to crack. Copper does not have this effect. It is cus-

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* *Chem. News*, **41**, 126, 266.

† *Bulletin* 253, U. S. Geological Survey.

‡ *Trans. A.I.M.E.* **60**, 706.

§ *Trans. A.I.M.E.* **46**, 783 (1913).

tomary, therefore, to add copper when none is present in the bullion. Being less readily oxidized than lead, it serves as an oxygen carrier and permits the entire elimination of lead from the bead.

These retained metals tend to compensate for the cupellation losses but do not do so entirely, so that ordinary assay results are still at least 1 or 2 per cent low. Experiments with fine silver, however, reveal the interesting fact that, by assaying slags and cupels and adding the metal recovered to the weight of the original bead, a very close check on the original silver is obtained, provided that the assay was carefully made and cupeled with crystals. This shows that the impurities in the assay beads balance the volatilization and other miscellaneous losses. This is true, however, only when cupellations and scorifications are run at a low temperature. Keller gives figures which show that if scorifications and cupellations are run hot a decided volatilization loss occurs and corrected figures are still far too low.

Portland Cement and Magnesia Cupels. Cupels of Portland cement and calcined magnesia have found favor in some localities, the former mostly in the United States and Canada, the latter principally in England and South Africa. Portland cement cupels are made from neat cement with 6 to 10 per cent of water, in the usual way. If properly made and handled, they do not 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: (1) beads from a bone-ash cupel were well rounded and stood on a small base, whereas those from Portland cement cupels were flatter and stood on a base as wide as the broadest diameter of the bead; (2) 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 almost entirely dissolved.

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* *Mining Sci. Press.* **100, 649.**

† *Technical Bulletin,* Vol. II No. 3, Missouri School of Mines, p. 33.

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. This is due to the greater conductivity of magnesite, which allows a more rapid dispersion of the heat of oxidation of the lead, with the result that magnesia cupels require a higher muffle temperature than bone-ash cupels. An especially high finishing temperature is required for magnesite cupels, to insure the elimination of the last 1 or 2 per cent of lead. A bone-ash cupel will finish in a muffle the temperature of which is sufficient to cause uncovering, but this is not true of the magnesia cupel, because the heat of oxidation of the lead is diffused too rapidly and is not conserved to help out at the finish.

Magnesia cupels absorb about two-thirds of their own weight of litharge; those of cement, about three-fourths of their weight.

Composite Cupels. As the result of a series of carefully controlled tests King* found that cupels made from a mixture of 70 per cent Portland cement and 30 per cent of bone ash by weight, moistened with about 8 per cent by weight of water, gave apparent silver losses as low as those obtained from cupels made entirely of bone ash. Since a good grade of bone ash costs delivered some 10 to 14 cents a pound as compared with about 1 cent a pound for cement, the advantage of the addition of cement is obvious. These cupels are firm and rugged and are thus less likely to be broken in handling. They must be well heated before use to insure the removal of all water of composition.

Improved Form of Cupel Cup. King† has developed an improved form of cupel cup, a vertical section of the surface of which is the product of three concave and two convex circular arcs. This exposes a large

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* "The Influence of Cupels on Silver Loss," *Bulletin* 147, University of Toronto Press, p. 66, 1934.

† *Op. cit.*, p. 64 et seq., 1934.

surface of lead at first, resulting in rapid cupellation in the early part of the process. The small and relatively deep finishing cup protects the alloy from the influence of the draft toward the end of the process, resulting in a correspondingly lower oxidation rate. It is reported that this shape gives much lower losses than can be obtained in a cupel of conventional shape and that it considerably reduces the tendency of silver beads to sprout.

Color Scale of Temperature. Starting from the lowest visible red the temperatures of incandescent bodies can be approximated by the color impressions produced on the eye. Such estimates are, of course, dependent upon individual judgment and the susceptibility of the eye, as well as upon the amount of illumination of the locality in which the observation is made and upon the nature of the heated body itself. The following color-temperature scale* will be found convenient for reference in cupellation.

	Degrees Centigrade
Lowest red visible in the dark	470
Dark red, blood-red	550
Dark cherry	625
Cherry-red, full cherry	700
Light red	850
Orange	900
Light orange	950
Yellow	1000
Light yellow	1050
White	1150–1200

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* Howe, *Eng. Mining J.* **69,** 75.

CHAPTER VI

PARTING

Parting is the separation of silver from gold by means of acid. In gold assaying nitric acid is almost exclusively used, although sulphuric acid is usually employed for parting large lots of bullion. Nitric acid cannot be used successfully to separate silver from gold unless there is present at least three times as much silver as gold. With this ratio the alloy must be in the form of a thin sheet, and it requires a long-continued heating with acid of 1.26 specific gravity to effect a separation. In parting beads from ore assays it is best to have at least eight or ten times as much silver as gold present, and for ease of manipulation this ratio of silver to gold is preferable to a greater one. With much less silver than this a long-continued treatment with acid is necessary; with much more silver than this, special precautions have to be taken to prevent the gold from breaking up into small particles which are difficult to manage. The idea of parting is to manipulate so that the gold will, if possible, remain in one piece.

The nitric acid for parting must be free from hydrochloric acid and chlorine in order to have no solvent action on the gold and also because any chlorides present would precipitate insoluble silver chloride on the gold. The acid strength is of great importance, the proper strength depending upon the composition of the alloy. The higher the ratio of silver in the alloy, the weaker should be the acid.

Great care is necessary in parting to avoid breaking up the gold and subsequently losing some of the small particles, as well as to insure complete solution of the silver.

Different authorities recommend different vessels for parting, but for ore assays, and especially for beginners in the art, a porcelain crucible or capsule is recommended.

Parting in Porcelain Capsules. A glazed porcelain capsule 1⅜ 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 writer in his laboratory. The strength of acid which may be used depends on the proportion of gold and silver in the alloy; the lower 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 invariably, but it 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 specific gravity 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. If 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 specific gravity, 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 milliliters of 1.26 specific gravity acid, made by diluting strong nitric acid, 1.42 specific gravity, with an equal volume of water, and heat almost to boiling for 2 to 10 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 a sharp-bladed penknife or a very 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 not all the silver has 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, and 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 or coke dust 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 $\frac{1}{32}$ 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 specific gravity acid for at least 10 minutes to insure 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. With 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 10-minute heating with 1.26 specific gravity acid is unnecessary.

4. Strong nitric acid (1.42 specific gravity) 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 in six times its weight of silver foil, and carefully cupel with lead; then re-part and weigh.

6. A small particle of gold floating on the surface of the liquid 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 2¼ 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.	2¼ to 1

Many assayers, when working for both gold and silver and suspecting an ore to be deficient in silver, add silver to the crucible or to the lead button before cupeling, part directly, and then run separate assays to determine the silver in the ore.

Preparing Beads for Parting. Beads which approach the maximum ratio of 25 per cent gold must be flattened on an anvil and rolled out to a thickness of about 0.01 inch before parting. During this process the alloy will require frequent annealing to prevent it from cracking. It should finally be rolled up into a little " cornet " before parting. (See " Assay of Gold Bullion.")

Parting in Flasks, etc. Parting in flasks, test tubes, etc., is exactly similar to parting in porcelain capsules, up to the completion of the washing of the gold. From this point on, however, the manipulations are different, as the annealing is not done in the same vessel but in an annealing cup. The annealing cup is a small unglazed crucible made of fire clay and very smooth on the inside.

PROCEDURE. After washing the gold, fill the flask or test tube with distilled water, invert over it an annealing cup, and then quickly invert the two so that the gold may fall into the cup. This operation should be done in a good light and preferably against a white background. Tap the flask if necessary, to dislodge any gold which may have caught on the side, and after all the gold has settled raise the flask slowly until its lip is level with the top of the annealing cup. Now, when all the

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*" Metallurgy of Gold," Seventh Edition, p. 502.

gold is at the bottom of the cup, slip the flask quickly from the cup and invert it. Drain the water from the cup, cover it, and set it on the hot plate to dry. When fully dry, it is ready to be annealed and weighed. Examine the flask once more to make sure that no gold has been left in it.

This method of parting has the advantage that the acid may be boiled, if necessary, with less danger of its boiling over and causing loss of fine gold. It is well suited for the parting of large beads where the porcelain cup would not contain enough acid to dissolve all the silver, and also to the parting of alloys in which the ratio of silver to gold is only 2 or 3 to 1, and which therefore require a long-continued heating at or near boiling temperature. The method, therefore, is recommended for the assay of gold bullion. The clay cups have the advantage of porosity so that they can absorb the last drops of water and give it off again slowly, thus preventing spattering if they are set on a hot iron plate to dry. They also stand sudden changes of temperature somewhat better than the glazed porcelain cups.

This method has the disadvantage that, if all the parted gold does not remain in one piece, there is greater danger of loss, because the fine gold settles with difficulty and because it cannot be watched so well through all stages of the process. There is also danger of small particles of the cup, and especially the cover, being broken off and mixed with the gold.

Influence of Base Metals on Parting. Pure gold-silver alloys of almost any proportions not exceeding 30 per cent of gold, with a proper strength of nitric acid and the right degree of heat, will part and leave the gold in a coherent mass similar in shape to the original alloy, although very much reduced in size when but little gold is present. Though a relatively strong acid may be used directly on alloys containing large proportions of gold, acid of this same strength cannot be used on alloys containing but little gold, without producing disintegration. Heating of the parting acid is more necessary, too, when but little gold is present. The fact that the gold holds together under these circumstances, and contracts, following the retreating surface of silver, very much simplifies the determination. When the gold breaks up, it increases the difficulty for the assayer and causes unavoidable losses in decantation. The high temperature of the parting acid increases the mobility of the gold and in pure alloys prevents it from breaking up.

Keller states that, although assay beads of not less than 997 parts gold plus silver fineness offer no difficulty in parting, yet when the fineness falls to 990 or lower the gold cannot be obtained in any form other than powder, no matter what acid and heat combinations are employed. The explanation of this difference may be that the whole gold-silver series form solid solutions in which the molecules of gold, even when in dilute solution, are uniformly distributed and almost if not quite in contact, or at least within spheres of mutual attraction. It may be imagined that impurities forming compounds or eutectic mixtures may so disrupt the uniformity of texture of the alloy, and 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 was noted in the chapter on cupellation, the assay beads may contain, in addition to traces of lead, bismuth, copper, and tellurium, practically all the platinum, palladium, rhodium, iridium, iridosmium, as well as more or less of the 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 is dissolved, the amount depending on various conditions such as the amount of silver present and the strength of acid.

PLATINUM has a disintegrating effect upon the gold when the gold 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 milligram in a small bead gives a distinct coloration to the solution.

IRIDIUM appears in the parted gold as detached black specks which retain 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, but for ore analysis a negligible, amount. According to F. P. Dewey this loss does not exceed 0.005 part per 1000 parts of gold. 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· they 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 sulphide or 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, put about 10 ml. of acid in a test tube and pour a few milliliters of silver nitrate solution cautiously down the side, 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.

CHLORATES. Nitric acid often contains chlorine in the form of chloric acid, and, since 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 put about 250 ml. in a beaker and add 1 ml. 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 insure its purity. Any chlorides in the wash water, of course, will 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 is then well mixed and allowed to stand until the silver chloride settles out. For obvious reasons, care must be taken to avoid adding an excess of silver nitrate. 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 proved 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 VII

THE SCORIFICATION ASSAY

The scorification assay is the simplest method for the determination of gold and silver in ores and furnace products. It consists 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 most common sizes are 2½, 2¾, and 3 inches in diameter.

The amount of ore used varies from 0.05 to 0.25 assay ton, the amount most commonly used being 0.10. With this are 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 assay ton 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 is required according to the relative difficulty with which the metals are oxidized and their oxides dissolved 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.

Scorification is particularly adapted to the determination of silver in ores which carry appreciable quantities of the sulphides, arsenides, and antimonides of the difficultly oxidizable elements. The chemistry of the process is essentially about as follows:

1. Decomposition of sulphide minerals by atmospheric oxygen with concurrent liberation of precious metals and subsequent collection of

the same by the metallic lead. During this stage there is also some alloying of undesirable constituents with the lead which brings about the necessity for:

2. Softening of the lead by continued oxidation to remove the undesirable constituents accompanied by (if conditions are properly controlled):

3. Slagging of the metallic oxides formed by the above reactions together with the earthy constituents of the ore charge.

After some oxides and sulphates of lead and other constituents have been formed by direct oxidation, the remaining sulphides may be decomposed by their interaction with the oxides and sulphates first formed. Examples of such reactions are to be found in a later section of this chapter. These reactions are, in general, endothermic and require a higher temperature to render them effective. It is not always of advantage, however, to attempt to speed up the process by working at too high a temperature, since this last type of reaction usually results in the precipitation of a metal and it may be one which we prefer to have remain in the oxide form.

Ignition Temperatures of Metallic Sulphides. Such minerals as stibnite, pyrite, galena, and sphalerite are decomposed primarily by roasting, and a knowledge of the ignition temperatures of the various mineral sulphides will serve as a guide as to the temperature requirements of that stage of the process. Table XIII contains such information, and reference to the data contained therein helps to explain the reason for the higher temperature necessary when assaying ores containing such minerals as sphalerite. Other factors, of course, must be considered; they will be taken in order.

TABLE XIII

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

Material	Formula	Ignition Temperature, °C.	Material	Formula	Ignition Temperature, °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, 170.

[2] In oxygen.

If the ore contains any difficultly oxidizable metals such as nickel, bismuth, or copper part of these metals will have become alloyed with the lead during the roasting stage of the process and should be removed as completely as possible before cupellation. This is accomplished by a continuation of the scorification in what may be termed the oxidizing-refining stage of the process. During this stage all the constituents of the alloy are oxidized to some extent but in different proportions and at different rates. The order, rate of removal, and proportion of each of the constituents which are finally eliminated are mainly dependent upon their greater or less affinity for oxygen, the effect of mass action, the effect of temperature upon each, and finally the time during which the scorification is continued. As has been known to metallurgists for many centuries and was so well stated by Rose* some years ago, " All metals are to some extent oxidized simultaneously . . . but a mixture of metals can be roughly separated by successive oxidation, each metal in turn partially protecting the metal next in order, while the latter acts as oxygen-carrier to the former."

Heats of Formation of Metallic Oxides. The metals in Table XIV are arranged in order of their heats of combination with oxygen, expressed in terms of a unit weight, 16 grams, of oxygen. This is the order in which they tend to be oxidized in scorification or cupellation.

TABLE XIV

HEAT OF FORMATION OF OXIDES[1]

Reaction	Heat of Combination with 16 gm. O	Reaction	Heat of Combination with 16 gm. O
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.

In a mixture containing a number of molten metals, that reaction in which the greatest amount of heat is evolved would naturally proceed at the fastest relative rate, so that if present in the melt those metals at the upper end of the table would be eliminated early in the process, and, as is well known, those metals appearing at the lower end of the table would be but little affected as long as an appreciable quantity of any of the metals preceding them in the table remained unoxidized.

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* " Refining Gold Bullion with Oxygen Gas," *Trans. I.M. & M.* **14** 390 (1905).

Since we have present in scorification a large amount of lead and a relatively much smaller amount of other metals and non-metallic elements it will help to note the position of lead in the table with respect to the other elements. With the exception of nickel, which will be referred to later, those elements which lie above lead in the table will be removed without difficulty. Those which lie below lead will be but slowly removed and only at the expense of a large amount of lead. Thus, during scorification or cupellation, bismuth, copper, and tellurium tend to concentrate in the residual unoxidized lead, and this explains why it is so difficult to separate these elements from silver by scorification and cupellation. Such a separation can never be entirely complete but may be sufficiently so for practical purposes. To accomplish this it is sometimes necessary to add fresh lead and repeat or continue the scorification, and, as might be expected, this may 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.

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 follows:

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.

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 XIII 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 ease or difficulty of their elimination in scorification may be determined; and a knowledge of the solubility of the metal oxides in litharge and in borax will indicate the relation between ore, lead, and flux that will give the most satisfactory results.

A small amount of nickel will cause more trouble in scorification and cupellation than any other metal. This is largely because of the insolubility of its oxide in litharge. The presence of copper seems to increase the difficulty of eliminating nickel from the lead. In scorifying ores containing nickel but no copper, practically all the nickel comes out in the first slag, making it lumpy, to be sure, but leaving the lead practically clean. When copper is also present the button requires rescorification and much nickel scoria is found in the second scorifier. Browne* calls attention to a similar action of nickel in converting copper-nickel matte. Here the nickel does not behave like iron, as it might be expected to do by reason of its heat of oxidation, but like copper, which has a much lower heat of oxidation. It was found impossible to slag off the nickel without at the same time removing a large part of the copper. In fact, the nickel-copper alloy acts like one metal and follows the same laws that govern the behavior of copper alone. No adequate explanation of this behavior is known.

SCORIFICATION ASSAY OF SILVER ORE

Procedure. Empty the bottle or envelope of ore onto a sheet of glazed paper or oilcloth, and mix thoroughly by rolling.

Take three scorifiers, 2½, 2¾, and 3 inches in diameter, respectively. Weigh out on the flux balance three portions of granulated lead 40, 50, and 60 grams, respectively. Divide each lot of lead approximately in halves, transfer one-half of each to the corresponding scorifier, and reserve the remaining portions. Weigh out three portions of exactly 0.1 assay ton of ore on the pulp balance, and place on top of the lead in the scorifiers. Mix thoroughly with the spatula, and cover with the remaining portions of lead. Scatter 1 or 2 grams of borax glass on top of the lead. The scorifiers are now ready for the muffle, which should be light red or yellow before the charges are put in. This temperature should be maintained during the first part of the roasting period.

FUSION PERIOD. Place the scorifiers about midway in the muffle, close the door, and allow the contents to become thoroughly fused. A minimum of 10 minutes is suggested.

ROASTING PERIOD. When the contents are thoroughly fused, open the door to admit air to oxidize the ore and lead. Any sulphides the ore contains will now be seen floating on 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.

Often the vapor rising from the assays indicates 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

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* *Trans. A.I.M.E.* **41**, 296.

of the lead is oxidized. Finally, when the whole of the lead is covered with slag, 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 insure 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 rescorifying 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 assay ton will truly represent the whole; 100-mesh may be fine enough for some ores, 150- or 200-mesh may be necessary for 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, put the pan back on the balance and use the hand with which it was held 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 one or two 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 and 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 one or two 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 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 means 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 taken 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 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 10 or 15 minutes, the assays require either more heat, more borax glass, or more lead. 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.

7. If the ore contains much tin, antimony, arsenic, nickel, or large amounts of basic oxides such as hematite or magnetite, 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 its eating a hole through the scorifier.

11. The lead button should weigh from 18 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 formed when the scorification temperature is low.

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

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.

Scorification is not to be recommended for pure ores low in silver because of the difficulty of handling and weighing the small beads obtained and also because with pure ores the crucible assay is preferable. All samples have to be weighed more carefully for scorification than for crucible assays, where usually five to ten times as much ore is taken, and the resultant beads must also be weighed more carefully if results are to be reliable. This is because in using 0.1 assay ton of sample all milligram weights are multiplied by 10 in computing the assay in ounces per ton.

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, or pyrolusite. 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.:

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

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:

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

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:

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

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 that we are justified in writing reactions such as the following:

$$2PbO + SiO_2 = Pb_2SiO_4.$$

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 heat of formation of silicates and borates from their component oxides is very small, and it is doubtful that 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, $x\text{PbO}\cdot y\text{Sb}_2\text{O}_5$. Arsenic behaves much like antimony.

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

REACTIONS BETWEEN SULPHIDES AND OXIDES. After enough PbO has been formed to slag the siliceous gangue the additional litharge formed is available to react with the partially decomposed sulphides, aiding in the elimination of sulphur, thus:

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

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

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

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 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, 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.

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 to heat for 10 or 15 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 with ores or products carrying zinc).

6. Nature 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 if any silver or gold is found a strict account must be kept of the lead used in each assay and a correction must be made for its precious-metal contents.

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, even if extremely small, must be made, as any error thus introduced would be multiplied by 10 in reporting the results in ounces per ton.

Scorification Assay for Gold. Because of the limit of sensitivity of the assay balance the scorification assay based on a charge of 0.1 assay ton does not give a sufficiently close determination of the value of the gold contents of a sample for commercial purposes. For example, with a balance capable of weighing to the nearest 0.01 milligram and using 0.1 assay ton of sample, each 0.01 milligram of gold obtained represents 0.1 ounce of gold, which means that we have determined the value of the substance only to the nearest $3.50 per ton. This is obviously not a commercially satisfactory situation, hence when, because of the nature of the substance, the scorification assay must be used it is customary to make a number of scorifications and to combine the beads for parting and weighing so that at least 1 assay ton of sample is represented by the gold on the scale pan when the final weighing of the gold is done. If, in addition to this combining of gold for weighing, a balance sensitive to 0.002 milligram is used it is perfectly possible to obtain the gold value to the nearest 7 cents per ton, which is generally commercially satisfactory.

SCORIFICATION ASSAY OF COPPER MATTE

Procedure. Take 3 portions of 0.1 assay ton 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, 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. Black 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 re-assayed 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 assay ton 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. Any decided loss by volatilization 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 or H_2O, etc. ($CaCO_3$, $CaSO_4{\cdot}2H_2O$), 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 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; in one series scorifications were run hot and in the other they were run cool. The results, each representing an average of twenty individual assays, are shown in Table XV.

TABLE XV
ASSAYS OF COPPER ANODE RESIDUES

Origin	Hot Scorification		Cool Scorification	
	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

When cool and hot scorification results are compared, the difference between both uncorrected and corrected silver results is seen to amount to about 76 ounces per ton, or a little more than 2 per cent, in favor of the cool scorifications. Since the silver loss in slags and cupels is substantially identical by both methods Keller concludes that there must have been a decided loss of silver by volatilization in the high-temperature scorification, and this is the most logical explanation of the difference. No better argument for cool scorification than these figures can be found. It should be noted, however, that this material, anode mud, not only contained copper but undoubtedly also carried a considerable proportion of tellurium and selenium. These elements may have had considerable influence on the volatilization loss.

Another interesting feature presented in these data is the very high loss of silver in the slag, about 1.5 per cent of the total, due undoubtedly to the repeated scorifications necessary to remove the copper and the above-mentioned non-metallic elements. The loss of gold in slags and cupels is extremely small, serving to illustrate the protective action of silver upon gold.

The gold lost in decantation, for beads resulting from cool work, is three times that for beads resulting from hot work. This difference Keller claims to be due to increased disintegration of the gold, because

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

of the presence of added impurities retained in the beads resulting from cool cupellation.

Use of Large Ore Charges in Scorification. Although 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 of only galena and quartz.

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

TABLE XVI

SCORIFICATION CHARGES

Material	Charge				Scorifier, inches	Heat High at First, then
	Ore, assay ton	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	–	½	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	–	2¾–3	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

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* "California Mines and Minerals," p. 226, 1899.

CHAPTER VIII

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 reagents 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 or sulphides of the charge, and these reduced shots of lead then 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 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 standpoints, first according to the character and quantity of their slag-forming constituents, and second according as they are oxidizing, neutral, or reducing in the crucible fusion with lead and lead oxide.

Ores Classified According to Slag-Forming Constituents. The principal slag-forming constituents of ores and gangue minerals, arranged approximately in the order of their occurrence in the earth's crust, are as follows:

Silica	SiO_2	Acids
Alumina	Al_2O_3	
Ferrous oxide	FeO	Bases
Manganous oxide	MnO	
Calcium oxide	CaO	
Magnesium oxide	MgO	
Sodium oxide	Na_2O	
Potassium oxide	K_2O	
Zinc oxide	ZnO	
Lead oxide	PbO	
Cuprous oxide	Cu_2O	

These oxides, with the exception of those of sodium, potassium, and lead, are infusible at the temperature of the assay furnace. To get them into the molten condition we add fluxes. All the common assay fluxes with the exception of silica are readily fusible by themselves. In general it may be said that to flux the acid, silica, it is necessary to add bases, and to flux any of the basic oxides, acids must be added. To flux alumina it is best to add both acids and bases.

Ores Classified According to Oxidizing or Reducing Character. According to their oxidizing or reducing character in the crucible assay, ores may be divided into three classes as follows:

Class 1. Neutral Ores. Siliceous, oxide, and carbonate ores or ores containing no sulphides, arsenides, antimonides, tellurides etc., *i.e.*, ores having no reducing or oxidizing power.

Class 2. Ores Having a Reducing Power. Ores containing sulphides, arsenides, antimonides, tellurides, carbonaceous matter, etc., or ores which decompose litharge with a reduction of lead in the crucible fusion.

Class 3. Ores Having an Oxidizing Power. Ores containing ferric oxide, manganese dioxide, etc., or ores which when fused with fluxes oxidize lead or reducing agents. Ores with any considerable oxidizing power are comparatively rare.

Determining the Character of a Sample. The mineral character of an ore can be most readily determined when the ore is in the coarse condition. However, as a large proportion of the samples received by the assayer are already pulverized, it becomes necessary for him to be able to form a close estimate of their composition in this condition. This may be best accomplished by washing a small sample on a vanning plaque or shovel, which should be of white enameled iron with a true spherical surface. The writer prefers the vanning shovel to the ordinary plaque, and this he would have made 12 inches in diameter with the center depressed about $\frac{3}{4}$ inch below the edges.

Place 1 or 2 grams of the ore on the vanning shovel, cover well with water, and allow it to stand until the ore is thoroughly wet; then shake in a horizontal plane until the fine slime is in suspension and all lumps are broken up. Allow to settle a moment, and decant off the water and fine slimelike particles. Repeat the washing, using ample water and giving the shovel a circular motion by which the heavy grains are settled and more slime brought into suspension. Decant the water and suspended slime again. Repeat the washing if necessary, and then with less water separate the ore according to the specific gravity of its different minerals by a combined washing and shaking. The water should be made to flow over the ore in one direction only, and the velocity of the shaking motion should be accelerated in a direction opposite to the flow of the water. The shaking tends to stratify the ore, heaviest next the pan, lightest on top, while the water tends to wash everything downward, the material on top being most affected because of its position, and also because of its lesser specific gravity. Finally, if a number of minerals are present, they should appear spread out in fan shape in

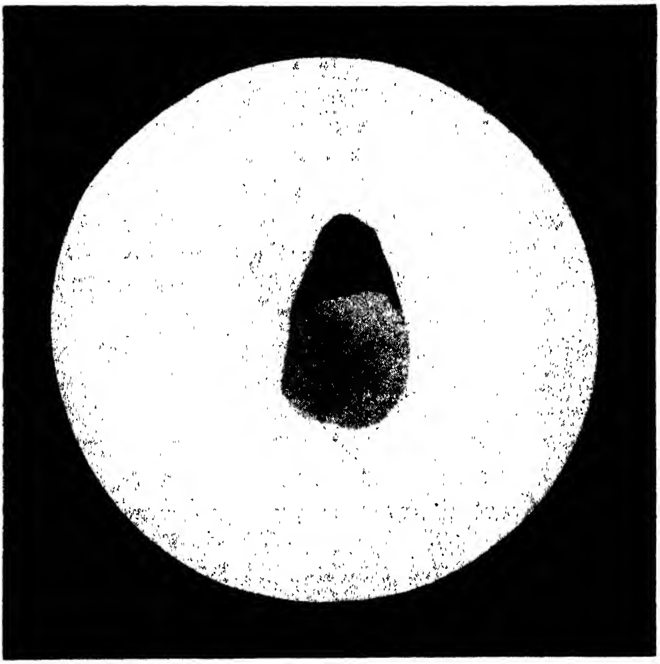

Fig. 48. Fan of galena and quartz on vanning shovel.

the order of their specific gravity, for instance, galena, pyrite, sphalerite, and quartz.

After the ore has been fanned out it is possible to form a good idea of the identity of the different common minerals from their color, streak, and specific gravity. The student should apply such confirmatory or investigatory tests as are suggested by his knowledge of mineralogy. For instance, to distinguish between quartz and other white minerals of about the same density draw the back of the fingernail over some of the mineral on the pan. Quartz can be felt biting into the pan while calcite will slide over it. If carbonates are suspected apply dilute hydrochloric acid directly on the pan.

Figure 48 shows a fan of galena and quartz on a vanning shovel. If account is taken of the specific gravity of the different minerals, an experienced operator can make a reasonably good estimate of the percentage of each of the common minerals present in an ore.

Crucible Slags. The slags obtained in the crucible assay may be regarded as silicates and borates of the metallic oxides dissolved in one another and in litharge. They also often contain dissolved carbon dioxide. The acid constituents of rocks, other than silica, so seldom play an important part in the formation of slags that they may be omitted at least from a preliminary discussion of the subject.

Assays slags high in litharge and low in silica, borax, and other acids are sometimes called oxide slags. Very little is known about the constitution of these slags.

Very acid slags are sometimes emulsions and not true solutions. That is, they may contain suspended solid or molten globules of other minerals.

A slag suitable for assay purposes should have the following properties:

1. It should have a comparatively low formation temperature readily attainable in assay furnaces.

2. It should be pasty at and near its formation temperature, to hold up the particles of reduced lead until the precious metals are liberated from their mechanical or chemical bonds and are free to alloy with the lead.

3. It should be thin and fluid when heated somewhat above its melting point, so that shots of lead may settle through it readily.

4. It should have a low capacity for gold and silver, and should allow a complete decomposition of the ore by the fluxes.

5. It should not attack the material of the crucible to any great extent.

6. Its specific gravity should be low, to allow a good separation of lead and slag.

7. When cold, it should separate readily from the lead and be homogeneous, thus indicating complete decomposition of the ore.

8. It should contain all the impurities of the ore and should be free from the higher oxides of the metals.

9. Except for the iron-nail assay it should be free from sulphides.

Color of Crucible Slags. As is also true in scorification, the color of the slags resulting from crucible assays is often indicative of the metals present. Owing to the larger proportion of silica and borax and the smaller amount of lead oxide in crucible slags the significance of the coloring is not always the same. Thus in crucible slags various shades of green may usually be ascribed to the presence of ferrous silicates and not of copper, as in scorification slags, while, in the absence of iron, copper gives the crucible slag a brick-red color due to the presence of cuprous silicate or borate.

Calcium, magnesium, aluminum, and zinc give white or grayish white slags, usually more or less opaque. The acid borosilicates of pure soda and lead are clear, colorless glasses. Cobalt gives the well-known cobalt blue. Iron and manganese in large quantities make the slag black. A small amount of manganese may, in the absence of interfering elements, yield a purple to a light pink; and, as is well known by all glass-makers, a small amount serves to neutralize the color effect of iron.

Classification of Silicates. Silicates are classified according to the proportion of the oxygen in the acid to oxygen in the base. Thus, a monosilicate has the same amount of oxygen in the acid as in the base; a bisilicate has twice as much oxygen in the acid as in the base, and so on.

The silicates which have been found to behave satisfactorily as assay slags lie within the following limits:

TABLE XVII

CLASSIFICATION OF SILICATES

Name	Oxygen Ratio Acid to Base	Formula. R = Bivalent Base
Subsilicate	½ to 1	$4RO \cdot SiO_2$
Mono- or singulosilicate	1 to 1	$2RO \cdot SiO_2$
Sesquisilicate	1½ to 1	$4RO \cdot 3SiO_2$
Bisilicate	2 to 1	$RO \cdot SiO_2$
Trisilicate	3 to 1	$2RO \cdot 3SiO_2$

The formation temperature and melting point of the different silicates depend not only on the relation of the silica to base, but also on the nature of the bases present. Thus we may say that within the above range the silicates of lead and the alkalies are all readily fusible, the iron and manganese silicates are difficultly fusible, and the silicates of calcium, magnesium, and aluminum are infusible at the temperature of the assay furnace. Note that so far we are referring to the individual silicates of the different bases and not to mixtures of the same.

Of these slags the bi- and the trisilicates have but little effect on the ordinary assay crucible while the subsilicates attack it strongly to satisfy their affinity for silica.

The student should distinguish between the formation temperature of a slag and the melting point of the same slag when already formed. It has been shown that, when the constituents of a slag are finely crushed and intimately mixed as in an assay fusion, the formation temperature of the slag is decidedly lower than the melting temperature. That is to say, the slag forms without melting and actually passes through a pasty stage before coming to perfect fusion.

Action of Borax in Slags. Borax ($Na_2B_4O_7 + 10H_2O$) melts at about 560°C. and gives up its water of crystallization, forming borax glass. Borax glass when molten is decidedly viscous and on account of its excess of boric oxide acts as an acid flux.

Although primarily an acid flux, borax exerts considerable solvent power upon the silicates as well. It lowers the temperature of slag formation and with non-sulphide ores helps to make the slag viscous during the reduction period. With basic ores particularly, it reduces the temperature of final complete fluidity. It seems to protect the crucibles from the solvent action of litharge, probably by coating them with a viscous aluminum borosilicate.

To determine what relation it bears to silica as regards its acid fluxing quality we may consider the matter first from a theoretical standpoint, and then from the results of experiments.

Considering the borates according to their metallurgical classification, *i.e.*, according to the amount of oxygen in the acid to that in the base, we may compute the weight of borax glass necessary to form a monoborate with a unit weight of sodium carbonate and compare this with the amount of silica required to form a monosilicate with the same amount of base. From the rational formula for borax glass ($Na_2O{\cdot}2B_2O_3$) we see that, to form the monoborate ($6Na_2O{\cdot}2B_2O_3$), borax glass requires five additional molecules of Na_2O. The equation may be written as follows:

$$5Na_2CO_3 + Na_2O{\cdot}2B_2O_3 = 6Na_2O{\cdot}2B_2O_3 + 5CO_2,$$

whence we may write the following proportion to find the amount of borax glass necessary to form a monoborate with 100 grams of sodium carbonate:

$$5Na_2CO_3 : Na_2O{\cdot}2B_2O_3 = 530 : 202 = 100 : x.$$

Solving, x is found to equal 38.1. In the same way we may find the amount of silica necessary to form a monosilicate with 100 grams of sodium carbonate,

$$2Na_2CO_3 : SiO_2 = 212 : 60 = 100 : y.$$

Solving, y is found to equal 28.3. Whence, from the theoretical standpoint, we may say that, with a monosilicate slag, 38.1 grams of borax glass is equivalent to 28.3 grams of silica, or when borax glass replaces silica in a monosilicate slag 1 gram has the same effect as 0.743 gram of silica.

For a bisilicate slag the relation is different, owing to the molecule of Na_2O already in the borax glass. The amount of borax glass required to form a biborate with 100 grams of sodium carbonate is 95.3, and the silica for a bisilicate is 56.6. Thus, with a bisilicate slag, 1 gram of borax glass is equivalent to 0.594 gram of silica.

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 6 to 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 $\frac{2}{3}(Na_2O \cdot B_2O_3) + 3RO \cdot \frac{2}{3}B_2O_3 \cdot 3SiO_2$. 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 metaborate of soda $Na_2B_2O_4$, it is a borosilicate 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 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 bisilicate 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 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 monosilicate, and the same may be said for borates.

Acidic and Basic Slags. Slags more acid than the monosilicate are generally termed acid, while those approaching a subsilicate are called basic. The acid slags are all more or less viscous when molten and during cooling may be drawn into long threads. Their viscosity is responsible for the fact that when cooled at the ordinary rate they are vitreous and still retain their heat of crystallization. Alumina and boric anhydride add to the viscosity and vitreous characteristics of acid slags; they also tend to render the solidified slags tough and to cause them to stick to the lead button. The basic slags usually crystallize to some extent during solidification. This is particularly true of the so-called oxide slags, which consist principally of litharge.

The ideal slag from the point of view of economy of time in the operation of " slagging " the lead buttons and completeness of recovery of lead is one which flies to pieces on cooling or on slightly tapping the cold cone of lead and slag leaving the bright button of lead ready for the cupel without any hammering.

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. The quantities of reagents recommended in this chapter have been held close to the minimum requirements of the ore, but it is only fair to say that many commercial and mine assayers, in this country at least, use considerably larger proportions. For example, many assayers use from 30 to 35 grams of sodium carbonate per ½ assay ton of ore whereas if the fluxing is properly performed 15 grams is usually sufficient. 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 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 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 substantially 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. As in target shooting it is not always possible to hit the exact center of the bull's eye so in aiming for a 28-gram lead button most assayers would be content to obtain a button weighing somewhere between 20 and 35 grams.

In some instances a much larger lead-fall seems to be of advantage, and many of these special cases have to be worked out by trial-and-error methods. When aiming for a larger lead button the litharge should be correspondingly increased since obviously when a charge is planned to yield a button of definite size all lead reduced in excess of that amount diminishes the quantity of litharge available as a flux and if excessive may seriously affect results.

The Cover. In practically all crucible assay work it was formerly customary to place a cover of some fusible substance, such as salt, sodium sulphate, borax, borax glass, and soda, as well as other flux mixtures, on top of the mixed charge in the crucible. The objects sought were to exclude the air, to prevent loss of fine ore by "dusting," to prevent losses due to ebullition, and to wash down the sides of the crucible after the boiling stage of the fusion. No one cover material can accomplish all these purposes equally well. Borax and salt were used more often than any of the others.

The borax cover fuses before the rest of the charge. It is thick and vesicular when first melted and serves to prevent loss of fine ore by "dusting," as well as to stop loss by ebullition. In muffle fusions it tends to act as an insulating layer and retards the melting of the top layer of the charge. Melting early, it makes a thick glaze on the sides of the crucible above the ore charge, and, as the fusion becomes quiet and the temperature rises, most of this glaze runs down to join the main charge, carrying with it particles of ore or lead globules left on the sides of the crucible by the boiling of the charge in the early part of the fusion. Some assayers omit the borax from the mixed charge and add it in the form of a cover. It finally enters the slag and so ceases to act as a cover after the fusion is well under way.

The salt cover is thinly fluid when melted. Usually it does not enter the slag but floats on top of it, thus serving to keep out the air and to some extent prevent loss by ebullition. The present tendency is to do away with salt covers except for reducing power fusions. Since both gold and silver chlorides are volatile alone or in connection with the chlorides of arsenic, antimony, copper, iron, etc., it does not seem wise to add salt deliberately. The use of salt is also objectionable for the reason that it fills the room with chloride fumes at the time of pouring, and since salt assists in the volatilization of lead compounds the fumes are not only offensive but actually injurious to health.

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 argol, 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 and as the melts are made in air with some inevitable oxidation 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; argol, 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

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

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 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 and silica.

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* *Trans. A.I.M.E.* **34**, 395.

The accompanying table gives the reducing power of some of the common sulphides. The theoretical figures are computed 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 grams; PbO, 80 grams; SiO_2, 2 grams; ore to yield an approximate 25-gram button.

TABLE XVIII

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 argol showed a reducing power of 11.04 when silica for a subsilicate was added, 10.93 for a monosilicate, 10.62 for a bisilicate, and only 9.26 for a trisilicate. 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 monosilicate 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 ferric oxide, we have silica sufficient for a bisilicate, 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 into account 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:

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

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 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 effective 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:

$$2KNO_3 + FeS_2 + SiO_2 = K_2O{\cdot}FeO{\cdot}SiO_2 + 2SO_2 + N_2.$$

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 to the higher stage 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 singulosilicate. 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 argol and flour are also found to vary in reducing power, and their reducing powers should 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 ½-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 10 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 5 or 10 minutes for a small fusion, break the cone of lead from the slag and hammer it into a cube to 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 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 each unit of 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 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 crucibles 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 lower the temperature decidedly.

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	Cornstarch	11.5–13
Argol	8–12	Sugar	14.5
Flour	10–12	Cream of tartar	4.5–6.5

ASSAY OF CLASS 1 ORES. SILVER, GOLD, OR SILVER AND GOLD

With the experience gained in testing reagents the student is now ready to proceed to the crucible assay of a simple ore. Class 1 ores, those having neither reducing nor oxidizing power in the crucible fusion, such as silicates, oxides, and carbonates, present the fewest difficulties and are therefore considered first. Actually, precious-metal ores with no trace of sulphides are somewhat of a rarity today, but the procedure and ore charges recommended under this section will ordinarily give entirely satisfactory results with any ore containing up to 5 per cent of sulphides.

The amount and nature of reagents required are determined from the appearance of the ore after washing on the vanning shovel supplemented by such additional tests as may seem pertinent. The students should bear in mind the general principle that for a siliceous ore a basic flux is needed, and for a basic ore, an acid flux.

Before attempting to decide on the nature and quantity of reagents to use it is desirable to divide Class 1 ores into one of the following groups based on the character of the gangue:

1. Siliceous, as ordinary quartz, with more than 60 per cent of silica.
2. Basic, containing an excess of calcium, magnesium, iron, or manganese all which enter the slag as oxides.
3. Ores high in alumina.

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 bisilicates of sodium 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 bisilicates 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 1 assay ton of pure silica will require either 51.2 grams of sodium carbonate, or 108 grams of litharge, to form a bisilicate.

As a mixture of sodium and lead silicates is generally more satisfactory than either one alone, it is common to use both these basic fluxes in every fusion, thus making a double or bibasic 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 sodium carbonate, leaving two-fifths of it to be fluxed with litharge. Taking these proportions, then, there will be required for 1 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 2⅓ 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)	2⅓	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 together with 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 bisilicate 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 bisilicate 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)	2⅓ "	2½ "	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 bisilicate, are regularly used by the writer 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 bisilicate 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 bisilicates with pure silica. This will be found useful in calculating assay charges for various quantities of siliceous ores.

TABLE XIX

Bisilicate Slag Factors for Siliceous Ores

SiO_2	Quantity of Bases Required			
	PbO, grams	Na_2CO_3, grams	K_2CO_3, grams	$NaHCO_3$, grams
1 assay ton	108.	51.2	66.8	81.2
10 grams	37.0	17.6	22.9	27.9

One gram of FeO neutralizes 0.84 gram 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 bisilicate slags for siliceous ores, and even if they did agree they might prefer different proportions of sodium carbonate and litharge from those mentioned above. Many assayers consider it better to make the slag less acid than the bisilicate; in fact, there are certain advantages in making what is approximately a sesquisilicate. The quantity of basic fluxes required for this silicate may be determined by increasing the figures found in the last table by one-third.

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, 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 bisilicate slag.

If the silica and borax are cut down so as to make monosilicates, 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 and prevents the coalescing of the reduced lead.

The following table of bisilicate slag factors will facilitate the calculation of charges for basic ores.

TABLE XX

BISILICATE SLAG FACTORS FOR BASIC ORES

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 grams PbO	2.7 " "
30 " $NaHCO_3$	10.8 " "
30 " Na_2CO_3	17.0 " "
10 " K_2CO_3	4.4 " "

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 borosilicates 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 bisilicate 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)	2⅓	"
Silica	12.8	"

The slag from this charge would contain 17.0 grams of $CaSiO_3$ and 34.6 grams of Na_2SiO_3, or about twice as much sodium bisilicate as calcium bisilicate. Figure 3 shows that such a combination will melt at a reasonably low temperature. The lead silicate and the borax glass would, 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	2⅓	"
Silica	28.3	"

The borax glass and litharge being disregarded for the moment, the slag from this charge would contain approximately equal amounts of sodium and calcium bisilicates, which mixture, according to data presented in Fig. 3, would melt at about 1150°C. Added to this there would be almost an equal weight of lead oxide and borax glass, both readily fusible substances. Though it is impossible to state exactly what would result it is safe to predict that the entire mixture would fuse at or below 1000°C. Experience proves that it fuses without difficulty, yielding a glassy slag and giving a good separation of lead.

Figure 49 shows at a glance the quantity of reagents other than flour required to flux 1 assay ton of any mixture of limestone and silica.

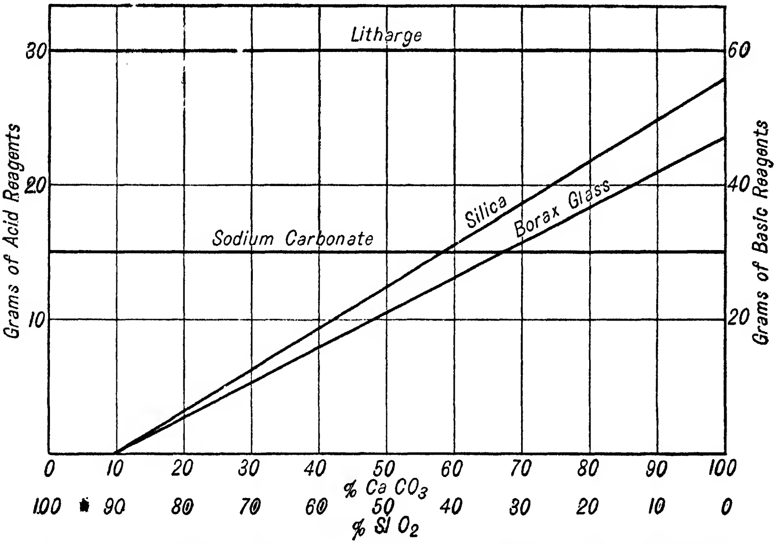

Fig. 49. Quantity of fluxes required for 1 assay ton of any mixture of limestone and silica.

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 bisilicate slags are the best.

Ores containing much calcium or magnesium carbonate cause considerable boiling in the crucible, owing 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. Metallurgists have never entirely agreed about the behavior of alumina in slags; some regard it as an acid, others as a base, and yet other authorities believe that it remains uncombined with any other oxide in slags, and therefore exists as a neutral substance held either in solution or in suspension in the liquid slag.

What we do know is that alumina is the most difficult to flux of any of the common metal oxides, and that it tends to make slags viscous. 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, $H_4Al_2Si_2O_9$, 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.

From the standpoint of assay fluxing the alumina in pure clay is already fluxed with silica and the aluminum silicate may be considered to be neutral. For ores which approach pure clay in composition such as some specimens of "gouge" and true slimes it is suggested that the sodium carbonate be increased to double the amount of ore, and that a moderate excess of litharge be used together with silica and borax glass for a sesquisilicate. The additional amount of flux will serve to dilute the aluminum silicate and yield a slag of more favorable characteristics. The addition of 5 or 10 grams of cryolite will be found beneficial when other means fail.

Assay Procedure for Class 1 Ores. 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	*

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

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

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 charges from the data given under the discussion, " Slags for Basic Ores."

For ores 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 entitled " Special Methods of Assay."

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 ½-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 it is 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 15 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, and the appearance and the degree of malleability of the lead buttons.

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 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 may 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, 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.

Notes. 1. The crucible should never be more than two-thirds full when the charge is all in.

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

3. 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.

4. The slag should be fluid on pouring and free from lead shot. If it is pasty or lumpy, either the fusion has not been long enough to decompose the ore thoroughly, 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. Lead shots 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.

5. 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 slag 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.

6. The lead button should be soft and malleable. If it is hard or brittle or weighs more than 40 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, or litharge or they may be rich alloys of lead and the precious metals.

7. 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 caused by incorrect fluxing or too short a time of fusion. If incorrect fluxing is the cause, decreasing the silica and increasing the soda and litharge will usually prevent the formation of this substance in a subsequent fusion.

* 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.

When assaying low-grade gold ore and tailings most assayers use at least a 1-assay-ton charge of ore and correspondingly more reagents. Either 25- or 30-gram muffle crucibles or G pot furnace crucibles are recommended for this quantity of ore.

ASSAY OF MISCELLANEOUS CLASS 1 ORES. STEP METHOD OF PROCEDURE

After determining and recording the character of each sample the student should decide on charges for each in a logical and systematic manner, taking into consideration their varying compositions so far as he has been able to determine them. The following outlined step procedure for the determination of a charge for Class 1 siliceous ores will serve to illustrate the method of approach and give some suggestions as to the solution.

1. Decide on silicate degree of slag to make:
   bisilicate or slightly less acid.
2. Decide on quantity of ore to use:
   ¼ to 4 assay tons.
3. Decide on quantity of sodium carbonate to use:
   equal to or greater than weight of ore.
4. Decide on quantity of litharge to use:
   at least 30 grams for the button plus an additional amount to flux part of the silica when soda is limited or to hold impurities in the slag.
5. Decide on quantity of borax to use:
   5 grams per ½ assay ton of ore plus extra amount for any basic oxides, etc.
6. Decide on quantity of flour to use:
   sufficient to yield a 28-gram button or more for large ore charges.

For Class 1 basic ores the procedure would be as follows:

1. Decide on silicate degree of slag to make.
2. Decide on quantity of ore to use.
3. Decide on quantity of sodium carbonate to use.
4. Decide on quantity of litharge to use.
5. Determine approximate weight of $CaCO_3$, $MgCO_3$, FeO, etc., and SiO_2 in ore charge.
6. Compute the weight of SiO_2 required to flux the CaO, MgO, FeO, and the other bases of the ore.
7. Compute the weight of silica required to flux the Na_2CO_3.
8. Compute the weight of silica required to flux that part of the PbO which is to go into the slag.
9. Compute total silica requirements of charge:
   sum of 6, 7, and 8 above.

10. Decide on quantity of borax glass to add:
    for ½ assay ton of ore use a minimum of 5 grams and for pure $CaCO_3$ *at least 10 grams.*
11. Determine quantity of silica reagent to add:
    No. 9 above minus silica in ore plus silica equivalent of borax glass.
12. Decide on quantity of flour to use.

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. In fact, so far as the size of lead button is concerned, we can assay an ore containing as much as 18 per cent of pyrite when using ½-assay-ton ore charges and still obtain no more than a 28- or 30-gram button. With these larger quantities of sulphides, however, the assayer must guard against their incomplete oxidation, which will result in the formation of matte with consequent loss and low results. Since both soda and litharge aid in the decomposition of sulphides it is well to increase each of these constituents in the charge as the sulphide in the ore increases.

The most important methods for the assay of Class 2 ores are as follows:

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 carefully regulated 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 it 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

As the sulphide content of his ores increase, the assayer is faced with the possibility of incomplete decomposition of the sulphides with the accompanying loss of precious metals in the form of matte. Since the character of the reactions in the crucible is governed both by the amount and nature of ore constituents and reagents used as well as by the heat treatment, no hard and fast and at the same time economically practical rule can be offered to fill in the gap between the ideal Class 1 non-sulphide and the really high-sulphide ore which requires the addition of niter for its assay. In general, the slag, which for an ideal Class 1 ore should be a bisilicate, should be made more basic by increasing the soda and the litharge as the sulphides increase.

With an ore containing 18 per cent of pyrite in a siliceous gangue the following charge, which will yield a slag of approximate monosilicate degree, should prove satisfactory:

Ore	0.5 A. T.
Soda	22.5 grams
Borax glass	5.0 grams
Litharge	60 grams

Neither flour nor niter is required, since the sulphide of the ore should reduce a button of about 28 grams. With ores containing more than 18 per cent of pyrite the lead buttons will be too large unless some oxidizing agent is added to counteract this extra reducing effect, and for this purpose potassium nitrate is commonly used. Figure 50 shows the quantity of flour, R. P. 12, or of niter, O. P. 4.2, which must be added to ½ assay ton of sulphide ore of any reducing power to obtain a 28-gram lead button.

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. If it does contain these so-called impurities, special measures have to be taken to eliminate them. 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.

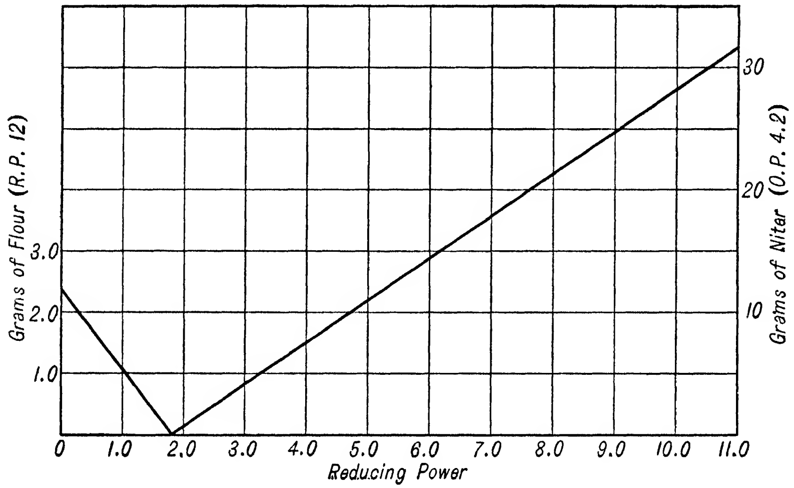

FIG. 50. Quantity of flour or niter required per 0.5 assay ton of ore of any reducing power.

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 ½ 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 with Class 1 basic ores, and the silica in the ore is deducted. A minimum of 5 grams of borax glass is generally used; with 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 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. It is desirable then to figure for a subsilicate slag. More detailed instructions for the assay of impure ores will be found in the next 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 assayer's "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 wish to use for a number of fusions. More important than this is the damage which is done if 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 slightly the quantity of silver which is held in the slag, so that no more litharge than is necessary to insure 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 today, 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 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 but very little.

For the best results in niter fusions the crucibles should be introduced into a hot muffle and brought rapidly to fusion, the actual fusion process not taking more than 10 or 15 minutes. This method of procedure insures a complete decomposition of the sulphide minerals of the ore and prevents the formation of a matte which is likely to result if the fusions take a long time. The crucibles should be in the furnace 30, or at the most 40, minutes. If only two or three fusions are to be made the muffle should be cherry red, 700°C. If a considerable number of crucibles are to be charged at one time the furnace should be at a bright red heat, 850°C. The cold crucibles will lower the temperature materially and the furnace 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, possibly due to volatilization.

To obtain good results, particularly when a large amount of litharge is used in the charge, the muffle door should be tightly closed and a reducing atmosphere maintained in the muffle.

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 skillful 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 28 grams and even 35 or more grams in large charges. The use of the large quantity of litharge and niter required in the assay of impure sulphide ores is thought to give high slag losses, owing to oxidation of silver and its solution in the heavy litharge slag.

Physical and Chemical Changes in the Niter Fusion. 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 and 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 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° to 750°C., 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., in which temperature range 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; these reactions are endothermic. The following are examples:

$$\mathrm{PbS + PbSO_4 = 2Pb + 2SO_2 - 92{,}380\ cal.}$$

$$\mathrm{PbS + 2PbO = 3Pb + SO_2 - 52{,}540\ cal.}$$

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:

$$\mathrm{3Fe_2O_3 + FeS + }x\mathrm{SiO_2 = 7FeO\cdot }x\mathrm{SiO_2 + SO_2 - 81{,}640\ cal.}$$

This reaction is of importance above 900°.

In this assay the niter is limited to less than that required to decompose all the sulphides of the 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 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 a 15 to 25 per cent excess above that required for the reducing power of the ore, but this is necessary only 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 temperature in the presence of an excess of silica, the litharge will be entirely converted into silicate before the completion of the reactions resulting in the oxidation of the sulphur, which require a comparatively high temperature. The litharge contained in the lead silicate is no longer available for the decomposition of the sulphides, all the niter is used up, and hence sulphide sulphur remains and a matte results. The slower the fusion, the more excess litharge there must be, and the more basic the slag must be, to insure the presence of enough undecomposed litharge to complete the oxidation of the residual sulphides. With only enough silica present for a subsilicate, the fusion may be relatively slow and yet afford complete decomposition of the ore. This type of slag is destructive of crucibles, and for this reason it is better to use a more acid slag whenever possible. It would be unwise, however, to make a slag much more acid than the monosilicate, for the monosilicate of lead is only partly reduced by metallic sulphides at the highest temperature of the assay furnace. With this silicate degree, however, rapid fusions are found to result in complete decomposition of the ore.

The silica which is added in the assay of high-sulphide ores helps to slag the metallic oxides which are derived from the oxidation of the sulphides; it helps to keep the iron in the ferrous condition; and it serves to protect the crucibles. If possible, no reaction between it and the litharge of the charge should be permitted until all the niter has been consumed and the remaining sulphide has been decomposed by litharge. It is impossible to realize this ideal entirely, but it may be approached by using comparatively coarse silica, 20- or 30-mesh, so that an appreciable time will be required for its complete solution in the slag.

Determining the Reducing Power of Ores. Van some of the ore and estimate the character and amount of the different sulphides present, as well as the amount and character of the slag-forming constituents. Take from 3 to 10 grams of ore according to the amount of sulphide present, 3 grams for pure pyrite and correspondingly greater amounts for ores containing less sulphides. If the ore is mostly galena as much as 10 grams may be taken, the idea being always to get a button of about 30 grams. (See "Reducing Power of Minerals.") Take twice as much sodium carbonate as ore, 60 grams of litharge, and silica sufficient to make a total of 5 grams when the silica of the ore is taken into account. Use an E crucible for the pot furnace or a 12- or 15-gram crucible for the muffle. Weigh out and add the fluxes first in the order given, and weigh the ore last, mixing thoroughly with a spatula. Place a $\frac{1}{2}$-inch cover of salt on top.

Fuse for 15 minutes, finishing at a good yellow heat. Pour into crucible mold, allow to cool, separate the lead from the slag, and weigh on the pulp balance to tenths of grams. Divide the weight of the lead by the weight of the ore taken.

It should be noted that this reducing power is not an absolute thing but depends upon many factors, such as the ratio of sodium carbonate to ore, the amounts of litharge and silica added, as well as the temperature at which the fusions are conducted. Reducing power fusions made in the soft-coal muffle furnace are likely to give low results on account of a partial oxidation of the sulphides and reduced lead during the fusion by the leakage of air into the muffle.

Estimating the Reducing Power of Ores. In many instances it is possible to estimate the reducing power of an ore within close limits. This requires a knowledge of the reducing powers of the common sulphide minerals as well as the knack of vanning. The ore is vanned and the percentage of the various sulphides estimated. From these data the reducing power is found. For instance, if the ore is 50 per cent pyrite and the rest gangue, the reducing power will be about 5.5, 50 per cent of the reducing power of pure pyrite. If it is 40 per cent galena and 10 per cent sphalerite, the reducing power will be 40 per cent of 3.4 + 10 per cent of 7.9 = 2.15 approximately. The reducing power of the ore is equal to the sum of the products of the reducing powers of the different constituents, multiplied by the percentage of each in the ore, divided by 100. For example, with an ore having three constituents, A, B, and C, whose reducing powers are respectively, a, b, and c, and which are present in the ore to the extent of x, y, and z per cent, respectively, the reducing power of the ore would be $\frac{ax + by + cz}{100}$.

In general if the amount of sulphides in the ore is comparatively small and especially if only 0.5 assay ton of ore is used, it is a very simple matter to obtain a lead button of suitable size for cupeling, by this means. If, for example, a mixture of galena and gangue mineral contains 50 per cent of galena the reducing power of the 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, $\frac{2}{3}$ gram of flour (R. P. 12) would have been added and the result would have been a 32.8-gram button which could still be cupeled. In a similar manner, if the galena had been estimated at 60 per cent about ½ gram of niter would have been added and the resulting button of about 22.7 grams would also have been considered to be within a satisfactory size range for collection of precious metals and suitable for cupellation.

Again, in dealing with practically pure sulphides, as 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	4 "	5 "
Lead obtained	24.31 grams	7.51 grams

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

Lead oxidized by 4 grams of niter $24.31 - 7.51 = 16.80$

Oxidizing power of niter $= \frac{16.80}{4} = 4.20.$

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 singulosilicate, 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 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 sodium sulphate, and because the soda thus used 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 of 1.75 grams of soda-ash, and every gram of pyrite above 2.33 grams requires 0.52 gram of soda ash. The computations for the actual charges need not be carried out in such detail, but it is done here to illustrate the principle.

The potassium and sodium sulphates formed by these reactions are only slightly soluble in silicate slags and, being lighter than the slag, form a layer on top of it. This sulphate cover is very liquid when molten and serves to keep the air away from the fusion. In the mold it appears on top of the slag cone as a crystalline white layer.

Quantity of Niter Required. The quantity of niter required for any charge is determined by multiplying the reducing power of the ore by the quantity of ore taken for assay, which gives as a result the quantity of lead which would be reduced from an excess of litharge if the latter were present and no niter were added. From this quantity is subtracted the weight of the lead button desired, and the remainder is divided by the oxidizing power of niter, expressed in terms of lead. For instance, in the example referred to above, the reducing power of pure pyrite being assumed to be 12, the oxidizing power of niter in this type of charge to be 4.2, the quantity of niter required for 0.5 assay ton of ore is determined as follows:

Total reducing effect of ore 14.58 × 12.0 =	175.0	grams of lead
Lead button desired	28.0	"
Difference, pyrite equivalent of which must be oxidized by niter	147.0	"

$$\text{Niter required } \frac{147.0}{4.2} = 35.0 \text{ grams.}$$

Silica Requirements of Bases. For ores which consist of the sulphides of iron, lead, and zinc, together with gangue minerals, and which are here classified as pure ores, a singulosilicate slag will give satisfactory results. The silica requirements for the different bases entering the charge in the example taken would be as follows:

For 8.65 grams of FeO resulting from the oxidation of 0.5 assay ton of pyrite there is required	3.64	grams	SiO_2
For 15 grams of sodium carbonate in the slag	4.25	"	"
For 30 grams of litharge	4.06	"	"
Total	11.95	"	"

Completed Charge. By combining these various quantities the charge for pure pyrite is found to be as follows:

Ore (Pyrite R. P. 12)	0.5	A. T.
Sodium carbonate	25	grams
Litharge	60	"
Niter	35	"
Silica	11.95	"

With the proper furnace treatment this charge will give a good decomposition of the ore with a clean lead button and greenish black, glassy slag.

Most assayers, however, would add a minimum of 5 grams of borax glass. If this is done the equivalent amount of silica should be omitted, and the charge would be

Ore	0.5	A. T.
Sodium carbonate	25	grams
Borax glass	5	"
Litharge	60	"
Niter	35	"
Silica	8	"

Zinc oxide is difficult to slag, and the zinc silicates fuse only at a very high temperature; $ZnSiO_3$ melts at 1479°C. and Zn_2SiO_4 at 1880°C. With pure sphalerite the borax glass may be increased to a maximum of 10 grams. It is interesting to note that the addition of borax increases the solubility of the sulphate salt in the slag. With pure sphalerite and no borax the slag is glassy and the weight of the sulphate cover closely approaches the theoretical amount. When 10 grams of borax glass is added the solid slag appears slightly stony and a much smaller sulphate cover is obtained. The alkaline sulphates are dissolved in the superheated slag but tend to crystallize out on cooling, resulting in the stony appearance of the solid slag.

The following are examples of suitable charges for pure ores:

	No. 1 Pure Galena R. P. 3.41	No. 2 Pure Sphalerite R. P. 7.87	No. 3 Pure Pyrite R. P. 11.05
Ore	0.5 A. T.	0.5 A. T.	0.5 A. T.
Sodium carbonate	19 grams	21 grams	25 grams
Borax glass	0 "	10 "	5 "
Litharge	50 "	60 "	60 "
Niter (O. P. 4.2)	5.2 "	20.6 "	31.6 "
Silica	5 "	6 "	8 "
Crucible	20-gram	25-gram	30-gram

Steps in the Computation of Charge for a Niter Assay

Having estimated the mineral contents of the ore after vanning, the student should make a preliminary assay to determine the reducing power of the ore; with the aid of that figure he is ready to compute a charge for the regular niter assay. The following outlined step procedure may serve to guide the student in his first few assays by the niter method.

A. Preliminary Assay to Determine Reducing Power of Ore.

1. Estimate reducing power of ore from reducing powers of component minerals.
   See Table XVIII.
2. Determine quantity of ore to use for preliminary assay.
   See rules on page 182.
3. Determine rest of charge.
   See rules on page 182.

B. Regular Niter Fusion.

1. Decide on silicate degree of slag to make.
2. Decide on quantity of ore to use.
   Depends upon the amount of impurities and the amount of sulphur present. Do not use much in excess of 25 grams of niter. One-half assay ton is the customary quantity.
3. Determine quantity of sodium carbonate to use.
   At least 15 grams per ½ assay ton of ore for the slag plus an additional amount to combine with sulphuric anhydride. See pages 184–185.
4. Determine quantity of litharge to use.
   A minimum of 60 grams and more if the ore contains impurities. See pages 178–179.
5. Determine the quantity of niter required.
   The oxidizing power of niter may be taken as 4.0 unless it is known to be different. See page 184.
6. Decide on the quantity of borax glass to use.
   Add a minimum of 5 grams except with coppery ores when it may occasionally be entirely omitted. See page 187.
7. Determine the quantity of silica to be added.
   Follow method outlined in step procedure for Class 1 basic ores. See also pages 186, 190.

Procedure. Regular Niter Fusion. Make up charges according to the rules outlined above. The fusions should preferably be made in large muffle furnaces regulated so as to have a slight reducing atmosphere. It is best to close the holes in the back of soft-coal muffles with bone ash, but this precaution is unnecessary with gas- or oil-fired furnaces. Crucible-type furnaces heated by gas or gasoline are satisfactory if thoroughly preheated before the crucibles are introduced. Coke-fired crucible furnaces are the least satisfactory of all for niter fusions because of the difficulty of careful temperature control, which is particularly necessary with this method. A salt cover is entirely unnecessary for muffle fusions.

Be sure that none of the reagents are lumpy and that the charges are thoroughly mixed. If this precaution is taken and the temperature is properly adjusted no trouble should be caused by boiling. However, if the soda and the niter are in lumps the results will be less satisfactory and the charges may boil over. Fuse at a high enough temperature, about 700°C., so that the charges will be well melted in 10 minutes and will have finished bubbling in 15 to 25 minutes. After audible bubbling has ceased, allow to remain at a yellow heat for 10 or 15 minutes more. Then pour and finish as usual. Examine the crucibles while hot to see whether the fusion has been satisfactory and note particularly whether 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 finish the new assay at a higher temperature. If sufficient silica is present to form bisilicates with all 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 the right-hand 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 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 monosilicate slag factors may be found useful in determining the quantity of silica required for any niter fusion.

TABLE XXI

MONOSILICATE 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	4.89
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 taken. 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, litharge is limited to 30 or 35 grams and even less if the ore itself contains lead. Therefore, the only basic fluxes available are the alkaline carbonates, and the quantity of these used is at least two or three times the quantity of ore. Just before pouring, the excess of iron is removed.

Chemical Reactions. The chemical reactions which take place in the crucible are entirely different from those of the other crucible methods. In the niter and roasting methods of assaying, the sulphides of the ore are oxidized by litharge, niter, or the oxygen of the air, and the sulphur either passes off as SO_2 or is converted into SO_3, which displaces the carbonic acid of some of the sodium carbonate, forming sodium sulphate. In the iron assay, part of the sulphur in pyrite and some of the other sulphides is volatilized, part of the sulphur is oxidized by the small amount of litharge used, and the rest remains as sulphide, appearing either as an iron matte on top of the lead button or dissolved in the excess of basic slag.

The following reactions will serve to illustrate the chemical changes which take place:

$$
\begin{aligned}
&FeS_2 = FeS + S,\\
&PbS + 2PbO = 3Pb + SO_2,\\
&Cu_2S + 2PbO = 2CuPb + SO_2,\\
&FeS + 3PbO = 3Pb + FeO + SO_2,\\
&Fe + PbO = Pb + FeO.
\end{aligned}
$$

When the litharge is all reduced the following occur:

$$
\begin{aligned}
&PbS + Fe = Pb + FeS \text{ (matte)},\\
&FeS_2 + Fe = 2FeS \text{ (matte)},\\
&Sb_2S_3 + 3Fe = 2Sb + 3FeS \text{ (matte)},\\
&As_2S_3 + 13Fe = 2Fe_5As \text{ (speiss)} + 3FeS \text{ (matte)},\\
&Cu_2S + Fe = Cu_2 + FeS.
\end{aligned}
$$

Finally, if a sufficient excess of alkaline flux is used, the iron matte is dissolved by this basic slag, probably as a double sulphide of iron and sodium.

From the equations it will be seen that copper, arsenic, and antimony are reduced, at least in part, and either go into the lead button, or in the case of arsenic form a speiss which appears as a hard, white globule partly embedded in the top surface of the lead button.

In Table XXII are shown the heats of formation of some of the common metallic sulphides expressed in terms of a unit weight of sulphur.

TABLE XXII

HEAT OF FORMATION OF METALLIC SULPHIDES

Formula	Calories	Formula	Calories
K_2S	103,500	CoS	21,900
CaS	94,300	Cu_2S	20,300
Na_2S	89,300	PbS	20,200
MnS	45,600	NiS	19,500
ZnS	43,000	$\frac{1}{3}Sb_2S_3$	11,500
FeS	24,000	Ag_2S	3,000

A glance at this table points to the theoretical possibility of reducing the sulphides of cobalt, copper, lead, nickel, antimony, and silver by metallic iron, and this is borne out by laboratory experience. From the thermochemical data it may also be predicted that but little zinc will be reduced, and therefore the lead button will be free from this metal.

Another reaction which is important in this connection is the oxidizing effect of alkaline carbonates on metallic sulphides. This reaction affords a considerable reduction of lead from galena when galena is fused with alkaline carbonate alone, and was the basis of the Upper Harz method for the assay of lead in galena ores. The reaction as given by Kerl is as follows:

$$7PbS + 4K_2CO_3 = 4Pb + 3(K_2PbS_2) + K_2SO_4 + 4CO_2.$$

At first glance this reaction may not appear to be reasonable, but a simple trial fusion with these two substances will serve to convince the most skeptical that something very much like this does occur. Taken step by step, starting with the reversible reaction:

$$(1) \qquad 3PbS + 3K_2CO_3 \rightleftarrows 3K_2S + 3PbCO_3,$$

the explanation is simple. Lead carbonate is readily dissociated by heat as follows:

$$(2) \qquad 3PbCO_3 = 3PbO + 3CO_2.$$

The CO_2 escapes and this allows equation (1) to proceed in the right-hand direction.

The lead oxide resulting from equation (2), in the presence of alkaline carbonate, reacts with more lead sulphide as follows:

$$(3) \qquad PbS + 3PbO + K_2CO_3 = 4Pb + K_2SO_4 + CO_2.$$

A condition of equilibrium appears to be reached when the simple double sulphide of alkali and lead is obtained, *i.e.*:

$$(4) \qquad 3PbS + 3K_2S = 3(K_2PbS_2).$$

Adding equations (1), (2), (3), and (4) we have Kerl's reaction:

$$7PbS + 4K_2CO_3 = 4Pb + 3(K_2PbS_2) + K_2SO_4 + 4CO_2.$$

It is obvious that sodium carbonate will have the same effect as potassium carbonate.

Limitations of the Method. The soda-iron method is an excellent one for suitable ores when the greatest accuracy is not desired, but is limited in its application to pure ores. It is known to give low silver results on high-sulphide ores such as nearly pure pyrite, but if the assay is properly conducted the results should not be more than 2 or 3 per cent lower than those obtained by the niter method, and the gold results differ but little in the two methods. This loss of silver is attributed by Hall* to the solubility of the silver in the iron sulphide of the slag, although, according to Fulton†, " Ferrous sulphide has practically no solvent action on silver or on gold." The slag obtained in the assay of pure pyrite contains a large amount of ferrous-alkaline-sulphide, which probably has a slight solvent action on silver, so that the silver is distributed between the slag and the lead button in proportion to the relative amounts of ferrous-alkaline-sulphide and lead present and according to its solubility in the one as compared with that of the other. If this is true, the less sulphide sulphur the slag contains and the greater the quantity of lead reduced, the higher the silver recovery and the more satisfactory the results should be. This points out one detail of the furnace manipulation of the iron-nail assay of pyritic ores which should be carefully regulated, *i.e.*, the temperature should be held at a dull red for some time to aid in the elimination of the first atom of sulphur from the pyrite, which breaks up at this temperature. It is also important to provide sufficient litharge to supply a good-sized lead button and more important still to reduce this as completely as possible. A 35-gram lead button is needed for pure pyrite. The excessively high slag losses often reported for this method are in part caused by too small a lead-fall and too short a time of fusion, which would result in leaving some lead sulphide, a good solvent for silver, in the slag.

In general it may be said that the method is not suited for ores carrying nickel, copper, cobalt, arsenic, antimony, bismuth, or tellurium. Even when an ore contains several per cent of copper, this metal may not enter the lead button in sufficient quantity to interfere seriously with cupellation; but the presence of copper always gives low results, probably because of the solvent action of the copper sulphide, contained in the slag, upon the silver. Ores containing nickel are least of all suited to the method.

The Slag. The slag made should not be more acid than a monosilicate, and a subsilicate is, perhaps, preferable. As the crucibles are not attacked by the slag to any extent, they may be used a number of times if care is taken to see that they do not retain any lead shot.

Atmosphere. A reducing atmosphere should be maintained in the furnace to prevent oxidation and corrosion of the nails. This may be accomplished by placing several crucibles containing soft coal in the front part of the muffle and renewing the coal in them if necessary. In

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* " Assay of Gold and Silver by the Iron-Nail Method," Trans. *A.I.M.E.* **47**, 37.

† *Trans. A.I.M.E.* **39**, 596.

an oxidizing atmosphere the nails are badly corroded. The ferric oxide scale formed causes the slag to become thick and pasty, and this tends to cause the retention of lead shot in the crucible.

Procedure. Van the ore; estimate and record its mineral composition. Note especially the amount of lead minerals. Use a 20-, 25- or 30-gram crucible according to the amount of reagents required. The following charges are suggested as capable of yielding better results than the customary 30 grams of sodium carbonate, 10 grams of borax glass, and 25 grams of litharge.

	Galena	Half Galena Half Pyrite	Pyrite
Ore	0.5 A. T.	0.5 A. T.	0.5 A. T.
Sodium carbonate	30 grams	40 grams	50 grams
Borax	10 "	15 "	20–25 "
Litharge	20 "	30 "	40 "
Silica	2 "	2 "	2 "

Insert from 3 to 5 twenty-penny cut nails, or preferably one 3½- or 4-inch track spike, point downward.

Heat gradually to fusion; fuse from 40 to 60 minutes. Examine the nails occasionally and if they are badly eaten add several fresh ones, leaving the old ones in the crucible if they cannot be removed free from lead. Fuse until the nails may be freed from lead by tapping them gently and washing them around in the slag. Remove all nails and pour as usual. The slag will be black and should separate easily from the lead button.

Notes. 1. If the ore contains 2 or more grams of silica none need be added.

2. This fusion requires a somewhat longer time than the niter fusion, owing to the fact that time must be allowed for all the charge to come in contact with the surface of the iron nails.

3. A matte indicates too much silica, too little alkaline carbonate, or too short a time of fusion.

4. The lead may not start to drive in cupeling quite as rapidly as other buttons owing to a small amount of iron which is often present.

E. A. Smith* believes that the soda-iron method is not suited for the assay of ores containing more than 25 to 30 per cent of pyrite. This is presumably because the presence of a large amount of ferrous sulphide in the slag is considered objectionable. Smoot† presents data which tends to show that by decidedly increasing the sodium carbonate content of the charge and adding an excess of argol this objection may be overcome and the results obtained on heavy sulphide ores equal those

* "The Assay of Complex Gold Ores," *Trans. I.M. & M.* **9**, 329.

† Discussion of Hall's paper, *Trans. Am. Inst. Mining Met.* **47**, 42.

obtained by the use of the litharge-niter method. By the use of argol Smoot doubtless was able to protect the fusion from oxidation and thus obtain a slag of better chemical and physical characteristics.

In the iron-nail assay as ordinarily conducted a large part of the iron of the nails is converted to oxide, which, to say the least, is of no advantage. Some assayers substitute a carefully regulated amount of iron in the form of small wire nails in place of spikes, long nails, or hoop iron. In addition 1 or 2 grams of charcoal is added. If the temperature is carefully controlled to provide a prolonged low-temperature fritting stage, it can be imagined that a considerable part of the litharge will react with the sulphides of the ore instead of with the iron. This will result in the removal of a part of the sulphur from the slag, which is to be preferred to the formation of the equivalent amount of ferrous sulphide. As the temperature rises and active fusion is in progress, lead will have begun to collect in the bottom of the crucible and the nails will float on top of this bath of lead in contact only with it and the lower stratum of slag, where also will be collected any undecomposed sulphides or matte. Allowed sufficient time, a properly regulated amount of nails will decompose all the sulphides and in so doing will be themselves entirely consumed. The carbon of the charcoal will serve to protect the iron of the slag from oxidation. The writer has seen this method used by British assayers in South America with apparently excellent results. The only serious objection observed was in the long fusion period apparently necessary to insure completion of the reactions and the absence of fragments of iron in the lead buttons.

The Roasting Method

This method of assaying sulphide ores is rarely used, but as it may be found of advantage for very low-grade pyritic ores it will be briefly described.

Procedure. Spread out from 0.5 to 5.0 assay tons of ore in a well-chalked roasting dish of sufficient size to allow of stirring without loss. Have the muffle at a dull red only and the fire so low that the temperature of the muffle may be held stationary, or raised slowly. Place the dish in the muffle, and, if the ore contains minerals which decrepitate, cover it and keep it covered until danger from this source is passed. The ore should soon begin to roast. When fumes are noticed coming from the ore, check the fire and hold it at this temperature for some time, stirring frequently. After all danger of fusing is over, gradually raise the temperature, stirring at intervals of 20 minutes or half an hour. Finally heat to about 700°C. for half an hour. If the ore contains only sulphides of iron and copper, practically all the sulphur will be removed within this time. If there is any doubt about the roast being complete, remove from the muffle, add a small amount of charcoal, and see if there is any odor of sulphur dioxide. If the ore contains zinc, a much higher temperature will be required to break up the zinc sulphate. It is not advisable, however, to carry the roasting temperature above 700°C. For ores which consist principally of pyrite, galena, or stibnite, place a weighed amount of silica on the dish before introducing the ore. A weight of silica equal to that of sulphide may be used. This will serve to prevent the roasted material from adhering to the dish and will be found useful as a flux in the subsequent fusion.

If the ore contains arsenic or antimony, the roasting operation is more difficult. The best conditions for the elimination of these elements are alternate oxidation and reduction at a low temperature. The presence of sulphur aids in the elimination of these elements, because their sulphides are volatile. To obtain the reducing action necessary for the elimination of arsenic and antimony, take the partially roasted ore from the muffle, allow it to cool for a few moments, and then mix powdered charcoal or coal dust with it and roast at a dull red heat until the coal is burned off. Then add more coal and re-roast. Repeat this until no more fumes of arsenic or antimony are noticed; then heat with frequent stirring to about 700°C.

After the ore is roasted, the dish is carefully cleaned out and the ore is charged into a crucible with fluxes and treated exactly as a Class 1 ore. If the sulphide mineral was mostly iron, the ore will probably be found to have a slight oxidizing power due to the formation of Fe_2O_3 and Fe_3O_4 in the roasting.

The roasting method of assaying is slow and takes up much muffle space. It is open to the liability of serious mechanical and volatilization losses. Its most useful field would seem to be the assay of low-grade pyritic gold ores where a very accurate determination of gold is desired. The method usually gives low results in silver.

The Combination Wet-and-Fire Assay

The combination wet-and-fire assay is used principally for the determination of gold and silver in impure ores, matte, speiss, and bullion. A description of the method, as applied to the assay of ores containing cobalt, nickel, and arsenic, will be found in the chapter entitled "The Assay of Complex Ores," and the application of the method to the assay of copper bullion may be found in the chapter, "The Assay of Bullion."

ASSAY OF CLASS 3 ORES

The principal ores belonging to this class are those containing some of the higher oxides of iron or manganese, *i.e.*, Fe_2O_3, Fe_3O_4, or MnO_2. These are reduced by carbon and tend to enter the slag as ferrous and manganous silicates, respectively. If the charge made up for these ores contained only the ordinary amount of flour, all this might be used up in reducing the oxides of the ore and no lead button would result. To remedy this, the oxidizing power of the ore should be known before the charge is made up.

To determine the oxidizing power of an ore, fuse a known weight of it, say 10 or 20 grams, with a regular crucible charge for that amount of ore and a carefully weighed amount of argol or flour of known reducing power, more than sufficient to reduce the ore. The weight of lead that the argol may be supposed to have reduced from an excess of litharge, minus the weight of lead obtained, is evidently the amount oxidized by the ore. This weight divided by the weight of ore taken gives the oxidizing power.

When the oxidizing power of the ore has been determined the assay is made in the same manner as for Class 1 ores, with the addition of the extra flour required.

PRACTICE ON MISCELLANEOUS SAMPLES

After having attained a working knowledge of the various principles of fluxing by actual practice with typical samples of the several types of ores described in this chapter, probably by assaying one sample at a time, during which he will have acquired a certain amount of manipulative skill, the student should next be given practice in carrying through a number of assays at the same time. This should be on a gradually increasing quantity basis with the object of permanently fixing in his mind the principles underlying the operations, of still further cultivating his powers of accurate and keen observation, of adding to his skill in manipulation, and of attainment of some degree of dispatch in quantity work. He should still work to attain accuracy, which is of primary importance, but should by concentrating on the work and particularly by carefully planning it out in advance develop an order of work or system which when perfected will enable him to get through a large amount of work in a surprisingly short time.

It will be well to read certain of the sections in the chapter "Practical Assaying" before attempting to adopt any system since the system there described is pretty much a standard the world over. All systems designed to secure dispatch depend on carrying through the various operations in as large batches as can be handled conveniently with the apparatus available, and all depend upon orderliness in every stage of the operation. To avoid confusion the crucibles, lead buttons, cupels, parting cups, etc., should always be kept in numerical order. If this is done in connection with a corresponding order in the notebook the necessity of numbering each crucible, cupel, etc., will be eliminated and this alone will result in a great saving of time. To be able to dispense with numbering of assays the student must have a desk and furnace to himself and to develop his capacity for handling a large amount of work must arrange to have a whole day in the laboratory without interruption. At this stage, after spending six or eight whole days in the laboratory he should be able, if provided with suitable apparatus, to make at least 25 duplicate assays in the course of a day's work.

CHAPTER IX

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.

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 ml. of acid is required for 0.25-

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* *Trans. Can. Mining Inst.* **17,** 244–250.

assay-ton portions and 100 ml. for 0.5-assay-ton portions. The solutions are heated on a steam bath until red fumes cease to be generated and are then diluted with 200 ml. 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 which 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 the silver as chloride, but any considerable excess of the precipitant is to be avoided. As long as some silver remains unprecipitated, the solution clears rapidly on stirring; toward the end the cloudiness persists for some time. 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 likely 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, with 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 insure 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 of an ounce 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 coordinating and elucidating much information which was hitherto widely 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 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 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; Pb to PbO, 52,500 calories; Te to TeO_2, 39,150 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.

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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**, 175.

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

In 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 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, *e.g.*, 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 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,* who has made a careful study of this process, 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 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 and 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°C., and the fusion should be finished in 20 to 30 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

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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,** 913.

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.

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 XXIII

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 ¼ inch of a mixture of 4 parts sodium carbonate, 2 parts borax, and 1 part silica. Fusions in 20-gram crucibles require about 30 minutes; those in 30-gram crucibles, about 50 minutes. It will be noticed that occasionally as much as 60 grams of niter are used in a single fusion. With the proper muffle temperature there is said to be no danger of a crucible boiling over even though the crucible is filled to within half an inch of the top.

ASSAY OF ZINC-BOX PRECIPITATE

The gold and silver precipitated from cyanide solutions by means of zinc always contains more or less metallic zinc as well as more or less copper, lead, and other readily reducible metals which may be present in the ore, or which may have been introduced during the process. Gold precipitate usually contains a good deal of metallic zinc and is generally given a preliminary acid treatment before being melted. Silver precipitate, on the other hand, is comparatively free from zinc and may be melted directly. Besides metals, the precipitates may also contain hydroxide, cyanide, and ferrocyanides of zinc, as well as iron oxide, silica, alumina, etc.

The materials as received by the assayer will usually have been passed through a 16- or 20-mesh screen for the purpose of removing the short zinc, and may or may not have been acid-treated. The peculiarities of this material are: (*a*) the presence of more or less metallic zinc which has a reducing power of 3.17 and which boils at 930°C.; (*b*) the presence of various compounds containing zinc oxide, which is difficultly soluble in litharge; (*c*) its richness and spottiness, which necessitate the most painstaking care to secure commercially satisfactory results.

On account of the amount of gold and silver contained, the sampling and grinding should be carried out in a special room, well separated from the regular assay office, to avoid danger of salting. A corner of the clean-up and melting room may be used if available, and there should be provided for this purpose a special bucking board, as well as special samplers, screens, brushes, etc.

The assay sample, weighing 2 or 3 pounds, should be thoroughly dried and ground to pass at least 80-mesh. A convenient quantity of the final pulp is 150 or 200 grams, and the 80-mesh sample may be cut down to this and then ground, preferably on the bucking board, to at least 150-mesh. This final sample should be thoroughly mixed and dried again, cooled in a desiccator and kept there until the final samples are weighed. This precaution is observed both to prevent the material from taking on moisture from the air and to prevent oxidation of the zinc, which in some cases would cause a measurable error due to change in weight of the sample.

The fine pulp may be assayed by crucible fusion and cupellation or by one of several wet or wet-and-fire methods. The crucible assay is always corrected by a re-assay of the slag, and corrections are also applied for cupel absorption.

The following crucible charge is recommended,

Precipitate.......	0.1 assay ton
Sodium carbonate.	10 grams
Borax glass.......	5 "
Litharge.........	70 "
Flour............	for 30-gram button
Silica.............	10 grams

A thoroughly glazed crucible should be used for this purpose, to insure against any of the precipitate adhering to the walls above the level of the fusion. A narrow-bladed spatula is convenient for sampling the precipitate. The weighing should be done on an analytical or an exceptionally accurate pulp balance. It is customary to make at least six assays and to average the results. The fusions should be heated rather gradually to the full temperature of the muffle since a high temperature at the beginning is productive of low results. Apparently it is better to oxidize the metallic zinc with litharge than to allow it to volatilize.

For silver-bearing precipitate the Volhard or Gay-Lussac volumetric methods may be used, but the latter should be avoided in the presence of mercury, which interferes. There is no great advantage in the combination wet-and-fire methods unless the precipitate contains considerable copper or other metals which might contaminate the bead or cause extra losses in cupellation.

THE ASSAY OF BLACK SANDS AND SIMILAR SUBSTANCES

The term " black sand " is used to embrace the heavy, residual, dark-colored minerals which are found accompanying gold and platinum in alluvial deposits on beaches and river bars and in sluice boxes used for the recovery of gold from placer gravels.

In a study of many hundreds of samples of black sands from the Pacific Coast of North America the principal heavy minerals found, arranged in descending relative order of abundance, were magnetite, ilmenite, chromite, hematite, and garnet. There were smaller amounts of olivine, monazite, zircon, and, of course, more or less quartz. It will be recognized that these are mainly higher oxides and silicates, with iron, titanium, and chromium predominating. Chromite is the most difficult of all these minerals to flux, but fortunately it is not ordinarily present in sufficient amount to cause any concern. Iron oxide is by far the most common basic constituent, and if suitable provision is made for taking care of this the other refractory constituents will ordinarily fall into line.

The iron in well-roasted pyrite is mainly in the form of ferric oxide so that the same assay charges and procedure which are indicated for black sands will be found to yield satisfactory results with such roasted ores.

Basic igneous rocks contain more magnesium, aluminum, and calcium than do ordinary black sands, and sometimes more sulphides, but the problem of assaying such of these as contain appreciable amounts of precious metals, for example the platinum-bearing ores of the Bushveld

Complex in South Africa, is in the main similar to the problem of the assay of black sands.

Preparing the Sample. Since magnetite, ilmenite, and chromite are all highly refractory the assay pulp should be finely ground in order to facilitate its decomposition in the assay fusion as well as to avoid the irregularities caused by the introduction of relatively coarse " metallics " into the assay portion. Grinding to minus 200-mesh is strongly recommended, particularly if chromite is present.

In river bar and beach deposits the gold and platinum particles are usually in fine, thin scales which are easily cut into minute particles by the quartz and other sharp fragments of the hard oxide minerals. Black sands from sluice boxes, however, often contain relatively coarse grains of gold and sometimes of platinum which have not been recovered in the primary concentrating or amalgamating operations; if present, these should preferably be removed and separately treated before the sample is ground. Amalgamation is recommended for gold and dry concentration for the platinum-group metals.

Some varieties of chromite are exceedingly tough as well as hard and together with hard steel particles resulting from abrasion of dredge buckets, etc., cause difficulty in grinding. When metallic particles, particularly steel, interfere with single stage grinding it will usually pay to grind in stages and remove the coarse metallics after each stage. If a magnet is used for removal of steel, care will have to be taken not to remove magnetite, and in any event the magnetic material must not be rejected. Not only is native platinum magnetic on account of its alloyed iron, but the iron and steel removed will almost invariably contain gold often in the form of amalgam. Other metallics commonly found consist of shot or other forms of lead, babbitt, copper, brass, etc. Usually these may be dissolved in nitric acid without loss of gold or platinum. Where the above method does not serve, owing to the presence of a large quantity of hard steel, Hopkins* recommends fusing 500 to 1000 grams in a graphite crucible with soda, borax glass, lead, and sufficient sulphur to form a sulphide with all the metallic iron present. The lead button is scorified and cupeled, and the slag is ground and assayed.

Assay of Ferric Oxide. It is a well-known fact that the ferric oxides, Fe_3O_4 and Fe_2O_3, are both infusible at the temperature of the assay furnace, and their presence as solid particles held in suspension tends to make the slag pasty and to prevent the coalescence of the lead. This is the principal cause of " shotty " slags in fire assaying. Even though the slag contains no shot, experience has shown that appreciable amounts

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* *U. S. Bureau of Mines Report of Investigations* 3265, 1934.

of ferric oxide causes the retention of notable amounts of gold and silver. In order to flux the iron of ferric oxides it must first be reduced to the ferrous state, and to do this in the assay fusion we have available carbon and carbon monoxide from the reducing agent, metallic lead, and possibly sulphur or a metallic sulphide. When once reduced, if free silica is present, ferrous oxide unites with it to form a readily fusible silicate. Fused borax will also combine with it, forming a more readily fusible compound.

Experiments by the writer clearly indicate that, if satisfactory slags are to be obtained in the assay of ores containing large amounts of ferric oxide, there must be present at least enough silica to form bisilicates with all the bases. If this minimum ratio of silica does not obtain, shotty slags with magnetic properties result. It would seem that the reactions

$$2Fe_3O_4 + C = 6FeO + CO_2$$

$$2Fe_2O_3 + C = 4FeO + CO_2$$

are reversible and required the constant removal of the reduced FeO by fluxing it with silica to make the reaction go in the right-hand direction. If sufficient silica is present the CO_2 phase is constantly being removed, which also serves to cause the reaction to go in the right-hand direction.

When the assayer uses an excess of litharge and a limited amount of carbonaceous reducing agent in order to control the size of the lead button, there are present both litharge and lead as well as ferrous oxide, and the following type of reaction is possible

$$3FeO + PbO = Fe_3O_4 + Pb.$$

As all metallurgists know, magnetite is the stable form of iron under any except the most intense reducing conditions, and the assay slag which contains excess litharge is also likely to contain some ferric oxide.

To avoid this contingency the writer prefers a high-soda, low-litharge charge together with excess reducing agent for this type of material. For those rare ores such, for example, as the platinum-bearing ores from the Bushveld Complex, where more or less copper and nickel are also present, these metals will come down with the lead button and may have to be removed by an extra treatment before cupellation. This contamination of the lead is likely to occur, however, even though an excess litharge charge is used. Since many of the platinum group of metals are oxidized on heating and some of the oxides are readily volatile, it follows that to collect these metals effectively in a crucible fusion with lead the conditions should be strongly reducing, and this is an additional reason for the use of a lead-free slag together with excess carbon when assaying platinum ores.

The following type charges conform to the above rules and have been found highly satisfactory for samples of practically pure black sand with little or no silica.

Ore	½ A. T.	1 A. T.
Sodium carbonate	20	40
Borax glass	15	30
Litharge	35	40
Flour	4	5.5
Fluorspar	5	10
Silica	15–20	30–40

If the ore contains appreciable amounts of silica the quantity of reagent silica may be correspondingly reduced.

THE ASSAY OF CYANIDE MILL SLIME PULP AND TAILING

Every cyanide metallurgist recognizes that unfinished cyanide residues yield low results* by the fire assay as ordinarily conducted in routine work. The discrepancy between the assay result and the true value is aggravated as the state of subdivision of the material is increased and particularly when the bulk of the precious-metal contents of the pulp is in the dissolved state. However, to a less pronounced extent, the same situation exists even in final residues.

The metallurgist is always conscious of these assay discrepancies, and they are always annoying, but particularly so when they appear in the assays of final residues since erroneously low assays at this point indicate a higher extraction than has actually taken place, and this leads to the finding of an apparent shortage of gold or silver in the clean-up. All gold metallurgists know that this is another word for grief.

There are several reasons for these assay discrepancies even with fully washed tailing, which will be taken up first. One of these is the fact that, from the percentage standpoint, the slag and cupellation losses are in inverse ratio to the actual precious-metal content of the material which is assayed. Thus a small assay discrepancy which in the case of mill feed is of little consequence may, even under the best conditions, be 4, 5, or 6 times as great in percentage when applied to the final tailings and, thus magnified, as it were, become of real consequence.

A second reason for these annoying discrepancies has its origin in the general high pressure under which many mine assay offices work. The

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* *J. Chem. Met. Mining Soc. S. Africa* **2,** 372 (1898); **6,** 271 (1906); **10,** 135 (1909); **33,** 190 (1932); *Eng. Mining J.* **138,** 353 (1937).

quantity of work which they have to put through in a day is large, and management is quite naturally interested in unit costs. A truly satisfactory tailing assay from a gold cyanide mill may well cost from 10 to 20 times as much as an entirely acceptable mine-sample assay, and the difference is fully warranted by the increased care and attention required to secure reliable results with material of this particular nature.

ASSAY OF FINAL TAILING. The principal difficulty in the assay of fully washed slime residues is that of the efficient collection of the infinitesimally small gold particles which it contains. The same type of fusion and conditions which yield satisfactory results with ores having their value in gold or silver particles of, say, 300-mesh size, may well fail with particles a few microns in diameter. As the metal particles decrease in size it is safe to say:

1. Both the litharge and reducing substance must be made correspondingly fine.
2. The mixing of sample and reagent must be correspondingly complete.
3. The sintering of the charge before melting must be prolonged to provide for the decomposition of the ore particles and the collection of the precious metals by the lead while the slag is still viscous. If this and the two preceding conditions are not accomplished, precious-metal particles too small to settle will be left floating in the slag.
4. At the high finishing heat more than ordinary time must be allowed even with fluid slag to permit of the complete collection of the unusually finely divided particles of lead alloy. All this takes much more time and more careful attention than the assay of the ordinary type of sample.

John Dixon* believes that coating the slime particles with a one-to-one mixture of saturated solutions of sugar and lead acetate prior to drying and regular fusion leads to better assay recoveries of gold from slime tailing.

ASSAY OF UNFINISHED SLIME SAMPLES. In addition to the reasons given above for low assay results, which apply here also, Benjamin† calls attention to other possible sources of loss when assaying ore pulp containing gold and silver in solution. These are:

1. By capillary attraction of the dissolved gold (silver) to the hotter sides and bottom of the vessel used for drying the sample, together with a loss by infiltration or incrustation of some of the concentrated gold-bearing solution.

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* "Assaying Mill Tailings for Gold," *Eng. Mining J.* **128,** 353 (July, 1937).

† *J. Cham. Mines West Australia,* September, 1914.

2. By expulsion of gold by the heat employed in drying.
3. By volatilization of gold from the assay charge during fusion.

He gives data to prove these contentions.

To overcome this difficulty the gold should be precipitated in the sample prior to drying. The precipitant ordinarily used is a copper salt, copper sulphate or cuprous chloride, the preference now being given to the latter. The gold is precipitated as cuprous aurocyanide and excess cyanide as cuprous cyanide. The copper chloride salt must be freshly prepared and in the cuprous condition, colorless. Comparisons made over a lengthy period between assays of slime dried in the ordinary way and samples treated with cuprous chloride prior to drying showed an increase of more than 30 per cent in favor of the latter.

Procedure. Treat 1500 to 2000 ml. of the well-mixed pulp, thinned down to 1.4 specific gravity, in a glazed metal or porcelain container with a few drops of a 5 per cent solution of alkaline ferrocyanide, and 10 ml. of fully reduced acid cuprous chloride solution. Agitate thoroughly, and then remove the excess solution by filtration followed by drying. Drying should be done in a porcelain or enameled container. When thoroughly dry pass the residue through an 80- or 100-mesh screen to break up lumps, mix thoroughly, and assay as usual. In assaying slimes it is important to have an exceedingly fluid slag and to heat for some time so as to insure collection of all the exceedingly fine particles of gold. The quantity of cuprous chloride added should be sufficient to bleach the first-formed chocolate-brown precipitate of cupric ferrocyanide. Refer to the assay of cyanide solutions for precautions to be taken in the presence of an excess of alkaline ferrocyanide, thiocyanates, etc.

ESTIMATION OF SOLUBLE AND UNDISSOLVED GOLD (SILVER) IN CYANIDE MILL PULPS. In cyanide plant operations it is often desirable to determine just how far dissolution has gone in a definite time, or to distinguish between soluble and undissolved gold in tailings, etc. Particularly during the early stages of treatment, it is necessary to stop the dissolving action at the instant the sample is taken. Experiments have shown that "drowning" the sample in a large excess of water may fail to stop the action of the cyanide. The use of freshly boiled water, because of the small amount of contained oxygen, would aid but not entirely eliminate the difficulty. White* has shown that an excess of alkaline permanganate solution would quickly destroy alkaline cyanides without precipitating any dissolved gold.

On the basis of this fact the dissolving action may be stopped instantly

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* *J. Chem. Met. Mining Soc. S. Africa,* **10,** 443–445; **12,** 90.

by running a sample of the pulp to be assayed into a bucket of water containing an excess of alkaline potassium permanganate with as little exposure to the air as possible. A pink color of the solution after addition of the slime sample guarantees an excess of permanganate. The bucket is then filled with water, a suitable coagulant added, and the slime allowed to settle. The solution is decanted, and the washing repeated three or four times to insure removal of dissolved gold. The residue is finally dried and assayed for determination of the undissolved gold.

Another sample taken at the same time and assayed by the cuprous chloride method is used to determine the total gold contents, and by a comparison of the two results the dissolved gold content of the sample may be determined.

THE ASSAY OF ORES AND PRODUCTS CONTAINING BISMUTH

As has been stated elsewhere, in assaying ores containing bismuth, or if the assay litharge contains bismuth, much of this metal passes into the lead button, and, being less readily oxidized than lead, it tends to remain with the silver until most of the lead has gone. Experience shows that, when the lead buttons contain bismuth, the cupel loss is greater than with pure lead and the beads left on the cupel retain bismuth.

Bismuth does not materially influence the results of gold assays, but it may cause serious errors in the silver determination. As will be shown later, the silver beads, obtained in assaying concentrates containing as little as 0.3 per cent of bismuth and the same amount of silver, were found to contain 2 per cent of bismuth. For careful control work, a correction for the bismuth in the silver bead is made.

Correction for Bismuth in Silver Beads. Bismuth is a common associate of lead and silver in many Mexican ores, and since, when this is the case, the assay beads may retain appreciable amounts of this metal, it is the practice of some of the Mexican smelters to make a correction for this retained bismuth.

Their practice is to make up composite samples representing the month's shipment, from the samples of concentrates received from each of the regular shippers. At the end of the month the composite samples are assayed for bismuth so as to get a figure to use in establishing the bismuth penalty, and at the same time they are assayed for silver. The beads after having been weighed are analyzed for bismuth, and the percentage found is applied as a correction to the assays of the following month.

The data relative to bismuth and silver content of concentrate, and of bismuth content of silver beads, for three shippers, are summarized in the accompanying tabulation.

	Mine A	Mine B	Mine C
Percentage of bismuth in concentrate	0.30	0.10	0.04
Silver assay, uncorrected, kilos per met. ton	3.000	1.600	0.800
Bismuth contents of beads, kilos per met. ton	0.060	0.019	0.005
Silver assay, corrected	2.940	1.581	0.795
Percentage of bismuth in concentrate going into bead	2.0	1.9	1.25

Determination of Gold and Silver in Bismuth Metal. Bismuth commonly occurs in nature in the metallic state, and as both gold and silver are frequently associated with it, the metal as produced may carry considerable quantities of the precious metals. Some lead and tin refinery slimes contain bismuth, and the bismuth recovered from them always contains some precious metals, whence a suitable assay procedure is necessary.

Bismuth is the only metal that behaves like lead in cupeling, and for approximate work the assay may be made by direct cupellation. The losses are higher than with lead, however, and the beads retain an indefinite amount of bismuth. For more exact results a combination wet-and-fire assay is recommended. The following method* gives reliable results if carefully carried out.

Weigh out 0.25 assay ton of borings in a large Pyrex beaker and add 85 ml. of concentrated sulphuric acid. Heat to boiling, and continue fuming for about 5 minutes to effect complete decomposition and solution of bismuth salts. Cool to the point where white fumes cease to be emitted and add very slowly, with constant stirring, 450 ml. of 1 to 1 sulphuric acid. Heat gently for about three-quarters of an hour. If this procedure is closely followed, almost all the bismuth oxysulphate will be dissolved. If not completely in solution, decant and fume the undissolved salts with 25 ml. more of sulphuric acid, finally diluting to 200 ml. with 1 to 1 sulphuric acid.

Pour both solutions into a liter beaker and cool to room temperature. Dilute to about 750 ml. with distilled water and add about 1 ml. of a saturated solution of sodium chloride to precipitate the silver. Any gold which was present in the bismuth will remain undissolved and will be collected by the precipitate of silver chloride. Filter and wash well with cold water. Dry residue and proceed with the fire assay, treating the filter paper and precipitate as in the combination assay for nickel and cobalt.

ASSAY OF ANTIMONIAL GOLD ORES

The niter method is universally recognized as being the best method for the sulphide ores of antimony. Considerable litharge is necessary

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* *Eng. Mining J.* **114,** 636 (1922).

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

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* William Kitto, *Trans. Inst. Mining Met.* **16,** 89; William Smith, *Trans. Inst. Mining Met.* **9,** 332.

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

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 followed in the assay of gold and other precious-metal bullions and sometimes in the assay of high-grade ores. A more detailed description of it 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 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, though approximating the actual contents of an ore, may occasionally give results a little too high, for although gold and silver lost by volatilization are 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 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 the basis of settlement, a deduction is made amounting to the average correction. This amounted to 1.1 per cent in certain Cobalt ores.

Assay of Slags. Assay slags are of such variable composition that no one method of 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 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 insure 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 separate carefully 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 it will be 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 insure decomposing all 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 singulosilicate. 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.

Assay of Cupels. Cupel materials are all refractory, particularly magnesia, and for this reason all unsaturated cupel material should always be rejected before the cupel is pulverized. The student should also bear in mind that both Portland cement and magnesia are basic and require the addition of a considerable amount of acid reagents to make a satisfactory slag. When a corrected assay is to be made the original lead button should not weigh more than 28 grams, or too large an amount of cupel material will have to be handled. The fluxes have to be carefully proportioned; and in order to get complete recovery of the silver all the absorbed litharge must be reduced. For this reason it is generally best not to use any litharge flux. In the charges which follow the proportions of reagents are all based on the weight of bone ash, dry cement, or magnesia in the material being assayed. This may be determined, closely enough for practical purposes, by calculating the weight of litharge corresponding to the lead button cupeled, and subtracting this calculated weight from the weight of saturated cupel material.

BONE ASH. To assay a bone-ash cupel, first remove and reject the unsaturated part of the cupel in order to have as little of this refractory material as possible to deal with. Weigh the saturated part, which will be about 50 per cent bone ash and 50 per cent litharge, and grind to 80- or 100-mesh on a clean bucking board.

Finally clean off what sticks to the board and muller by grinding a quantity of 20-mesh quartz equal to the silica requirements of the charge. For an ordinary assay this will be about 10 grams. This quartz, added to the charge, serves as a flux for some of the bases.

To flux bone ash add one and a half times its weight of normal sodium carbonate, two-thirds of its weight of borax glass, half its weight of fluorspar, and one-third its weight of silica. In assaying a cupel, an excess of flour is added to reduce all the litharge. For example, the charge for a bone-ash cupel would work out as follows:

Cupel material (30 grams bone ash, 30 grams litharge)	60	grams
Sodium carbonate	45	"
Borax glass	20	"
Silica from cleaning the bucking board	10	"
Fluorspar	15	"
Flour	4	"

Put into a 30-gram crucible, mix, and place in a hot muffle so that it will fuse rapidly. Have the atmosphere neutral or slightly reducing, and finally bring to a light yellow heat. Pour after half an hour at this temperature. The lead button obtained should weigh almost as much as the button first cupeled, *i.e.*, the assay of a cupel in which a 30-gram lead button was cupeled should yield somewhat more than 28 grams of lead.

The slag will be an almost colorless, clear glass. The lead button is cupeled, and the bead weighed and parted.

CEMENT. To assay a Portland-cement cupel, remove and reject the unsaturated part. Weigh the saturated part, which may contain as little as 40 per cent of cement, and grind it to 80- or 100-mesh. Clean the bucking board and muller by grinding 15 grams of 20-mesh quartz, and add this to the charge, where it will serve as a flux for some of the bases. It must be included when considering the quantity of silica required for the charge.

To flux, add twice as much sodium carbonate as there is cement, an equal amount of borax glass, and twice as much silica. Add 4 or 5 grams of flour and fuse rapidly in a neutral or reducing atmosphere. The charge for a Portland-cement cupel would work out as follows:

Cupel material (20 grams cement, 30 grams litharge)	50 grams
Sodium carbonate	40 "
Borax glass	20 "
Flour	5 "
Silica	40 "

This yields a clear-green glassy slag and a lead button weighing about 90 per cent as much as the original button. The silver recovery is not so good as that obtained from bone-ash cupels, probably because the lead recovery is not so good.

MAGNESIA. To assay a magnesia cupel proceed as for Portland cement. The patent magnesia cupels are the least porous and therefore the least of all suited for corrected assays, because so very much more flux will have to be provided for them. The saturated part of a magnesia cupel is almost 60 per cent magnesia. Therefore, the quantity of magnesia used in absorbing a given quantity of litharge is more than twice the quantity of Portland cement required to absorb the same quantity of litharge. Consequently twice as much of the reagents will have to be used to assay the magnesia.

CHAPTER X

SAMPLING AND ASSAYING OF BULLION

Bullion, from an assayer's point of view, is an alloy containing enough of the precious metals to pay for parting.

The different bullions are usually named to correspond to their major components, for instance, copper bullion, an alloy of copper with small amounts of other impurities, as well as some gold and silver. In the same way we have lead, silver, and gold bullions. Doré bullion is silver bullion containing gold as well as a small percentage of base metals. Doré bars differ in silver content from 600 to 990 parts per thousand; the base metals consist chiefly of copper, lead, and antimony. The term base bullion is used in two different senses. According to the lead smelter's definition, base bullion is argentiferous lead, usually the product of the lead blast furnace; according to the mintman's and refiner's definition it is bullion containing from 10 to 60 per cent of silver, usually some gold, and a large percentage of base metals, particularly copper, lead, zinc, and antimony. Fine gold bars are those which are free from silver and sufficiently free from other impurities to make them fit for coinage and use in the arts, usually 990 to 999 fine.

The results of lead and copper bullion assays are reported in ounces per ton as in ore assays, but in the assay of silver, gold, and doré bullions the results are reported in " fineness," *i.e.*, so many parts of silver or gold in 1000 parts of bullion. Thus sterling silver is 925 parts fine, that is to say, it is 92.5 per cent silver.

Weights. In assaying gold, silver, and doré bullion, a special set of weights, called gold-assay weights, are used. This is termed the " millième " system; the unit, 1 millième, weighs 0.5 milligram, and therefore the 1000-millième weight equals 0.5 gram. Ordinary weights in the gram system may be used, but as 0.5 gram is the quantity of bullion commonly taken for assay the use of the millième system saves computation in obtaining the fineness.

SAMPLING BULLION

Bullion may be sampled either in the molten or in the solid condition. When it may be melted and kept free from dross the dip or ladle sample is usually the more accurate method. As the weight, as well as the assay, of the bullion must be known in order to value it, the sampling of large lots of bullion by the dip sample method often presents difficulties, owing to changes in weight or purity in the considerable length of time necessary for pouring. Again, it is not always convenient to melt a lot of bullion to obtain a sample, and other means must be found. Sampling solid bullion by punching, drilling, sawing, or chipping, under certain conditions, may be made to yield good results. Lead bullion is usually sampled by punching one or more holes in each bar, and combining and melting the punchings. Copper bullion is now generally cast in the form of slabs or anodes, and these are drilled.

Sampling Molten Bullion. The most satisfactory method of sampling bullion is to melt the whole in a suitable vessel, stir thoroughly with a graphite rod or iron bar to mix, and then, immediately before pouring, ladle out a small amount and granulate it by pouring into a pail of water. If these operations are correctly performed there is no chance for segregation, and each particle of the granulated metal should be a true representative of the whole. If a granulated sample is not desired, a ladleful of the mixed molten metal may be poured into a thick-walled flat mold so that it chills almost instantly, and a drill or saw sample may be taken from this. When a ladle sample is taken, the ladle must be so hot as not to allow the forming of any solidified metal or " sculls," as this would interfere with the homogeneity of the sample. This method of sampling is most satisfactory for bullions which do not oxidize or form dross on melting, as this, of course, adds a complication for which it is difficult to allow.

Sampling Solid Bullion. The principal difficulty encountered in sampling bullion in the form of bars or ingots is due to the irregular distribution of the various constituents caused by segregation in cooling. If it were possible to cool a bar instantly, segregation could be prevented, and a chip or boring taken from any part would be representative. As instant cooling is impossible, the sampling of bars of the ordinary dimensions is usually a difficult problem. An occasional bar of bullion may be entirely homogeneous, but this happens rarely; and unfortunately there are no characteristics by which this homogeneity can be recognized. Heterogeneity is the rule, and the explanation for this common condition is found in the presence in almost every bullion of constituents having different freezing points. In slow cooling, solidification begins first on the walls of the mold and the constituent having the highest freezing point starts crystallizing here, forcing the part which is still liquid away from the walls. Solidification progresses away from the walls and sometimes also away from the surface, toward the center of solidification, at which locus the alloy of lowest melting point freezes.

This naturally results in a certain amount of migration of the different constituents, toward or away from the various cooling surfaces and in a direction normal to these surfaces. According to their amount, as well as upon the nature and amount of the other constituents of the alloy, the gold and silver may concentrate either toward or away from the center of solidification.

Figure 51 shows the distribution of silver and gold in a block of blister copper. To obtain these figures the block was cut in two, half of the section was laid off into squares as indicated, and a sample was taken by drilling a hole in the center of each square. The upper figure of each pair represents the silver assay, and the lower one gold, in ounces per ton.

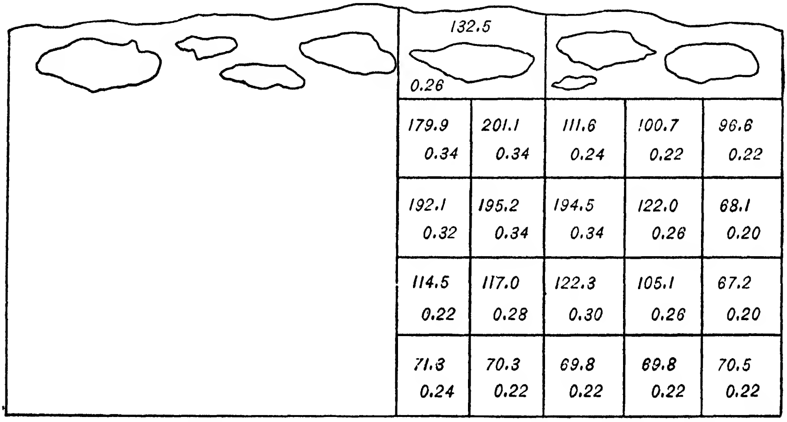


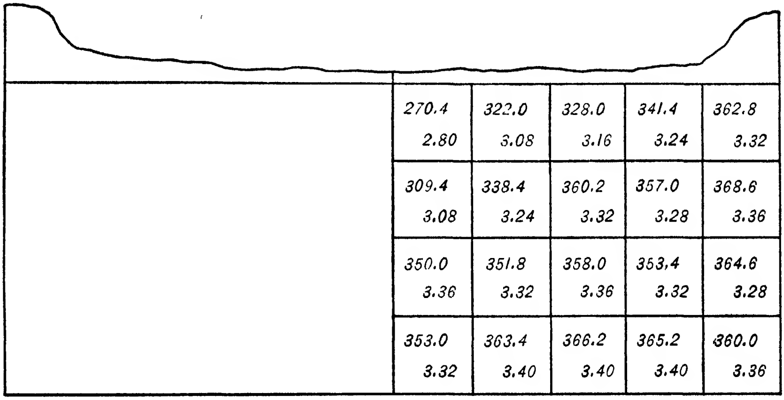
FIG. 51. Distribution of silver and gold in a block of blister copper.

In this sample, the precious metals, particularly the silver, have concentrated toward the center of solidification, which is slightly above the geometrical center of the solid. It is obviously next to impossible to locate a drill hole which would take a representative sample of such a block, and no chip taken from a corner could possibly give anything like the truth. A saw section through the center would probably be satisfactory, provided that the entire amount of sawings were assayed. Figure 52 shows another example of the distribution of the precious metals in copper bullion; but here the concentration was in the opposite direction, *i.e.*, toward the part which solidified first. The same thing which is illustrated here for copper is true to a lesser extent for lead bullion and for impure precious-metal bullions, and in these too the concentration may be either away from or toward the center of solidification.

The amount of this diffusion or segregation is dependent upon a number of factors, the most important of which are the composition of the alloy and the rate of cooling. The shape and thickness of the mold, as well as its initial temperature and the temperature of the alloy when poured, are also important factors in this problem.

It has been conclusively demonstrated that it is impossible to obtain samples of sufficient accuracy from copper bars or pigs of the usual dimensions, except by sawing, which is entirely too expensive a proceeding for everyday use.

To eliminate the difficulty of sampling from a bar, Keller* recommends casting the metal in a thin plate or slab, and this practice has now been almost universally adopted by the copper smelters. The slabs are usually made some 30 or 40 inches square and only 1 or 2 inches thick.



270.4 2.80	322.0 3.08	328.0 3.16	341.4 3.24	362.8 3.32
309.4 3.08	338.4 3.24	360.2 3.32	357.0 3.28	368.6 3.36
350.0 3.36	351.8 3.32	358.0 3.36	353.4 3.32	364.6 3.28
353.0 3.32	363.4 3.40	366.2 3.40	365.2 3.40	360.0 3.36

FIG. 52. Distribution of silver and gold in a block of refined copper.

Of course, some concentration takes place here, also, but as the plate solidifies so much faster than the same metal cast in a bar or ingot this factor has less weight.

Figure 53 is an ideal section through a part of such a slab. The concentric lines indicate the progressive cooling toward the center of cooling. It may be assumed that solidification progresses so as to form even layers from all the surface planes of the slab and that each successive layer differs in composition from its predecessor. On the right-hand side of the figure, just beyond the center of solidification, is shown a region, not wider than the thickness of the plate, where segregation has taken place both horizontally and vertically. All around the slab there will be a strip like this. Therefore, the solid constituting this strip contains in its entirety a fair proportion of all the constitutents of the alloy, but it is impossible to sample this correctly. Inside of this strip, the width of which is the same as the thickness of the slab, there can be movement only in a vertical plane. The solid inside of this strip also

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* *Trans. A.I.M.E.* **27,** 106.

contains a fair proportion of all the constituents of the alloy, and as here there is segregation in the vertical direction only, a hole drilled through the plate anywhere should yield a correct sample of the whole. This method, first advocated by Keller, has been demonstrated to yield satisfactory results and has now become standard in the copper industry.

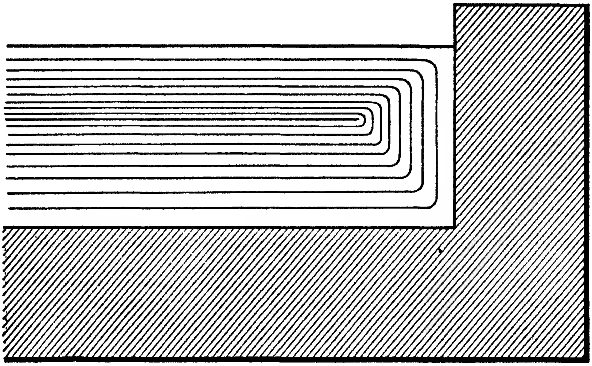

FIG. 53. Diagrammatic section through a plate of metal illustrating direction of segregation toward or away from center of solidification.

Some typical methods of sampling bullion follow.

Sampling Lead Bullion. Lead bullion is sampled both in the liquid and in the solid state. In either event it is now customary to transfer the lead from the blast furnace either into a reverberatory furnace or into large kettles holding 20 to 30 tons. Here the lead is purified by cooling to a little above the melting point of pure lead. By doing this, a large part of the impurities which are held in solution by the superheated lead separate out as a dross which is carefully removed by skimming. The remaining lead, now in a better condition to sample, is drawn off and cast into bars of about 100 pounds.

In taking a dip sample, a small ladleful is removed at regular intervals from the stream coming from the drossing kettle. These individual samples are carefully remelted at a dark red heat in a graphite crucible, the melt is well stirred and cast in a heavy-walled shallow mold, making a cake about 10 inches long, 5 inches wide, and ½ inch thick. This cools so quickly that there is little or no chance for segregation. The final assay samples are obtained from this cake by sawing and taking the sawdust, or by boring entirely through the slab in a number of places and taking the borings, or by cutting out four or more 0.5-assay-ton pieces from different parts of the bar and using these directly.

Another and more modern method of sampling lead bullion, which does away with the remelting, is to take a number of dip samples in the shape of gumdrops. While the material in the kettle is being thoroughly stirred, the mold, which has six or eight conical depressions and is provided with a long handle, is inserted and heated to the same temperature as the molten metal. The " gumdrops " are dipped out and cooled in the mold, by placing the bottom of the mold in water.

Bars of solid lead bullion are sampled by means of a heavy punch which takes a cylindrical sample about 2 inches long and $\frac{1}{8}$ inch in diameter. There are naturally a number of different systems, but the most common method is to place five bars side by side and face up, and punch a hole in each extending halfway through. Each bar is punched in a different place and in such a way that the holes make a diagonal across the five bars. The bars are then turned over and another sample is taken from each along the opposite diagonal. Usually a carload of about 20 or 30 tons is sampled as one lot. The punchings from such a lot, weighing from 8 to 15 pounds, are melted in a graphite crucible and cast into a flat bar, from which the final assay samples are taken by sawing, drilling, or cutting.

Sampling Copper Bullion. The sampling of copper bullion may be classified into smelter methods and refinery methods. The bullion known as blister copper is quite universally cast in the form of anodes at the smelter, and shipped to the refinery in this form. This renders remelting at the refinery unnecessary, and the result is that the refiners sample the solid bullion by drilling. The smelters, having the bullion in the molten condition, generally sample it in this condition on account of the greater ease and less expense.

Probably the most satisfactory smelter method of sampling is the " splash-shot method," which consists in shotting into water a small portion of the molten stream of copper as it flows from the refining furnace, by " batting " the stream with a wet stick. This operation is repeated at uniform intervals during the pouring, the amount taken each time being kept about the same. The samples are dried, and dirt and pieces of burned wood are removed. All material over 4-mesh and under 10-mesh is rejected, the remainder being taken as the sample. This method, when properly carried out, gives results which check within practical limits with the drill sample of the anodes taken at the refinery.

Another method which is used to some extent for sampling molten copper bullion is known as the " ladle-shot method." This consists in taking a ladleful from the furnace or from the stream of the casting machine and shotting it by pouring over a wooden paddle into water. At least three ladlefuls are taken, one near the beginning, one at the middle, and one near the end of the pour. The shots are treated in the same manner as before. This method is not thought so well of as the previous one on account of segregation toward or from the "sculls" which are left in the ladles.

Instead of shotting and taking the shot for the final sample, W. H. Howard of Garfield, Utah, recommends ladling into a flat disc. This "pie sample" is sawed radially a number of times, and the sawdust is used for the final sample.

The following description of the method of sampling anodes at Perth Amboy, N. J., is typical of refinery methods of sampling blister copper; it is the method developed by Dr. Edward Keller. The copper is received in the form of anodes 36 inches long, 28 inches wide, and 2 inches thick. These are carefully swept to remove foreign matter, and then drilled with a 0.5-inch drill completely through the anode, all the drillings being carefully saved. A 99-hole template is used to locate the holes, which are spaced $3\frac{1}{16}$ inches center to center, and the outside row is approximately $2\frac{1}{2}$ inches from the edge of the anode. The holes of the template are used in continuous order, one hole to the anode. The best practice is to drill half of the holes from top to bottom and the remainder from bottom to top.

For very rich anodes some refiners use a template having as many as 240 holes, but it seems doubtful that this arrangement of spacing a single hole in each anode will yield any better sample.

With low-grade uniform bullion every fourth anode only is drilled. A 30-ton lot of anodes in which each one is drilled will yield 6 or 8 pounds of drillings, which are ground in a drug mill fitted with manganese-steel plates and reduced by quartering to about 2 pounds. This sample is reground until it will all pass a 16-mesh screen, and is then divided into the sample packages.

Sampling Doré Bullion. Doré bullion is sampled in the molten state by dip sampling and in the solid state by drilling.

The doré bullion at one plant is cast into plates 18 inches by 7 inches by $\frac{3}{8}$ inch and sampled by drilling $\frac{9}{32}$-inch holes in it, on the checkerboard plan. The drillings are ground to pass a 30-mesh screen. An electromagnet is used to remove from the sample all the iron from the drills and mill.

Sampling Gold Bullion (United States Mint Method). Every lot of bullion or dust received at any United States Assay Office or Mint is immediately weighed and given a number. It is then melted in a graphite crucible with borax to make the deposit uniform, and cast into a bar, except as noted hereafter. Occasionally, with very impure bullions, a small dip sample is taken and granulated, but in general the whole melt is cast and sampled as noted below. The slag is poured with the bar and when solid is ground and panned, and the recovered prills are dried, weighed, and allowed for in computing the value of the bar.

After the bar is cleaned of slag it is dried, weighed, and numbered, and if it is thought to be homogeneous, two samples of 3 or 4 grams each are chipped from diagonally opposite corners. These are flattened with a heavy hammer, annealed, and rolled into sheets thin enough to be cut easily with shears.

Because of the prejudice of so many depositors due to a misunderstanding of the reason for loss of weight in melting, the United States Mint service for a long time attempted to avoid oxidation during melting. Bars which did not yield checks from chipped samples were remelted and again chip sampled and assayed. In the event of a second discrepancy of minor nature bars were often drilled halfway through on two opposite corners of the top at a point about 1 inch from each edge. These drillings were mixed and assayed as the top sample. The bottom sample was taken in the same manner, except that the drilling was done on the other two corners. The top and bottom samples were kept separate.

Bullion from cyanide plants is particularly subject to segregation due mainly to the presence of zinc, and the Mint service no longer tries to avoid loss of weight in melting. Instead, if segregation is known or even suspected the disturbing elements are removed by fire refining in the crucible before even dip sampling is attempted. If the bullion is to be dip sampled the best procedure is to use for this purpose a graphite rod in the lower end of which is a cup-shaped cavity capable of holding from 5 to 25 grams of metal. After the metal is ready for pouring it is well stirred with a graphite paddle, the graphite rod is introduced and allowed to attain the heat of the melt, and the sample is poured into a mold under its cover of borax slag or granulated by pouring into water.

THE ASSAY OF LEAD BULLION

The cupellation assay of lead bullion has already been described in the chapter on cupellation. In smelter control work the assay is usually made in quadruplicate. If the bullion contains sufficient copper, arsenic, antimony, tin, or other base metals to influence the results of the cupellation assay, three or four portions of 0.5 or 1.0 assay ton are scorified with the addition of lead until the impurities are eliminated, when the resultant buttons are cupeled.

The " gumdrop " dip samples now so commonly used are weighed without trimming either in grams or with a special set of decimal assay-ton weights. The weights of the gumdrops together with those of the beads and of the gold go to the office, and calculations are made there by machine. Under this system the results are less subject to error since the assayer is not tempted to make his results check.

CORRECTION FOR CUPEL LOSS. Sometimes the slags and cupels are re-assayed and the weight of the gold and silver found is added to that obtained from the first cupellation. There is no fixed custom as yet regarding the use of corrected assays. In most of the custom smelters, the uncorrected assay is taken as the basis of settlement; but some of the large concerns which have their own refineries are using the corrected assay in their interplant business.

THE ASSAY OF COPPER BULLION

Copper bullion may be assayed by the scorification method, by the crucible method, or by a combination of wet-and-fire methods. In the combination method the bullion is treated with sulphuric or nitric acid, which dissolves the copper and more or less of the silver but leaves the gold. The silver is precipitated by suitable reagents and filtered off together with the gold. The filter paper and contents are put into a scorifier or crucible with reagents and the assay finished by fire methods.

The Scorification Method. The following, commonly referred to as the "all-fire" method, is one of many modifications of the general method of assaying copper bullion which depends upon repeated scorification for the removal of the copper.

Sample down the finely ground bullion on a split sampler in such a way as to obtain a sample which will include the proper proportion of the finer and the coarser parts of the borings. This sampling must be conducted carefully, as the precious-metal content of the finer portion differs somewhat from that of the coarser portion of the sample.

Weigh out four portions of copper borings of 0.25 assay ton each, mix with 50 grams test lead, put in 3-inch Bartlett scorifiers, cover with 40 grams test lead, and add about 1 gram SiO_2. Scorify hot, heating at the end so that they will pour properly. Add test lead to make weight of buttons plus test lead equal to 70 grams, add 1 gram SiO_2, and scorify rather cool. Pour, make up to 60 grams with test lead, adding 1 gram SiO_2, and scorify again.

Combine the buttons two and two, and make up each lot to 85 grams with test lead, adding 1 gram SiO_2, and scorify very cool. Make up buttons to 70 grams by adding test lead, add 1 gram SiO_2, and scorify for the fifth time. The buttons should be free from slag and weigh 14 or more grams.

Cupel at a temperature to feather nicely, and raise the heat at the finish. Cupels should be made of 60-mesh bone ash, and should be of medium hardness.

Weigh the beads and part as usual. Dry, anneal, and weigh the gold. The two results should check within 0.02 ounce per ton, and the average figure is to be reported. If the silver content of the bullion is low, add enough fine silver before the first scorification to make the total silver in the mixture equal to about eight times the amount of gold.

The scorification method was until recently accepted as standard for gold, and most smelter contracts involving this material stated that "gold shall be determined by the all-fire method or its equivalent." The silver results obtained by the scorification method are not acceptable, owing to the considerable slag and cupellation losses which average perhaps as much as 5 or 10 per cent.

The Crucible Method. The crucible method for gold and silver in copper bullion was first described by Perkins* and as described by him showed no great advantage over the scorification method as to saving in time, cost of materials, or increased furnace capacity. The following modified procedure requires about one-third of the materials, time, and furnace capacity necessary for that described by Perkins, and yet gives buttons sufficiently free from copper to be cupeled directly.

Sample down the finely ground bullion to about 0.25 assay ton and adjust the weight of the sampled portion to exactly 0.25 assay ton. Place in a 20-gram crucible and mix with it 1.2 grams of powdered sulphur. Cover this with a mixture of 15 grams of sodium carbonate, 240 grams of litharge, and 8 grams of silica; but do not mix with the sulphur and copper, which should be allowed to remain in the bottom of the crucible. Cover with salt or flux mixture and place in a hot muffle so that the charge will begin to melt in 6 or 8 minutes. The fusions should be quiet and ready to pour in 25 or 30 minutes.

If a salt cover is used the lead buttons should weigh about 32 grams; if a flux cover is used they may be somewhat smaller. With a properly conducted assay the buttons are soft enough for direct cupellation; but the cupels are quite green. If the assayer prefers, the buttons may be made up to 60 grams with test lead and scorified in a 3-inch scorifier to further eliminate the copper. After cupellation the beads are weighed and parted as usual. It is well to make four fusions, and to combine the beads, two and two, for parting.

REMARKS. As soon as the sulphur melts it combines with the copper to form a matte. This matte is later decomposed and most of its copper

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* "An 'All-Fire' Method for the Assay of Gold and Silver in Blister Copper," W. G. Perkins, *Trans. A.I.M.E.* **33**, 670.

is oxidized and slagged by the litharge of the charge. The fusions melt down very quietly, almost without boiling, and with a short period of fusion the crucibles are not badly attacked. The final temperature need not be higher than a good bright red or full yellow. The slag is heavy but very fluid, and should not contain any lead shot.

The method gives results in gold equal to the scorification method; but, as in any method using high litharge, the silver is likely to be somewhat low.

Nitric Acid Combination Method.* Sample down the finely ground bullion on a split sampler in such a way as to obtain a sample of about 1 assay ton which will include the proper proportion of the finer and coarser parts of the borings. This sampling must be conducted carefully as the precious-metal content of the finer portion differs somewhat from that of the coarser portion of the sample. Portions "dipped" from the sample bottle or from the sample spread out on paper are likely to contain undue amounts of coarse or of fine.

Weigh out two portions of copper borings of 1 assay ton each, and carry the assay through, on each portion, as follows:

Place in a No. 5 beaker, add 100 ml. of distilled water and 90 ml. HNO_3, specific gravity 1.42, the acid being added in portions of 30 ml. each, at intervals of about 1 hour. When all is in solution, precipitate a small amount of silver chloride with salt solution in order to collect the gold, filter through double filter papers, and wash the filter papers free from copper. To the filtrate add the calculated amount of salt solution to precipitate all the silver and a slight excess, measuring the solution with a buret and varying the amount added with the richness of the bullion. Allow to stand over night after stirring well. Filter the silver chloride through double papers, wash papers free from copper, then sprinkle 5 grams of test lead in the filter paper and fold into a 2½-inch Bartlett-shape scorifier, the bottom of which is lined with sheet lead. To this add also the filter papers containing the gold. Dry and ignite the filter papers carefully, cover with 35 grams of test lead and a little borax glass, and scorify at a low heat so that the resultant button will weigh about 12 grams. Cupels should be feathered nicely. Cupels should be made of 60-mesh bone ash and should be of medium hardness. Weigh the bead and part. Anneal and weigh the gold. The two results on gold should check within 0.02 ounce per ton, and the silver within 1 per cent.

The nitric acid combination method has for a long time been the standard for the determination of silver in copper bullion. In laboratories where many such determinations are made, a number of most

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* Procedure kindly supplied by Mr. D. H. Greenwood, Chrome, N. J.

ingenious labor-saving devices have been developed. For a description of these the student is referred to two papers* by Edward Keller.

The nitric acid combination method is recognized as giving low results in gold. Van Liew attributes this to the solution of the gold in the mixture of nitrous and nitric acids present. He found a loss of 33.7 per cent of gold, on treating gold leaf with a mixture of nitrous and nitric acids for 2½ hours. He gives a method of slow solution in cold dilute acid which reduces this loss to a minimum.

The uncorrected silver results obtained by this method are from 1.5 to 4 per cent low, according to the amount of silver contained, and unless this loss is taken into account, it is certain to cause perplexing discrepancies in the metal inventories of the smelting companies.

Keller† recommends the following method for determining the slag and cupel loss. The slag and cupels are crushed, ground, and thoroughly mixed. The whole or an aliquot part is fused in G crucibles with the following charge:

Slag and cupels	200	grams
Sodium carbonate	70	"
Borax	70	"
Flour	10	"

The resulting lead buttons are scorified and cupeled. Keller believes that it is necessary to reduce practically all the lead in the slag and cupels in order to obtain full recovery of the silver and gold.

Mercury-Sulphuric Acid Method. The copper bullion sample, which has been ground to pass a 16-mesh screen, is first separated into two portions by means of a 40-mesh screen, and each portion is weighed. As the precious-metal content of the fine differs somewhat from that of the coarse portion, it is important to include a proper proportion of each in the sample taken for assay. Calling C the weight of the coarse and F the weight of the fine, weigh out $\frac{29.166}{\frac{F}{C} - 1}$ grams of coarse and make up the remainder of the assay ton with fine. Transfer to an 800-ml. beaker; add 30 ml. of water and 10 ml. of mercury nitrate solution (Hg, 0.25 gram). Shake the beaker until the copper is thoroughly amalgamated, then add 100 ml. of strong sulphuric acid; cover the beaker, place on the hot plate, and heat until all the copper is dissolved.

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* "Labor-saving Devices in the Works Laboratory," *Trans. A.I.M.E.* **36,** 3 (1906); **41,** 786 (1910).

† "Recent American Progress in the Assay of Copper Bullion," *Trans. A.I.M.E.* **46,** 782.

This will take from 1 to 2 hours, depending on the temperature and the state of division of the sample. The apparent boiling of the liquid during this time is only bubbling and is due to the evolution of sulphur dioxide gas. This completed, the supernatant liquid assumes a dark green color, finally changing to a light grayish blue, which is the indication of the finishing point.

Remove the beaker and allow to cool. The contents will be a semi-liquid sludge. When this is cool, add about 100 ml. of cold water and mix; then add 400 ml. of boiling water and stir until the copper sulphate dissolves. Add sufficient salt solution to precipitate all the mercury and silver present. With 100 milligrams of silver and 0.25 gram of mercury, 30 ml. of a solution containing 19 grams of NaCl per liter is sufficient. Any material excess should be avoided.

Boil the solution to coagulate the silver chloride, remove from the hot plate, dilute to 600 ml. with cold water, and allow to cool. Filter through double filter papers, wash the beaker, and filter with hot water. Finally wipe the inside of the beaker with filter paper and add this to the material in the filter. Thorough washing of the filter is not necessary.

Transfer the wet filter and its contents to a 2½-inch scorifier which has been glazed on the inside by melting litharge in it and pouring away the excess.

Burn off the filter paper at a low temperature, preferably in a closed oven which may be heated to, say, 175°C. This chars the paper slowly without danger of loss of silver. When the paper is consumed, add 40 grams of test lead and scorify; pour so as to obtain an 18-gram button, cupel as usual to produce feather litharge, weigh the gold and silver bead, and part with dilute nitric acid.

The assays should be made in triplicate, and the average results reported. Differences in silver seldom exceed 0.2 ounce; the gold results are usually exactly the same. The sulphuric acid used should be chemically pure and full strength (1.84 specific gravity).

The mercury solution may be made by dissolving 12.5 grams of mercury in the least quantity — about 25 ml. — of hot nitric acid, making the solution up to 500 ml. with just sufficient nitric acid added to keep the solution clear. The object of adding mercury is to help in the solution of the copper by forming a galvanic couple.

Notes. 1. Since copper is but sparingly soluble in sulphuric acid it is important that the copper borings be finely divided for this method. The grinding mill should be sharp and designed to cut the borings into fine particles since a dull mill simply rounds and compacts the copper, making it harder than ever to dissolve.

2. With comparatively pure copper the amount of mercury nitrate may be reduced; with copper high in sulphur or arsenic an increase in the amount will be required.

3. The gold is in a very fine state of division in copper bullion, and great care must be taken so to entangle it with copper or silver sulphide or silver chloride that it will not be lost during filtration.

4. In the assay of high-grade gold-bearing copper which contains but little silver, it is of advantage to add the silver necessary to protect the gold during cupellation, to the beaker along with the copper before adding the acid, rather than to the scorifier or cupel.

5. It is important to keep the funnels well filled during filtration since if they are allowed to drain the copper sulphate will crystallize and expand the pores of the filter papers, which is likely to result in subsequent loss of gold. After the beakers have been emptied and washed the solution level should be maintained in the funnels by additions of hot water.

6. Provided that the sulphuric acid is not actually boiled no silver is dissolved when the bullion is low in precious metals, say below 50 ounces. No gold dissolves, whatever the grade.

The mercury-sulphuric acid combination method with average bullion of moderate silver content gives silver results equal to the nitric acid combination method and superior to the all-fire or scorification method. According to Smoot* it is limited in its application to silver assays to those grades of bullion which do not contain an excessive proportion of impurities and where the silver is not in excess of about 80 ounces per ton. When the scorification and cupellation losses are taken into account, the gold results obtained by the mercury-sulphuric acid and the scorification methods are substantially identical, and the method is now generally accepted as standard for gold.

THE ASSAY OF DORÉ BULLION

This method is the one generally adopted by assayers in this country and may also be used for the assay of silver bullion. A better method for the accurate determination of silver in doré or silver bullion is probably the Gay-Lussac or salt titration, also known as the mint method. It requires considerable equipment and preparation, however, and for this reason the occasional assay is more easily performed by fire methods.

The Check. In order to correct for the inevitable losses in cupeling as well as for any other errors in the assay, silver, doré, and gold bullions are always run with a check. This check or " proof center " is a synthetic sample made up of known weights of pure silver, gold, and copper, to approximate as closely as possible the composition of the bullion to be assayed. It is cupeled at the same time and under the same conditions as the regular assays, and whatever gain or loss it suffers is applied as a correction to the regular assay. To obtain data to make up the

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* " Commercial Practice in Sampling and Assaying Copper," *Eng. Mining J.* **120,** 609 (1925).

check a preliminary assay is made. This gives the approximate composition of the bullion.

The following description of procedure was designed to aid the student in his first bullion assay. It calls for triplicate determinations with two checks so that the student may see for himself how closely the checks themselves agree. It is assumed that he has a good knowledge of cupellation and will protect his working cupels with an extra row of blanks and will take such other precautions as will result in having all conditions uniform during the assay.

Preliminary Assay. A sample of 500 milligrams of bullion, or as nearly this amount as possible, is weighed out on the assay balance, and the exact weight recorded. This is compactly wrapped in 6 or 8 grams of lead foil and cupeled in a small cupel with a few feather crystals of litharge. The cupel should be pushed back in the muffle for the last 2 or 3 minutes, to insure the removal of the last of the lead. After the play of colors has ceased it should be drawn toward the front of the muffle and then covered with a very hot cupel to prevent sprouting. It is then removed gradually from the muffle, and when it is cool the bead is cleaned, weighed, and parted in the ordinary manner. The gold will require more than the ordinary amount of washing, on account of the large quantity of silver present.

If the cupeling has been properly conducted it will be fair to assume a loss of 1 per cent of silver in determining the approximate silver. The weight of gold may be taken as substantially correct. The sum of the weights of approximate gold and silver is subtracted from the weight of bullion taken to obtain the amount of base metal. This will usually be copper, but the assayer should be able to determine what it is from the appearance of the bullion and the cupel.

Final Assay. Three portions of approximately 500 milligrams are weighed accurately and wrapped in the proper amount of lead foil as shown by Table XXIV in which the impurity is assumed to be copper.

TABLE XXIV
LEAD RATIO IN CUPELLATION

Fineness of Au + Ag	Weight of Lead, grams	Fineness of Au + Ag	Weight of Lead, grams
950	5	750	11
900	7	700	12
850	8	650	13
800	10	600	15

Bullion assayers have long recognized that a minimum of 20 parts of lead per part of copper must be supplied to carry the copper into the cupel, and in practice a much

larger ratio is employed. Over one hundred years ago D'Arcet of the Paris Mint found that the ratio of lead to copper required for the cupellation of a silver-copper alloy increased with the proportion of silver in the alloy, so that, for instance, while an alloy of these two metals containing 20 per cent silver could be cupelled with a lead-copper ratio of 20 to 1, an alloy containing 90 per cent of silver required a lead copper ratio of 70 to 1. A study of this table, which is the outgrowth of an infinite amount of experience, will bear out D'Arcet's findings.

Two checks are made up with C.P. silver and proof gold, equal to the approximate silver and gold found by the preliminary assay, and the necessary amount of copper or other base metal. These are wrapped up in the same amount of sheet lead as was used for the bullion. The lead for these assays is best cut into equal-sized rectangles with proportions approximately 1½ inches by 2½ inches, and twisted into the shape of little cornucopias with the bottoms folded up. The bullion and metals going to make up the check are transferred to these directly from the scale pans, and are then folded over and made into compact bundles.

The cupels are placed in a row across the muffle, and when they are hot, the buttons are dropped quickly into them with the checks in the second and fourth cupels. They should be cupeled at a low temperature so that a few crystals of litharge are obtained all around the buttons, but toward the end the temperature should be increased to make sure of driving off the last of the lead.

The beads are cleaned, weighed, and parted, and the gold is weighed. The percentage loss of gold and silver is determined and a corresponding correction made to the weights of gold and silver found. From these corrected weights the fineness in both gold and silver is determined. The gold should check within 0.1 part and the silver within 0.5 part.

Precision: 1. Adjust the weight of bullion to 500 milligrams ± 1.0 milligram, and weigh accurately to 0.01 milligram.

2. Adjust the weight of silver for the checks to agree with the estimated silver content ±1.0 milligram and weigh accurately to 0.01 milligram.

3. Adjust the weight of gold for the checks to agree with the estimated gold content ±0.1 milligram and weigh accurately to 0.01 milligram.

As this method is accurate for silver only to about 0.5 part per 1000, report individual results only to the nearest 0.1 part per 1000 and final result only to nearest 0.5 part per 1000.

Report final gold results only to the nearest 0.1 part per 1000.

Notes. 1. In umpire work 1-gram portions are commonly used for the final assay and the work is done in quadruplicate.

2. In quantity work with bullion of more or less uniform tenor and cupeled in multiple rows it is customary to use one check in each row but to have the checks occupy different positions in the different rows.

3. Avoid cupeling at extremely low temperature since with large beads a higher finishing temperature is required to remove the last of the lead.

4. When the doré contains antimony the samples are weighed into 2.5-inch scorifiers with 30 grams of test lead. Proofs are made up according to the preliminary assay. All are scorified in the same muffle at the same time. Should the weight of these lead buttons vary over a gram, they are made up to the same weight with lead foil before cupeling. The assay is carried on from this point as if no impurities had been present.

5. When the doré contains bismuth, selenium, or tellurium, three ½-gram portions are weighed out into 2½-inch scorifiers with 40 grams of test lead and scorified, and the lead buttons are flattened out into sheets about 3 inches square. These sheets of lead are dissolved in about 200 ml. of dilute HNO_3 (1–3), and the solutions are boiled to expel all red fumes. They are then diluted to 400 ml. and filtered through triple-folded 15-cm. filters; the precipitate is washed once. To the filtrate is added sufficient NaCl solution to precipitate all the silver. The solutions are heated to boiling and allowed to stand over night. The silver chloride is filtered off through 15-cm. filters, and the precipitate is washed only once. The two filter papers are placed in a 2½-inch lead-lined scorifier, dried and burned in an oven, then covered with 30 grams of test lead and scorified. When the scorifiers have entirely closed over, the muffle door is closed and the heat raised. When hot, the fusions are poured and the lead buttons treated exactly as those from bullion containing antimony.

6. If the silver fineness of the doré is not three or more times greater than the gold fineness, another set of assays must be run with the addition of sufficient proof silver to allow for parting.

UNITED STATES MINT ASSAY OF GOLD BULLION

Preliminary Assay. Assay for Bases. To determine the approximate composition of the bullion a preliminary assay is made. A sample of 1000 millièmes (500 milligrams) is weighed out, wrapped in 5 grams of lead foil, and cupeled. The assay portions are clipped from the flattened chip samples usually with 6-inch Brown's snip shears. The use of the shears can be learned only by practice, but assayers become very skillful after a time and it is no unusual thing to see a bullion assayer weigh out five samples in almost as many minutes. The weight of the bullion taken, less the weight of the bead obtained, gives the base metals.

The bead now consists of gold and silver, the approximate relative proportions of which must be determined. This may be done by adding silver, cupeling, and parting, or by touchstone. The touchstone method consists in rubbing the sample on a piece of black jasper and comparing the mark with marks made by alloy slips, "needles," of known composition. The needles range from 500 to 1000 fine and are 20 points apart. This gives the fineness within 2 per cent, which is close enough to show how much silver to add in order to inquart the main assay and to make up the check or proof center.

Final Assay. The final assay is usually made by two assayers, each working on one of the chip or drill samples. For a small bar, each makes one assay; for a large bar each assayer makes two or more assays. The balance used for the assay is usually adjusted so that a deviation of the needle of 1 division on the ivory scale amounts to some simple fraction of the weights used. Thus, at one assay office a deviation of the swing of 1 division on the ivory scale amounts to 0.1 milligram = 0.2 millième. With this adjustment it is not necessary to make so many trials with the rider to get the final weight, nor is it necessary to weigh out exactly an even half gram of bullion for the assay. Instead we weigh out 1000 ± 3 divisions on the ivory scale, record the difference, and make a corresponding correction when the gold cornet is weighed.

As stated above, the weight of bullion taken for each assay is 1000 millièmes. To this is added sufficient silver to make the ratio of silver to gold 2 to 1, and the whole is wrapped up in 5 or 6 grams of lead foil. The lead foil pieces are all cut to exact size, about 1½ inches by 2½ inches, and rolled up into the shape of a cornucopia with the bottom pinched in. The bullion is poured directly into these from the scale pan. The silver is added in the form of discs made, for convenience, in four of five different sizes. These discs are punched out of sheets carefully rolled to gage, so that the punchings will weigh exactly even tens and hundreds in the gold weight system. If the bullion contains no copper it is advisable to add about 30 millièmes. This copper may be alloyed with the silver used for parting.

One or more proofs of pure gold weighing usually 900 millièmes (0.450 gram) are also weighed and made up to the 2 to 1 ratio, and copper is added to approximate that in the bullion. These are wrapped in the same quantity of lead foil as the bullion, and one or more are run in each row of cupels in the muffle. The lead packets are pressed into spherical shape with " balling pliers " specially designed for the purpose.

The lead packets are put in order as prepared in the numbered compartments of a wooden tray and taken to the furnace room where they are cupeled in a rather hot muffle, about 1000°C. The cupels are surrounded by a row of extra cupels so that the temperature may be kept as uniform as possible for all the assays. The cupels are withdrawn while the beads are still fluid. With a 2 to 1 ratio of silver to gold, and with copper present, there is no danger of sprouting.

The beads are removed from the cupels by means of pliers, carefully cleaned from all adhering bone ash, and then placed on a special anvil and flattened by a middle blow and two end blows with a heavy polished hammer. They are next annealed at a dull red heat and passed twice through the rolls which are adjusted each time, so that after the second passage they are about 2½ inches long by ½ inch wide, and about as thick as an ordinary visiting card. It is important that the fillets be all of the same size and thickness and that they have smooth edges. They are then reannealed and each one is numbered on one end with small steel dies to correspond with the number of the assay, after which they are rolled up into " cornets " or spirals between the finger and thumb, with the number outside. It is important that an even space be left between all turns of the spiral, in order that the acid shall have easy access to all parts of the gold.

The cornets are parted in platinum thimbles, which are supported in a platinum basket, and the whole is placed in a platinum vessel containing boiling nitric acid of 32° Bé. (specific gravity 1.28). They are boiled for 10 minutes and then transferred to another vessel containing acid of the same strength and boiled 10 minutes longer. The basket, with its contents, is then washed by dipping it vertically in and out in three changes of distilled water. It is then drained, dried, and annealed, usually in the muffle.

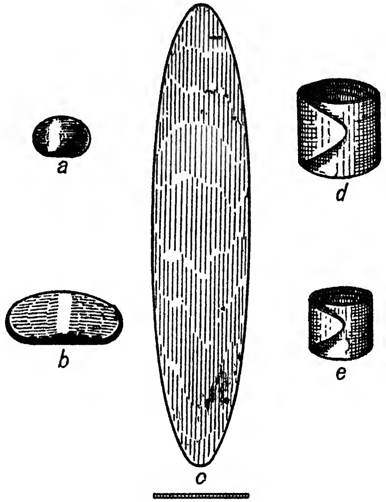

FIG. 54. Stages in preparing bead for parting in gold bullion assay. (*a*) bead; (*b*) after flattening; (*c*) fillet; (*d*) cornet before parting; (*e*) cornet after parting and annealing.

The various stages in the conversion of the bead to the parted cornet are shown in Fig. 54.

When cold, the cornets are ready to be weighed. The gold should be entirely in one piece, and the original numbers easily discernible on the parted cornets. The proofs are weighed first and the corrections applied to the weight of the other cornets. The proofs always show a slight gain in weight. The correction thus determined is termed the "surcharge," and is really the algebraic sum of all the gains and losses.

When more than fourteen cornets are parted at one time the lot is given a preliminary 3-minute treatment in an extra lot of acid, followed by the two regular 10-minute boilings.

The purpose of the copper which is added to the assays is to render the button tough and permit of its being rolled out into a smooth-edged fillet. Without the copper, the fillet is likely to crack in rolling, or to come through with a ragged edge which might give rise to a loss in parting. The action of copper is probably due to its effect in aiding in the removal of the last of the lead in cupeling. The time required for cupellation is approximately 12 minutes.

CHAPTER XI

THE ASSAY OF SOLUTIONS

A great variety of methods for the assay of gold- and silver-bearing solutions have been published in the technical press and have been adopted by assayers. These methods may be classified as follows:

1. Methods involving evaporation in lead trays with subsequent cupellation, or scorification and cupellation, of the tray and contents.
2. Methods involving evaporation with litharge and other fluxes, followed by a crucible fusion and cupellation.
3. Methods in which the precious metals are precipitated and either cupeled directly, or first fused or scorified and then cupeled.
4. Electrolytic methods in which the precious metals are deposited directly on cathodes of lead foil, which are later wrapped up with the deposit and cupeled.
5. Colorimetric methods (for gold only) all of which depend upon obtaining the " purple of Cassius " color which may be compared with proper standards.
6. Volumetric methods (for silver only). The silver is precipitated by means of zinc dust with or without lead acetate and sulphuric acid. The precipitate is dissolved in nitric acid and titrated with thiocyanate, using ferric alum as an indicator.

Evaporation in Lead Tray. This method is a good one for rich, neutral solutions containing only salts of the precious metals. A tray of suitable size is made by turning up the edges of a piece of lead foil. If many of these assays are to be made it is well to have a wooden block as a form on which the trays may be shaped. A tray 2 by 2 inches and $\frac{3}{4}$ inch deep is about right to hold 1 assay ton of solution.

Having made a tray which will not leak, the assayer adds the solution and carefully evaporates it to prevent spattering. The tray is then folded into a compact mass and dropped into a hot cupel.

Among the disadvantages of the method are the following: It does not permit of the use of a large quantity of solution, and therefore is suited only to rich solutions. If the solution is acid it will corrode the tray, and if it contains salts other than those of gold and silver these will interfere with cupellation. As both $AuCl_3$ and $KAu(CN)_2$ are volatile at moderate temperatures, many assayers do not consider the method a reliable one for solutions of these salts on account of the possibility of loss of gold.

Evaporation with Litharge. A measured quantity of the solution is placed in a porcelain evaporating dish and 60 grams of litharge is sprinkled over the surface. The mixture is allowed to evaporate at a gentle heat to prevent both spitting and baking of the residue. When dry the residue is scraped out, mixed with suitable fluxes, transferred to a crucible, and fused in the ordinary manner. The last portions remaining on the dish may be removed by means of a small piece of slightly moistened filter paper together with fine silica, both of which are afterwards added to the charge.

Some assayers add a little fine silica and charcoal with the litharge. The soluble constituents of a crucible charge, soda and borax, should not be added to the solution as they form a hard cake which is difficult to remove from the dish. The most important point in the process is the proper control of the temperature. If this is right, there will be no spattering and the dry residue will come away from the dish practically clean, after it has been pried up with the point of a spatula.

The evaporation method, though somewhat long, is the most reliable and accurate one known and the standard with which all other methods are compared. If arrangements are made for allowing the evaporation to run over night, the samples taken one night may be assayed and reported early next morning. The method is adapted to the treatment of solutions in any quantity and of almost any character. If the solution contains much sulphuric acid, the litharge may be converted into lead sulphate, which is not suited either to act as a flux or to provide lead for a collecting agent. A fusion made on such a substance with a carbonaceous reducing agent will give either no button at all or a button of matte. The reaction between lead sulphate and carbon is as follows:

$$PbSO_4 + 2C = PbS + 2CO_2.$$

If the solution is one of $AuCl_3$, a little charcoal should be added during the evaporation, to insure the reduction and precipitation of the gold, as in this way we avoid the danger of loss of gold by volatilization as the chloride. The gold, being precipitated on the charcoal, is in the best possible position to be alloyed with the lead which will be reduced by the carbon.

Precipitation by Zinc and Lead Acetate. The Chiddey Method. (For Cyanide Solutions.) This method, which was first described by Alfred Chiddey, is suitable for both gold and silver and is used almost exclusively in this country for the assay of cyanide solutions. It works equally well on strong or weak, foul or pure solutions, and almost any quantity may be taken. Many changes of detail have been suggested, and innumerable modifications of the original process have been described in the technical press. The following method has been found satisfactory:

Heat from 1 to 20 assay tons of solution in a beaker or evaporating dish. Add 10 or 20 ml. of a 10 per cent solution of lead acetate containing 40 ml. of acetic acid per liter. Then add 1 or 2 grams of fine zinc shavings rolled lightly into a ball or an equivalent amount of zinc dust in the form of an emulsion. The gold, silver, and lead will immediately commence to precipitate on the zinc. At first the solution may become cloudy but will soon clear as more of the lead is precipitated. Heat, but not to boiling, until the lead is well precipitated. This usually takes about 15 or 20 minutes. Then add 10 to 20 ml. of strong hydrochloric acid to dissolve the excess zinc. Continue heating until effervescence stops. It is often found that action ceases while some undissolved zinc still remains. This is entirely covered and thus protected from the acid by the spongy lead. To be sure that all the zinc is dissolved, feel of the sponge with a stirring rod and drop a little hydrochloric acid from a pipet directly on it.

As soon as the zinc is dissolved decant off the solution and wash the sponge two or three times with tap water. Next, moisten the fingers and press the sponge, which should be all in one piece, into a compact mass. Dry by squeezing between pieces of soft filter paper or by placing on a piece of lead foil and rolling with a piece of large glass tubing. Finally roll into a ball with lead foil, puncture to allow for escape of steam, add silver for parting, and place in a hot cupel.

Notes. 1. The solution must be clear and free from slime or colloidal matter or the sponge may break up. Add a little lime water, boil for a moment to coagulate the slime, and then filter if necessary before beginning the assay.

2. Some assayers bring to boiling after adding the zinc and lead acetate solution, then decant off the solution as completely as possible, after which they add an equal volume of dilute hydrochloric acid and proceed to dissolve the excess zinc.

3. As the lead sponge begins to dissolve and break up as soon as all the zinc is dissolved, no time should be lost in decanting the solution after the zinc has disappeared.

4. Some assayers dry the assays before cupeling to avoid danger of spitting caused by retained moisture.

5. In those rare cases where because of special impurities or for other reasons the sponge cannot be successfully collected by the above-described method the solution may be filtered on a rapid paper and quickly washed. The filter paper with precipitate is removed and the excess water squeezed out. It is placed in a small scorifier with lead and borax glass together with silver for parting if gold only is sought. The filter paper is burned off and the assay finished in the usual way.

6. When working with small quantities of solution it is best to add water occasionally to maintain the original volume of solution or else the hydrochloric acid will become too concentrated and cause the sponge to disintegrate.

Both gold and silver are precipitated and may be determined in the same assay. Assays may be completed in 2 hours, and with the reservations mentioned in the first paragraph the results are good on both low- and high-grade solutions.

Notes. 1. The potassium ferrocyanide acts as a coagulant and as a precipitant for silver. No more than the stated quantity should be added, however, since an excess leads to a loss of gold.

2 The sodium sulphite, an active reducing agent, is added to insure complete reduction and precipitation of all the gold.

3. The precipitate consists in the main of cuprous cyanide; it is white, curdy, and insoluble in weak acid.

4. If the precipitate tends to pass through the filter paper pour a little suspended paper pulp into the folded filters. This will insure rapid filtration and minimize loss of fine precipitate.

THE CUPROUS CHLORIDE METHOD. The cuprous chloride method requires fewer reagent solutions than the copper sulphate method, but the cuprous chloride solution is somewhat troublesome to prepare and does not keep well. It is therefore not so popular with assayers as the sulphate method. For a description of the assay and particularly for methods of preparation and storage of the cuprous chloride solution the reader is referred to a paper on this subject by King and Wolfe in the January, 1938, issue of the *Canadian Mining Journal.*

The Electrolytic Assay of Cyanide Solutions. The following method is abstracted from the *Journal of the Chemical, Metallurgical and Mining Society of South Africa,** in which is described the method and installation used at the Kleinfontein Group Central Administration Assay Offices.

Ten-assay-ton samples of the solution to be assayed are placed in No. 3 beakers, which are held in a frame, and electrolyzed with a current of 0.1 ampere. The anodes used consist of ordinary $\frac{5}{16}$-inch arc lamp carbons held in position in the center of each beaker by suitable clamps. They are arranged so that they may be lifted out of the solution when no current is passing. The cathodes are made from strips of ordinary assay lead foil $2\frac{1}{2}$ by 9 inches, with the lower edge coarsely serrated to allow for circulation of the solution. To connect with the battery a $\frac{1}{4}$-inch strip is almost severed from one end of the foil, and turned upward to make a terminal. The two ends of the lead are brought together and connected by folding the edges, making a cylinder about 3 inches in diameter.

The time required for the complete deposition of the gold is 4 hours, after which the carbons are removed and the lead cathodes disconnected

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* Vol. **12,** 90, C. Crichton.

and dried on a hot plate. When dry, they are folded into a compact mass and cupeled.

With weak solutions a small quantity of cyanide should be added in order to decrease the resistance and thus accelerate the deposition of the precious metals. The author reports no difficulty in obtaining a complete and adherent deposit of the gold, which separates as a bright yellow deposit.

This, of course, was the only metal worked for on the Rand, but there seems to be no reason why silver as well as gold cannot be determined by this method.

The principal advantage of the method lies in the small amount of actual personal attention required. The method works as well for a 20-assay-ton sample as for one of 10 assay tons. The principal disadvantage of the process appears to be that the time required for the deposition of the gold is somewhat longer than for some of the precipitation methods.

Colorimetric Method of Testing Barren Cyanide Solutions for Gold.* This test is made as follows:

Pour 1000 ml. of cyanide solution into a wide-necked bottle; to this add 3 drops of a saturated solution of lead acetate, and shake the mixture. Add 0.75 gram of zinc dust and shake again. Add 20 ml. of saturated cyanide solution and shake for 30 seconds. Pour into an evaporating dish and allow the dust to settle. Pour off the solution, put the dish on a spirit lamp, and dissolve the zinc dust with about 10 ml. of aqua regia; boil this until the bulk is reduced to a volume of about 4 ml. Allow the chloride of lead to settle, and then pour the solution into a test tube. Cool the solution in the tube, and add 2 drops of a solution of stannous chloride. If gold is present to the extent of 0.02 dwt. per ton of the original cyanide solution, a very slight coloration will be perceived in the liquid; 0.03 shows a slight yellow; 0.04 a slight pinkish yellow; 0.06 a strong pink; 0.08 the purple of Cassius.

The great advantage of a test of this nature lies in the fact that a shiftsman can make it in a very few minutes, and he can be certain that precipitation is going on satisfactorily. There is no need to wait for assays to be made.

John Dixon† describes the Kirkland Lake Gold Mining Company's modifications of the above method. To 750 ml. of solution in a 1000-ml. Erlenmeyer flask add 20 ml. of saturated cyanide solution. Then add from 2 to 4 drops of lead acetate solution and 0.5 gram of zinc dust,

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* C. B. Brodigan, *Trans. Inst. Min. Met.*, **22,** 190.

† *Eng. Mining J.* **111,** 629 (April 9, 1921).

and shake thoroughly. After the lead sponge is formed, invert the flask over a 3-inch porcelain casserole, and admit air into the flask until the casserole is half full. The flask may be held in position by means of a wooden stand until the sponge has settled out.

After the sponge has settled, invert the flask quickly and reject the clear solution. Decant the remainder of the solution from the sponge in the casserole, and add 10 ml. of aqua regia. Evaporate until a thick brown syrup remains. Add 5 ml. of hydrochloric acid and evaporate until 5 ml. remains. Pour the solution into a test tube and cool under the tap. Allow the precipitate of lead chloride to settle, and add 2 drops of stannous chloride solution from a dropper. From the color of the ring formed, estimate the gold in the sample.

	Per Ton
Colorless	0 cents
Straw-yellow	0–2 cents
Light purple	2–4 cents
Dark purple	over 6 cents

The color disappears quickly but can be brought back again by adding more stannous chloride. The determination can be made in about 15 minutes, and if desirable, several samples can be handled at the same time.

STANNOUS CHLORIDE. Make a saturated solution of the C.P. salt in 1 part hydrochloric acid and 15 parts distilled water. Place a few shavings of metallic tin in the bottle to keep it in the stannous form. Not over two weeks' supply of stannous chloride should be prepared at a time, as it deteriorates on standing.

The compound which yields this purple color is thought to be a mixture of red colloidal gold and colloidal stannic acid. The test is more sensitive when the stannous chloride contains a small amount of the stannic salt. This is always present except in a freshly prepared solution. In this case some of the tin may be oxidized by the addition of a little chlorine water.

CHAPTER XII

THE LEAD ASSAY

The fire assay for lead consists of a reducing fusion with iron, fluxes, and some carbonaceous reducing agent, and is conducted much as is the iron-nail assay for gold and silver ores, except, of course, that no litharge or other lead-bearing flux is added. The object of the fusion is to reduce and collect all the lead in a button free from other elements.

Lead Ores. Lead ores are classified by metallurgists as oxidized or sulphide ores, also as pure or impure ores. The oxidized ores contain the lead principally in the form of carbonate, occasionally as sulphate, and rarely as oxide or in combination with phosphorus, molybdenum, vanadium, chromium, etc. The corresponding lead minerals are cerussite, $PbCO_3$ (77.6 per cent Pb); anglesite, $PbSO_4$ (68.3 per cent Pb); minium, Pb_3O_4 (90.6 per cent Pb); pyromorphite, $Pb_5Cl\ (PO_4)_3$ (75.6 per cent Pb); vanadinite, $3Pb_3(VO_4)_2\ PbCl_2$ (72.4 per cent Pb); and wulfenite, $PbMoO_4$ (56.5 per cent Pb). The most important sulphide lead minerals are galena, PbS (86.6 per cent Pb); jamesonite, $Pb_2Sb_2S_5$ (50.8 per cent Pb); and bournonite, $PbCuSbS_3$ (42.5 per cent Pb). The principal associated minerals are argentite, pyrite, chalcopyrite, sphalerite, stibnite, quartz, calcite, and dolomite, as well as the oxidation compounds of the above sulphides. Impure ores, from the assayer's point of view, are those containing more or less arsenic, antimony, bismuth, copper, zinc, and other rarer metals which interfere with the lead assay.

Besides ores, the assayer may have brought to him various furnace products such as litharge, slag, matte, flue dust, and cupel bottom.

The fire assay for lead is not so accurate as a carefully made wet determination, but it is so simple, inexpensive, and rapid that for a long time it served to govern the purchase and sale of all lead ores. Today it is still sometimes used by the smelters and others for the assay of pure ores, although for ores containing such base metal impurities as antimony, copper, and zinc the wet method is usually preferred. The results of the fire assay may be either lower or higher than the actual lead content, depending on the nature and quantity of the other minerals present in the ore.

Pure ores give low results due to losses of lead by volatilization and slagging. Both the sulphide and the oxide of lead are volatile at moderate temperatures, and for this reason great care must be taken to maintain the lowest temperature consistent with a proper decomposition of these minerals, during the early part of the assay. Lead oxide begins to volatilize at about 800°C., and the loss due to this cause is rapid at 1000°. Lead sulphide is more easily volatilized than the oxide. In a neutral or reducing atmosphere at 860°C., it loses 18 per cent in an hour, while at 950° it is vaporized at the rate of 45 per cent per hour. Lead compounds, particularly the oxide, also tend to pass into the slag, and this tendency is increased by the presence of zinc, and to some extent by arsenic and antimony.

Impure ores containing arsenic, antimony, bismuth, and copper usually give high results, as these metals are partly or wholly reduced and pass into the lead button.

Quantity of Ore and Reagents Used. The amount of ore used is generally 10 grams, occasionally 5 grams. With low-grade ores 20, 25, or more grams may be used. The reagents used are the alkali carbonates, borax glass, some reducing agent, usually argol or flour, and occasionally sulphur. Iron in some form is always used. It may be in the form of nails or spikes, or coiled wire, or the crucible itself may be of iron; an iron crucible can be used over and over again until worn out. A satisfactory way of introducing iron is to use a rail- or boat-spike 2½ or 3 inches long and about ½ inch through. In this assay it is customary to use a mixture of sodium and potassium carbonates, as the mixture fuses at a lower temperature than either one alone. The alkali cabonates act as fluxes for the silica and serve to give a basic slag which is necessary in this assay. Usually two or three times as much alkaline carbonate as ore is taken. Borax glass acts as a flux for the metallic oxides, for limestone and the other alkaline earths. From one-half to twice as much borax glass as ore is used. An excess of reducing agent is always used to maintain the highly reducing character of the slag which is required. Sulphur is used when an oxidized ore containing copper is being assayed.

In the lead assay it is customary to use a mixed flux called a "lead flux." This may be bought already prepared or may be made up in the laboratory. Many different formulas are given, including the following:

	1	2	3
Sodium carbonate	12 parts	4 parts	6.5 parts
Potassium carbonate	15 "	4 "	5.0 "
Borax glass	7 "	–	2.5 "
Borax powdered	–	2 "	–
Flour	2 "	1 "	2.5 "

Formulas 1 and 2 are found in use in the Coeur d'Alene lead district where the fire assay for lead has been brought to the highest degree of perfection. Formula 1 is better for ores having a basic gangue; 2, for siliceous ores; formula 3 is perhaps the best of all for general use.

About 30 grams of flux are intimately mixed with 10 grams of ore, one spike or four or five 10-penny nails are inserted and a cover of 8 or 10 grams more of flux is added. Very few assayers use a cover of salt in the lead assay on account of the danger of the loss of lead as chloride.

The fusion should always be made in a muffle furnace because of the better control of temperature available. In fact, the secret of the successful fire assay for lead is largely in the proper manipulation and control of the temperature throughout the process.

At first the muffle should be just visibly red and the crucibles should be allowed to remain at this temperature for about 20 minutes. Then the heat should be gradually raised until fusion begins, and kept at this temperature for some time.

This is necessary because in the early part of the assay the charge is in active motion and particles of the various lead compounds are continually being brought to the surface, where, if the temperature were high, they would suffer an appreciable loss by volatilization. When the charge has finished boiling and most of the lead is reduced and collected in the bottom of the crucible there is less danger of loss by volatilization, first, because lead itself is not so readily volatile as some of its compounds, and second, because it is difficult for the vapor to escape through the heavy layer of reducing slag which covers the lead.

After the boiling has entirely ceased the temperature is raised to the highest heat of the muffle to decompose the lead compounds which still remain in the slag. These are principally the silicate and the double sulphide of lead and sodium or potassium, and they require a bright-yellow heat for their complete decomposition. The fusion period is finished when the nails can be removed free from shots of lead. Sulphide ores require a much longer fusion than oxides, owing to the fact that their decomposition is effected principally by iron, and therefore time must be allowed for every particle of the charge to come into contact with the iron. Oxide ores, on the other hand, are decomposed by the carbon of the charge, and as this is uniformly distributed a much shorter time will suffice. Sulphide ores will require from 1½ to 2 hours of fusion, oxide ores from ¾ to 1 hour.

Influence of Other Metals on Lead Assay. SILVER. Practically all the silver in an ore is reduced and passes into the lead button. If it is present in sufficiently large quantities a correction for it may be made, *i.e.*, 291.66 ounces per ton equals 1 per cent.

GOLD. This metal is also reduced and passes into the lead button, but it is usually present in such small quantities that it may be disregarded.

ARSENIC. Arsenic is occasionally found in lead ores, usually in the form of arsenical iron pyrite. During the assay, part of the arsenic is volatilized as metal or as arsenic sulphide but the larger part remains in the crucible. Here it usually enters into combination with the iron, forming speiss. After the contents of the crucible have been poured, the arsenic will be found as a hard white button on top of the lead, from which it may be removed by hammering. Little if any arsenic enters the lead button. Under certain conditions, *e.g.*, a long fusion at a low temperature with high soda excess, the formation of speiss may be prevented.

ANTIMONY. This metal is frequently found associated with lead, usually, however, only in small amounts. In the assay with iron, antimony is reduced and passes into the lead button. Buttons containing antimony are harder and whiter than those from pure lead ores, and when they contain much antimony they are brittle, breaking with a bright crystalline fracture.

If much antimony is present (over half as much as the lead) an antimony speiss will be found lying on top of the button.

BISMUTH. This metal is rarely found associated with lead ores, but if present will be reduced and pass into the lead buttons.

COPPER. Copper is often found in lead ores in the form of chalcopyrite, chalcocite, and oxidized copper compounds. If the ore is fully oxidized and a high temperature is employed most of the copper will pass into the lead button. If the ore contains much pyrite, or sulphur in other forms, most of the copper will remain as a sulphide and be dissolved in the alkaline slag. A button containing copper will be hard and tough and may show a reddish tinge.

IRON. This metal is often present in lead ores, usually in the form of iron pyrite. It goes into the slag, forming either a silicate or a double sulphide of iron with sodium or potassium. The lead button is practically free from iron.

ZINC. Zinc is often found associated with lead in ores, usually in the form of the sulphide. During the assay, part of the zinc is volatilized and part remains in the slag. Zinc sulphide is decomposed by iron only at a very high temperature, so that but a very small amount of zinc passes into the lead button. Zinc sulphide is practically infusible; it makes the slag thick and pasty, and thus, if present in too great proportion, interferes with the separation of the lead.

Procedure. Assay ores in duplicate, using 10 grams of ore and 40 grams of prepared lead flux. Use a 12- or 15-gram muffle crucible. Weigh out first 30 grams of lead flux, place the ore on top of this, and mix thoroughly with the spatula. Insert a spike or nails, point downward, and finally cover with 10 grams more of lead flux. Have the muffle just visibly red and bring up the heat very gradually so that after the charges are put in it will take at least 45 minutes to boil them down. Close the door of the muffle as soon as the crucibles are in, and after the charges are melted place two crucibles partly full of soft coal in the mouth of the muffle just inside of the door, which should be kept as tightly closed as possible. Raise the temperature gradually to a bright yellow and continue at this temperature until the nails can be removed free from lead.

Finally take the crucibles from the muffle, using a pair of muffle-crucible tongs, and without setting them down quickly remove the nails with a large pair of steel forceps, tapping against the side of the crucible and washing the nails in the slag to remove all adhering lead globules. Then pour into a deep, pointed mold. Work as fast as possible to prevent too great chilling of the slag in the crucible before pouring.

When cool separate the lead from the slag and hammer clean. Weigh to centigrams, and report the results in percentage. Duplicates should check within 0.2 per cent.

The slag should be black and glassy. If it is dull, more borax glass should be added. It should pour well from the crucible, and immediately after it is poured, the crucible should be examined for shots of lead. These if found are usually an indication of too low a temperature at pouring.

Notes. 1. If the ore is an oxide and contains copper add a gram or two of finely pulverized sulphur to the charge to prevent the copper from entering the button.

2. The soft coal is added to provide reducing conditions in the muffle, and it may be renewed if necessary. When a muffle is used solely for fusion purposes the hole in the back is stopped up, preventing the entrance of so much air.

3. The nails must be removed and the pouring done without a moment's delay as the charges are small and cool rapidly.

4. If the ore contains much silver the button should be cupeled and the weight of silver found deducted.

5. The lead should be soft and malleable, and a fresh cut surface should have the bluish gray color of pure lead. The button should be capable of being hammered out into a thin sheet without breaking or cracking. A button that is bright, brittle, and brilliantly white in the fracture indicates the presence of antimony.

6. The lead button should be carefully examined for speiss before it is hammered. With a little care this may be pounded off without serious loss of lead.

7. If there is doubt regarding the purity of the lead button it may be tested by cupellation. The only metals, except lead, likely to be present are gold, silver, antimony, copper, and possibly bismuth; each of these gives characteristic indications in cupeling.

8. Crucibles may be used a number of times as they are but little corroded, but those used previously for gold and silver assays must not be taken for this assay as the slag left in them contains lead. It is well to keep a special size of crucible for the lead assay in order to avoid errors due to mixing crucibles.

9. If the fusion has been properly conducted the nails will show but little corrosion. If they are much corroded the results are bound to be decidedly low.

Assay of Slags, Furnace Products and Low-Grade Ores or Tailings. In the assay of low-grade materials, such as slags and tailings, a larger quantity of ore and a different mixture of fluxes should be used. The slag should be between a singulo- and a subsilicate and part of the iron may be added in the form of small wire nails. On account of the size of the charge it is well to add a number of the larger nails, as this will lessen the time necessary for complete reduction.

The following charges have been found satisfactory:

Limestone		Slag		Slag	
Ore	25 grams	Slag	25 grams	Slag	100 grams
Na_2CO_3	25 "	Na_2CO_3	25 "	Na_2CO_3	50 "
K_2CO_3	20 "	K_2CO_3	20 "	K_2CO_3	— "
$Na_2B_4O_7$	20 "	$Na_2B_4O_7$	10 "	$Na_2B_4O_7$	10 "
Flour	10 "	Flour	10 "	Flour	10 "
Nails	5 "	Nails	5 "	Nails	5 "
(20-penny)		(20-penny)		(20-penny)	
20-gram crucible		20-gram crucible		30-gram crucible	

Allow some time at a high temperature, so that all the slag may have a chance to come in contact with the iron.

Corrected Lead Assay. To recover any lead which may have been left in the slag the following procedure is recommended: Save all the slag and remelt in the original crucible with the spikes or nails formerly used. If the first slag was quite glassy and viscous in pouring, add from 5 to 15 grams more of sodium carbonate. Heat to redness, and drop into each crucible a lump of about 5 grams of potassium cyanide. Close the door of the muffle, heat to a bright yellow, and pour as soon as quiet. Add the weight of any small button found to the lead from the original fusion.

Chemical Reactions of the Lead Assay. With an ore containing $PbCO_3$, $PbSO_4$, PbS, SiO_2, and $CaCO_3$ the following reactions may occur:

$PbCO_3 = PbO + CO_2$. (Begins at 200°C.)
$2PbO + C = 2Pb + CO_2$. (Begins at 550°C.)
$PbO + SiO_2 = PbSiO_3$. (Begins at 625°C.)
$PbSO_4 + 2C = PbS + 2CO_2$. (Begins at a dark red heat.)
$7PbS + 4K_2CO_3 = 4Pb + 3(K_2PbS_2) + K_2SO_4 + 4CO_2$. (Begins at a red heat.)

If carbon were not present some oxide and sulphate would probably remain to react as follows:

$PbS + 2PbO = 3Pb + SO_2$. (Begins at 720°C.)
$PbS + PbSO_4 = 2Pb + 2SO_2$. (Begins at 670°C.)
$2PbSO_4 + SiO_2 = Pb_2SiO_4 + 2SO_2 + O_2$. (High heat.)

Toward the end, as the heat is raised to a bright red and above, the reactions with iron become important, particularly the following:

$PbS + Fe = Pb + FeS$.
$PbSiO_3 + Fe = Pb + FeSiO_3$. (Requires a bright yellow heat for completion.)

$K_2PbS_2 + Fe = Pb + K_2FeS_2$. (Requires a bright yellow heat for completion.)

CHAPTER XIII

THE ASSAY OF ORES AND PRODUCTS CONTAINING METALS OF THE PLATINUM GROUP

The elements of the platinum group consist of platinum, iridium, osmium, palladium, rhodium, and ruthenium. All the metals of this group are rare, heavy, white to grayish white in color, and highly resistant to corrosion, and all have high melting temperatures. Arranged according to atomic weight and specific gravity they may be divided into two groups: platinum, iridium, and osmium, with specific gravities ranging from 21.40 to 22.50; and palladium, rhodium, and ruthenium, with specific gravities ranging from 12.00 to 12.44. The color in order of whiteness ranges from rhodium, a brilliant white, iridium somewhat less brilliant, palladium a trifle less white than silver, platinum white with a grayish tinge, ruthenium gray, and osmium bluish gray. Of these six metals palladium only is soluble in nitric acid, and in the pure state only platinum and palladium are at all readily soluble in aqua regia. Their melting points range from that of palladium, 1550°C., to that of osmium, about 2700°C. According to Carter* the platinum metals appear to form numerous oxides which are capable of existence only within narrow limits of temperature. Some of these oxides are decidedly volatile, and for this reason a knowledge of their behavior in this respect is particularly important to the fire assayer. Their comparative volatility in air at 1300°C., as may be seen in the following table of properties, ranges from 1 for rhodium, 2 for platinum, 6 for palladium to 1000 for osmium.

OCCURRENCE

Platinum was first discovered in Colombia in the middle of the eighteenth century, where it was known by the natives as *oro blanco*, white gold, on account of its nobility and color.

The principal source of the platinum metals is in the several native alloys of the metals found in alluvial deposits in various parts of the world. The richest deposits are in the Ural Mountains in Russia, and next in importance come those of Colombia. Nuggets as large as 10 to 20 pounds have been found, but most of the native platinum is in

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* "The Platinum Metals and Their Alloys," *Trans. A.I.M.E.* **78**, 763.

TABLE XXV

PROPERTIES OF THE METALS OF THE PLATINUM GROUP

Property	Heavy			Light		
	Platinum	Iridium	Osmium	Palladium	Rhodium	Ruthenium
Atomic weight	195.2	193.1	190.9	106.7	102.9	101.7
Specific gravity	21.40	22 42	22.50	12.00	12.44	12.10
Melting point, °C.	1774	2450 ±	2700 ±	1550	1985	2450(?)
Relative volatility	2	60	(1000)	6	1	200
In boiling concentrated HNO_3[1]	Insol.	Insol.	Insol.	Slowly soluble	Insol.	Insol.
In aqua regia[1]	Soluble	Insol.	Insol.[1]	Soluble	Insol.	Insol.

[1] The solubilities of the pure metals in nitric acid and aqua regia are substantially as indicated in the table, but the degree of purity has a bearing and also the crystalline state of the metal. For instance, aqua regia does not attack crystalline osmium but it does dissolve the amorphous variety, and so does fuming nitric acid. Some of these metals are soluble when in the form of alloys even though insoluble in the pure state. The best-known example of this is platinum, which when pure is insoluble in nitric acid but which when alloyed with silver or numerous other metals is partially or wholly soluble in the same acid.

the form of rounded or flattened grains the size of rather fine sand, with occasional irregular lumps the size of peas. The particles have a metallic luster and are usually of a steel-gray color. They may be distinguished by their high specific gravity, 16 to 19, their infusibility in the hottest part of the blowpipe flame, and their insolubility in any single acid. Platinum predominates in most of the native alloys, which usually contain all six metals of the group together with 4 to 20 per cent of iron. In certain of the natural occurrences some of the metals may be absent, as in some iridosmium deposits, which contain no platinum or palladium. In alluvial deposits the platinum minerals are usually associated with the heavy oxide minerals collectively described as black sand, which consists of a mixture of magnetite, hematite, chromite, ilmenite, rutile, zircon, cassiterite, garnet, and other heavy minerals.

A few compounds of the metals, such as platinum arsenide and ruthenium sulphide, are known. At the Boss Mine near Good Springs, Nevada, the platinum-group metals, notably palladium with some platinum, were found together with gold and silver in a quartz vein associated with a mineral known as plumbojarosite. The platinum metals are often found associated with copper and nickel sulphides, and as a by-product may contribute to the value of the ores. The most important examples of this are the nickel mines of the Sudbury district in Ontario, from which are extracted several thousand ounces of platinum and palladium annually. The most recent discoveries of lode platinum are in two districts in South Africa. In one area about 50 miles in length there occur outcrops of dunite, a basic peridotite, carrying platinum values running as high as 1 ounce per ton. Owing to the low price of platinum, however, none of the mining enterprises which sprang up there have proved profitable, and as yet nowhere in the world has a profitable platinum lode mine been developed.

Other sources of the platinum metals are the anode muds from electrolytic copper refineries and the gold ores of the South African Rand, which latter carry appreciable quantities of iridosmium.

MINERALS

The following platinum-group minerals have been identified:

CRUDE PLATINUM. Ordinarily contains 70 to 90 per cent of platinum.

NATIVE PALLADIUM. A very rare white to steel-gray mineral.

IRIDOSMIUM. A very hard and tough mineral containing 55 to 60 per cent iridium; 30 to 40 per cent osmium.

PLATINIRIDIUM. A native alloy practically free from osmium. White, very rare, and the heaviest of known minerals.

SPERRYLITE. A platinum diarsenide, $PtAs_2$.

LAURITE. A sulphide of ruthenium, probably RuS_2, usually contains osmium.

COOPERITE. A platinum sulpharsenide, $Pt(AsS)_2$.

STIBIO–PALLADINITE. A native alloy of antimony and palladium containing, when pure, about 70 per cent palladium; possibly Pd_3Sb.

RHODITE. A rhodium-gold native alloy carrying 30 to 43 per cent rhodium.

PORPESITE. A palladium-gold native alloy.

SAMPLING

Besides ores containing or suspected of containing the platinum metals the assayer may have brought to him for analysis black sands, various industrial alloys, scrap, filings, etc., sweeps, base bullion resulting from the melting of mixed scrap, electrolytic slime, as well as matte and speiss. Each one of these may require a different method of attack, and to begin with, a good knowledge of sampling and allied problems is essential. Many assaying difficulties may be traced back to the question of sampling, and any material containing the rich mineral in tough and sometimes malleable particles, such as grains of native platinum, is bound to give difficulties because of this condition.

DIFFICULTIES IN ASSAYING FOR PLATINUM

The platinum metals themselves are much more difficult to detect, separate, and determine than gold and silver, and as yet, even after a great deal of careful investigation by thousands of chemists, the methods are far from satisfactory. Their correct determination is considered the most difficult analysis in the realm of inorganic chemistry. Part of the difficulty is due to the fact that the metals of this group rarely occur alone. More likely all six will be found in one sample, and not only are all valuable, so that it is desirable to determine each one separately, but also the determination of any one alone is complicated by the presence of other metals of the group and by gold and silver which are usually found associated with them. In ordinary ores the quantities involved are so small that the difficulties, because of this feature alone, are greatly multiplied.

FIELD OF THE FIRE METHOD

The analysis of rich alloys, nuggets, and grains, *i.e.*, alluvial concentrates, may best be accomplished without the use of fire, and a description of these wet methods is not appropriate to a book of this title. Only those methods will be described here which begin with an igneous concentration of the precious metals in metallic lead, or with cupellation. These methods apply to ores, black sands, matte, speiss, base bullion, sweeps, and slimes, and are the only ones available for the determination of small amounts of platinum and palladium in ores, etc.

INDICATIONS

Platinum in small amounts gives the surface of the assay bead a characteristic frosted appearance. As little as 1.6 per cent in a silver bead is distinctive. Palladium behaves much like platinum but is not quite so distinctive. Other metals of the group give even more marked indications of their presence by changes in the appearance of the surfaces of the beads. For further details refer to pages 119–122. The rate of cooling and other factors will have a bearing on the surface appearance, but an experienced assayer can tell quite accurately what metal of the platinum group is present and about how much, by observing the surface of the assay bead. He might be deceived by tellurium, which if present in large amounts in the ore might, in part, go along with the silver in sufficient amount to give the bead a marked frosted appearance.

All the platinum group of metals other than palladium prevent the flashing of assay beads, and this characteristic provides another indication.

Both palladium and platinum impart peculiar colors to the nitric acid used for parting, for details of which see page 131. Likewise, since ordinarily not all the platinum is dissolved in a single parting operation, and since the remaining platinum discolors the gold, leaving it more or less steel-gray instead of yellow, this too provides another means of attracting the assayer's attention to the probability of the presence of members of the platinum group of metals.

DETECTION

In the event that heavy metallic grains, more or less grayish white, and suspected of belonging to the platinum group of metals, have been found in black sand or elsewhere, they should first be tested for fusibility and resistance to acid attack. If they are infusible at the highest heat of the blowpipe flame and are not attacked by any single acid they probably belong to the platinum group. The simplest confirmatory test is probably that known as the "glow reaction," which depends upon the catalyzing action of finely divided platinum-group metals on the oxidation of the hydrogen in illuminating gas. The test will show the presence of as little as 0.0005 milligram of palladium, 0.0009 milligram of rhodium, 0.002 milligram of platinum, and 0.005 milligram of iridium. It does not reveal osmium or ruthenium, but fortunately these are of least importance, and ruthenium at least is present in amounts of only a fraction of 1 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 previously been removed by evaporation.

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 ml. 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 sensitivity 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 insure 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.

FORMIC ACID precipitates all the platinum from neutral, boiling solutions in the form of a black powder. Neutralization is best accomplished with sodium carbonate. Silver and many other metals are also precipitated by formic acid.

OXALIC ACID does not precipitate platinum, thus providing a means for the separation of gold from platinum.

ALUMINUM, magnesium, cadmium, zinc, and many other metals may be used to reduce platinum salts to the metallic state. The precipitated metal is in a finely divided condition and tends to run through the filter. The addition of salt to the wash water will prevent loss due to this cause.

Palladium. Palladium, like platinum, forms two series of salts corresponding to the oxides PdO and PdO_2. The palladous oxide is the more stable and may be formed by the prolonged heating of the metal slightly above 700°C.

Palladium, alone of the platinum group, is soluble in nitric acid, forming $Pd(NO_3)_2$, which is soluble in dilute nitric acid. Dilution, evaporation, or standing causes decomposition with precipitation of a basic nitrate. Palladous sulphate, $PdSO_4$, is readily soluble in water but decomposes upon standing. Palladium is more readily soluble in aqua regia, forming mainly the more stable brownish yellow chloropalladous acid, H_2PdCl_4.

Nearly all palladium compounds are reduced to the metallic state on strong ignition. It should be noted, however, that if ignition is in air the palladium sponge will become coated with oxide, and if it is desired to get the sponge into solution the oxide should first be reduced to metal, in which form it is more readily soluble.

From a solution containing palladous chloride:

AMMONIUM CHLORIDE produces no precipitate, thus providing a means of separating palladium from platinum and iridium.

POTASSIUM IODIDE precipitates black palladous iodide, insoluble in water or alcohol but soluble in excess of potassium iodide. This reaction is very sensitive and will indicate 1 part Pd in 500,000 parts of the solution.

DIMETHYLGLYOXIME gives a yellow precipitate insoluble in water, in 50 per cent alcohol, and in dilute acids. The precipitate is readily soluble in ammonia or in solutions of potassium cyanide. This reagent also precipitates metallic gold. Platinum dimethylglyoxime is precipitated, but only on boiling. It does not react with any other members of the platinum group.

MERCURIC CYANIDE produces a yellowish white gelatinous precipitate of palladous cyanide, $Pd(CN)_2$, difficultly soluble in hydrochloric acid, but soluble in ammonia and in potassium cyanide to $K_2Pd(CN)_4$.

HYDROGEN SULPHIDE precipitates, from acid or neutral solutions, black palladous sulphide insoluble in ammonium sulphide.

POTASSIUM NITRATE gives a yellow crystalline precipitate of $K_2Pd(NO_2)_4$ if the solution is not too dilute.

FORMIC ACID, sulphurous acid, ferrous sulphate, zinc, iron, mercury, silver, and numerous other reagents reduce palladium salts to the metallic state.

STANNOUS CHLORIDE in the presence of hydrochloric acid gives at first a red or brown precipitate which finally dissolves, yielding an intensely green solution. In the absence of acid, stannous chloride causes a partial reduction to the metal, and the solution becomes green.

Iridium. Iridium forms at least two oxides, Ir_2O_3 and IrO_2, and salts corresponding thereto. Heated in air to 800°C. it begins to oxidize, going to IrO_2; heated to 1000° it begins to volatilize as oxide.

In the dense form iridium is practically insoluble in aqua regia. It may be converted into a water-soluble form by being heated with salt in a current of chlorine, which converts it into Na_2IrCl_6. The tetrachloride, $IrCl_4$, yields a dark brown to black solution. The trichloride and its double salts yield dark green and brown solutions. The iridium salts are much less readily reduced to the metallic state than those of platinum and palladium.

Ignition on charcoal reduces all iridium compounds to metal. In consequence of the ease with which it oxidizes, the final ignition of such a precipitate as $(NH)_2IrCl_6$ should be in an atmosphere of hydrogen, in which case metallic iridium is obtained.

From a solution containing Na_2IrCl_6, sodium chloriridate:

AMMONIUM CHLORIDE precipitates dark red to black ammonium chloriridate, $(NH_4)_2IrCl_6$, which is insoluble in a saturated solution of ammonium chloride.

POTASSIUM CHLORIDE precipitates brownish black K_2IrCl_6, insoluble in potassium chloride and in cold alcohol. The K_3IrCl_6, on the other hand, is readily soluble in water and in potassium chloride solution.

HYDROGEN SULPHIDE. Iridium is the hardest of all the platinum metals to precipitate with hydrogen sulphide. Hydrogen 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 that too much mineral acid is not present. To insure 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 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 if 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.

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 ml. of solution.

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

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," to Volume I of W. T. Hall's Ninth English Edition of Treadwell's " Analytical Chemistry " (1937) and to a paper by Thompson, Beamish, and Scott, *Ind. Eng. Chem., Anal. Ed.* 9, 421.

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 are 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. First a large piece of smooth paper is spread out 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 insure 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 1 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, platinum, palladium, and rhodium 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 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 partially oxidized and either volatilized or carried into the slag. The extent to which this oxidizing process will proceed depends 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 platinum and palladium and part of the rhodium in alloy form, and most of the iridium and iridosmium which was collected in the lead button, mechanically held. Some of the rhodium, ruthenium, and 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, and part of the rhodium, 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 may 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 insure 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 5 or 10 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 insure 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; this loss ordinarily amounts to 20 to 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 15 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 will part but yet will not break up during parting, Smith* states that experience shows that, in order to get an alloy such that practically no silver will remain undissolved in sulphuric acid parting of the assay cornet, enough gold must be present to make the ratio of gold to platinum about 10 to 1. This makes the desirable ratio of platinum : gold : silver equal 1 : 10 : 33. He admits that satisfactory results may be obtained by using a ratio of 8 of gold to 1 of platinum but states that, if the ratio is less than this, the cornets retain more silver. Robinson, in outlining a rapid method for the estimation of palladium in connection with the sulphuric acid parting method, states that the sample should contain "gold in amount equal to ten times the platinum and palladium together," but gives no reason.

Palladium in the alloy is attacked and in part goes into solution with the silver, yielding a solution which ranges from orange-yellow to a rich brownish red, depending upon the amount. The relation between platinum and palladium present appears to have an influence upon the amount of palladium passing into solution in sulphuric acid, as does, of course, the proportion of silver. Double parting will ordinarily be necessary for a complete separation of palladium by sulphuric acid. If the alloy contains ruthenium in appreciable amounts, enough of this may dissolve to impart, in the absence of palladium, a pink color to the solution. The other metals of the platinum group are not soluble in sulphuric acid of this strength and will be left behind with the gold and platinum.

Any lead left in the bead after cupellation will be converted into sulphate, and for this reason, if for no other, care should be taken to finish the cupellation at a high temperature to keep the residual lead as small in amount as possible. Since lead sulphate is much more soluble in hot concentrated sulphuric acid than in cold dilute acid, the parting acid should be poured off while it is still hot. If one or two additional treatments with hot sulphuric acid are given, followed by the usual hot water washes, practically no lead should remain with the gold-platinum residue.

* "The Sampling and Assay of the Precious Metals."

Nitric Acid. As has already been pointed out, platinum when alloyed with silver is soluble in nitric acid. The extent of this solubility depends upon the amount of dilution and the degree of diffusion of the platinum in the silver. The solubility is probably increased by the presence of gold and palladium but diminished when iridium, rhodium or ruthenium are present. The strength and the temperature of the nitric acid may likewise have an influence on the reaction, but here the data are contradictory.

In nitric acid parting of alloys high in platinum, the color of the solution ranges from light straw-yellow to brown, almost to black, depending upon the amount of platinum present, whereas when parting alloys containing only gold and silver, the solution is colorless. The dissolved platinum appears to be in the colloidal state, since the brown solution will pass through a filter paper, but if allowed to stand for several days, a very fine black powder separates and the solution becomes almost colorless. Robinson, in discussing the colorimetric estimation of palladium in nitric acid parting solutions, confirms the opinion of others that in many cases the platinum in the nitric acid solution is in a colloidal state, but goes on to say that, in his opinion, if a ratio of eight or more times as much gold as platinum is maintained, with, of course, the necessary amount of silver, the platinum forms a true solution in the nitric acid.

If platinum is present in appreciable amount, it is impossible to separate it entirely from gold in one nitric acid treatment. The gold-platinum residue invariably retains silver, and this increases with the increase of platinum in the alloys treated. To complete the separation it is necessary to alloy the residue with more silver by cupellation and to repeat the nitric acid treatment. Several repetitions will ordinarily be necessary. The extent to which the platinum has been removed in each parting may be estimated by observing the color of the annealed residue. If much platinum remains the residue will be black, but as the platinum is gradually removed by successive partings the color changes to steel-gray and finally to the yellow of pure gold. Ordinary commercial work usually calls for three partings.

Since at 20°C. platinum is soluble in silver only up to 22 atomic per cent, and beyond that a complex system of mixed crystals results, the platinum-silver ratio should not exceed this amount. With a larger proportion of silver, diffusion will probably take place more quickly, and for this reason a higher ratio of silver to platinum 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 platinum, is entirely separated from gold by double parting, and in the absence of platinum in a single parting, provided that silver is present in amount equal to 15 or more times the combined gold 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 is 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; it 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 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 of an alloy, or as much as 5 or 10 assay tons of 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 oxidizable 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 or more 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 10 minutes.

The alloy thus obtained 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 3 to 10 times its weight of silver, which 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; the writer prefers 10 milligrams for most purposes.

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 10 or 15 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 cupel loss, the results obtained from check assays being applied.

SULPHURIC ACID PARTING. Sulphuric acid parting is best conducted in a 30-ml. pear-shaped parting flask. The parting acid is made up by diluting 100 ml. of concentrated sulphuric acid with 22 ml. of water. Ten milliliters of this acid is placed in each flask, and these are then put on the asbestos-covered hot plate and heated to about 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 two or three 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.

Parting acid made up as above described yields a solution containing 90 per cent H_2SO_4 by weight which boils at 262.5°C. It is slow in action and the first treatment may last 1 or 2 hours for a 300- to 900-milligram bead. Some authorities prefer a 95 per cent H_2SO_4 strength which is much more rapid in action but is more likely to cause the residue to break up.

Two flasks similar to those used for parting but containing respectively metallic tin and metallic bismuth, placed on the hot plate adjacent to the flasks actually used for parting, provide a cheap, simple, and satisfactory temperature indicator. Tin melts at 232° and bismuth at 271°C. With the heat regulated so that the tin is melted and the bismuth remains solid a sufficiently accurate temperature control is provided. If another and higher temperature control point is desired a third metal, cadmium, which melts at 321°C., may be used.

Heat at about 240°C. until chemical action ceases and then for an additional 10 minutes. If an orange-yellow color, indicating palladium, appears at this point, the procedure must be modified as described later. The acid is decanted as completely as possible and at least one additional acid treatment of 10 minutes is given, after which the residue is carefully washed. For the second acid treatment sulphuric acid of 95 per cent strength is recommended. This acid boils at 295°C., and for this treatment the temperature may be raised until the bismuth melts. This acid strength is made by diluting 100 ml. of concentrated sulphuric acid with 10 ml. of water.

The solution 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. Silver sulphate is difficultly soluble, even in hot water, so that more than ordinary care in washing is required to insure its removal.

Since the assay bead is likely to have retained some lead which will have been converted to sulphate during the parting process some authorities recommend several washings with hot 50 per cent ammonium acetate solution, alternating with hot water, to remove lead sulphate. Final washing with hot water will serve to remove the ammonium acetate.

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 cup 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 10 minutes at 800° to 850°C. Clean the bead and part as in the gold assay. Wash, dry, and anneal; 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.

ALTERNATIVE TO NITRIC ACID TREATMENT. Instead of repeated inquartations with silver followed by nitric acid partings with the additional inevitable cupellation losses which one must attempt to correct for by means of check assays, the gold-platinum residues may be dissolved in aqua regia, the nitric acid removed in the customary way (see p. 278), and the gold precipitated by hydroquinone. According to Beamish,* precipitation in hot, 1.2 *N* hydrochloric acid is rapid, the gold is readily filtered, and the occlusion of the platinum metals is negligible. Use 3 ml. of a 5 per cent aqueous solution of hydroquinone for every 25 milligrams of gold, and boil for 20 minutes. Allow the

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* "The Determination of Gold," Beamish, Russell and Seath, *Ind. Eng. Chem., Anal. Ed.* **9**, 174 (1937).

solution to cool and filter off the gold, ignite, and weigh. The platinum may be determined by difference, or in the absence of palladium it may be precipitated by formic acid after destruction of the hydroquinone.

If palladium is present it may be precipitated as dimethylglyoxime directly from the filtrate of the gold precipitation. The excess hydroquinone and glyoxime may be removed from the filtrate by evaporation and heating to destroy the organic matter and the platinum dissolved by treatment with a little aqua regia. The nitric acid is then eliminated and the platinum precipitated with formic acid in the presence of 3 grams of sodium acetate for each 100 ml. of solution. This precipitate should be allowed to digest in contact with the mother liquor at near boiling temperature for several hours.

Palladium may also be determined by this alternative method, but the procedure is more complicated since palladium will be found partly in the sulphuric acid solution and partly with the gold-platinum residue.

Notes on Sulphuric Acid Method. Experiments in cupeling and sulphuric acid parting in which definite weights of pure gold and silver were run as checks against the same weights of gold and silver but with included platinum brought out the following interesting results:

1. In spite of the higher melting point of platinum which should have tended toward an increased retention of lead in the beads, cupellation losses in those assays which carried platinum were materially higher than those in which platinum was omitted, averaging 4.12 per cent against 3.78 per cent. Evidently platinum induces extra losses of silver (and gold) or itself suffers more under this treatment than do the gold and silver in the parallel assays.

2. Parting with 90 per cent sulphuric acid as described above accompanied by very thorough washing invariably resulted in a positive surcharge for assays both with and without platinum, but without any constant trend with respect to presence or absence of platinum. The gain in weight, which averaged 0.6 per cent, can be due to retained metallic silver, to metallic lead, or to the sulphates of these metals.

3. Those beads which contained platinum broke up, leaving a black to dark brown residue, while the gold-silver alloys parted with the residue holding together in one piece and yellow in color. Platinum seemed to accelerate the parting action since in those beads containing it chemical action came to completion much quicker than with those containing only gold.

4. After annealing, the gold residues were of a good gold color and in one piece. The gold platinum residues varied in color according to gold-platinum ratios from dark lead-gray for the 2 : 1 ratio, through a true platinum-gray for the 5 : 1 ratio, to a tea-rose shade for the 8 : 1

ratio. The first was badly broken up, the second not so finely divided, and the third semi-coherent.

Quantities of metals taken for these experiments were: platinum, 10 milligrams in all cases; gold, 20, 50, and 80 milligrams, respectively; and silver, 300, 600, and 900 milligrams, respectively. In the tertiary precious-metal combinations the ratio of 10 silver to 1 gold and platinum was selected to insure practically complete elimination of lead in cupellation and the complete elimination of silver in sulphuric acid parting. Since for each pair the gold and silver quantities were maintained constant the silver-gold relationship (ratio) in those assays which contained no platinum was 15 to 1. Twenty-five grams of lead was used for cupeling, and the cupels were run hot as is indicated by the cupellation losses. Finished beads were annealed at 800°C. for 10 minutes in the muffle to allow for diffusion.

THE DIRECT DETERMINATION OF PALLADIUM, PLATINUM, AND GOLD

This method requires considerably more time and manipulation than the one involving sulphuric acid parting, but since the platinum and palladium are directly determined it may appeal to some operators more than the method involving difference and colorimetric measurements. Where the sample contains considerable palladium this method is preferable. Any iridium, rhodium, or ruthenium which have been collected in the bead may be determined, and the gold results corrected to correspond.

Epitome. The assay beads are parted directly in nitric acid, which dissolves the silver, palladium, and platinum. The residue is inquartated and the parting repeated until all the palladium and platinum are dissolved. From the combined solutions containing the silver, palladium, and platinum, the silver is precipitated as chloride, and filtered. After removal of nitric acid from the filtrate, the palladium and platinum are precipitated as metals with formic acid, or as sulphides with H_2S. They are filtered, ignited, and weighed as metals, and then redissolved in aqua regia, after which the palladium is precipitated with dimethylglyoxime. The platinum may be obtained by difference, or it may be again precipitated and weighed alone.

It was formerly thought impossible to precipitate palladium in the presence of platinum with dimethylglyoxime, but the separation has recently been developed until it is now considered the best available. C. W. Davis* describes the separation and gives results of analyses

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* *Bureau of Mines Reports of Investigations* 2351, May, 1922.

showing that palladium can be completely precipitated at room temperature, and that practically no contamination with platinum occurs.

Preliminary Assay. *Unless the approximate metal contents are* known it will be necessary to make one or two preliminary assays to determine the approximate composition, and so ascertain how much silver to add. The skilled assayer may be able to estimate the approximate composition of the material from the weight and appearance of the assay bead, followed by a simple nitric acid parting. The color of the parting solution gives an indication of the amount of palladium present, and the appearance and weight of the ignited residue yield information as to the amount of gold and platinum.

Procedure. Take a quantity of ore sufficient to yield an amount of platinum and palladium such that errors of weighing the final metals 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 or 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 silver is added to the crucibles or to the lead buttons to give a ratio of silver to platinum of about 15 to 1. The buttons are cupeled first 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 10 or 15 minutes, after which they may be removed. Weighing of the beads is not ordinarily necessary, since for an exact determination of silver a different assay must be made.

PARTING. Since the palladium and platinum going into solution are to be determined, the nitric acid parting should be done in a small flask with a lip. Some loss of solution is inevitable in decanting from a porcelain crucible or capsule, but the lip of the flask makes it possible to recover all the solution in decanting. A 30-ml. pear-shaped parting flask is most suitable for this purpose.

Treat first in hot, weak acid, and when no further action occurs, decant the solution into 300-ml. casseroles, taking care not to pour off any of the residue. Then add about 10 ml. of 1.26 specific gravity acid and heat almost to boiling for 5 or 10 minutes, depending upon the amount of the residue. Decant this solution also into the casserole, and wash carefully by decantation, saving the washings. Finally, transfer the residue to a parting capsule in the manner described on page 273, dry, and anneal. If only a small amount of palladium was present in the material, practically all may have been removed by one parting; but if much platinum was present, the parting must be repeated. Add silver equal to 15 times the weight of the residue, wrap in lead foil, and cupel and anneal as before. Part, wash, and add the solution to that which resulted from the first parting. Transfer to capsules, anneal, and examine the color of the gold. Repeat the operation as many times as necessary to get gold of good color. An alternative method of judging when the platinum is all out is to continue inquartation and parting until the gold is of constant weight. Weigh the gold, and if it is thought to contain iridium, rhodium, ruthenium, or osmium these may be separated by a method to be described later.

TREATMENT OF NITRIC ACID SOLUTION. To the combined nitric acid solutions and washings from each assay, preferably diluted so that there shall not be more than 0.1 or 0.2 gram of silver for each 100 ml. of solution and heated to about 70°C., add slowly and with constant stirring dilute hydrochloric acid, 0.2 to 0.5 normal, until no more precipitate is formed. Avoid the addition of more than a slight excess of the acid. Allow the precipitate to stand in a warm place for several hours, preferably over night. Keep away from direct sunlight or too strong reflected 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

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* "Determination of Platinum, Palladium, and Gold," *Eng. Mining J.* **99**, 700 (1915).

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 hydrochloric acid (1 : 3) and again evaporate to dryness to remove all nitric acid. Finally take up with 5 drops of dilute hydrochloric acid and not more than 25 ml. of water, and filter on a small paper in a 1½-inch funnel, catching the filtrate in a 100- or a 150-ml. beaker. Wash fully, using a small wash bottle which will deliver a very fine stream of water.

PRECIPITATION OF PLATINUM AND PALLADIUM. Make the filtrate slightly alkaline with sodium carbonate, add 10 ml. of formic acid, and heat to boiling in a covered beaker. Boiling for about 30 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 insure 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 ml. of hydrochloric acid, dilute to 100 ml. with hot water, heat to 70°C., and pass in a rapid current of hydrogen sulphide for some time. Filter and wash the platinum and palladium sulphides with hot hydrogen sulphide water containing a little hydrochloric acid. 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 sulphide 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 hydrochloric acid, diluted to 50 ml. or less, depending 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, from 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 hydrochloric acid, and diluted with a little distilled water. The solution is made alkaline with sodium carbonate 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.

DETERMINATION OF SMALL AMOUNTS OF PLATINUM IN CUPELLATION BEADS BY MICROTITRATION

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.

Anyone who has attempted to determine such small amounts of platinum in ores by the usual gravimetric methods cannot fail to recall the great amount of care and time required to obtain something which could be weighed and identified as platinum after having been collected together with the other precious metals in the assay bead. Only those who have actually had the above experience can truly appreciate the work of Dr. W. B. Pollard* in developing a simple volumetric method for this purpose. With solutions already standardized the platinum in a bead may be determined in not more than 10 minutes as contrasted with almost as many hours for the usual gravimetric separation. As little as 0.01 milligram of platinum may be quickly identified and determined.

The method is based on the reaction between stannous chloride and chloroplatinic acid whereby the platinum salt is reduced to chloroplatinous acid and yields yellow or red solutions. The color is then

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* "The Micro-Titration of Platinum in Cupellation Beads," *Trans. Inst. Mining Met.* **47**, 331 et seq. (1938).

discharged by titration to a colorless liquid with an organic reagent, diethyl dithiocarbamate, with the aid of a layer of benzene which dissolves the compound formed by the reaction, thus removing it and leaving a clear liquid.

Epitome. The assay bead containing not more than 6 milligrams of silver and not to exceed 1.5 milligrams of platinum and gold is treated in a dry test tube with 2 drops of nitric acid, 1.26 specific gravity, which dissolves the silver and part of the platinum. Six milliliters of strong hydrochloric acid is then added which, when the tube is shaken, quickly dissolves the silver chloride first precipitated. The tube is then gently heated, resulting in the rapid dissolution of the gold and remaining platinum.

If an excess of a concentrated solution of stannous chloride is now added and the solution heated just to the boiling point, gold is precipitated as metal. Under the conditions of this work, *i.e.*, just below the boiling point and in the presence of strong hydrochloric acid, stannous chloride precipitates gold as metal and not as " purple of Cassius." The platinum is reduced to the highly colored platinous condition and any small excess of nitric acid destroyed. Now if the solution is cooled, a small amount of benzene added, and the tube closed with a rubber stopper and well shaken, the gold passes from the hydrochloric acid solution and is held in suspension in the benzene layer. After the benzene layer has been allowed to separate, as little as 0.01 milligram of platinum is easily detected when the tube is held against a white background.

If a solution of sodium diethyl dithiocarbamate is now run in from a microburet and the tube again closed with a rubber cork and well shaken, the platinum salt reacts with the reagent to form a compound which is soluble in benzene, leaving the hydrochloric acid layer paler in color. The reagent is added and the tube shaken until the hydrochloric acid has become colorless. The reagent is standardized against a platinum solution of known strength.

STANNOUS CHLORIDE SOLUTION. Four hundred grams of stannous chloride and 200 ml. strong hydrochloric acid are placed in a covered beaker and heated with granulated tin on a water bath for several hours. Any acid lost by evaporation is replaced and the solution filtered through asbestos-wool on a Büchner funnel. It is essential that the filtrate should be colorless. When cold, 8 mg. of potassium iodide is added and the solution well mixed. The reagent is much more reactive with chloroauric acid in the presence of a trace of iodide,* but the amount stated should not be exceeded when gold is also to be estimated.

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* W. B. Pollard, " The Volumetric Assay of Gold," *Trans. I.M.M.* **41,** 439 (1931–2).

SODIUM DIETHYL DITHIOCARBAMATE SOLUTION. In a standard 250-ml. flask, 0.591 gram of the salt is dissolved in 50 ml. of alcohol and 150 ml. of water is added. The mixture is allowed to cool, the volume made up to 250 ml. with distilled water, and filtered.

The solution should always be standardized against decimal platinum solutions before use and the necessary correction applied.

DECIMAL PLATINUM SOLUTION. (FREE FROM NITROSYL COMPOUNDS.) One-half gram of pure platinum in the form of foil is dissolved in a beaker in 6 ml. of hydrochloric acid and 2 ml. of nitric acid. The solution is taken to dryness on the water bath and then evaporated to dryness three times with 10 ml. of strong hydrochloric acid. Six milliliters of strong hydrochloric acid is added and the solution made up to 500 ml. with distilled water in a standard flask.

STANDARDIZATION OF SODIUM DIETHYL DITHIOCARBAMATE SOLUTION. To standardize the sodium diethyl dithiocarbamate solution, measure various amounts of decimal platinum solution into 6-inch by ¾-inch test tubes with a 1-ml. graduated pipet; add 6 ml. of strong hydrochloric acid and then 1 ml. of stannous chloride, which will reduce the platinum to the highly colored platinous condition. Then add 5 ml. of benzene, and run in the sodium diethyl dithiocarbamate solution from a 2-ml. microburet graduated in hundreths of a milliliter.

The first addition of this reagent causes a white precipitate to form, and this becomes greenish when the solutions are mixed. On shaking, the green compound dissolves in the benzene, which then becomes yellow. After each addition the tube is closed with a rubber stopper and the contents well shaken. The end point is found very rapidly as the depth of color of the hydrochloric acid solution gives a clear indication of the amount of platinum present. When the hydrochloric acid is colorless as viewed against a white background, the reading is recorded and the titration is finished.

FINAL ASSAY PROCEDURE. The cleaned and flattened bead is placed in a dry test tube and 2 drops of nitric acid, 1.26 specific gravity, added. The tube should be held in a nearly horizontal position with the bottom resting on a hot surface. Vapor rising from the acid condenses on the cooler part of the tube and runs back to the bottom. Parting can be done in this way with very small amounts of acid. Any silver nitrate crystallizing out should be dissolved by the addition of 1 or 2 drops of water. If palladium in appreciable amounts is present the parting acid will appear yellowish when viewed against a white background.

Add 6 ml. of strong hydrochloric acid, shake, and warm the test tube to dissolve the silver chloride. After the silver chloride has dissolved, heat the tube gently when the gold and platinum will quickly dissolve.

Since all the silver chloride is in solution, the dissolution of the gold and platinum is readily observed. Should any trace of residue remain, the presence of the more insoluble members of the platinum group is indicated.

Now add 1 ml. of stannous chloride and heat the contents of the tube almost to the boiling point; hold at that temperature for about 5 minutes, then cool. Add 5 ml. of benzene, close the tube and shake well, and titrate the platinum in the manner already described under the subject of standardization.

In the method as described 1 milligram of palladium if present in the bead would be returned as 1.83 milligrams of platinum, hence when palladium or other metals of the platinum group are present, the hydrobromic modification* of the method should be used.

It has been found that, when hydrobromic acid and stannous bromide are substituted for hydrochloric acid and stannous chloride, metallic palladium is precipitated with the gold and that neither rhodium or ruthenium interfere. The original method, however, is somewhat simpler and is, therefore, given first preference.

When it is desired to determine the amount of gold present in the same bead a second modification is given.

Notes. 1. Enough silver should be present in the bead to cause the parted platinum-gold residue to break up, since in this condition it is more readily soluble in aqua regia.

2. The nitric acid is limited to 2 drops since all nitric acid and nitrates must be eliminated before the titration can proceed. Tests with 0 and 2 drops respectively of nitric acid gave identical results. When 4 drops of nitric acid were used, 2 ml. of stannous chloride solution had to be employed since 1 ml. was not sufficient to reduce all the nitric acid to ammonia.

3. Tests made with platinum solutions from which nitrosyl compounds had not been removed proved that it is not necessary to remove them.

4. Tests have shown that small amounts of lead and of copper, traces of which might be present in the assay bead, cause no displacement of the end point.

5. As it is believed that the carbamate solution is somewhat sensitive to light, it is suggested that it be kept in a dark place when not in use.

6. Should an ore contain very large amounts of silver this would not dissolve in the amount of strong hydrochloric acid used in the assay. A preliminary sulphuric acid parting, followed if necessary by microfiltration, would remove the excess silver, after which the regular procedure should be followed.

7. Care should be taken to obtain a pure white paper to be used as a background during titration.

8. In place of a microburet, which costs $5.00, the writer has had good results with a much less expensive 2-ml. graduated pipet carrying on its upper end a short piece of rubber tubing capable of being closed and controlled with the aid of a glass bead.

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* "The Micro-Titration of Platinum in the Presence of Other Platinum Metals," *Bull. Inst. Mining Met.* July, 1938.

Volumetric Determination of Small Amounts of Platinum in the Presence of Other Platinum Metals

It has been found that, if bromides are substituted for chlorides in the method last described, palladium will be precipitated as metal by stannous bromide. The precipitated palladium joins the gold in the benzene layer and does not interfere with the platinum titration. Apart from the substitution of bromides for chlorides the method remains almost unchanged. The other metals of the platinum group which may be found in the bead do not interfere.

STANNOUS BROMIDE SOLUTION. Ten milliliters of hydrobromic acid (specific gravity 1.265) is put in a small beaker and 1 ml. of bromine added. The bromine quickly dissolves, forming a brown solution. A few pieces of granulated tin are then added to form yellow stannic bromide and to remove all traces of bromine.

A plug of glass wool is pushed to the bottom of a 25-ml. buret fitted with a rubber tube and pinchcock. (Glass taps were not found very satisfactory.) The buret is then filled with granulated tin.

The stannic bromide, free from bromine, is poured into the buret and the top tightly closed with a rubber stopper. The liquid is then left in contact with the tin until it has become colorless.

Any yellow liquid in the glass wool is drawn off and poured in at the top of the buret, which should be closed at once with the rubber stopper. The absence of any yellow color is an indication that the bromide is entirely in the stannous condition. The stannous bromide should never be allowed to drain completely from the buret. Fresh stannic bromide should always be added before this occurs. When required, the rubber cork should be removed so as to allow the solution to be drawn off.

HYDROBROMIC ACID. Acid of specific gravity 1.265 containing 30 per cent of hydrobromic acid should be used. The chief impurity to be avoided is arsenic, which causes the precipitation of metallic platinum in the presence of stannous bromide in a hot solution.

$$(a) \qquad 2AsBr_3 + 3SnBr_2 = 3SnBr_4 + 2As.$$

$$(b) \qquad 3PtBr_2 + 2As = 2AsBr_3 + 3Pt.$$

The reaction continues until all the platinum is precipitated. Tellurium acts in the same way but is an improbable impurity.

The acid can be obtained with an arsenic content as low as 0.0005 per cent and is entirely satisfactory. The arsenic can be detected by the Gutzeit test* but not by the Reinsch test. The following tests should also be made: One milliliter of decimal platinum solution is put in a

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* C. R. Fresenius, "Qualitative Chemical Analysis," J. and A. Churchill, London, Seventeenth Edition, Section 89, Par. 11 and 14.

test tube with 6 ml. of hydrobromic acid, 10 drops of stannous bromide is added, and the solution is titrated as described below. The test is then repeated, but the contents of the tube are heated up to the boiling point and kept at this temperature for 5 minutes after the addition of the stannous bromide. Insoluble matter should not separate. The tube is then cooled and titrated as before. The readings obtained in both titrations should be the same. If these conditions are fulfilled, the acid may be regarded as satisfactory.

Final Assay Procedure. The bead is dissolved in 2 drops of 1.26 specific gravity nitric acid as in the method last described. If palladium is present, the parting acid will be yellowish brown in color. Six milliliters of hydrobromic acid is added and the test tube shaken and warmed to dissolve the silver bromide first formed. After all the silver bromide has dissolved, the tube should be further carefully heated until bromine and nitrosyl bromide vapors begin to be evolved. It should be held at this temperature for about 5 minutes to effect the dissolution of all the gold and platinum. The dark color of the liquid may obscure this part of the process, but if the parted platinum and gold show a tendency to break up on nitric acid parting, its solution can be readily effected at this point by carefully following directions and avoiding undue loss of bromine by overheating.

A few small crystals of hydroxylamine hydrochloride are now added to the contents of the tube. This is to destroy the bromine and nitrosyl bromide. Nitrogen gas will be evolved, and the contents of the tube will become paler in color. Heat nearly to the boiling point; add a little more of the hydroxylamine hydrochloride until the liquid is pale yellow and other small additions cause no further evolution of gas. If bromine is not removed at this stage stannic bromide will be formed in the succeeding step, and this in large amounts colors the solution yellow and interferes with the end point of the titration.

If the contents of the tube are allowed to settle any insoluble residue can be readily detected, since the solution is now only faintly colored. Provided that the foregoing step has been properly performed an insoluble residue here is an indication of rhodium, iridium, or ruthenium.

After removal of all excess bromine, add 1 ml. of stannous bromide, heat the contents of the tube to boiling, and hold at this temperature for 5 minutes. Gold and palladium are precipitated as metals by this treatment, and platinum is reduced to platinous bromide, which colors the solution reddish brown, the intensity of which coloration affords a clear indication of the amount present.

Cool, add 5 ml. of benzene, and titrate the platinum in the manner already described.

Notes. 1. Hydrobromic acid is a very delicate test for copper. Should the bead have retained any copper, the addition of hydrobromic acid will cause a purple color to appear unless it is masked by palladium.

2. Owing to the small amount of damage caused in sampling, micro methods such as here described have an important advantage in testing precious-metal alloys such as jewelry and the like where it is not permitted to destroy the material tested. In this way it is akin to the assay for gold by a touchstone.

3. It would seem, by titrating beads from duplicate assays, one by the hydrochloric acid method which yields a measure of both platinum and palladium content, and the duplicate bead by the hydrobromic acid modification by which only the platinum content is found, that the palladium content could be found by difference.

Determination of Both Gold and Platinum

When it is desired to determine the amount of gold present in the same bead as the platinum, the gold precipitated by the stannous chloride is separated from the silver-bearing platinum solution on an immersion-type microfilter. The filter is made from a capillary glass tube 2 mm. in outside diameter and 0.5 to 1.0-mm. bore. One end is expanded into a funnel head similar to that of a thistle tube some 6 or 8 mm. in diameter. The filtering medium is a small plug of asbestos-wool. The tube has a double right-angle bend, the short arm of which passes through a double-hole rubber stopper which is inserted in a test tube similar to the one which contains the material to be filtered. A short length of glass tubing passes through the second hole in the rubber stopper and serves to connect the system with a vacuum pump.

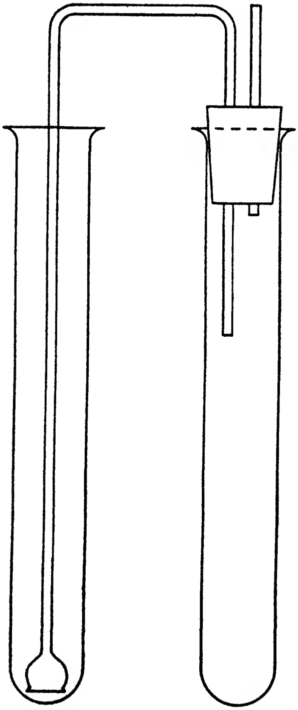

FIG. 55. Immersion-type Microfilter.

The prepared filter is inserted with its funnel head in the bottom of the test tube containing the precipitated gold, and the strongly colored platinous solution is drawn over into the second test tube. The sides of the first test tube are washed down with 2 ml. of strong hydrochloric acid which is run around the top of the tube from a small pipet. The washing acid is drawn through the filter into the second tube, which is afterwards disconnected from the filter and the contents titrated in the usual way.

This precipitated gold dissolves very readily in bromine water acidified with 2 drops of hydrochloric acid. By sucking the bromine solution through the filter, the gold is almost instantly dissolved. The dissolved gold can now be titrated by a method recently described by Pollard* or may be precipitated, collected, and inquarted with silver on a cupel, parted, and weighed in the ordinary manner. So far as the gold determination is concerned the advantage of the volumetric method is in the substitution of a microburet costing a few dollars for a high-grade gold balance which costs several hundred dollars. Where many such determinations are to be made, the volumetric method would have the advantage since once the solutions are prepared and the procedure established it is easier to dissolve the gold and titrate it than to collect and weigh it.

THE DETERMINATION OF SILVER IN ORES, CONCENTRATES, WASTES, AND ALLOYS CONTAINING PLATINUM AND PALLADIUM

The silver in ores, concentrates, and simple alloys containing only gold and platinum is usually determined by cupellation followed by sulphuric acid parting; but when palladium is present, or high accuracy is required for any reason, a different method may be required.

The high cupellation temperature employed with platinum alloys causes high and sometimes irregular losses of silver, and to a lesser extent of gold and platinum, none of which losses are necessarily properly corrected by means of checks. The presence of gold and platinum affects the amount of lead retained in the beads. The corrections for added gold and silver and the uncertainties connected with the behavior of these in cupellation and in sulphuric acid parting further complicate the cupellation process, so that even in the absence of palladium, where reliable silver results are essential, a special assay for silver is best.

The method used by A. M. Smoot† has been found reliable, and his method is here described with minor modifications.

Procedure. Make the usual crucible fusion on ¼, ½ or 1 assay ton, according to the amount of silver present. In some cases, scorification would be indicated as a starting method rather than crucible fusion. Instead of cupeling the lead button, hammer it free from slag and dissolve it in dilute nitric acid. Most of the silver passes into solution together with the palladium and a small proportion of the platinum. The gold and most of the platinum, together with a small fraction of the silver, remain undissolved. Filter out the insoluble residue and

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* *Analyst*, **62**, 597 (1937).

† *Eng. Mining J.* **99**, 701 (1915).

wash it thoroughly with hot, dilute nitric acid, followed by hot water. Scorify the residue once with a little lead, and dissolve the lead button as before, filtering into the beaker containing the first filtrate. The silver in the combined filtrates is precipitated as chloride* by the slow addition of a limited quantity of dilute hydrochloric acid with constant stirring. If the amount of silver is small, so that difficulty in settling and filtering is anticipated, add about ½ ml. of strong sulphuric acid to form a precipitate of lead sulphate. Allow to settle over night, or until the supernatant liquid is clear, filter through double filter papers, and wash.

The filter paper containing the silver chloride is burned off at a low temperature, observing precautions appearing elsewhere in this text, and the residue is scorified with lead. If the amount of palladium contained in the sample is small, the silver bead obtained by cupeling this lead button may be considered sufficiently pure for ordinary purposes. It contains some palladium, and for a more accurate silver determination the lead button resulting from scorifying the first silver chloride precipitate should be redissolved and the silver reprecipitated. This is filtered and scorified as before, and the lead button is cupeled. The amount of palladium retained after the second precipitation is so small as to be negligible. Correction assays for slag loss, solubility, and cupel absorption may be carried through and corrections applied, if desired.

ASSAY OF ORES AND OTHER MATERIAL CONTAINING IRIDIUM, IRIDOSMIUM, RHODIUM, AND RUTHENIUM

When ores containing iridium, iridosmium, rhodium, and ruthenium are fused with lead under the right conditions, the rhodium will be alloyed with the lead, but the other metals either will remain practically unattacked or will form with iron a separate alloy containing no lead. The iridosmium and the unattacked iridium, because of their high specific gravity, will sink through the molten lead to the very bottom of the crucible. When it is desired to recover these metals the assay slag should be neutral, the fusion should be of a reducing nature, and the crucible should preferably be removed from the furnace without agitating the contents, and left to cool. If the charge is poured, there is danger of a loss of some of these metals; but if the contents of the crucible are cooled, without agitation, they are held mechanically by the lead.

When the lead button containing these metals is cupeled, the iridium and iridosmium sink to the bottom of the lead and some of the fine particles may be lost on the cupel. That which remains will be found near the bottom of the bead of precious metals. When the presence

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* Based on the fact that $PbCl_2$ is almost 10,000 times as soluble as AgCl.

of iridium or iridosmium is suspected, it is advisable to clean the lower surface of the bead by immersing it in hydrochloric acid to remove all bone ash, rather than to brush it, as that might serve to detach some of the fine particles. The rhodium in the lead button, because of its lower density, will be distributed throughout the final precious-metal bead. Part of the rhodium and ruthenium will be oxidized during cupellation, giving the surface of the bead a bluish black color; the remainder will be distributed throughout the bead.

When the bead or cornet is parted in nitric acid, in the ordinary manner, the residue, in addition to gold, will contain all the iridium and the iridosmium which the bead contained, as well as most of the rhodium and ruthenium. These will ordinarily be weighed and reported as gold, and in most ore analyses these metals are so small in amount that it makes little material difference if this is done. Some sweeps or other manufacturer's wastes, however, contain appreciable quantities of the first three of these constituents, and when they do, a separation may be justified, particularly for the reason that iridium and rhodium are worth so much more than gold.

Estimation of Iridium, Iridosmium, and Rhodium in Gold Cornets. After the cornet, dried but not annealed, is weighed, it is treated with 20 per cent aqua regia as long as chemical action continues. This dissolves the gold and any residual platinum or palladium, but has practically no effect on the rest of the metals of the platinum group. Wash, ignite, and weigh the residue, which now consists of iridium, iridosmium, and rhodium as well as any ruthenium which escaped oxidation during cupellation.

To confirm the reliability of this separation, the aqua regia solution may be evaporated and re-treated with hydrochloric acid to insure removal of all nitric acid, and then diluted and the gold precipitated with hydroquinone. The precipitate obtained is washed, dried, and weighed.

It should be evident, from the description, that the method given here for the determination of iridium, etc., is a proximate one, with the advantage that it is fairly simple. For material such as black sands and relatively low-grade wastes, it is sufficiently accurate for most commercial purposes. To control the sale of large quantities of high-grade wastes, or for the assay of alloys containing large proportions of the platinum-group metals, more accurate methods involving a greater expenditure of time and money are warranted. One method of this sort, inasmuch as it starts with a fusion with lead, is described under the title "Determination of Iridium in Platinum Alloys." Most of these more exact methods, however, deal mainly with wet chemistry and are not relevant to a textbook dealing with fire assaying and are therefore not included here. For descriptions of these the student is referred to the standard authorities on quantitative analysis.

DETERMINATION OF IRIDIUM IN PLATINUM ALLOYS

This method depends upon a discovery of Deville that when platinum alloyed with iridium, rhodium, palladium, iron, and copper was fused with lead at a high temperature he was able to effect a very distinct separation of the platinum metals. All the platinum, palladium, rhodium, and copper alloyed with the lead. The iridium, ruthenium, and iron formed a separate alloy containing no lead. Boiling dilute nitric acid removed the bulk of the lead, together with the palladium and copper and a small proportion of the platinum and rhodium. Digestion of the residue with warm, dilute aqua regia left insoluble only the alloy of iridium, ruthenium, and iron.

Gilchrist* studied the details of this method, using specially prepared alloys made from highly purified metals, and confirmed the quantitative separation of iridium and ruthenium from the rest of the platinum group by this method. Gold was found not to interfere. Iron separates nearly quantitatively with the iridium. His modified procedure for the method is given below together with some discussion.

Lead Fusion. Fuse the carefully sampled platinum alloy with 10 times its weight of granular test lead for a period of 1 hour at a temperature of about 1000°C. A covered crucible, whose outside dimensions are 1½ inches in diameter and 2½ inches in height, machined from Acheson graphite, is suitable for fusions using from 20 to 40 grams of lead. The inside of the crucible should possess a slight taper to facilitate the removal of the cooled ingot. Do not pour the fusion from the crucible, but allow it to solidify, since the iridium will have largely settled to the bottom of the melt. The crucible is best heated in an electric furnace.

Disintegration with Nitric Acid. Brush the cooled lead ingot free from carbon with a camel's-hair brush, and place it in a beaker. Add nitric acid of the concentration 1 volume of acid (specific gravity 1.42) to 4 volumes of water, using 1 ml. of acid per gram of lead. Place the beaker on the water bath or on a hot plate which will maintain the temperature of the solution at about 85°C. Disintegration of the lead ingot is usually complete in about 2 hours, leaving a rather voluminous grayish black mass. Dilute the solution to twice its volume and decant the liquid through a double filter, consisting of 9-cm. paper of fine texture, such as S. & S. No. 589 blue ribbon filter, on which is superimposed a

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* *Scientific Paper* 483, U. S. Bureau of Standards, **19**, 325–345 (1924).

7-cm. paper of looser texture, such as No. 589 black ribbon. Wash the residue quite thoroughly with hot water and pass the washings through the filters. The residue is not transferred to the filters at this point. The lead nitrate solutions and washings are best caught in an Erlenmeyer flask to make it easier to detect the presence of any residue which has passed through the filters. This is done by whirling the liquid in the flask. Any particles of the residue collect at the center of the bottom of the flask. Return the filters to the beaker without ignition.

Solution of the Lead-Platinum Alloy by Aqua Regia. Add in order 15 ml. of water, 5 ml. of hydrochloric acid (specific gravity 1.18), and 0.8 ml. nitric acid (specific gravity 1.42) for each gram of platinum alloy taken. Heat the solution in the beaker on the water bath or on a hot plate which will maintain the temperature at about 85°C. The lead-platinum alloy is usually completely dissolved within 1½ hours. Dilute the solution with twice its volume of water and filter through a double filter, similar to the one used for the lead nitrate solution. The iridium, insoluble in the aqua regia, will be in the form of fine crystals, possessing a bright metallic luster and having a high density. Pass the clear solution through the filter first, and then transfer the thoroughly macerated paper. It is very important to examine the beaker to see that no iridium remains. To do this wipe the interior of the beaker with a piece of filter paper to collect any metal adhering to the sides. Then, whirling a small quantity of water in the beaker causes any remaining iridium to gravitate toward one place, whence it can be removed with a piece of paper. Wash the filters and iridium thoroughly, first with hot water, then with hot dilute hydrochloric acid (1 : 100), and lastly with hot water. The chloroplatinic acid filtrate and washings should be examined for iridium which may have passed through the filters in the manner described under the nitric acid treatment. The last washings should be tested for the absence of lead.

Ignition and Reduction of the Iridium. Place the washed filters and iridium in a porcelain crucible and dry before igniting in air. After the destruction of the filter paper ignite the iridium strongly with the full heat of a Tirrill burner. After all carbon is burned out, cover the crucible with a Rose lid, preferably of quartz. Introduce into the crucible a stream of hydrogen, burning from the tip of a Rose delivery tube (a quartz tube is preferred). After 5 minutes remove the burner, and a few minutes later extinguish the hydrogen flame by momentarily breaking the current of hydrogen. This is best done by having a section of the rubber delivery tube replaced by a glass tube, one end of which can easily be disconnected. Allow the iridium to cool in an atmosphere of hydrogen and then weigh as metallic iridium.

Notes. 1. The residue consists of iridium and any ruthenium which may have been present in the original alloy, together with most of the iron.

2. In commercial analyses no effort is made to correct the weight of iridium for small amounts of ruthenium.

3. A very small part of the iridium may go into solution during the aqua regia treatment, but the loss is negligible.

4. A small amount of insoluble matter may be introduced into the iridium during the analysis, and when dealing with small amounts of iridium blank analyses should be run to provide data for a correction for this error. Gilchrist ran blank analyses using 40 grams of test lead and obtained residues weighing 0.5 milligram.

5. Two methods of correcting for the iron are suggested. (*a*) The iron is determined in a separate sample of the alloy. (*b*) The other method involves the fusion of the iridium residue with pure zinc in a quartz crucible. The iridium forms a zinc-iridium alloy which is insoluble in dilute hydrochloric acid, which is used to dissolve the zinc and iron. The insoluble portion is washed by decantation through a filter, the filter is ignited in a porcelain crucible, and then the main portion of the zinc-iridium alloy is added and dried. The dried material is fused with potassium pyrosulphate to render the zinc soluble. After disintegration with very dilute sulphuric acid the material is filtered and washed with hot dilute ammonium chloride solution. The filter paper containing the iridium is carefully dried, charred in hydrogen, and ignited in air. The ignited residue is treated to remove silica, ignited in an atmosphere of hydrogen and weighed. For complete details as to methods for this correction see Gilchrist's original article, pages 340–341.

CHAPTER XIV

PRACTICAL ASSAYING

The main purpose of this book is to provide for the college student a scientific approach to the ancient art of fire assaying. He is presumably working in groups of considerable size with the assistance of a laboratory instructor, and his laboratory work and assigned reading are supplemented by lectures. Certain features which the author has chosen to present to his own students in lecture form have been purposely omitted from previous editions of this textbook. For the considerable group of persons who are forced to learn the essentials of fire assaying from textbooks alone it has been decided to attempt to make up for some of the omissions of past editions, and, without going back to the old rule-of-thumb approach, to try to help them by gathering together numerous odd ends of the subject which now appear in other chapters of the book. The beginner who is attempting to educate himself finds difficulty particularly in the calculation of crucible charges. An attempt will be made to find a way around this difficulty.

Because of the limitations of time and more specifically because none of his students aspire to become routine analysts, no attempt to develop any great amount of speed has been contemplated in the author's teaching. It is recognized, however, that the young graduate may very likely and profitably spend some time in the assay office before advancing to the operating work of some mine, mill, or smelter. There are included here a number of matters which may be of assistance to such a man or to one who finds himself in the position of chief assayer with the responsibilities which that involves.

REQUIREMENTS IN COMMERCIAL ASSAYING

In the regular routine of any commercial assay laboratory a large volume of work must be handled with a minimum of personal attention and with no lost motion, since both speed and expense must be taken into consideration. Whether the laboratory is a one-man one-shift affair, or a twenty-four-hour continuous plant employing some two dozen men and turning out 1200 to 1500 determinations a day, the work must be carefully standardized and the various operations well coordinated to accomplish the purpose for which it is established — a maximum of service at a minimum cost. The element of time is important. In a custom laboratory, samples brought in one day must be assayed and reports delivered the following day. In a mine where stoping or chute drawing is governed by the results of assays, samples brought in some time before noon must be assayed and reports prepared for the foreman before he goes off shift in the afternoon. The young graduate thrown on his own resources in a small mine or smelter laboratory will have his hands full for the first several months until he learns exactly how to plan his work and make every moment and movement count. He will soon learn how to keep everything moving and, by concentrating on the work and giving attention to securing accuracy through discovery and elimination of those features of defective manipulation or procedure which lead to avoidable errors, he will quickly gain in skill and power of independent work with consequent increase of productive capacity without sacrifice of precision.

Starting with a thorough knowledge of the underlying principles and provided with suitable apparatus and facilities, any capable man can by application and practice master the small but valuable details of manipulation which make for avoidance of errors and accomplishment of the most work with the least effort. System, order, and cleanliness are indispensable. Assayers may be required to make from 40 to 80 determinations in a day, and to accomplish this they must not only possess skill, which comes with practice, but must also carry through the various operations of pulping, fluxing, fusing, cupeling, parting, and weighing in as large batches as can be handled with the muffles and other equipment available. They must adhere to some system and order of work which eliminates the necessity for marking assay vessels so that a large amount of work can be done in a limited time without confusion of samples or sacrifice of accuracy. Much of what follows in this chapter will deal with individual items which bear on this question of routine assaying.

VARYING DEGREES OF PRECISION

Depending upon the purpose for which the assay is made, the practice has developed, particularly in the western part of the United States, of making assays with different degrees of care and with different degrees of precision. In custom laboratories these are known as specimen, control, and umpire assays. Specimen assays are those ordinarily made on hand specimens from any source as well as on face and car or muck samples for control of underground mining where the utmost accuracy is not required. Control assays are in general used to establish the value of ores changing hands in the process of marketing or for greater certainty in underground control and in important ore-testing work as well as for internal mill and smelter control. Such assays must always be made in duplicate or triplicate to increase the precision and to reduce the possibility of a variety of errors of chance or of technique. Samples for control assay are more carefully prepared than those for specimen determinations. Where control assays between buyer and seller do not agree within reasonable "splitting limits," recourse is had to some particularly reputable assayer who presumably takes still more pains to attain the maximum of precision in his results, which are usually accepted as final in making settlements.

The prices for these three grades of assays are usually in geometric proportion, *i.e.*, 1, 2, and 4 dollars, respectively, or some multiple, and presumably the time and material spent in obtaining the results are in like proportion. In the eastern part of the United States there is less demand for specimen assays, and many custom assayers do not care to jeopardize their reputations by undertaking to do such, to them, cut-price assaying.

PREPARATION OF SAMPLES

Samples delivered to the assay office may vary in weight from a few ounces of pulp already prepared for control or umpire assaying, to lots of 100 or more pounds of lump ore which will require drying, crushing, sampling, pulping, and further sampling before they are ready to be spread out before the pulp balance for weighing up charges.

Some simple form of marking and maintaining the identity of samples and assays of same in various stages is essential and will result in the saving of much time. This will be referred to later on. A suitable arrangement of assay office and equipment will greatly facilitate the work of any laboratory, but it is most evident in large laboratories.

In gold and silver mines when stoping or drawing is controlled by the results of assays of face, muck, or car samples the utmost accuracy is not so important as economy in time and cost. For this reason some liberties are taken with respect to the principles of sampling, or it might be more exact to say that a 5 or 10 per cent error in sampling is acceptable instead of the more common 1 per cent. This permits of a very large reduction in the safe weight of sample cut out after any definite crushing operation and corresponding saving of time and effort in crushing and grinding. By far the greatest saving of time in the preparation of samples comes in the omission of screening the pulverized sample to insure that it all will pass 100-mesh or some other limiting screen. This last is absolutely necessary for all control samples but is customarily omitted in specimen determinations and work of like grade. Careful screen sizing with inspection for and handling of "metallics" is the greatest single time-consuming operation in fire assaying, and the omission of this one feature may well result in saving some 5 or 10 cents per assay. In a laboratory handling 1000 samples a day this $50 to $100 a day saving is too large for any manager to overlook. To overcome some of the objections to this method of sample preparation some mining companies supply their underground sampling staff with two colors of tags. For instance, the ordinary sample is marked with a white tag but especially important ones are given a colored tag, which calls for somewhat more care in preparation and for duplicate assays.

One recent important development in assay laboratory practice is the recognition of the harmful effect of long-continued breathing of the mineral and chemical dusts and fumes to which the assay staff is exposed. Not only should the crushing rooms be ventilated by means of exhaust fans capable of quickly changing the air, but also the crushers and pulverizers should be provided with suitable hoods or entirely closed-in dust boxes which are likewise connected with an exhaust system of even higher vacuum. The tables where the ore is mixed previous to weighing should be ventilated, and the mixing of flux and ore, at which stage the lead-dust hazard commences, should be performed in a suitably ventilated cabinet or hood. The furnace room too requires ventilation to remove fumes and to carry off excess heat.

AVOIDANCE OF CONFUSION OF SAMPLES

Small numbered brass or copper tags which can be placed in the pan of assay pulp provide a convenient means of identification, but from the time the pulp is placed in the crucible to the final weighing and computation of assay results some other method of keeping track of things must be adopted. It is a waste of time to mark all the various crucibles, cupels, parting cups, etc., and hence it is not done. Instead the assayer adopts some system dependent upon orderly arrangement and definite sequence which can be learned in a few days. Obviously this order must be adhered to by everybody handling the work, and one of the problems of the chief assayer at a large laboratory is to put such a system into operation and then to devise some means of checking to insure against any breakdown of it.

The system usually adopted depends primarily on keeping the work progressing in batches the size of which is governed by the number of crucibles which can be placed in the muffle at one time. Crucibles come to the pulp balance in numbered trays which are designed to hold one muffle charge. If the muffle holds six rows of four crucibles each, the trays will correspond in capacity and arrangement. Here, in the furnace and throughout its entire progress through the process, the sample is known by its relative position.

Outside of the furnace the samples may conveniently be arranged in the order of the written page, *i.e.*, left to right and top to bottom. This applies to charges ready for the furnace, melts in pouring molds, lead buttons, cupels, parting cups, etc. Inside of the furnace it is convenient to use a reverse order so far as rows go but to maintain the left-to-right arrangement.

For example, if the muffle holds six rows of four crucibles each, the order outside the furnace will be as illustrated below:

1	2	3	4
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—
21	22	23	24

intervening numbers being represented by dashes. It is convenient to weigh out the charges, add extra reagents, and mix in orderly sequence from 1 to 24.

In charging the crucibles into the muffle it is convenient to reverse the order, placing crucible 24 in the right-hand back corner of the muffle and continuing the sequence until crucible 1 is placed in the left front corner, thus:

21	22	23	24
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—
1	2	3	4

This enables one in pouring to start with crucible 1 and to return to the normal order of the printed page with fusions in the slag molds. In order to carry out the scheme of identification by position, slag molds as well as trays for lead buttons, cupels, and parting cups should permit of the same general order and arrangement as the muffle.

This system makes it possible for one to tell at any time just which sample is contained in any vessel at any stage of the work. If an accident occurs, from any cause, a note is made in the record, but in order to retain the regular arrangement even though the assay is lost the system is maintained by carrying through an empty mold, cupel, and parting cup just as if the assay were satisfactory. This reverse-order system provides for transferring crucibles, scorifiers, cupels, etc., to and from the muffle with the least difficulty.

A similar system of sequence and placement of batches throughout the various stages must be developed to avoid confusion in the numerous lots which may be in process in a large laboratory.

A large proportion of the errors which occur in routine work are due to a momentary failure of someone to abide by the system adopted. The result is interchange of two or more trays or of assays within a single batch in some stage of the process. Practically everyone is subject to such lapses at times, and the system to be described is designed to show at a glance when such errors have been made. Particularly when a large number of persons are working on the same batch, some check is necessary.

Because Rand gold ores contain practically no copper an ingenious method for detecting misplacements has been developed there.* It depends upon the addition of small quantities of copper in the form of wire or foil to certain of the crucibles in each lot in accordance with some predetermined pattern. A different pattern is adopted for each succeeding lot of crucibles during the day's work. If the cupels corresponding with any lot of fusions present the adopted pattern in stains it is rather conclusive evidence that no mistakes have occurred. The double copper stain check uses additions of both 50 and 100 milligrams of copper, resulting in unmistakable light and dark stains respectively. When fusions are made in lots of 24, no less than 1152 assays may be conducted without fear of confusion with the aid of the double copper stain check system. The main advantage of such a check system is that fewer mistakes are made when assistants know that blunders will advertise themselves. The chief assayer's confidence in results for which he is responsible is further advanced by the fact that interchange of trays is immediately detected.

Another method of checking routine work is by means of blanks. It does not so completely enable the detection of the misplacement of individual crucibles, cupels, or parting cups but it does prevent the mixing of whole lots. In this system each tray carries one blank crucible containing only flux. Its position in the tray identifies the number of the tray. When fusions are made in lots of 24 crucibles at a time, No. 4 blank signifies No. 4 tray, and so on up to No. 24, after which the series repeats. After the fusions are poured in the molds and the slag is cooled the blank is recognized by its clear color. After cupellation, the blank is easily recognized by the absence of a silver bead on the cupel. In

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* H. Monckton, "Notes on Routine Mine Sample Assaying." *J. Chem. Met. Mining Soc. S. Africa,* **8,** 54 (August, 1907).

parting, which is done in lots of 24, the parting cup corresponding to the blank in the cupel tray is turned bottom up and again indicates the number of the batch.

ASSAY OFFICE RECORDS

Whether it is a custom or a mine assay office a careful record should be made of all samples received for assay and of the results obtained. Such a record is usually kept in a "sample book," and all samples may well be given a running number never to be repeated. By so numbering all samples and, of course, by dating all records it is possible to reproduce an assay certificate even after the lapse of years. Custom assayers will naturally record the name of the client and should include a description of the sample. Mine assay records vary somewhat from this for obvious reasons.

The form of laboratory record on pages 300-301 has been found generally satisfactory for routine assay work under the system described here, although it is not sufficiently complete for a student's record. The first assay made each day is numbered 1, and each succeeding assay is numbered in sequence or each tray is numbered similarly. The records may be kept in a large notebook or, where the tray system is used, there is usually a separate record sheet for each tray.

DIRECTIONS FOR ASSAY FLUXING

It should be said at the outset that no two assayers working on the same ore will agree exactly on the flux proportions to use, so that it is safe to say that for any given ore there is a comparatively wide range within which the four common flux constituents may be varied and still, in the hands of an able assayer, yield practically identical results. It is fortunate that this is so since we seldom know very exactly the composition of the material we are called upon to assay and if each different ore combination required a different proportion of the different fluxes we would always be pretty much at sea. Instead, we know that different assayers working on duplicate samples of ore pulp, each employing his own method of fluxing, are obtaining substantially identical results in a large majority of cases. This is being demonstrated thousands of times each day in assay comparisons required in connection with settlements for shipments changing hands at different smelters and custom mills. This does not mean, however, that there is not one best flux proportion, lead-fall, fusion time, and temperature control that will give slightly lower slag and volatilization loss accompanied by higher recovery in the lead button than any other condition. The writer is of the opinion that there is one such optimum condition. Nevertheless, all assayers recog-

LABORATORY

X.Y.Z. Mine Assay

Tray No.______________

Assay No.	Mark	Mineral Composition	Wt. Ore A.T.	Type Flux	Red. Flux	Ox. Flux	Xtra PbO	Xtra B.G.	Xtra SiO_2
1				A					
2				B					

nize that the benefit derived from some slight gain during this stage of the assay may be easily rendered of no avail by some offsetting subsequent loss in some other stage of the assay, as for example an unduly high cupeling temperature. The best we can hope to accomplish in commercial work is to attain some happy medium between economy of materials and time on the one hand and the ideal perfection of theory and practice on the other hand.

The known principles and something of the practice relating to the conduct of fire assays have been covered in the earlier chapters of this book, and it is not intended to repeat them here. It may be of some help, however, to summarize some of the rules which must be followed and some of the broad principles which should be observed if satisfactory results are to be expected, and nothing stated here or hereafter should be interpreted as denying the fact that the more we know as to the composition of the ore to be assayed and of the reactions which take place between ore minerals and assay reagents, the better should be the chances for attainment of satisfactory assay results. With this qualification, the following rules are offered, first as a guide in the determination of assay flux requirements for any given ore, and second as a check on a charge which the student may have worked out by following some other source of directions for assay fluxing.

General Rules for All Gold and Silver Crucible Charges. 1. Always use at least as much alkaline carbonate as ore.

2. Always use at least two and one-half or three times as much " active " flux as ore.

3. Always plan to obtain at least a 28-gram lead button.

4. For Class 1 and Class 3 ores, *i.e.*, neutral or oxidizing in character, aim to make a bisilicate slag.

5. For Class 2, pure ores, if reducing power is greater than 1.0, aim for a monosilicate slag.

6. For Class 2, impure ores, aim for a subsilicate slag using mainly litharge to provide the additional basic material.

RECORD

Office Record

Date________________________

Wt. Doré	Wt. Au	Wt. Ag	Oz. per Ton		Notes on Conduct of Assay. Remarks
			Au	Ag	

7. Use a minimum of 7.5 grams of borax per half assay ton of any ore, and as much more as judgment or experience indicates for the specific ore to be assayed.

Notes and Comments. The following notes and comments may serve to clarify and amplify the foregoing rules. The numbers correspond to the corresponding numbers above.

1. No assayer uses less than 15 grams and some use as much as 35 grams of alkaline carbonate, usually soda, for ½-assay-ton ore charge.

2. By "active" flux is meant that part of the flux which reports in the slag; hence that part of the litharge which is reduced to metallic lead to serve as a collecting agent, and that part of the alkaline carbonate which is decomposed to form sulphate, are not "active" fluxes.

3. With exceptionally rich ores, large ore charges, high-litharge and iron-nail assays, larger lead buttons are required to obtain the best recoveries. For 2-assay-ton charges lead buttons should weigh 35 to 40 grams. For underground grab samples where the greatest accuracy is not required and economies of time, furnace space, and material are considered paramount some liberties may be taken with the amount of lead-fall, for instance an 18- or 20-gram lead button from ½-assay-ton ore may be thought satisfactory.

4. For Class 1, acid ores, rule 4 makes for economy of reagents and extends the life of crucibles. For Class 1 or Class 3 basic ores it makes for better slags of lower fusion temperature and helps to insure complete decomposition with consequent better recoveries.

5. All Class 2 ores call for curtailing the amount of carbonaceous reducing agent. For assay-ton charges of ore having a reducing power greater than 1.0, and for ½-assay-ton charges of ore of reducing power greater than 2.0, the addition of niter is required to avoid obtaining too large lead buttons.

6. Impure ores require more excess litharge to enable the slag to dissolve the impurities present. As the litharge content of the slag is increased the size of the lead button should also be increased.

TIME AND LABOR SAVING

If many assays are to be made on ore of about the same character it is neither necessary nor desirable to take the time to weigh out each individual unit of flux. Instead, flux mixtures are made up and then a unit weight of one of these mixtures 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.

No one flux mixture will serve all ores, but since all assays require a minimum of soda, borax, and litharge, such a flux will serve as a start even for the general laboratory which receives the greatest variety of ores for assay. By adding extra litharge, borax, and silica as indicated by the character of the ore, together with suitable quantities of reducing or oxidizing agents, a mixture suited to any combination of ore minerals is quickly assembled, leaving nothing to be weighed but the ore itself.

Either flour alone or a reducing flux consisting of flour mixed with soda can be measured out with sufficient accuracy to provide a lead button of the right size, provided, of course, that the reducing effect of the ore itself is known or correctly estimated.

When a number of niter assays are to be made it will be found convenient to provide an oxidizing flux mixture consisting of niter and sodium carbonate. Some assayers include a certain proportion of borax glass, silica, and litharge in such a mixture. By increasing the bulk of the oxidizing agent we cut down the unit oxidizing effect, which facilitates the addition of the correct quantity of niter by means of graduated scoops. The incorporation of sodium carbonate in this mixture has the additional advantage that the quantity of sodium carbonate in the charge is automatically increased as the reducing power of the ore increases, thus providing sodium oxide, to combine with the sulphuric anhydride formed by the oxidation of the sulphur of the ore. The addition of borax glass, silica, and litharge to the oxidizing flux serves likewise to increase these constituents automatically if in the opinion of the chief assayer such additions are desirable. Most assayers will probably agree that as the sulphide content of an ore charge increases it is logical to increase the alkaline content of the slag other than for the reason given above and also to increase the litharge content. Both these reagents are considered to help in the complete decomposition of the sulphides, and the litharge, if not entirely required in the fluxing of silica, will aid in holding the probably increased quantity of impurities in the slag, resulting in a cleaner lead button for cupellation.

ASSAY FLUXING IN ROUTINE ASSAYING

Classification of Ores for Routine Assay Fluxing. Most ores and mill products which are subject to routine assaying fall into one of four general divisions of which the first is the most common and the last is relatively rare. These are (1) siliceous ores; (2) sulphide ores, with galena, pyrite, and sphalerite predominating and classed as pure ores; (3) sulphide ores with or without the three above-mentioned sulphides, but with appreciable amounts of sulphides of copper, nickel, cobalt, arsenic, antimony, or bismuth classed as impure ores; and (4) basic ores with a preponderance of hematite, calcite, or dolomite. This last group may be either neutral, oxidizing, or slightly reducing in action.

Of the two commonly used crucible assay methods for gold and silver in ores the excess litharge method is quite generally used in North America for all the above general classes of ore. The method in which only sufficient litharge is used to give the required size of lead button, metallic iron in some form being added to the charge with sulphide ores is more commonly used in Europe, Africa, India, and some parts of South America for all except the impure ores of the third class above.

Using the excess litharge method and having regard for expense by holding down the quantity of the most expensive reagent, litharge, it is possible to start with a single stock flux in assaying any of the four above-mentioned classes of ore and to add to the crucibles requiring it such other reagents as are needed by the individual ores. Ores containing a small percentage of sulphides require less reducing flux; ores containing a large percentage of sulphides require no reducing flux but do require the addition of niter with a moderate amount of extra litharge. Impure ores need an additional amount of litharge. Basic ores require the addition of silica and extra borax glass.

Regular Flux. For the sake of consistency, so that the proportion of lead oxide in the slag shall be the same for both ½- and 1-assay-ton charges, two different flux mixtures are suggested for these two different quantities of ore.

For ½-A.T. Ore Charges		For 1-A.T. Ore Charges	
A		*B*	
Sodium carbonate	15 parts	Sodium carbonate	30 parts
Borax	7.5 parts	Borax	15 parts
Litharge	45 parts	Litharge	60 parts
	67.5		105

Use 67.5 grams of *A* for ½-assay-ton ore charges and 105 grams of *B* for 1-assay-ton ore charges. For convenience make scoops or standardize porcelain crucibles or capsules to deliver these quantities of the above flux mixtures, and always keep the measures in the respective flux containers. Using these quantities of reagents and the appropriate amount of reducing flux to yield a 28-gram lead button will give a ratio of

" active " flux to ore of about 2.85 to 1, which is within the limits of general rule 2 given for all crucible charges.

In mine laboratories having to deal largely with ores of low and uniform sulphide content the proper amount of reducing agent will naturally be incorporated in the regular flux, thus reducing by one the operations required in the assay process. Where gold only is to be determined, a suitable proportion of silver, usually in the form of chloride, is also well mixed with the flux, and this again reduces and simplifies the operations to be performed.

Reducing and Oxidizing Fluxes. In smelter and other laboratories where ores of all degrees of reducing power have to be assayed it will be found convenient to have a supply of both reducing and oxidizing fluxes to be added to each crucible according to the demands of the ore. The following have been found satisfactory. The ingredients should be well mixed by stirring or rolling after a preliminary elimination of lumps. A final mixing by screening is recommended to insure uniformity.

	REDUCING	OXIDIZING
Sodium carbonate	3000 grams	1000 grams
Borax glass	0	1000 "
Flour	1000 "	0
Potassium nitrate (granular)	0	2500 "
Silica (granular)	0	1000 "

The reducing flux has several advantages over flour used alone. It is more bulky and less compressible, so that the required amount can be measured in scoops with greater precision, and because of the added soda it does not attract mice. Obviously, too, a quartzose ore with no sulphides contains more silica and yields no compensating bases from oxidation of sulphides to assist in fluxing the acid of the ore. Requiring the maximum quantity of reducing flux the diluting soda will help to balance the extra silica, thus killing two birds with one stone.

It will be observed that $9\frac{1}{3}$ grams of this reducing flux will contain $2\frac{1}{3}$ grams of flour, which is just sufficient to yield a 28-gram button since flour can be counted on to have a reducing power of 12. The additional 7 grams of sodium carbonate are available as basic flux. Since the reducing effect of ores containing minor amounts of sulphides is usually estimated after vanning a sample of the ore, it is customary and obviously equally exact to measure out the reducing flux with a special set of scoops or a graduated scoop.

The oxidizing flux may seem at first glance to be of unduly complex composition. If the reader will refer to the discussion and computations relating to the niter assay in Chapter VIII he will be reminded first that extra sodium carbonate has to be added in proportion to the niter which is used if the sodium oxide content of the slag is to be held constant. This is accomplished by the addition of sodium carbonate to the oxidizing flux. Second, as the sulphides in the ore increase, the base metals iron, zinc, etc., associated with them necessarily also increase while the silica must naturally decrease. For this reason it is both logical and necessary to add both borax glass and silica in the assay of high-sulphide ores and by the use of the above oxidizing flux these additions become automatic with the addition of niter and are made proportional to the necessary niter. Thus we condense four necessary additional operations into one.

In those assays which require the addition of an oxidizing agent to control properly the size of the lead button, the assayer is likely to have made a preliminary or reducing power fusion since the estimation of high reducing powers is none too simple and in that case the oxidizing flux may well be weighed out rather than measured in a scoop. The dilution is such that the oxidizing effect of 1 gram of the flux serves to prevent the reduction of about 1.9 grams of lead, and with this small oxidizing power the flux balance is sufficiently accurate, which materially simplifies the operation of weighing. There is no reason, however, why a scoop may not be used for this purpose if the operator prefers it.

Provided with the above fluxes together with extra litharge, which may be measured with a scoop, and very occasionally extra borax glass

	1	2	3	4
Composition	Generally siliceous	20% pyrite siliceous	35–60% sulphides	75–90% sulphides
Reducing power	none	2.0	4.0	8.0
Wt. ore	0.5 A.T.	0.5 A.T.	0.5 A.T.	0.5 A.T.
Flux *A*	67.5 g.	67.5 g.	67.5 g.	67.5 g.
Reducing flux	9⅓ g.	..	..	..
Oxidizing flux	..	..	16	46
Extra litharge	..	15	15–30	15–45

	5	6	7	8
Composition	Low-grade impure	Pure Fe_2O_3	Limestone	Fire clay
Reducing power	4 to 6	none	none	none
Wt. ore	1 A.T.	1 A.T.	1 A.T.	1 A.T.
Flux *B*	105 g.	105 g.	105 g.	105 g.
Reducing flux	..	(Flour 5.5g.)	9⅓ g.	9⅓ g.
Oxidizing flux	44 to 74	..	..	..
Extra litharge	60–90 g.	..	..	..
Extra borax glass	..	25	22.5	25
Extra silica	..	25	22.5	20

and silica, the assayer is ready to prepare the flux charge for practically any and all ores.

The preceding examples will illustrate the application of the above-mentioned reagent mixtures to the fluxing of selected ores from each of the four general divisions mentioned in the first paragraph of this section.

HIGH-PRECISION WEIGHING

In the assay of final tailing from gold cyanide plants and in experimental work on low-grade ores an assay accuracy of approximately $0.01 per ton is practically mandatory. Besides requiring extremely accurate work in all other parts of the assay the final weighing must be done with the greatest of care by skilled men provided with the best equipment available. With gold at $35 per ounce, an accuracy of $0.01 per ton is equivalent to a precision of 1 part in 100,000,000. The best assay balances have a rated sensitivity of 0.002 milligram, but until one has tried it he does not appreciate the difficulty of actually weighing to this degree of precision.

To obtain an assay tailing value good to approximately $0.01 per ton, it is customary to make twelve fusions on 1-assay-ton portions of tailings with the corresponding twelve cupellations and individual partings, each with the utmost of care in all the various steps involved. The ideal balance room should be windowless and air conditioned with a temperature of 98°F., so that no radiant heat passes from the body of the operator to the beam of the balance, and sufficiently low humidity so that the operator can work in comfort in a room held at body temperature. Other requirements as to balance support, lighting, air circulation, etc., are or should be obvious.

The system to be used in weighing the gold from the twelve 1-assay-ton samples is about as follows, credit for which goes to J. W. Martell, Chief Assayer, Lake Shore Mine.*

Adjust balance very accurately.
Weigh combined gold from assays 1, 2, and 3. Note weight.
Check balance.
Weigh combined gold from assays 4, 5, and 6. Note weight.
Check balance.
Weigh combined gold from assays 7, 8, and 9. Note weight.
Check balance.
Weigh combined gold from assays 10, 11, and 12. Note weight.
Check balance.
Each of these four weights must check within 0.004 milligram.

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* "Milling Investigations at Lake Shore," *Trans. Can. Inst. Min. Met.* **39**, 331.

Combine gold from all twelve assays and weigh. Their total weight must check accurately the sum of the four previous weighings. The resultant total is divided by 12 to arrive at the final assay figure with the desired precision.

EQUILIBRIUM IN FIRE ASSAYING

A knowledge of the principles of chemical equilibrium and of its applications to fire chemistry is important in many metallurgical operations. The student of fire assaying should know the underlying facts relating to the distribution of silver and gold between slag and lead button even though, in his assay practice, he may not attain true equilibrium.

Distribution Equilibrium Law. In general, when two or more immiscible phases, in this case liquids, are in contact and a third substance soluble in each is added to them, a part of it will pass into solution in one phase and a part in the other. If opportunity is afforded for the establishment of equilibrium, the solute will distribute itself between the solvents in a perfectly definite manner, which is dependent upon: (*a*) the nature of the substances; (*b*) the relative amounts of each; and (*c*) the temperature.

The application of this law to our subject is best illustrated by the specific example of a crucible assay. Reducing the matter to its simplest terms, we may consider that we have pure lead as one solvent, a slag of some definite composition as a second, and metallic silver soluble in both, all in contact in the liquid state. At the temperature of the crucible fusion it is well known that silver is readily soluble in lead and slightly soluble in slag to an extent which is dependent upon the nature of the slag. Boyd Dudley* believes that he has established the following additional facts with relation to this type of system:

1. A true state of equilibrium is attainable.
2. Litharge is the most active of the slag-forming constituents with respect to the dissolution and retention of silver.
3. Other conditions remaining constant, the amount of silver retained by the slag is in direct proportion to the molecular concentration of litharge and is independent of the silicate degree of the slag.
4. The concentration of silver in the slag increases with increasing temperature.

If his conclusions are correct it follows that, other conditions remaining the same, the total amount of silver retained by a slag is proportional to the weight of the slag.

The data with respect to solute distribution in any system are based

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* *Met. Chem. Eng.* **14**, 636–641 (June 1), 695–701 (June 15, 1916).

on the solute content of a unit weight of the several phases involved. The so-called distribution coefficient is the ratio of solute content in unit weights of the contacting phases. For example, Dudley reports that, at 1150°C., 1 gram of lead-silver alloy in contact with a sodium-lead borosilicate slag of approximately 1 to 1 oxygen ratio and 72 per cent PbO will contain 600 times as much silver as a gram of slag. Much painstaking work remains to be done before we have sufficient specific data to answer all the questions which might be raised in regard to this matter or thoroughly to convince all assayers of the accuracy of all the facts given by Dudley in his paper. The above-cited distribution coefficient does seem, however, to be in general accord with the writer's experience, and it serves to give the student at least some quantitative measure of this important relationship. Without having to resort to specific data a general understanding of the equilibrium relationships helps to explain why the size of the lead button should be increased as the litharge content of the assay slag is increased.

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