A MANUAL

OF

FIRE ASSAYING

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To his Mother

THIS BOOK IS LOVINGLY DEDICATED BY

THE AUTHOR

PREFACE

The author has long recognized the need of a work on fire assaying that treats the subject from the scientific and rational point of view rather than from that of the "rule of thumb." Strangely enough, this last governs most modern works on the subject. The book is closely confined to the subject of fire assaying, which it treats in detail. The chapters on "Reduction and Oxidation Reactions," "Crucible Assay and Assay Slags," and "Cupellation," outline scientifically the principles of assaying. A large part of these chapters is new and some of the material is presented for the first time. The chapter on the "Errors in the Assay for Gold and Silver" outlines and discusses the accuracy of the assay in greater detail than has been attempted heretofore.

The author has had experience with practically all of the methods of assay discussed in the book; first as a manipulator, then as a teacher, and finally in charge of works. The book is intended for the use of students in technical schools and for the assayer in actual daily practice who frequently feels the need of a reference book.

The author wishes to acknowledge his indebtedness to the writers cited in the text, especially to the late Professor E. H. Miller, of Columbia University, whose work and personality has ever been an inspiration to the author. He also expresses his thanks to Mr. J. B. Read and Mr. Ivan E. Goodner, chemist and assayer respectively for the Standard Smelting Company, Rapid City, and to Mr. Frank Bryant, his assistant at the School of Mines, for valuable aid in the testing of methods; to Professor M. F. Coolbaugh for the inspection of those chapters containing chemical equations, etc., and to Miss Ethel Spayde and Miss Della M. Haft for invaluable aid received in the preparation of the manuscript for publication. The author also desires to express his appreciation of the courtesy of the Denver Fire Clay Company and of Ainsworth & Son, Denver, Colorado, of F. W.

Braun and Company, Los Angeles, California, and others, in furnishing photographs and electrotypes of apparatus used in the book.

CHARLES HERMAN FULTON.

RAPID CITY, S. D.
April, 1907.

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A MANUAL OF FIRE ASSAYING

I

ASSAY FURNACES AND TOOLS

The furnaces used in assaying are many in design, varying mainly with the kind of fuel used. The furnaces are classified as follows: (1) Pot furnaces, in which the assay is in direct contact with the fuel; (2) Muffle-furnaces, in which a muffle or receptacle containing the assay is externally heated.

As the muffle-furnace is practically essential[1] for carrying on the operations of scorification and cupellation, and crucible fusions can be made satisfactorily in the muffle if it be large enough, muffle-furnaces have largely replaced pot furnaces for general assaying. In general, they are cleaner, more easily operated, better controlled as to temperature, and if large enough are of great capacity, which makes them especially desirable for smelter, mill and mine assay offices, where frequently a great number of assays are performed daily. The choice of fuel for heating the furnaces is usually dependent on locality. Bituminous and lignite coal, coke, anthracite, gasolene, wood, fuel and illuminating gas are all used. Of these, coke and anthracite are the fuels least desirable for muffle-furnaces, as these fuels, being flameless, must surround the muffle. This makes the firing difficult, requiring considerable attention. The best fuel, usually also the most easily obtainable, is bituminous or good lignite coal, yielding a long or reasonably long flame. One-, two- and three-muffle furnaces, constructed of fire-clay tiling, fire-brick, and common hard brick, tightly bound with stays and rods, are in common use, and for general utility, where much work must be turned out, are very desirable.

Fig. 1 shows such a two-muffle furnace in perspective, and Figs. 2 and 3, in cross-section. The essential parts of the furnace,

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[1] "Koenig's Furnace," in *Trans.* A. I. M. E., XXVIII, p. 271. This furnace is practically a pot furnace fired by gasolene, and with an air blast can be used to scorify and cupel without a muffle.

as the tiling, *A*, *B*, *L*, *K*, etc., can be readily purchased, although the interior of the furnace may also be built of fire-brick. The tiling furnace, however, is more easily set up and is more durable. In the design of the soft-coal furnace, the essential dimensions are: area of fire-grate; distance from the grate to the bottom of the lower muffle; the "fire space," *i.e.*, the distance between muffles and side and end of furnace, and between the top of the upper muffle and the top of the furnace, giving the proper space for combustion of the gases. These dimensions depend upon the nature of the coal. In Figs. 2 and 3 the grate area is 17.25 x 21.0 in.; distance from grate to lower muffle, 18 in.; fire space, 2.5 in.; external dimension of muffle, 19 in. long, 12.25 in. wide, 7.75 in. high. The flue should be from one-sixth to one-eighth of the grate area. It is best placed forward of the center of the muffles to get the full sweep of the flame around them, although this, with poor draft, is apt to cause smoky muffles.

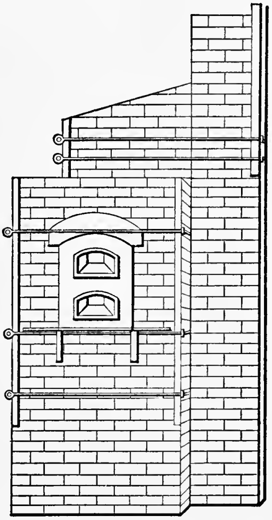

FIG. 1.—TWO-MUFFLE FURNACE. Perspective view

The walls of the furnace are thick (13 in.) to prevent radiation. The front of the furnace above the muffle is arched. The arch tiling has in it a duct, leading to the flue, to carry off lead fumes. The muffles are supported by two sets of tiles, set into the side walls or into the rear end wall. These tiles frequently prove weak, and in falling away leave the muffle without support, causing it to be short lived. The supports are best made in such shape, of two pieces, that they will join under the center line of the muffle and arch over, supporting each other. The writer has used supports of this type, which were perfectly satisfactory and increased the life of the muffles greatly. A furnace of the kind described has a capacity of 25 to 30 fusions (20-gram crucible) per hour, including the necessary cupellations. If the fusions are made in 30-gram crucibles or in 2.5-in. scorifiers, the

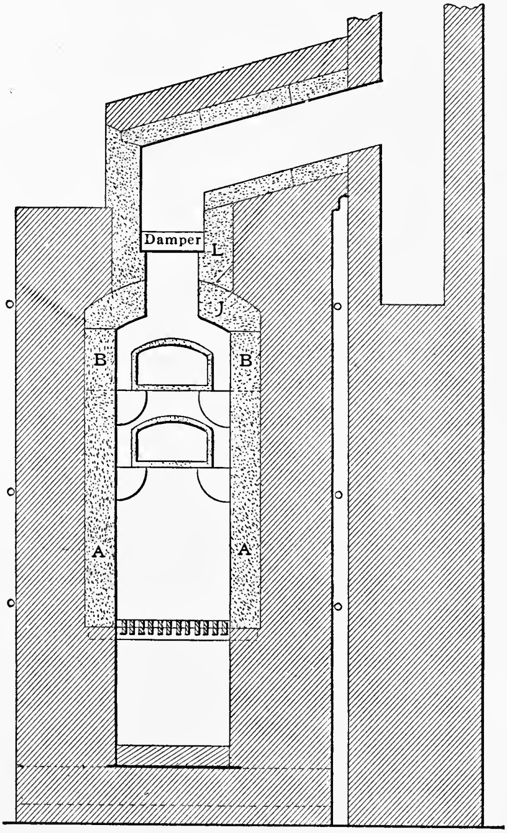

FIG. 2. — TWO-MUFFLE FURNACE. Cross-section

capacity is from 20 to 24. With good draft, this furnace burns from 37 to 47 lbs. of coal per hour, which, at $7.00 per ton, makes the cost per assay for fuel amount to from 0.65c. to 0.80c. With a good grade of coal (6500 to 7500 calories), a maximum temperature of 1150° to 1200° C. can be obtained in this furnace. Figs. 4 and 5 show a three-muffle furnace of similar type.

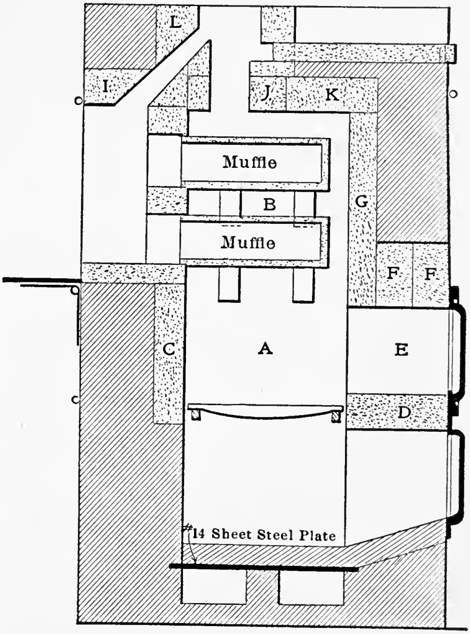

FIG. 3. — TWO-MUFFLE FURNACE. Longitudinal section

Coal furnaces may also be readily modified to burn crude oil. This can be done by placing tiling in the fire-box, and making the necessary pipe and burner connections.[1] Figs. 6 and 7 show a wood-burning muffle-furnace.[2] In some districts wood is the only available cheap fuel. If the fire-box and fire spaces are properly designed (*i.e.*, of larger size than in the coal furnace) and a deep bed of fuel is provided for (*i.e.*, the distance from the

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[1] F. C. Bowman, "Crude Oil in Fire Assaying," in "Eng. and Min. Journ.," LXXIX, p. 221.

[2] See also E. H. Nutter, in "Min. and Sci. Press," XCII, p. 329; Louis Janin, Jr., in "Eng. and Min. Journ.," LXXIV, p. 810.

grate surface to the bottom of the fire-door is from 8 to 10 in.), sufficient temperature for ordinary assaying can be attained in this type of furnace. Almost any wood may be used.

Coke and anthracite muffle-furnaces, when used, are usually smaller, although large furnaces may be specially designed and built of the general type of the coal furnaces described.

Fig. 8 shows a small coke or anthracite furnace. The fuel is fed in at the top and kept well heaped around the muffle. A furnace of the kind shown in Fig. 8 will consume from 32 to 38 lbs. of coke per hour, according to draft. With a muffle 11 x 16 x 7 in., 10 assays per hour, including cupellation, can be made at a cost of 1.7c. per assay with coke at $10 per ton.

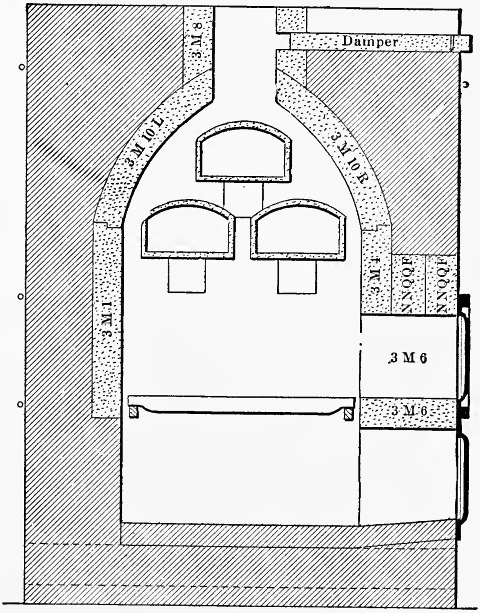

Fig. 4. — Three-Muffle Furnace. Cross-section

Fire-clay muffles for furnaces are made in varying sizes and shapes. The best shape for general use is one of nearly rectangular cross-section, with but a slightly arched top. The largest muffles ordinarily used are 19 in. long, 14.5 in. wide and 7.75 in. high (outside dimensions). Muffles 19 in. long, 12 in.

wide and 7.75 in. high are very common in coal furnaces. The muffles have two holes in the rear end to induce an air draft through them.

Gasolene-fired Furnaces. — Furnaces of this type are in common use, and for small offices, where the pressure of work is not great, they afford a convenient and cheap method of operation. Gasolene, on account of ease of transportation and great calorific power, is also employed in out-of-the-way districts for extensive daily work. Where coal is reasonably cheap, not above $6.50 per ton, gasolene at 30c. per gal. cannot compete with it in large offices or schools, where the assay furnaces are operated continuously for the greater part of the day.

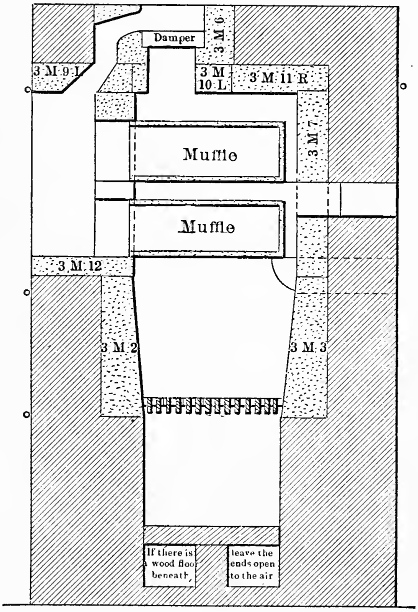

Fig. 5. — Three-Muffle Furnace. Longitudinal section

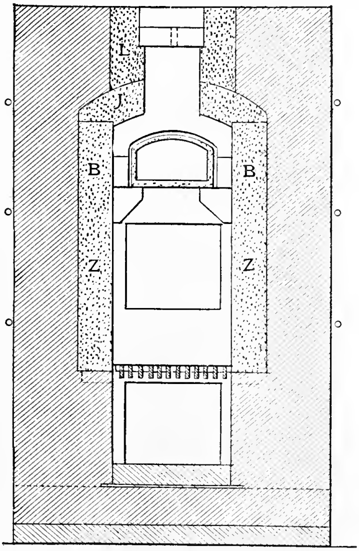

Fig. 6. — Wood-Burning Muffle-Furnace. Cross-section

Fig. 9 shows a gasolene furnace apparatus. The furnace, divided into crucible and muffle compartments, is made of fire-clay tiling, bound with sheet iron. It is heated by a brass and copper burner, provided with a generating device. The burners

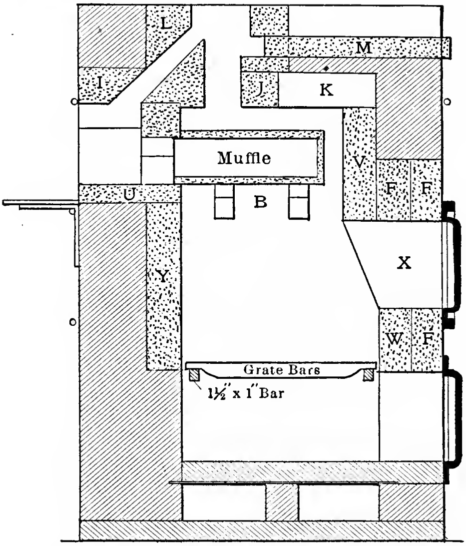

FIG. 7. — WOOD-BURNING MUFFLE-FURNACE. Longitudinal section

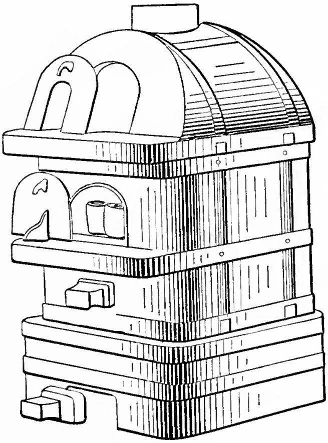

FIG. 8. — MUFFLE-FURNACE FOR BURNING COKE

are made in varying sizes to suit different furnaces. The gasolene is stored in a steel tank, of 5 or 10 gal. capacity, provided with an air pump to furnish pressure. A pressure gage is attached to the tank. Generally, 0.25- to 0.375-in. piping joins the tank and the burner. The burner and piping are connected by a special universal joint, so that the burner can be swung into and out of position. The burner (if the Carey) should fit tightly against the fire-clay ring or boss in the opening of the furnace, so that all the air for the combustion of the gasolene is drawn in through the burner tube. To insure tight joints, glue or soap, not white or red lead, must be used in the screw connections.

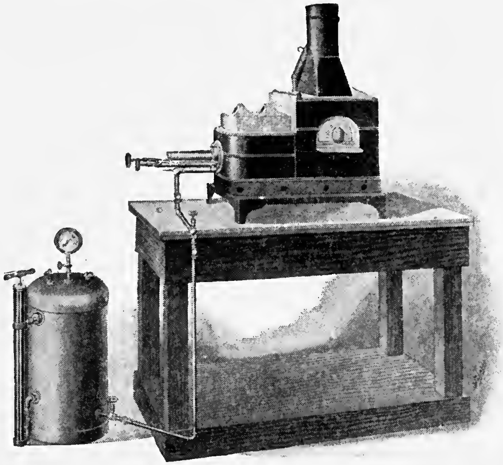

Fig. 9. — Gasolene Furnace Apparatus

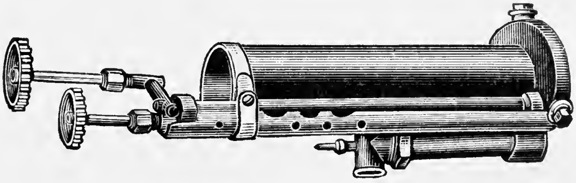

Fig. 10. — The Carey Gasolene Burner

The gasolene is fed to the burner under a pressure of 10 to 20 lbs., though for special purposes higher pressures are used.

Fig. 10 shows a detailed view of the Carey burner. The upper valve controls the main gasolene supply, and the lower one controls the generator. The burner is heated by the generator, so that the gasolene issuing from the main needle-valve is vaporized, and in its passage to the furnace draws in air through the burner tube, the mixture igniting and burning at the mouth of the burner in the hot furnace. Burners are listed by the diameter of their tubes. Five sizes are made, from 1.25 to 2.25 in., each size varying by 0.25 in.

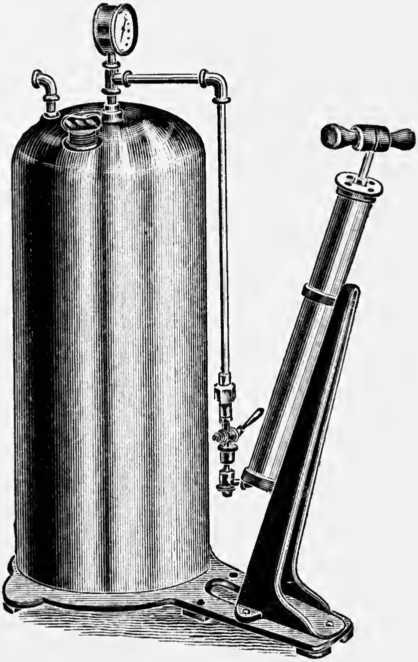

Fig. 11. — Gasolene Tank and Pump Apparatus

Fig. 11 shows the tank and pump apparatus. It is best to place this at a considerable distance from the furnace, in order to avoid accidental explosions. Fig. 12 shows a crucible furnace, and Fig. 13 a large gasolene muffle-furnace. The writer has attained a temperature of 1350° C. in small gasolene furnaces, such as Fig. 12 represents, and 1250° C. in large furnaces, as represented by Fig. 13. By a special construction of furnace, with graphite muffle and heavy insulation against radiation, with good draft, the writer has attained (for metallurgical experimentation) temperatures of 1500° to 1530° C., after three hours, by a 2-in. gasolene burner as shown in Fig. 10, with gasolene at a pressure of 55 lbs. and a consumption of 1.53 gal. per hour. A 2-in. Carey burner, under 10 lbs. pressure, will consume from 0.65 to 0.75 gal. per hour. A No. 31 Carey combination furnace, holding at a charge in the crucible compartment six 20-gram crucibles and having a muffle 7 x 10.5 x 4.5 in. in size, has a capacity of 10 fusions per hour, including cupellation. With gasolene at 30c. per gallon, the cost of fuel per assay is 2.25c.

Fig. 12. — Gasolene-Burning Crucible Furnace

Gas Furnaces. — Where municipal illuminating gas or other gaseous fuel is available, gas-fired furnaces are convenient and cheap of operation. The Reichhelm furnace (American Gas Furnace Company) is frequently used. The furnaces require air at low pressure, which is mixed with gas in proper proportion before it enters the furnace through the several burners. The proportion of gas to air is controlled by valves. Fig. 14 shows the furnace. Gas furnaces permit of close control of heat and are desirable for accurate temperature work.

Furnace Tools. — Convenient tools are necessary for the handling of crucibles, scorifiers and cupels. The features essential in these tools are that they be light, grasp the crucible, etc., firmly, with no danger of tipping, and take up little room in the furnace. As an illustration of a tool deficient in these qualities and therefore undesirable, Fig. 15 is given. This shows a pair of crucible tongs designed to grasp the body of the crucible. It cannot be handled in a muffle full of crucibles, owing to the space it takes up in opening. Fig. 16 shows a pair of crucible tongs to grasp the sides of the crucible, and operating in little space.

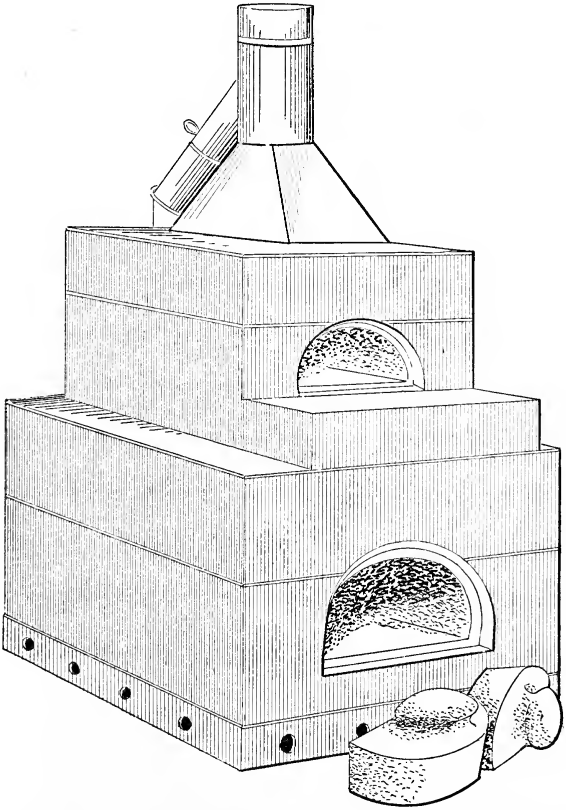

Fig. 13. — Gasolene-Burning Muffle-Furnace

Fig. 17 shows two types of cupel tongs. Fig. 18 shows a good form of scorifier tongs, and Fig. 19 another form.

For large offices where much work must be quickly accomplished, special forms of tools may be used. Figs. 20 and 21 show a multiple tongs[1] for scorifiers. This apparatus will handle 20 scorifiers, practically a muffleful at one time. It is composed of quintuple tongs, corresponding to the five longitudinal rows of scorifiers in the muffle. The lower part of each pair of the tongs consists of a fork on which the scorifiers rest, and one of whose prongs is rectilinearly extended through two bearings in a

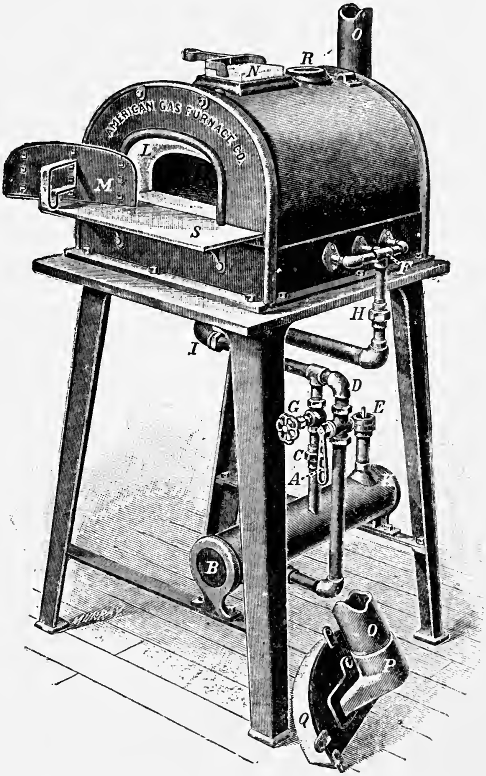

Fig. 14. — Gas-Burning Muffle-Furnace

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[1] Edward Keller, "Labor-Saving Appliances in the Works Laboratory," in *Trans.* A. I. M E., XXXVI, p. 3.

frame and held in position by collars. This extension is free to revolve on the bearings, and it is the axis of rotation of the tongs. To each of them is attached, at a right angle, a lever extending upward at 45°, and all the levers are connected by slotted joints to a cross-rod. Therefore if, by means of a crank fastened to the end of one of the extended prongs, one of the forks is turned and the scorifiers tilted to the desired angle, the others rotate to the same extent. The center of gravity of the scorifiers lies to one side of the rotation point, and they would therefore, on being lifted, tilt in that direction; this, however, is prevented by the cross-bar resting against a post at that end of the frame toward

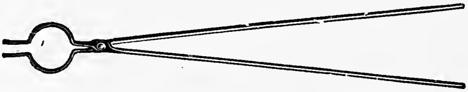
FIG. 15. — CRUCIBLE TONGS. Undesirable model


FIG. 16. — CRUCIBLE TONGS

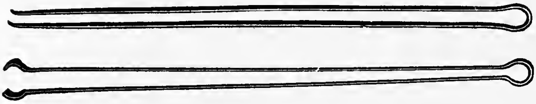
FIG. 17. — CUPEL TONGS


FIG. 18. — SCORIFIER TONGS


FIG. 19. — SCORIFIER TONGS

which the inclination tends. The scorifiers are clutched by the upper prongs of the tongs, which is fastened to a spring on a post of the fork below, and which is free to move in a vertical plane,

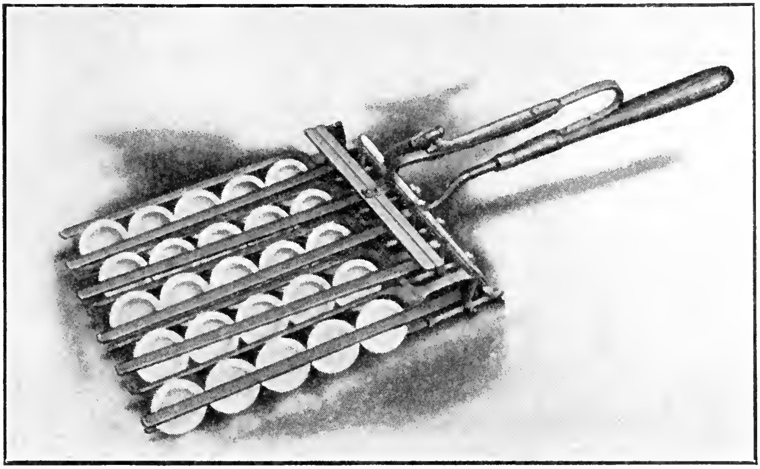

Fig. 20. — Multiple Scorifier Tongs. (Keller)

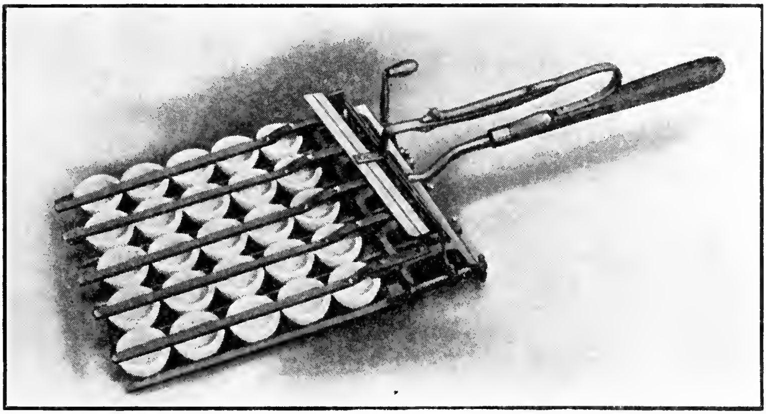

Fig. 21. — Multiple Scorifier Tongs. (Keller)

the pivotal point lying over the spring and post. By bringing pressure on the extended ends of these clutch bars behind the pivot, their other end will rise above the scorifiers, and thus release them, or permit the placing of them onto the tongs. The pressure exerted on the rear ends of the clutches is accomplished by means of a cross-bar fastened to a spring bar, which is itself fastened to the handle of the instrument. An ordinary mold with 20 holes, arranged to receive the contents of the scorifiers, goes with the tongs.

Fig. 22 shows a device to charge 30 cupels at one time. It comprises a top sliding plate with openings corresponding exactly to the position of the cupels. The openings in the lower plate correspond exactly with those of the upper one; the plate, however, rests on two adjacent sides extended downward at right angles to the plate and to each other, thus forming two closed sides of the instrument; one at the front and the other at the right-hand side. The hight of these sides is such that when resting on the bottom of the muffle the bottom plate will be some distance above the cupels, and by a slight pull forward and a push to the left with the handle of the instrument the set of cupels will be perfectly alined in both directions and the apertures in the lower plate will exactly cover the tops of the cupels. The lead buttons are placed in the apertures of the upper plate and rest on the lower plate before introducing the instrument into the furnace, and when it is placed over the cupels, which have been properly alined in the muffle, the upper plate is pushed forward to a stop-point, bringing the apertures of the two plates into register, thus causing the lead buttons to drop down into the cupels. The handle of the upper plate runs through guides fixed to the handle of the lower plate; both handles are connected with a spring, which acts as a brake when the upper plate is pushed forward to drop the buttons, and also serves to bring it

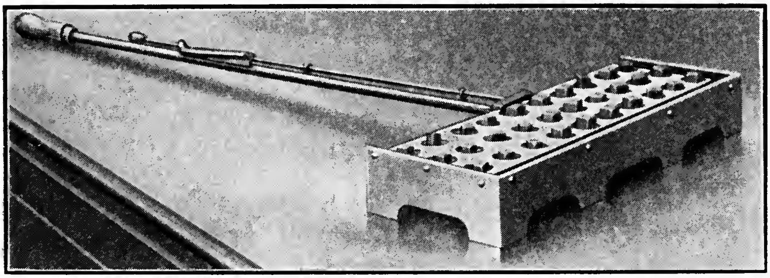

FIG. 22.— CUPEL CHARGING DEVICE. (Keller)

back into its original position, in which the buttons cannot drop through the apertures in the lower plate.

Molds. — Fig. 23 shows machined cast-iron molds to receive the molten fusions. The sharp cone-shaped mold is preferable to the shallow hemispherical type, as the lead buttons are then sharp and well defined and separate easily from the slag. The mold is best made with a screw-handle, so as to be easily repaired in case of breakage. The inner surface of the molds should be machined smooth, to permit the ready separation of slag and lead button from the mold.

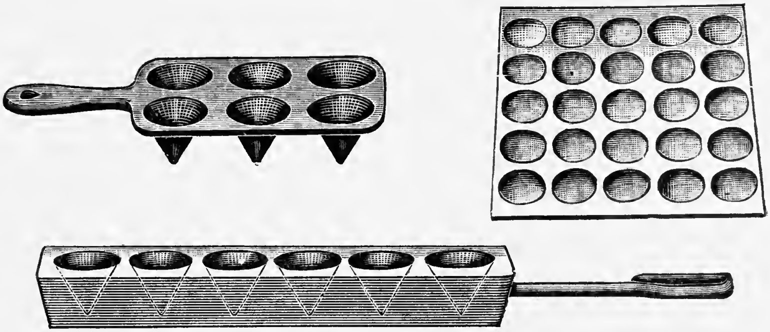

Fig. 23. — Crucible Pouring Molds

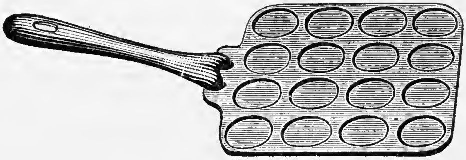

Fig. 24. — Cupel Tray

For scorification fusions, smaller molds are often used. For the transfer of cupels to the parting room, iron cupel trays, as illustrated in Fig. 24, are used. The handle is removable, and one handle serves for a number of trays. For the annealing of gold beads, or cornets, fire-clay trays as shown in Fig. 25 are

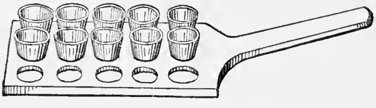

Fig. 25. — Fire-Clay Annealing Cup-Tray

employed. Fire-clay, however, is very easily broken, and more satisfactory trays are made of sheet iron and heavy asbestos board.

Crucibles and Scorifiers. — Fire-clay crucibles are largely used in the United States, and fire-clay ware for assay purposes is made to a large extent in some of the western States. Following is the analysis of a Colorado crucible clay:

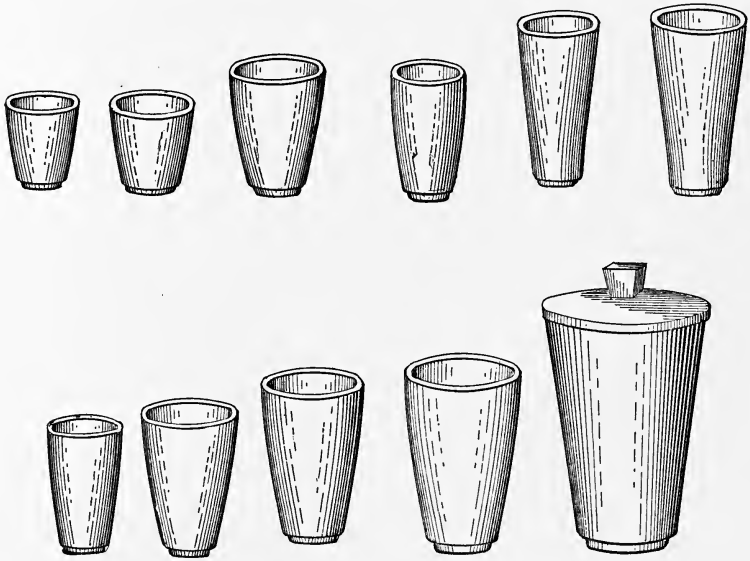

FIG. 26. — FIRE-CLAY CRUCIBLES

Loss on ignition	10.14 per cent.
Alumina	15.09 per cent.
Silica	71.81 per cent.
Ferric oxide	1.75 per cent.
Lime	0.14 per cent.
Magnesia	0.05 per cent.
Alkalies	1.02 per cent.

The crucibles are rated by "gram" capacity, that is, by the number of grams of ore with the proper amount of fluxes necessary for fusion which the crucible will hold. The chief sizes are 5, 10, 12, 15, 20, 30 and 40 grams; of these the 20- and 30-gram sizes are mostly used, the 20-gram crucible for the 0.5 assay ton, and the 30-gram for the 1 assay ton fusions. Fig. 26 shows the various shapes employed. Imported Hessian triangular crucibles and sand crucibles are also used, but in small quantities. Scorifiers are made of the same clays as the crucibles and are designated in size by their outside diameters; 1. 5-, 2-,2.5- and 3.5-inch sizes are made. These will hold a volume of 15 c.c., 25 c.c., 37 c.c. and 100 c.c., respectively. The 2.5-inch scorifier is the one commonly used. Fig. 27 shows the ordinary type of scorifiers. Roasting dishes are shallow fire-clay dishes similar to scorifiers, but not so thick. They are rated by their diameters; the common sizes being 3, 4, 5 and 6 inches. Fig. 28 shows the ordinary buck board and muller, and Fig. 29 buck board brushes. For the description of other minor tools and apparatus, as screens, pliers, and crushing and grinding machinery, necessary to the assay laboratory, the reader is referred to the voluminous and

Fig. 27. — Scorifiers

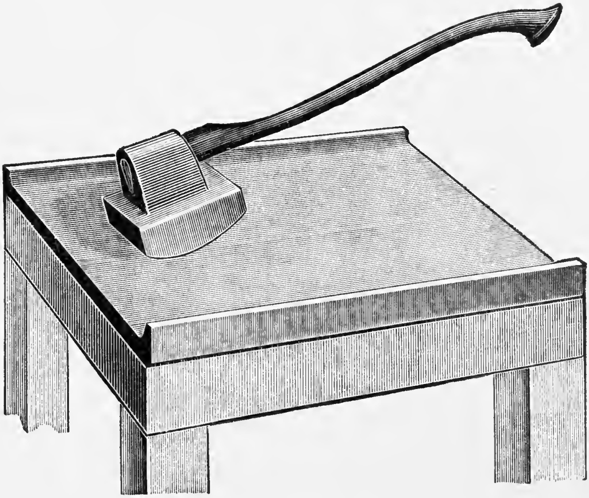

Fig. 28. — Buck Board and Muller

well-illustrated catalogues of the assay supply houses. Balances, weights, sampling tools, cupels, parting devices, etc., are discussed under their respective chapters.

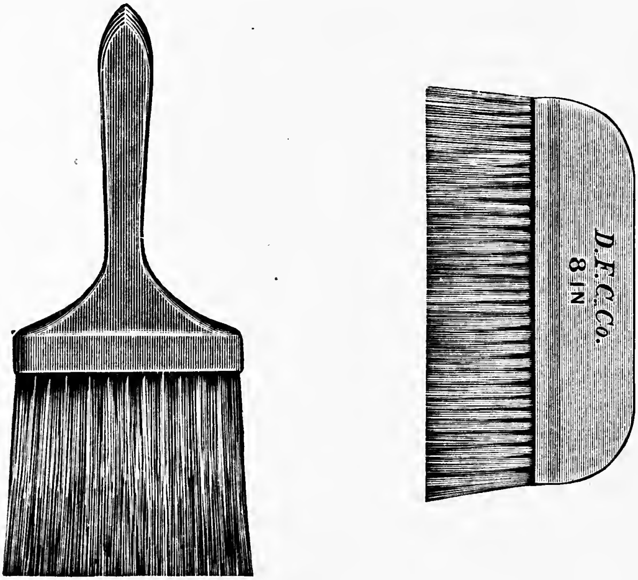

FIG. 29.—BUCK BOARD BRUSHES

II

DEFINITIONS; REAGENTS; THE ASSAY OF REAGENTS

Assaying includes all those operations of analytical chemistry which have for their object the determination of the constituents of ores and metallurgic products. Three methods are used: (1) Fire assaying (dry methods); (2) gravimetric analysis (wet methods); (3) volumetric and calorimetric analysis (wet methods). This work treats of fire assaying only, with a few exceptions. The quantitative determination of the following metals is discussed: gold, silver, platinum, etc., lead, antimony, bismuth, tin and mercury; chiefly, however, gold and silver.

Fire assaying comprises the separation of the metal sought from the other components of the ore, by heat and suitable fluxes, and then the weighing of it in a state of greater or lesser purity.

Gold and Silver. — Gold and silver are determined in their ores, or metallurgic products, by collecting them with lead, forming an alloy, which may be accomplished either by the crucible or the scorification fusion, the lead being then driven off by cupellation, and the resultant bead of the gold and silver alloy weighed. The separation of gold from silver is accomplished by parting in most instances with nitric acid, rarely by sulphuric acid.

In order to successfully collect the precious metals by means of lead, it is essential that the ore be mixed with suitable fluxes, so that in fusion the ore is thoroughly decomposed chemically, and a liquid slag of the proper constitution produced, enabling the lead with its alloyed gold and silver to settle from the slag by gravity, thus affording a ready separation.

REAGENTS COMMONLY USED IN ASSAYING

Name	Formula	Nature (chemical)
1. Litharge	PbO	basic
2. Sodium carbonate	Na_2CO_3	basic
3. Sodium bicarbonate	$NaHCO_3$	basic
4. Potassium carbonate	K_2CO_3	basic
5. Silica	SiO_2	acid
6. Borax	$Na_2B_4O_7.10H_2O$	acid
7. Borax glass	$Na_2B_4O_7$	acid
8. Fluorspar[1]	CaF_2	neutral
9. Lime	CaO	basic
10. Hematite	Fe_2O_3	basic
11. Test lead Sheet lead	Pb	basic
12. Argol	$KHC_4H_4O_6$	basic
13. Charcoal	C	
14. Coke dust		
15. Flour		
16. Lead flux		
17. Black flux		
18. Black flux substitute		
19. Potassium cyanide	KCN	neutral
20. Potassium nitrate	KNO_3	basic
21. Salt (sodium chloride)	$NaCl$	neutral

1. Litharge is acted on in the crucible by reducing agents, such as charcoal, etc., and metallic lead produced as follows:

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

The litharge not reduced is acted on by silica and borax glass, producing silicates and borates of lead, as follows:

$$PbO + SiO_2 = PbSiO_3, \text{ etc.}$$

Litharge melts at 906° C.

2, 3. Sodium carbonate and bicarbonate is decomposed by heat in the crucible, as follows, at high temperature:

$$2NaHCO_3 = Na_2O + H_2O + 2CO_2$$

Or, in the presence of silica,

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

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[1] Not decomposed in the crucible by temperatures ordinarily used in assaying.

The Na_2O, with silica, forms sodium silicates, as Na_2SiO_3, etc., which are very fusible. It also possesses the property of readily forming sulphides and sulphates and, in the presence of metallic Fe, of freeing lead in the charge from sulphur.

Na_2CO_3 melts at 814° C.

4. Potassium carbonate acts in a similar manner to sodium carbonate. It melts at 885° C.

5. Silica is a powerful acid flux and combines with the metallic oxides or bases present in the charge to form the slag, which is mainly composed of silicates. It is present in most ores in considerable quantity, ranging from small amounts in basic ores to the main bulk of the ore in quartz ores. It melts at 1775° C.[1] (Quartz). — (Roberts-Austin, 1899.)

6, 7. Borax and borax glass act as an acid flux. The formula may be written $Na_2O, 2B_2O_3$. It contains an excess of boric acid, which can unite with metallic oxides to form a borate slag. Boric oxide and boric acid yield a very fluid slag with zinc oxide, either alone or with one-half its weight of borax. It acts very corrosively on clay crucibles. Borax melts at 560° C.

8. Fluorspar is occasionally used in assaying. It fuses at a comparatively high temperature, but when fused is very thinly fluid. The greater part of it remains unchanged throughout the fusion, and hence its lime cannot be considered as available for fluxing silica. It gives the slags containing it a stony appearance. Owing to its great fluidity, it has the property, shared by soda and litharge to some extent, of holding in suspension unfused particles, thus still making a fluid slag. Where the decomposition of the ore to be assayed is essential, as it is in most cases, its use is not to be advocated.

9. Lime is used either as the carbonate or as the oxide or hydrate. In the crucible it is converted into oxide, the carbonate beginning to lose its CO_2 at 700° C. In itself it is extremely infusible (1900° C.; Hempel, 1903), but with silica, when joined with other bases and in moderate quantities, it makes very desirable slags. It is found in many ores. Magnesia acts in a similar way. Its melting-point is 2250° C. (Hempel, 1903.)

[1] Day and Shepard give the melting-point of SiO_2 at approximately 1625° C.; "Journ. Am. Chem. Soc.," XXVIII, p. 1096.

10. Hematite, or natural ferric oxide, and limonite, are of frequent occurrence in ores, and are sometimes added as a flux. Ferric oxide is very infusible. In the crucible it is converted by reducing agents, such as argol, charcoal, etc., to ferrous oxide (FeO), and then unites with silica to form silicates. The fact that it is reduced to ferrous oxide, conversely gives it an oxidizing power. Manganese oxides acting in a similar way are also frequently found in ores. Alumina, Al_2O_3, is often found in ores, and unites with silica to form silicates. It has no oxidizing power. Al_2O_3 melts at 1880° C. (Hempel, 1903.)

11. Test lead and sheet lead are used chiefly in the scorification assay and in cupellation. In both of these operations the lead is oxidized by the oxygen of the air ($2Pb + O_2 = 2PbO$) to litharge. In the scorification assay part of this PbO volatilizes; the greater part becomes fluid and holds in suspension and solution other metallic oxides derived from ores, thus forming what is termed an oxide slag. In cupellation, part of the lead is volatilized as PbO, and part is absorbed by the cupel as PbO. Lead melts at 326° C.

12. Argol is a crude bitartrate of potassium, separating out in wine casks, from the wine on standing. On heating, it breaks up as follows:

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

The carbon and carbon monoxide set free give it its reducing power. The K_2O left acts as a basic flux.

13, 14, 15. Charcoal, coke, coal dust, sugar and flour are reducing agents by virtue of the carbon or hydrogen, or both, that they contain.

16. Lead flux is a ready-prepared flux used mainly in the assay of lead ores for lead. It has the following composition:

Sodium bicarbonate	16 parts
Potassium carbonate	16 parts
Borax glass	8 parts
Flour	4 parts

It is also made up in other proportions.

17. Black flux is made of 1 part KNO_3 and 3 parts argol, deflagrated. It is sometimes used in the tin assay.

18. Black flux substitute consists of 3 parts of flour and 10 parts of $NaHCO_3$. It is used in the tin assay.

19. Potassium cyanide (KCN) is a powerful poison, and when powdering it great care must be taken not to inhale it. The mortar in which it is powdered should be covered by a cloth and the operation conducted at an open window. It fuses at 526° C. (commercial, 98 per cent. KCN), and remains unchanged at a fair red heat when air is excluded. Crucibles in which it is used for fusion should be covered. It is a powerful reducing and desulphurizing agent, acting as follows:

$$PbO + KCN = KCNO + Pb$$
$$PbS + KCN = KCNS + Pb$$

It is used mainly in the assay of base metals, as bismuth, tin, etc. The cyanide used in assaying should be as pure as possible; pure sodium cyanide is preferable to the usually more or less impure potassium cyanide. No material rated less than 98 per cent. KCN should be used.

20. Potassium nitrate or niter is used as an oxidizing agent. With metallic lead it acts as follows:

$$7Pb + 6KNO_3 = 7PbO + 3K_2O + 3N_2 + 4O_2 \text{ (approximately).}$$

It is frequently used in assaying to oxidize impurities in the charge, such as sulphur, arsenic, etc. It acts as a basic flux. Potassium nitrate fuses at 339° C.

21. Salt ($NaCl$) is used as a cover. It is very thinly fluid and is not decomposed during the fusion. It melts at 772° C.

The Assay of Reagents. — It is essential for the assayer to be assured of the fact that his reagents are pure, or at least to know to what extent they are impure and what the impurity consists of. For this reason it is necessary to examine lots of reagents from time to time, as they come into the laboratory, by approved chemical methods, to determine their purity. Sometimes reagents or fluxes, as a result of being left exposed in the laboratory, become accidentally or purposely "salted" or contaminated with gold, silver or base-metal values. A blank assay for metals on the reagents will readily determine this. In general, it may be stated that the labeling of a chemical "c. p." does not necessarily make it so.

It is necessary to determine the silver in litharge and test lead, as these two reagents frequently contain some silver, due to their being usually made from lead bullion refined by the Parkes' or zinc-desilverization process, which leaves some silver in them. As litharge is almost invariably used in the crucible assay, and test lead in the scorification assay, any silver or, possibly, gold introduced into the results by their use must be subtracted, so as not to be ascribed to the ores. Most assay supply houses now furnish practically silver-free litharge and lead containing only traces of silver and no gold.

The method of determining silver and gold in litharge and test lead is as follows:

The following charge is weighed out in duplicate:

Litharge	3 assay tons
Sodium carbonate	20 grams
Silica	7 grams
Argol	2 grams
Borax glass	5 grams (as a cover)

The various ingredients are put from the scale pan on a sheet of glazed paper and thoroughly incorporated by mixing. It is essential to weigh the litharge and argol as accurately as possible with the pulp balances in use.

The incorporated charge is then transferred to a 20-gram crucible, a shallow cover of borax glass being put on top of the charge, and then fused in the muffle-furnace for from 25 to 35 minutes at a yellow heat (1000° C.). The fusion is considered complete when the charge is in quiet fusion, that is, when there is no more bubbling and boiling in the charge and when the only motion observable is that due to convection currents. The charge is then poured into an iron mold and allowed to solidify, which takes approximately 10 minutes. The lead button is then separated from the slag by the hammer and formed into a cube. It is weighed and its weight recorded in grams and tenths of a gram in the assay note-book, a definite assay number being assigned to this assay and its duplicate. The lead button is then cupeled, the cupel being first placed in the muffle for 10 to 12 minutes before the lead button is dropped into it. If the button weighs from 15 to 20 grams, as it should, it will take 25 or 30 minutes to finish the cupellation, that is, to drive off the lead. The end of this operation, in this particular instance, is denoted by the darkening of the small silver bead. The bead is then removed from the cupel after this has become cold, flattened on a small anvil with a blowpipe hammer, cleaned of adhering bone-ash from the cupel by a button brush, and weighed carefully on the assay balances, the weight being recorded in milligrams and hundredths of a milligram. The weight of the bead, divided by the number of assay tons (3) taken in the assay, gives the number of ounces contained in a ton (2000 lbs.) of litharge, or the number of milligrams per assay ton of litharge.[1] If the presence of gold is suspected in the litharge, the silver bead from the cupellation, after weighing, is dropped into a parting-cup filled with hot nitric acid (9 parts water to 1 part concentrated nitric acid, sp. gr. 1.42), which will dissolve the silver and leave the gold as a black residue. This residue is washed three times by decantation with cold distilled water, carefully dried and annealed at a red heat in the muffle; after cooling it is weighed as already described for silver. The weight of the gold is recorded and then subtracted from the weight of the original gold and silver bead. The difference in weight gives the amount of silver.

To determine the silver and gold in test lead, weigh out 3 assay tons, place in a 2.5-in. scorifier, add a pinch of borax glass, and scorify in the muffle at a yellow heat (1000° C.). As the lead oxidizes to litharge, this melts and forms a slag which, owing to the convexity of the meniscus of molten lead, falls to the side of the surface and forms the slag ring, leaving a disk of fresh lead exposed. The scorification is finished when the slag finally covers all the lead. The charge is then poured into an iron mold, the further method of procedure followed being identical with the one described for the litharge assay.

It is possible to obtain test and sheet lead with only traces of silver, and litharge practically free from silver. It is often desirable that the litharge should contain a uniform amount of silver, for whenever low-grade gold ores, deficient in silver, are assayed, silver would have to be added at some stage of the assay in order to assure parting, or the complete separation of the gold from the silver. In assaying very low-grade gold ores, in which practically only gold is present, the final bead might be so small as to sink into minute cracks in the cupel and thus be

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[1] For a discussion of weights used in assaying, cupellation and weighing, reference should be made to these subjects.

lost. The addition of silver in this case, either by adding it in the metallic state or by its presence in the litharge, obviates this difficulty.

Litharge will frequently contain from 0.20 to 0.32 mg. of silver per assay ton. It is, however, not safe to assume the above figures. The test lead ordinarily bought from the supply houses contains only traces of silver.

III

SAMPLING

Proper sampling is of the utmost importance, for unless the sample to be assayed accurately represents the lot of ore or metallurgic product from which it is taken, in other words, unless it is a true sample, the greatest care in the assay itself means nothing. Large amounts of money are involved in settlements made on the assay of final samples representing many tons of rich ore, matte, bullions, etc. Mills and smelters purchase ores by the carload on the assay of the final sample, and even slight errors mean loss either to the shipper or the purchaser. Where so-called "specimen" assays are made, the sampling of the small amount of pulp is usually a simple matter, although accuracy is also required. In most cases the samples, representing large lots, are handed to the assayer, so that he is usually not directly concerned as to how the samples were obtained; but in general he should be familiar as to how sampling is conducted. Sampling may be classified under two heads:

1. Hand sampling:
    - *a.* Coning and quartering.
    - *b.* Alternate shovels.
    - *c.* Split shovels.
    - *d.* Riffling.
2. Machine sampling:
    - *a.* Part of the ore stream for the whole time.
    - *b.* The whole of the ore stream part of the time.

Whatever the method of sampling used, a distinct relation must exist between the weight of the sample and the size of the ore particles. Thus, if the ore particles are large (10 to 12 in. diameter), a large sample must be taken; if the particles are small (0.10 to 0.20 in.), a small sample will, if properly taken, accurately represent the lot of ore.[1] An old rule in force on Gilpin County, Colorado, ores, carrying from 1 to 4 oz. gold, illustrates this:

Diam. of largest piece, in inches...	0.04	0.08	0.16	0.32	0.64	1.25	2.50
Minimum weight of sample, in lbs...	0.0625	0.50	4	32	256	2048	16348

The proper weight of sample for any desired size of ore particle is obtained by multiplying the known weight for the given size by the cube of the ratio of the desired size to that of the given size.

As an example of mill practice by machine sampling on Cripple Creek ores of from 2 to 6 oz. gold per ton, the following is given:

The ore is crushed to pass a 1.5-in. ring, and from the total bulk a Vezin sampler cuts out one-fourth. This is passed to crushing rolls, which reduce it to 0.25-in. size. It is then elevated to another Vezin sampler, which takes out one-tenth of the bulk, the final sample being one-fortieth of the ore, or 2.5 per cent. This is then cut down and crushed finer and sampled in the usual way (alternate shovels, etc.), described further on. In smelting works, where it is desirable to have the product going to the furnaces as coarse as possible, the above method is modified by not crushing so fine and by taking larger samples; or hand sampling is employed. The size of the sample depends not only on the size of the ore particles, but also on the nature of the ore. If the values are uniformly distributed, smaller samples will do than are necessary where they are "spotted" or irregularly distributed. While machine sampling, with properly constructed apparatus, is largely in use, and is most desirable when applicable, hand sampling may be accurately performed; it is still widely used by smelting plants, as it avoids crushing a large part of the ore.

The method of "coning and quartering" has been in use for many years, and is still employed, but it is being displaced largely by the "alternate-shovel" method. Coning and quartering, unless carefully performed, which is difficult to do, is apt to be inaccurate. In this method, the thorough mixing of the ore is

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[1] Brunton, "The Theory and Practice of Ore Sampling," in *Trans.* A. I. M. E., XXV, p. 826. "Notes on Sampling," in "Min. Rep.," XLV, Nos. 7–16 (inclusive).

essential, and the mixing is supposed to be effected by coning. The cone is built up by men moving around the circumference of a circle and shoveling the ore upon the point of a cone formed by the angle of repose of the material falling vertically upon one point. The samplers — from 4 to 8 men — move so as to be always diametrically opposite each other.

In order to fix the point of the cone, a rod is driven into the ground as a guide. It is evident that the shoveling must be very conscientiously done in order to have the ore distribute itself uniformly (fines and coarse) over the surface of the cone; but this uniformity is essential to the obtaining of a true sample. When the cone has been built up, it is then pulled down by the men walking around the pile and scraping the ore from the apex to the base, until a flat plaque of ore is made about 12 or 18 in. thick. Then, in the form of a cross, plates of iron are carefully centered on the pile and driven in, dividing the plaque into quarters. Two opposite quarters are removed to the bins, and the other two, representing the sample, are reshoveled into a cone and the operation repeated. The ore is then recrushed and coned and quartered again, until finally a sample of from 25 to 30 lbs. is obtained. The number of recrushings depends upon the size of the first sample and the nature of the ore. The sample is then ground fine and prepared for the assay office by cutting down with a split sampler or other approved device. The whole process is slow and laborious. Three men can handle from 20 to 25 tons of sample per shift at a cost of from 45 to 50 cents per ton.

The Alternate-Shovel Method. — The fundamental law of sampling may be stated thus: In order to properly take a sample of ore, it is necessary to take the sample frequently, or in as many places as possible, and to take the same quantity each time at regular intervals. These conditions are fulfilled by the "alternate-shovel" method, which is conducted as follows:

The ore from the cars is dumped on a platform and men with the proper sized and shaped shovels put it into the bins, taking out for the sample a certain number, dependent on the nature and size of the ore pieces; viz., nine shovels are thrown into the bins and every tenth shovel is taken as a sample. If the ore is difficult to sample, sample shovels may be taken more frequently; or if the ore is uniform, less frequently. It is usual to cut out from one-fifth to one-twentieth of the ore. The alternate-shovel method possesses the following advantages:

1. It is more reliable and accurate than coning and quartering.
2. It is cheaper in operation.
3. It is quicker.

The "quartering" and the "split-shovel" methods are not reliable and need not be described.

At the plant of the Standard Smelting Company, at Rapid City, S. Dak., the shovel sample is passed to a Blake crusher with a 9 x 15 in. mouth opening, having an A discharge, so as to halve the crushed sample. One of the halves is fed directly to a pair of 24 x 12 in. rolls, the discharge from these being again automatically halved. If a 100-ton lot is taken as a unit, the sample at this point is 2.5 tons (taking every tenth shovel), with no particle larger than 0.375 in. in diameter. The rolls discharge directly upon a plate-iron floor, where the ore is reshoveled, every fifth to tenth shovel being taken as a sample, which now amounts to 500 or 1000 lbs. This is put through a pair of 12 x 12 in. sampling rolls and crushed fine, and then sampled by a large Jones split or riffle sampler, which takes halves, until finally a sample of between 15 and 20 lbs. is arrived at. This is put through a small cone grinding mill, and after a determination of moisture on the sample floor is sent to the assay office. Here it is cut down to about 2 lbs. by a small Jones sampler, and then crushed on a buck board to pass a 120-mesh screen, furnishing the assay sample. This sample is supposed to contain no moisture, as this was eliminated on the sample floor, where the percentage of moisture is determined; but as all settlements are made on dry samples, the final assay sample is again heated at 120° C. for some time in order to expel any moisture which the sample may have absorbed in its passage from the sampling works to the assay office. The assay sample is divided into 4 parts and put in paper sacks. One part is assayed by the seller of the ore or product; one part by the purchaser; a third part is kept for emergency; and a fourth part is laid aside for an umpire assay, if such becomes necessary.

The assays made by the seller of the ore and those made by the purchaser of the ore are called "control assays." If the seller and purchaser agree within a certain limit, depending on the value of the ore, settlement is made on the purchaser's assay, or sometimes on the average of the two assays. If they do not agree, it is the practice for the buyer and seller to reassay their own samples or to exchange pulp samples and reassay. If they do not then agree, an umpire assayer is chosen who makes an umpire assay, by the results of which all parties abide, and on which settlement is made. The party that is farthest away from the result of the umpire has to pay for the assay.

Controls are made with three check assays, and umpires with four check assays. In sampling small lots in the laboratory and cutting down for the assay sample, the principles already enumerated also apply. Riffle samplers are commonly used as well as the coning and quartering method, although this last is not recommended, even for small lots. The final pulp sample is put through a 100- or 120-mesh screen; for high-grade material, 150- to 200-mesh is better. It is then thoroughly mixed on a rubber sheet or on heavy glazed paper, spread out in a thin, broad plaque 0.25 in. thick, and small lots taken with a spatula at regular intervals, until the required weight is obtained. Fig. 30 shows the Jones riffle sampler and Fig. 31 the umpire mechanical ore sampler.

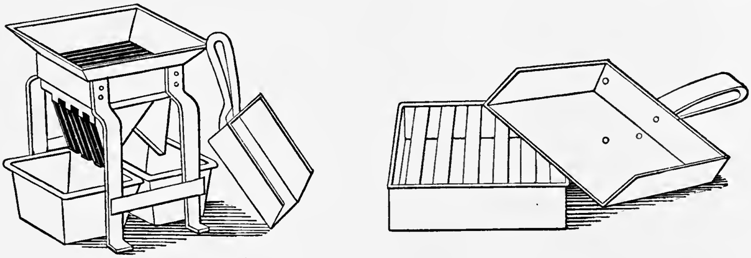

FIG. 30.— JONES RIFFLE SAMPLER

Great care should be taken to clean all sampling apparatus after sampling each lot, so as to avoid "salting" samples. This also applies to all the crushing machinery employed in the sampling.

Sampling Lead Bullion.[1] — Lead bullion is molded into bars

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[1] G. M. Roberts, "Experiments in the Sampling of Silver Lead Bullion," in *Trans.* A. I. M. E., XXVIII, p. 413. Edward Keller, "The Distribution of the Precious Metals and Impurities in Copper," *ibid.*, XXVII, p. 106.

NOTE.— For a complete discussion of machine sampling, consult A. W.

of approximately 80 lbs. weight and shipped in this form. The best method of sampling is to take dip samples at regular intervals while a lot of bars are being molded at the furnace. When the solid bars are to be sampled, about the only reasonably accurate method is to take a "saw sample." This is carried out as follows:

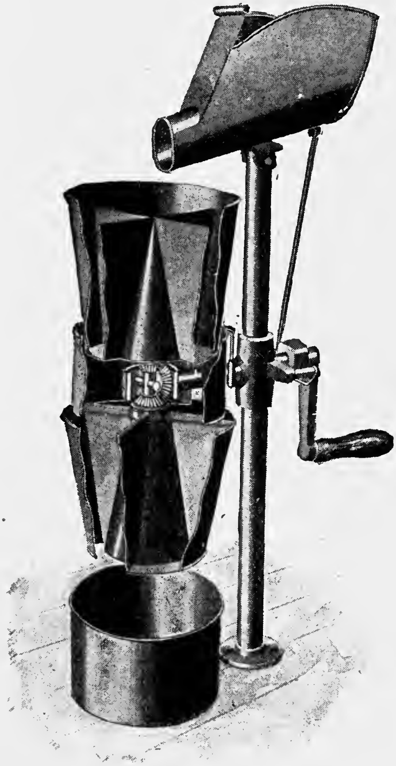

Fig. 31. — Umpire Ore Sampler

Out of a lot of bars, every fifth or tenth bar is sawed across the middle into two pieces. The saw dust is then further cut down to the proper amount for sample and assayed.

Copper bullion is sampled in a similar manner.

Chip or gouge samples are almost invariably inaccurate.

Warwick, "Notes on Sampling," published by the Industrial Publishing Co. Denver, Colorado (50 cents).

IV

WEIGHING; BALANCES AND WEIGHTS

THE balance used in weighing the minute quantities of gold and silver is a delicate piece of apparatus and must be carefully adjusted and handled in order to give accurate results. The balance should be set upon a firm foundation, not subject to vibration; otherwise it is apt to be frequently thrown out of adjustment. Stone or concrete piers set some distance into the ground and free from the floor are the best foundations, when the vibrations induced by moving machinery are absent. Where such vibrations occur, insulated shelf supports should be used.

Construction. — The balance-beam is made of aluminum, gold-plated brass, special silver-aluminum alloys, etc., and as light as possible consistent with the requisite strength. The material from which it is made should be non-magnetic, and have a small coefficient of expansion, so that temperature changes will have but slight effect on the length of the beam. The pan-hangers are frequently of a nickel-silver alloy, or of german silver, and the pans of aluminum. The standards and other metal-work are best made of gold-plated brass. The knife-edges and the plates on which they rest are made of agate, accurately polished and ground true. The balance-beam has three knife-edges, which should be in line in the same plane in order to give equal sensibility with varying loads.[1] The two balance-arms, or the distance from the central knife-edge to each of the outer knife-edges, should be equal in length. This can never be absolutely accomplished, but may be very closely approximated. The accompanying illustration (Fig. 32) shows the essential features of the balance.

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[1] Gottschalk, "The Balance," in "*West. Chem. and Met.*," Vol. II, April, May and June, 1906.

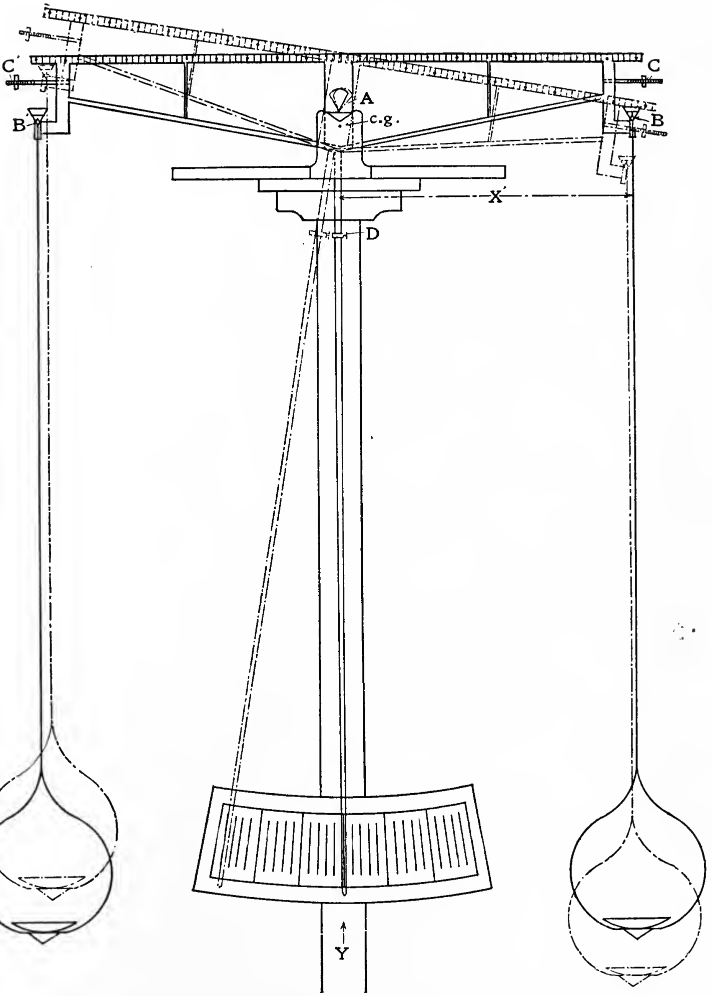

FIG. 32. — DIAGRAM OF ASSAY BALANCE

A	the central knife-edge.
B, B'	the outer knife-edges.
D	adjustment for center of gravity of the balance system.
C, C'	adjustments for equal moment of arms.
$c.\ g.$	center of gravity of the balance system.
Y	pointer-arm.
x..........	distance of deflection of center of gravity, or the gravity lever-arm.

x' ....lever-arm of small weight m' in pan.
m' ....small weight.
M ....mass of balance system.

When the small weight m' is put into the pan it will cause a deflection of the pointer, and the center of gravity of the balance system shifts. The condition of equilibrium is then expressed by the equation

$$Mx = m'x'$$

From this it follows that if M increases, that is, if the mass of the balance system becomes greater, and other conditions remain constant, the weight m' must increase to cause the same deflection; *i.e.*, the sensibility of the balance will be lessened, the sensibility being the amount of deflection caused by a given mass. Assay balances must show a sensibility of at least one-half division of the scale with a weight of 0.01 mg. or even 0.005 mg. This shows the necessity for an extremely light construction, or a small mass of the balance system. It is evident from the equation that the sensibility might be preserved by increasing x', *i.e.*, by lengthening the arms of the balance; in practice, however, this would also very materially increase M, so that the gain is more apparent than real. Long arm balances are also very slow of vibration. Formerly, long arm balances were common, but in modern assay balances the arm rarely exceeds 2.5 in.

From the equation it also follows that, if the center of gravity of the balance system is placed at A, the knife-edge x becomes zero, and we have

$$M \times 0 = m'x'; \text{ or } m'x' = 0;$$

or m' approaches 0 for x' is practically constant; in other words, the balance will become extremely sensitive, an infinitely small weight in the pan causing rotation. While the balance would be very sensitive, it would also be very unstable and "cranky."

The screw-ball D is provided to adjust the center of gravity, which should be somewhat below the knife-edge A. The center of gravity is adjusted so that a weight of 0.01 mg. in the pan or on the beam will cause a deflection of from one-half to one division of the pointer. The lower the center of gravity of the balance system, the more rapid the oscillation of the balance. The higher or the nearer the point of suspension, the slower the oscillations and the greater the sensibility.

Before weighing, the balance is always thoroughly cleaned in every part from dust by a soft camel's-hair brush, made perfectly level by adjusting the leveling screws, and the pointer standardized to 0 by the little thumb-screws *C*, *C′*. To do this, the balance is set in motion until the pointer swings to from 5 to 8 divisions on the scale each side of the zero mark. If the balance-arms are equal in moment, the pointer will swing practically an equal number of divisions on each side, losing, however, a trifle on each swing, thus: $+8, -7.75, +7.5, -7.25, +7, -6.75$, etc., the loss being due to friction and a gradual settling back into equilibrium. If the swings are not as outlined, the adjustment is made until they become so. The balance is then tested for sensibility as described, and the adjustment made for it, if necessary, by moving the center of gravity. If the balance-arms are suspected of being unequal in length (though this is rare in good balances), weighing by "substitution," or double-weighing, is adopted. In this method, the object to be weighed is placed first in one pan and weighed, and then in the other, the true weight being the square root of the product of the two weights found. When the sensibility of the balance is accurately known, no adjustment for equal moment of arms need be made, but weighing may be done by deflection, after the true zero or equilibrium point is found. This is found as follows: Start the balance swinging and count swings to the left as minus and to the right as plus. Suppose the swings are as follows: $-8, +3, -7.5$. The zero-point then is

$$\frac{-8+(-7.5)}{2}\,(+3) = -4.75 \text{ (divisions).}$$

Then place the particle to be weighed on the right-hand pan and weigh again. The swings are as follows: -10, $+2$, -9.5. The sensibility of the balance being 0.5 deflection for each 0.01 mg., the weight of the particle will be

$$\left(\frac{-10+(-9.5)}{2}+2\right)-(-4.75) = -3 \text{ (divisions).}$$

Sensibility, 1 div. = 0.02 mg. The weight is therefore $3 \times 0.02 = 0.06$ mg.

This method, however, is not generally to be recommended; the "rider" should be used for the determination of the fractional parts of the milligram. The balance should also be adjusted for equal moment of arms, as described, before weighing.

In order to detect inequality in the length of the arms, standardize the balance to the true zero, place a 1-gram weight on the right pan, and an old or worn 1-gram weight on the left pan, and bring the balance into approximate equilibrium by adding minute quantities of old rider-wire to the short weight.

Let the gram weight in the right pan be called A.

Let the counterpoise in the left pan be called B.

Let R be the right lever-arm and L the left lever-arm.

Determine the zero-point of the balance in the manner described. If this zero-point differs from that of the unloaded balance, bring the balance to the old zero-point by moving the rider on the left or right arm, as required.

Let the weight indicated by the rider be called $+m$ or $-m$, as it may act with or against B to bring the balance system back to the original zero-point.

Now shift the weight A to the left pan and B to the right pan; remove the rider and again determine the zero-point, and then manipulate the rider to bring the balance system to the zero-point of the unloaded balance and call the weight indicated by the rider $\pm n$, as it may act with or against A. The following equations will then result:

$$1. \quad AR = (B \pm m)\,L \qquad\qquad A = (B \pm m)\,\frac{L}{R}$$

$$2. \quad BR = (A \pm n)\,L \qquad\qquad B = (A \pm n)\,\frac{L}{R}$$

$$3. \quad A + B = (B + A \pm m \pm n)\,\frac{L}{R}, \text{ or } \frac{L}{R} = \frac{A + B}{(B + A \pm m \pm n)}$$

$$4. \quad \frac{L}{R} = 1 - \frac{\pm m \pm n}{A + B \pm m \pm n}, \text{ or, approximately, } \frac{L}{R} = 1 - \frac{\pm m \pm n}{2A}$$

If $m = -n$, or the reversal of the masses shifts the zero-point exactly as much to one side as it was before on the other of the actual 0, the balance has equal arms; *i.e.*, $\frac{L}{R} = 1$. $\frac{L}{R}$ should not exceed 1 ± 0.000003.

Some assayers weigh by "no deflection." They adjust the balance to the true zero, place the bead to be weighed in the right-hand pan, and then by the addition of weights and the moving of the rider by repeated trials, balance the bead, so that finally, when the balance is lowered gently on its knife-edge, no deflection of the pointer takes place. This method, however, is not recommended, as it disregards friction and inertia, and for small weights gives inaccurate results. Care must be taken to have an even temperature in the balance room, preferably about 60° F. The balance must not be exposed to a source of heat which will radiate unsymmetrically, otherwise unequal expansion of balance-arms will cause incorrect weights. In weighing, the balance-door should always be closed to avoid the disturbing effect of slight air currents. The true weight of a mass can be determined only by correcting for the buoyant effect of air. The error, however, is so small that it may ordinarily be neglected.[1]

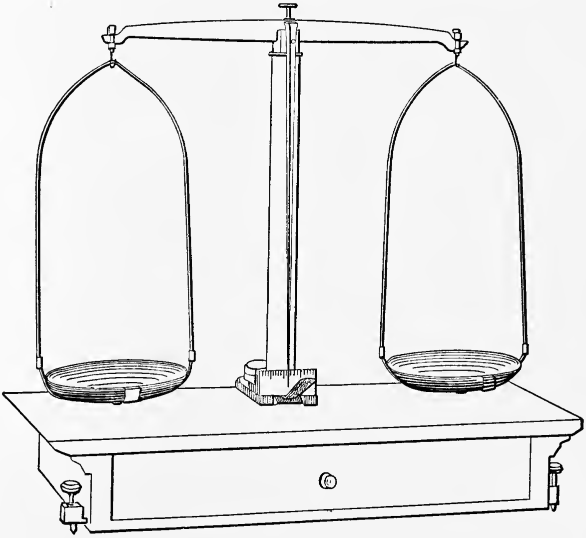

FIG. 33. — PULP BALANCE

Pulp and reagent balances are shown in Fig. 33. A modern assay button balance is shown in Fig. 34.

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[1] Ostwald, "Physico-Chemical Measurements," 1894, p. 38. Ames and Bliss, "A Manual of Experiments in Physics," p. 151.

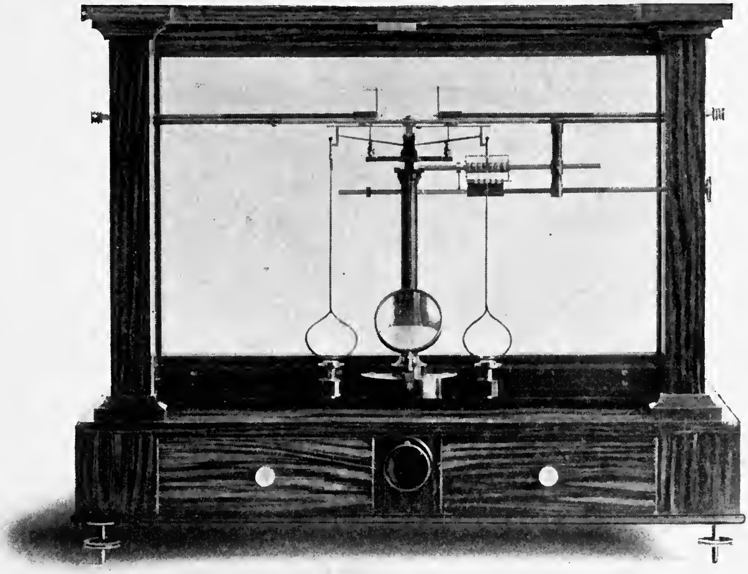

FIG. 34. — ASSAY BUTTON BALANCE.

Weights. — The weights used in weighing beads are milligram weights, usually from 1 mg. up to 1000 mgs., the units being as follows: 1, 2, 5, 10, 20, 50, 100, 200, 500 and 1000 mgs. They are best made of platinum, as the material must be non-corrosive, so that the weight will remain constant. Riders are used to determine weights up to 1 mg. the balance-beams being divided into 100 equal spaces, each space being equivalent to 0.01 mg. with a 1-mg. rider. Riders are made of fine platinum wire, and for assay balances usually come as 0.5- and 1-mg. riders. One-milligram riders are commonly used. Where the balance can readily be made sensitive to 0.005 mg., 0.5-mg. riders can be used with profit; otherwise 1-mg. riders are preferable, as they are not so readily injured by handling. Riders are frequently sold which are not of true weight, and it is essential to check them before using. The same is true of weights. It is desirable for every assay office to have a set of standardized weights for comparison. These standardized weights can be purchased from the balance firms; or a set may be corrected by the Government Bureau of Standards.

The Assay-Ton System. — Gram and assay-ton weights are used to weigh pulp and fluxes. The assay-ton system was devised by Professor Charles F. Chandler, of Columbia University, New York, and reconciles the difficulties arising from the fact that all ores, etc., are weighed by the avoirdupois system, while precious metals are weighed by the troy system. The basis of the assay ton is the number of troy ounces in 1 ton (2000 lbs.) avoirdupois.

1 ton = 2000 lbs.;
1 lb. (avoirdupois) = 7000 troy grains;
therefore, 1 ton = 14,000,000 troy grains.
1 oz. (troy) = 480 grains;

$$\text{therefore, } \frac{14{,}000{,}000}{480} = 29{,}166 \text{ oz. (troy).}$$

Then, taking 1 mg. as the unit, 1 assay ton = 29,166 mgs., or 29.166 grams, and 1 mg. bears the same relation to 1 assay ton as 1 oz. troy bears to 1 ton of 2000 lbs. avoirdupois.

From this it follows that if 1 assay ton of ore is taken, and the silver and gold from this is weighed in milligrams, this weight will represent ounces troy per ton of ore. Fig. 35 shows a set of platinum assay weights; Figs. 36 and 37 show a set of assay-ton and gram weights, respectively.

FIG. 35. — Platinum Assay Weights

FIG. 36. — Assay Ton Weights

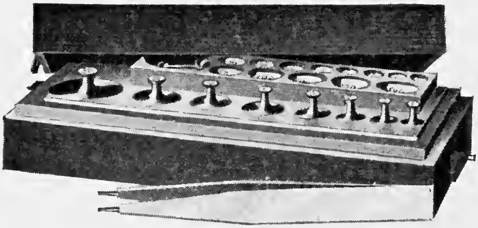

FIG. 37. — Gram Weights

V

REDUCTION AND OXIDATION REACTIONS

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

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

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

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

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

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

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

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

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

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

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

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

$$(a)\quad \underset{240}{2FeS_2} + 15PbO = Fe_2O_3 + 4SO_3 + \underset{3105}{15Pb}$$

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

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

Pyrite	3 grams
$NaHCO_3$	10 grams
PbO	100 grams

The result could not be obtained were the pyrite to be fused with litharge alone, as the presence of soda, a strongly alkaline base, induces the formation of sulphuric anhydride (SO_3), which combines with soda to form sodium sulphate (Na_2SO_4). This sodium sulphate will float on top of the slag and is not decomposed by the temperature usually attained in the muffle. It separates out on cooling as a fused white mass. Its melting-point is 861° C. When the oxidizing action in the above charge is diminished by decreasing the litharge[1] to below 70 grams, the iron is only partially oxidized to the ferric condition and the two following equations express the reactions:[2]

$$FeS_2 + 7PbO = FeO + 2SO_3 + 7Pb$$
$$2FeS_2 + 15PbO = Fe_2O_3 + 4SO_3 + 15Pb$$

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

TABLE I. — REDUCING POWERS OF AGENTS

Name of Reducing Agent	Quantity of Lead in Grams reduced by 1 gram of Reducing Agent
Argol	9.61
Flour	10.53
Sugar	11.78
Charcoal	26.0
Sulphur	18.11 (See Table II)
Pyrite	12.24
Pyrrhotite	8.71
Stibnite	7.17
Chalcocite	4.38
Sphalerite	8.16

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

$$\underset{120}{FeS_2} + 5PbO = FeO + 2SO_2 + \underset{1035}{5Pb};$$

or 1 gram of pyrite reduces 8.6 grams of lead.

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

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

In the assay, as ordinarily performed, the foregoing conditions are modified by the presence of other substances, in the main by silica. Lead oxide readily forms silicates with silica, and the mono-, bi-, and tri-silicates are easily fusible, while those of a higher degree are fusible with difficulty. When a reducing agent (argol, sulphides, etc.) is fused with a silicate of lead, or with a charge containing litharge and silica, practically no lead is reduced when the silica is present in amounts to form a trisilicate or above, and little lead is reduced when the silica is present in amounts to form a mono- or bisilicate. The reason for this is that the silicates of lead are not reduced by sulphides or carbonaceous reducing agents at temperatures below about 1000° C. Above that temperature reduction takes place more readily. The higher the silicate degree the more difficult is the reduction. If, however, certain other bases, such as ferrous oxide (FeO), soda (Na_2O), or lime (CaO), are present (as is the case with most ores), reduction of lead from the silicate occurs, with ferrous oxide or soda, at a comparatively low temperature; but with lime alone, only at a high temperature. The following equation expresses this condition:

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

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

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

Reducing agent	1 gram	Soda bicarbonate	10 grams
Litharge	45 grams	Silica	7 grams

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

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[1] "The Reduction of Lead from Litharge," *ibid.*

TABLE II. — REDUCING POWER OF AGENTS

Name of Reducing Agent	Quantity of Lead reduced by 1 Gram of Reducing Agent
Argol	9.6
Flour	10.92
Sugar	11.74
Charcoal	26.08
Pyrite	9.30
Sulphur	18.11 [1]

NOTE. — Compare Table I with this.

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

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

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

1. By the addition of potassium nitrate (KNO_3) to the charge (or other oxidizing agents).

2. By roasting the ore, thus using the oxygen of the air for the oxidation of impurities.

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

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

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

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

or 1 gram of niter oxidizes 0.15 gram of carbon.

Taking the reducing power of pure carbon as 34.5 grams of lead, the oxidizing power of niter against carbon, expressed in terms of lead, is 0.15 × 34.5, or 5.17 grams. Ten fusions of a charge composed of 85 grams PbO, 1 gram charcoal, 3 grams KNO_3, with 5 grams PbO as a cover, gave very concordant results, and showed the oxidizing power of niter to be 5.10.

The reducing power of the charcoal was determined by five fusions with the same charge, omitting the KNO_3.[1] These results, of course, can also be obtained by an impure charcoal; for, taking one which has a reducing power of 26 grams of lead (this was used in the above fusions), it then contains $\frac{26.0}{34.5}$ or 0.765 gram pure carbon. If 3 grams of niter have been added to the charge, the available carbon for reduction will be $0.765 - (3 \times 0.15)$ or 0.315 gram, which will reduce 34.5×0.315, or 10.75, grams of lead. The oxidizing power of niter expressed in lead, then, is

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

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

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

or 1 gram of niter oxidizes 0.39 gram of pyrite. In the litharge-soda charge, 1 gram of pyrite reduces 12.22 grams of lead; therefore, 1 gram of niter in this instance would oxidize 12.22×0.39, or 4.76, grams of lead. The accompanying table[2] shows actual results obtained for the oxidizing power of niter against different reducing agents.

TABLE III. — OXIDIZING POWER OF NITER

REDUCING AGENT	OXIDIZING POWER OF NITER IN TERMS OF LEAD
Pyrite	4.73 grams
Charcoal	5.15 grams
Flour	5.09 grams
Argol	4.76 grams

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

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

[2] *Ibid.*

When the assay charge contains silica and borax glass, the above figures no longer hold, for in their presence oxygen is evolved by the niter, which escapes from the charge, as in the case of the oxidation of metallic lead by niter. The amount of oxygen lost (thus reducing the oxidizing power of niter) is probably a function of the rate of rise of temperature, but evidence also points to the fact that silica reacts with the niter, setting free oxygen, at a temperature very close to that at which niter reacts with charcoal, or at which oxygen will react with carbon. Niter fuses at 339° C., but does not give off oxygen when fused alone until 530° C. is reached. Charcoal ignites at temperatures[1] ranging from 340° C. to 700° C., depending upon the temperature at which it was burnt, while silica begins to react with niter at very nearly 450° C., probably according to the following reaction:

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

Thus, during the period in which the temperature in the crucible gradually rises to a yellow heat (that of the muffle), oxygen escapes during the range from 400° C. to 500° C., etc., this last being taken as an average temperature at which charcoal will begin actively to oxidize.[2]

Niter will begin to react with argol and pyrite at practically its melting-point.

The oxidizing power of niter against charcoal in charges containing silica will frequently vary between 3.7 and 4.2 grams of lead, averaging about 4 grams. This is 1.1 grams lower than in the litharge-soda charge. The oxidizing power of niter against sulphides is but little lowered by the presence of silica or borax glass. When the oxidizing power of niter against pyrite (sulphides) is considered, and expressed in terms of lead, the varying reducing power of sulphides in different charges has to be taken into account. Taking as an example a charge containing considerable silica, so that a large part of the soda (alkaline base) is absorbed as a silicate, leaving but little to form sulphate from the oxidation of the pyrite, it is found that the reducing power

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

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

of pyrite is 9 grams of lead, as already noted. In this charge, niter will react with pyrite as follows:

$$4FeS_2 + 10KNO_3 = 4FeO + 5K_2SO_4 + 3SO_2 + 5N_2;$$

or 1 gram of niter oxidizes 0.475 gram pyrite. The oxidizing power of niter expressed in lead is then 9 × 0.475, or 4.275 grams. Actually, it will be very little lower than this, as but little oxygen escapes without action. The actual figure obtained by experiment is very close to 4.20.

It is evident from this that the oxidizing power of niter varies with the type of charge used. It ranges, for pyrite, from about 4 grams in acid charges to 4.76 in basic charges (containing no silica). It varies still more with other sulphides. It has been the practice of assayers in making the niter fusion to run a preliminary assay in a comparatively basic charge (approximately the litharge-soda type), and use the figure obtained for the reducing power of the ore in this charge in calculating the amount of niter for the final fusion, usually made quite acid. In this way discordant results are obtained, for both the reducing power of the ore and the oxidizing power of niter vary in the different charges.

Supposing that the preliminary assay showed the reducing power of a nearly pure pyrite to be 12 grams of lead per gram of ore. Using a 0.5 assay ton in the final fusion, on this basis the amount of lead reduced would be 12 × 15, or 180 grams. Subtracting the weight of the lead button, 20, from this leaves the equivalent of 160 grams of lead to be oxidized. Taking 4 as the oxidizing power of niter in the final charge, 40 grams of niter would be added. But in the final charge, owing to its acidity, the reducing power of the pyrite is but 10 grams of lead per 1 gram of ore, and the total reducing power of $\frac{1}{2}$ assay ton is 150 grams. It therefore follows that the final result will show no button. The oxidizing power for niter which should have been used is $\frac{12}{9} \times 4$, or 5.3, and 31 grams of niter added. This, then, would give approximately the proper sized button. As the range of reducing power for pyrite is from about 9 to 12.2 grams of lead, according to whether the charge is acid and contains little soda, or is of the litharge-soda type, the most satisfactory way to determine the amount of niter to add is to have the nature of the preliminary charge the same as that of the final charge, and then use the figure 4 to 4.2 as the oxidizing power of niter.[1] The following charges are recommended to determine oxidizing and reducing powers:

Preliminary Assay, No. 1

5 grams of pyritous ore
8 grams of SiO_2
100 grams of PbO
12 grams of Na_2CO_3
Borax glass cover

Preliminary Assay, No. 2

5 grams of pyritous ore
8 grams of SiO_2
100 grams of PbO
12 grams of Na_2CO_3
3 grams of KNO_3
Borax glass cover

The difference in weight of the lead buttons of preliminary assays Nos. 1 and 2, divided by 3, will give the oxidizing power of niter in the type of charge used. The weight of the button of preliminary assay No. 1, divided by 5, gives the reducing power of the ore.

Preliminary Assay, No. 3

5 grams of pyritous ore
100 grams of PbO
12 grams of Na_2CO_3
Salt cover

It will be noticed that the reducing power of the ore is greater than that obtained in preliminary assay No. 1. In order to determine the reducing power of argol and charcoal, make up the following charges in duplicate:

Preliminary Assay, No. 4

5 grams SiO_2
60 grams PbO
10 grams Na_2CO_3
2 grams argol
Borax glass cover

Preliminary Assay, No. 5

5 grams SiO_2
60 grams PbO
10 grams Na_2CO_3
1 gram charcoal or coke or coal dust
Borax glass cover

In order to determine the oxidizing power of niter as compared to charcoal, make up the following charge in duplicate:

Preliminary Assay, No. 6

5 grams SiO_2
60 grams PbO
10 grams Na_2CO_3
1 gram charcoal, etc.
3 grams KNO_3
Borax glass cover

Calculate results as directed for niter in pyritous ores.

Certain basic ores will have an appreciable oxidizing power,

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[1] This has reference to pure dry KNO_3.

so that when the usual amount of reducing agent is added to the charge to obtain a 20-gram lead button, it is found that, due to the oxidizing power of the ore, the button is deficient in size. The oxidizing ingredients of an ore are generally hematite (Fe_2O_3), magnetite (Fe_3O_4), and manganese oxides; *i.e.*, MnO_2. The reaction which takes place is as follows:

$$2Fe_2O_3 + C = 4FeO + CO_2$$

One gram of Fe_2O_3 requires 0.037 gram of carbon to reduce it to FeO.

In order to determine the oxidizing power of an ore, make up the following charge, if the ore consists mostly of base. When considerable silica is present in the ore, decrease the silica in the charge:

1 assay ton of ore
20 grams Na_2CO_3
90 grams PbO
15 grams SiO_2
1.5 grams coal
Borax glass cover

VI

THE CRUCIBLE ASSAY; ASSAY SLAGS

In almost every instance, when a crucible assay is to be made, the ore and the fluxes added are thoroughly incorporated by mixing, so that, theoretically at least, every particle of the ore is in contact with a particle or particles of fluxes and reducing agent, the most favorable condition to produce a thorough reaction among them. The separation of the precious metals is dependent upon their affinity for metallic lead, forming an alloy of lead, gold and silver, in which lead greatly preponderates, and which readily settles by gravity from the balance of the ore and fluxes which have united to form a slag. The ore to be assayed must, in all instances, be in a finely crushed condition, varying, in American practice, from 80-mesh up to 200-mesh material. What takes place within the crucible depends upon some or all of the following factors:

1. The fineness of crushing. Are all the particles of gold and silver, or their alloy, present, entirely set free from the inclosing gangue? In some ores this takes place with much coarser crushing than in others. In other ores the values are so finely disseminated that all are not set free within the limits of crushing as carried out.

2. The mode of occurrence of the gold and silver. Is it in the free state, as is most generally the case with gold, or are the precious metals in the form of a more or less complex mineral compound (tellurides, argentite, etc.), which must be decomposed before the gold and silver will alloy with the lead?

3. The physical properties of the slag produced; *e.g.*, its formation point, its fluidity at temperatures somewhat above its formation point, and its fluidity after superheating.

4. The chemical nature of the slag, its acidity or basicity, the nature of the bases present, more particularly copper, zinc, antimony, manganese, iron, etc.

If a crucible be broken open and its contents examined shortly after fusion has commenced, these will be found to consist of a heterogeneous mass through which are scattered innumerable particles of lead, both microscopic and macroscopic. The larger particles have been formed by the coalescence of the smaller particles, gradually settling through the charge toward the bottom of the crucible to form the final lead button as the temperature rises and the charge becomes more fluid and less resistant. It is evident that the completeness of the collection of the precious metals depends upon the main factors already outlined. The temperature at which charcoal or argol, etc., begins to react with PbO to form Pb[1] is well below 906° C., the melting-point of PbO. The formation point of a borate silicate, $PbO,Na_2O,4SiO_2,2B_2O_3$ (Seger Cone No. 0.022) the constituents of which are contained in nearly all assay charges, is 590° C.

In the fusion of a mixture containing silica, various bases and borax glass, that silicate-borate having the lowest formation point will form, and then as the temperature rises absorb either silica or base or both, as these are in excess of the ratio required to form the lowest formation-point compound. If the temperature does not rise high enough to cause this absorption, the excess of silica or base or both will remain in suspension in the formed silicate-borate, practically in an unaltered condition. If the formed silicate, etc., constitutes the greater part of the mass, there will be an imperfect non-homogeneous slag; if the excess of silica or base forms the greater part of the material, there will be a slightly fritted mass.

Taking the simplest case, and also the rarest, that of an ore containing free gold completely liberated by crushing, the particle of lead,[2] formed at a comparatively low temperature, can unite at once, as soon as formed, with the gold particle not inclosed in gangue and commence settling to the bottom to form the lead button. It is evident that in this instance the homogeneous fusion and chemical decomposition of the ore are immaterial. Taking, however, the far more common case, in which the values

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[1] CO reacts with PbO to form Pb at 100° C. H reacts with PbO to form Pb at 310° C. — Roscoe and Shorlemmer, 1892, Vol. XI, part 1, p. 282.

[2] There will probably be many particles of lead for each gold particle present, so that no gold will escape for lack of lead.

are not completely liberated by crushing, it is evident that the particle of gold still inclosed within the gangue cannot be reached by the lead already reduced, and it becomes practically essential to hold the lead in place until the ore particle containing the gold is thoroughly broken up chemically and liquefied, so that the lead can absorb the gold. If the lead settles through the charge before this decomposition takes place, gold will remain in the slag. The only way to control this condition is:

(*a*) By fine crushing, liberating the values as completely as possible.

(*b*) By the choice of a slag having the proper physical properties, *i.e.*, a low formation point and a viscous nature near the formation point.

(*c*) By a comparatively slow fusion during the early stages of the assay, to prevent as much as possible the rapid settling away of the lead particles through the still existing interstices of the charge.

Where compounds of the precious metals are in the ore, such as argentite (Ag_2S), tellurides, calaverite and sylvanite (Au, $AgTe_2$), etc., these are readily decomposed by the litharge as follows:

$$Ag_2S + 2PbO = 2PbAg + SO_2$$

The tellurides will be especially considered in Chapter X, on "Special Methods of Assay."

Assay Slags. — An assay slag from the crucible assay consists in most instances of silicates and borates of the metallic bases. While usually of a homogeneous nature, a slag is not to be considered a chemical compound, but rather as an isomorphous mixture of certain compounds. There may, perhaps, be no chemical compound in the slag; litharge, for example, will readily unite with SiO_2 in varying proportions, and after fusion will be homogeneous, in all respects appearing similar to solutions, as salt and water. Salt can be dissolved in water in all proportions up to 23.6 per cent., the solution being homogeneous. In the same way it may be said that PbO can dissolve SiO_2 within certain limits, or vice versa. It is probable that in this mixture certain chemical compounds exist which go into solution in the excess of PbO or SiO_2 present. Since these mixtures or solutions are fluid only at comparatively high temperatures, and solid at ordinary room temperatures, the term "solid solutions" is used for them. In a similar way all the common bases, FeO, Na_2O, K_2O, CaO, MgO, Al_2O_3, ZnO, MnO, etc., form silicates which are relatively soluble within each other, so that a slag may be a complex solution of various silicates. Boric acid and alkaline borates act in a similar way to silica, and the assay slag may consist, and in most cases does consist, of a solution of silicates and borates of various bases.

Silicates are defined in degree by the ratio of oxygen in the base to that in the acid. The chemical classification is as follows:

TABLE IV.—SILICATE DEGREES

NAME	OXYGEN RATIO, BASE TO ACID	EXAMPLE
Orthosilicate	1 to 1	$MgO.FeO.SiO_2$
Metasilicate	1 to 2	$MgO.CaO.2SiO_2$
Sesquisilicate	1 to 3	$K_2O.Al_2O_3.6SiO_2$
Bisilicate	1 to 4	$CaO.2SiO_2$

The metallurgical classification is made on the same basis, *i.e.*, oxygen in the base to that in the acid, but is somewhat different. It is the one adopted in these notes.

TABLE V.—SILICATE DEGREES

FORMULA, RO (BASE)	NAME	FORMULA, R_2O_3 (BASE)
$4RO, SiO_2$	Subsilicate	$4R_2O_3, 3SiO_2$
$2RO, SiO_2$	Monosilicate	$2R_2O_3, 3SiO_2$
$4RO, 3SiO_2$	Sesquisilicate	$4R_2O_3, 9SiO_2$
RO, SiO_2	Bisilicate	$R_2O_3, 3SiO_2$
$2RO, 3SiO_2$	Trisilicate	$2R_2O_3, 9SiO_2$

Borates may be classified in a somewhat similar manner.

In general, it may be stated that the higher the silicate degree, the more infusible is the mixture, and that a polybasic mixture, one of many bases, is more easily fusible than one of few. These general statements are not without exceptions, for certain bisilicates and trisilicates have a lower fusing point than the corresponding monosilicate, etc. It also depends greatly upon the base what the fusibility of the silicates will be. PbO, Na_2O, and K_2O give easily fusible silicates; FeO and MnO give, comparatively, readily fusible silicates; Al_2O_3, CaO, and MgO give difficultly fusible silicates. When, however, silicates of all these various bases are mixed and go into solution as a homogeneous mass, the effect of this mixture on the melting-point of the mass is often to lower it. In fact, the silicate mixtures are to be looked upon from the same point of view as metallic alloys; there may be eutectic mixtures, *i.e.*, mixtures of two or more constituents which have a lower melting-point than either of the constitutents, as is illustrated in the accompanying diagram.[1]

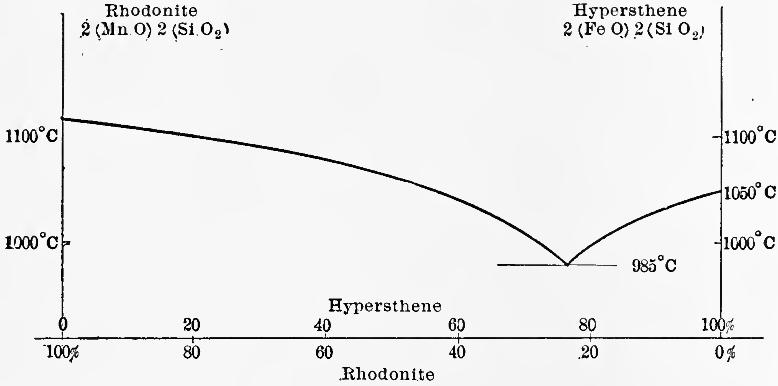

Fig. 37a. — Freezing-Point Curve; Rhodonite Hypersthene

When approximately 80 per cent. of rhodonite (the bisilicate of manganese) is fused with 20 per cent. of hypersthene (the bisilicate of iron), the melting-point is appreciably lowered. $CaSiO_3$ ($CaO.SiO_2$) and Na_2SiO_3 ($Na_2O.SiO_2$) thus form a eutectic mixture of 80 per cent. Na_2SiO_3 and 20 per cent. $CaSiO_3$.

Typical Assay Slags. — A slag of low formation temperature and considerable viscosity at that temperature corresponds to Seger Cone No. 0.022 — $Na_2O.PbO.4SiO_2.2B_2O_3$, 590° C. This may be written: $PbO.4SiO_2.Na_2B_4O_7$ (borax glass).

By calculation from the atomic weights the following charge will yield this slag:

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[1] J. H. L. Vogt, "Die Silicat-Schmelzlösungen, II, Christiana.

PbO	33.3 grams
SiO_2	36.2 grams
$Na_2B_4O_7$	30.4 grams

The slag, corresponding to Seger Cone 0.017 and melting at 740° C., may be desirable for aluminous ores:

($Na_2O.PbO.Al_2O_3.6SiO_2.2B_2O_3$), which may be written ($Na_2B_4O_7$, PbO, Al_2O_3, $6SiO_2$).

The following charge will yield this slag:

$Na_2B_4O_7$	22.9 grams	Al_2O_3	11.5 grams
PbO	24.9 grams	SiO_2	40.7 grams

TABLE VI. — ASSAY SLAGS[1]

FORMULA	SILICATE DEGREE	Approximate temperature (Centigrade) at which fluid	REMARKS
1. $2Na_2O.SiO_2$	Monosilicate	1070	Vitreous, colorless, transparent.
2. $Na_2O.SiO_2$	Bisilicate	1090	Stony, white, crystalline.
3. $2PbO.SiO_2$	Monosilicate	1030	Vitreous, lt. yellow, transparent.
4. $PbO.SiO_2$	Bisilicate	1050	Vitreous, lt. yellow, transparent.
5. $Na_2O.FeO.SiO_2$	Monosilicate	1070	Very fluid, stony black.
6. $Na_2O.FeO.2SiO_2$	Bisilicate	1070	Vitreous, black.
7. $PbO.FeO.SiO_2$	Monosilicate	1100	Resinous, black.
8. $Na_2O.PbO.SiO_2$	Monosilicate	1020	Vitreous, yellow-green.
9. $Na_2O.PbO.2SiO_2$	Bisilicate	1030	Vitreous, yellow-green.
10. $2(PbO.FeO.CaO)3SiO_2$	Monosilicate	1110	Vitreous, black.
11. $Na_2O.PbO.FeO.CaO.2SiO_2$	Monosilicate	1030	Vitreous, black, contains sq. crystals.
12. $Na_2O.PbO.FeO.CaO.4SiO_2$	Bisilicate	1100	Vitreous, black.
13. $2(Na_2O.PbO.CaO)3SiO_2$	Monosilicate	1090	Stony, light yellow.
14. $2(Na_2O.FeO.CaO)3SiO_2$	Monosilicate	1150	Viscous, stony, gray-brown.
15. $2(Na_2O.PbO.FeO)3SiO_2$	Monosilicate	1030	Vitreous, black.

[1] Elmer E. West, Laboratory, S. D. School of Mines, 1904.

Stony slags indicate incomplete solution of some of the ingredients.

A partial replacement of the silica by borax glass in the foregoing slags will appreciably lower the formation points.

Bases such as FeO, CaO, MgO, MnO, BaO, and Al_2O_3 are present in greater or lesser quantity in almost all ores, and SiO_2 is present in practically every ore, so that such slags as those outlined must necessarily be made. The easily fusible bases PbO and Na_2O serve to lower the formation point of the slag. If it is accepted that the composition of the slag in the assay is practically the constant factor, it is evident that when the approximate composition of the ore is known, we will add either basic or acid fluxes, in such proportions as to produce the proper slag decided upon. The most desirable constitution for an assay slag in general is that of a monosilicate or a sesquisilicate, sometimes, but more rarely, a bisilicate. If the ore is basic a bisilicate may be approached, if acid a monosilicate, or even a sub-silicate, in order to insure complete decomposition.

The accompanying table will simplify slag calculations:

TABLE VII.—THE CALCULATION OF SLAGS[1]

Unit Molecular Base Ratio; e.g., PbO: Na_2O: FeO, etc. = 1: 1: 1

One Part of Base by Weight	Parts of Other Bases Necessary						Parts of SiO_2 Necessary for Monosilicate
	Na_2O	PbO	CaO	Al_2O_3	FeO	ZnO	
Na_2O	1.000	3.590	0.903	1.646	1.160	1.311	0.486
PbO	0.279	1.000	0.252	0.459	0.323	0.365	0.136
FeO	0.862	3.095	0.779	1.419	1.000	1.130	0.419
CaO	1.108	3.976	1.000	1.823	1.284	1.452	0.539
Al_2O_3	0.608	2.181	0.549	1.000	0.705	0.797	0.886
CuO	0.780	2.801	0.704	1.284	0.905	1.023	0.379
ZnO	0.763	2.738	0.689	1.255	0.885	1.000	0.371

One Part by Weight of SiO_2 requires to form the Monosilicate	Na_2O	PbO	CaO	Al_2O_3	FeO	ZnO	CuO
	2.07 parts	7.36 parts	1.86 parts	1.14 parts	2.40 parts	2.70 parts	2.63 parts

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[1] Based on Balling's table.

When a bisilicate is to be calculated, the silica required for a monosilicate is determined and then multiplied by two. Vice versa, when the bases for the monosilicate have been calculated and a bisilicate is to be formed, the bases must be divided by two. The same reasoning applies to other silicate degrees.

Example of the Calculation of an Assay Slag. — The problem is to calculate a charge to produce the following monosilicate: $Na_2O.PbO.FeO.CaO.2SiO_2$. Taking as the unit 10 grams of Na_2O, it follows from the preceding table that the weights of the substances required are:

Na_2O .... 10 × 1 = 10.0 grams
PbO .... 10 × 3.59 = 35.9 grams
FeO .... 10 × 1.16 = 11.6 grams
CaO .... 10 × 0.903 = 9.03 grams

The silica required will be:

for the Na_2O .... 10 × 0.486 = 4.86 grams
PbO .... 35.9 × 0.136 = 4.86 grams
FeO .... 11.6 × 0.419 = 4.86 grams
CaO .... 9.03 × 0.539 = 4.86 grams
Total .... 19.44 grams SiO_2

The silica may be determined by calculating it for one base and multiplying that figure by the number of oxygen molecules in the bases present, after having reduced the slag formula to its lowest possible terms. Before making up the charge, it is essential to remember that the Na_2O in this instance is furnished in the form of $NaHCO_3$, which contains approximately 40 per cent. of Na_2O, and that the FeO is furnished by an iron ore of the following approximate composition:

Fe_2O_3, 80 per cent.; SiO_2, 17 per cent.

The lime is furnished by limestone, $CaCO_3$, practically pure.

It is also necessary to provide a lead button; so extra litharge must be furnished. To reduce the lead, coal dust is added. Some of the coal will be used up to reduce the Fe_2O_3 to FeO. Hence the following calculations are to be made: 10 grams Na_2O are required; therefore $\frac{10}{40} \times 100 = 25$ grams of $NaHCO_3$ must be added. PbO contains 92 per cent. of Pb; therefore, in order to obtain a 20-gram lead button, $\frac{20 \times 100}{92} = 22$ grams of PbO must be added, in addition to the 35.9 grams for the silicate – a total of 57.9 grams of PbO. Eleven and six-tenths grams of FeO are required. Fe_2O_3 consists of 90 per cent. of FeO and 10 per cent. of O_2; and as the ore is 80 per cent. of Fe_2O_3, $\frac{11.6 \times 100}{90 \times 80} = 16.1$ grams of ore will be required. The limestone contains 54 per cent. CaO; therefore, $\frac{9.03 \times 100}{54} = 16.7$ grams of limestone will be required.

The coal in use has a reducing power of 20 grams of lead per gram of coal.

The following reaction takes place between carbon and the Fe_2O_3.

$$2Fe_2O_3 + C = 4FeO + CO_2.$$

One gram of Fe_2O_3 requires $\frac{12}{320} = 0.037$ gram of charcoal. But as the coal used is only $\frac{20 \times 100}{34.4} = 58$ per cent. as strong as charcoal, the following quantity will have to be added to the 16.1 grams of Fe_2O_3 to reduce it:

$$\frac{0.037 \times 16.1 \times 80}{0.58} = 0.82 \text{ gram coal}$$

To this must be added .1 gram for the reduction of the 20-gram lead button, giving 1.82 grams of coal to be added.

Since the iron ore contains silica, this is to be deducted from the silica calculated. The amount of SiO_2 in the ore is 16.1 × 17 per cent. = 2.74 grams.

The correct charge then is:

25	grams........$NaHCO_3$	16.7	grams........limestone
57.9	grams........PbO	16.7	grams........silica(19.44 − 2.74)
16.1	grams........Fe_2O_3 (iron ore)	1.82	grams........coal

Salt cover

Following is the calculation of the same slag, but for a quartz ore containing 95 per cent. SiO_2. The formula for the slag is: $Na_2O.PbO.FeO.CaO.2SiO_2$. Taking as the unit 1 assay ton of ore, or, in round numbers, 30 grams, this will contain 28.50 grams of SiO_2. These 28.5 grams are to be divided into 4 equal parts to satisfy the 4 bases present. Therefore, 7.1 grams of SiO_2 will go to such an amount of each base as will form a monosilicate.

7.1 grams SiO_2 require $7.1 \times 2.07 = 14.7$ grams Na_2O
7.1 grams SiO_2 require $7.1 \times 7.36 = 52.25$ grams PbO
7.1 grams SiO_2 require $7.1 \times 2.40 = 17.04$ grams FeO
7.1 grams SiO_2 require $7.1 \times 1.86 = 13.20$ grams CaO

The bicarbonate of soda required is $\frac{14.70 \times 100}{40} = 37$ grams.

The PbO required is $52.25 + 22 = 74.25$ grams for the lead button.

The $FeCO_3$ (siderite) required is $\frac{17.04 \times 100}{62} = 27$ grams.

The limestone required is $\frac{13.20 \times 100}{54} = 24.4$ grams.

The complete charge is:

1	assay ton of ore	27	grams............$FeCO_3$
37	grams............$NaHCO_3$	24.5	grams............$CaCO_3$
74	grams............PbO	1	gram............coal

Salt cover

In one case the ore is of a basic nature — hematite and limestone (17 grams of each), and in the other case it is of an acid nature — quartz; yet the slag produced is the same in both cases. This brings out the fact that the slag is the constant and that fluxes are added of such nature and in such quantity, determined by the ore, as to produce a slag of fairly constant composition. It is to be noted that the slag made in the two assays contains four bases, PbO, Na_2O, FeO, CaO, and that these are present in unit molecular base ratio. As a matter of fact, the assayer rarely adds CaO or FeO as fluxes, but when these are present in the slag, they are derived from the ore. The bases added as fluxes are practically limited to three, PbO, Na_2O and, at times, K_2O, so that when an ore consisting chiefly of SiO_2 is to be assayed, the slag made will approximate a monosilicate and borate of lead oxide and soda.

The table of assay slags given mentions only those in which the bases are present in the unit molecular ratio. It is evident that where an ore is considered in which numerous bases are present, these are not contained in the unit molecular ratio, so that the formula of the slag made will rather have this general form:

$$(xPbO, yNa_2O, zFeO, tMgO)\ vSiO_2,$$

in which, for a monosilicate, considering the letters as oxygen coefficients, $x + y + z + t = 2v$. In order to get a slag of low formation point, the coefficients of the more infusible bases, such as CaO, MgO, Al_2O_3, will have to be materially smaller than those of the more fusible bases, PbO, Na_2O, and FeO.

In assay practice, it is neither possible nor desirable to make analyses of ore before assaying for gold and silver. The assayer, however, is supposed to have a good working knowledge of lithology and mineralogy, which will enable him to form a correct judgment of the contents of his ore within fair limits. It will be comparatively easy for him to tell at once whether he has limestone or dolomite, or an ore containing much limonite or hematite or the iron sulphides; or whether magnesia, barium or other minerals are present, and in what general proportions. Following are analyses of silicious and lead antimonial ores:

TABLE VIII.—SILICIOUS ORES

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Gold	0.63 oz.	0.85 oz.	3.35 oz.	2.00 oz.	0.78 oz.	0.90 oz.
Silver	2.00 oz.	6.08 oz.	1.75 oz.	0.62 oz.	1.00 oz.	——
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Silica	65.38	80.00	80.90	84.80	77.38	93.72
Iron	13.40	7.50	9.94	7.50	3.54	2.67
Sulphur	11.40	4.40	4.53	0.75	4.42	0.69
Arsenic	0.90	2.00	0.29	0.00	0.55	0.02
Antimony	trace	trace	trace	trace	trace	0.089
Tellurium	0.003	trace	0.007	trace	——	——
Zinc	——	——	——	——	——	——
Copper	0.02	0.004	0.013	0.008	trace	——
Manganese ...	trace	0.54	trace	0.96	——	0.082
Alumina	5.43	1.79	1.70	1.02	2.80	3.53
Lime	2.10	1.70	0.50	0.90	0.56	——
Magnesia	0.20	——	trace	——	trace	——

TABLE IX. — LEAD ANTIMONIAL ORES

	No. 1	No. 2	No. 3
Silica	60.1 per cent.	57.65 per cent.	59.50 per cent.
Ferrous oxide	5.2 per cent.	0.70 per cent.	4.60 per cent.
Alumina	9.5 per cent.	1.40 per cent.	9.00 per cent.
Magnesia	2.68 per cent.	2.09 per cent.	3.00 per cent.
Lime	trace	trace	trace
Lead	10.6 per cent.	16.86 per cent.	10.1 per cent.
Antimony	4.4 per cent.	11.84 per cent.	7.55 per cent.
Sulphur	0.5 per cent.	——	0.44 per cent.
Water	0.3 per cent.	——	0.40 per cent.

TABLE X. — HEMATITE

Analysis of a Hematite	
Silica	14.20 per cent.
Ferrous oxide	73.68 per cent.
Alumina	5.03 per cent.
Lime	0.57 per cent.
Manganous oxide	0.19 per cent.
Phosphorus	0.101 per cent.

TABLE XI. — LIMESTONE

Analysis of a Limestone	
Silica	1.94 per cent.
Alumina and ferric oxide	0.68 per cent.
Magnesia	0.18 per cent.
Lime	53.61 per cent.
Carbonic acid	43.81 per cent.
Water	0.11 per cent.

These analyses are given to show what the chief base constituents may be, and how ores will range from acid types to basic ones. Whenever sulphides are present, it is to be noted that the oxidation of these leaves basic oxides to be fluxed.

At times, instead of silicate and borate slags, it is desirable to make oxide slags in the crucible assay. This, of course, can only be done when silica is absent from the ores, or when a very large excess of litharge is used in the fusion. Litharge, which melts at 906° C., possesses the property of dissolving or holding in suspension certain quantities of other metallic oxides. These slags are discussed in the chapter "Assay of Impure Ores."

The charge for the monosilicate of lead and soda is (using the unit molecular base ratio):

0.5 assay ton silica or quartz ore
39 grams $NaHCO_3$
55 grams PbO
Borax glass cover

For the bisilicate it is:

0.5 assay ton silica or quartz ore
20 grams $NaHCO_3$
28 grams PbO
Borax glass cover

Allowing for a 20-gram lead button, the charges are:

No. 1 Monosilicate Ore (quartz), 0.5 assay ton	No. 2 Sesquisilicate (Approximate) Ore (quartz), 0.5 assay ton	No. 3 Bisilicate Ore (quartz), 0.5 assay ton
$NaHCO_3$ ...... 39 grams	$NaHCO_3$ .... 30 grams	$NaHCO_3$ ...... 20 grams
PbO .... 77 grams	PbO .... 60 grams	PbO .... 50 grams
Coal .... 1 gram	Coal .... 1 gram	Coal .... 1 gram
Borax glass cover	Borax glass cover	Borax glass cover

All of the above charges will yield satisfactory slags in an ore assay if the ore is of the nature described. No. 3 is the cheapest in point of cost; No. 2 is the one most frequently made.

Color of Slags. — Most slags from ore assays will be from light to very dark green in color or almost black, this color being due to various proportions of ferrous silicate. When iron is absent, the color of lead silicates (yellow) may predominate, or white and gray or colorless slags, due to silicates of CaO.MgO.ZnO, etc., be produced. Copper produces red slags, due to cuprous silicate. Cobalt gives blue slags. When much lime is present in an ore, this is best calculated to a bisilicate or even higher, while the other bases can be calculated to the monosilicate.

VII

CUPELLATION

CUPELLATION has for its object the oxidation of the lead in the gold, silver, etc., alloy to PbO, which in part (95 per cent.) is absorbed by the cupel, and in part (5 per cent.) volatilized. The silver and gold of the alloy are left as a metallic bead. The process is carried out in cupels. Cupels are shallow porous dishes, made generally of bone-ash. Leached wood-ashes (particularly from beech-wood) and lime and magnesia have also been used for cupels. A mixture of bone-ash and leached wood-ashes, in the proportion of 1 to 2 and 2 to 1 respectively, has been used, and is said to give a much smaller absorption of the precious metals than bone-ash cupels.[1]

The bone which yields the bone-ash on calcining has the following composition.[2]

	SHEEP BONES	CATTLE BONES
$Ca_3(PO_4)_2$	62.70 per cent.	58.30 per cent.
$CaCO_3$	7.00 per cent.	7.00 per cent.
$Mg_3(PO_4)_2$	1.59 per cent.	2.09 per cent.
CaF_2	2.17 per cent.	1.96 per cent.
Organic matter	26.54 per cent.	30.58 per cent.

These bones will produce bone-ash of the following composition:

	No. 1	No. 2
$Ca_3(PO_4)_2$	84.39 per cent.	83.07 per cent.
$CaCO_3$	9.42 per cent.	10.00 per cent.
CaF_2	4.05 per cent.	3.88 per cent.
$Mg_2(PO_4)_3$	2.15 per cent.	2.98 per cent.

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[1] Kerl, "Probir Kunst," 1886, p. 91.

[2] Hemtz, "Erdman's Jour. of P. Chem.," Bd. 48, S. 24.

The bone-ash used for cupels must be specially treated by washing with an aqueous solution of ammonium chloride (this salt to the extent of 2 per cent. of the weight of the bone-ash to be treated).[1] This reacts with $CaCO_3$ and any CaO present, converting them into $CaCl_2$, which is removed by washing with water. The presence of $CaCO_3$ is very undesirable in bone-ash for cupels, as it begins to give off CO_2 at 700° C., about the proper temperature for cupellation, causing a serious spitting of the lead button, which entails a loss of the precious metals. Cupels should not be kept where the nitrous fumes from parting can be absorbed by them, as these will form $Ca(NO_3)_2$ with any CaO that may be present, which also is decomposed about the temperature of cupellation. Bone-ash melts at about 1450° C. (Hempel).

The physical nature of the cupel, especially as regards porosity, is very important. For this reason there should be a careful adjustment of the relative amounts of different sized particles present. Practically, only the fraction of 1 per cent. of the bone-ash should remain on a 40-mesh screen. If there is an insufficiency of fine particles in the bone-ash, the cupel will be too porous and cause a relatively heavy absorption of gold and silver. If the bone-ash is too fine, the cupels made from it will be too dense, prolonging the cupellation and causing losses, mainly by increased volatilization.

The following is a screen analysis of the bone-ash commonly purchased, but which is rather coarse:

Through a	20-mesh screen,	100	per cent.
On a	30-mesh screen	2.00	per cent.
On a	40-mesh screen,	6.40	per cent.
On a	60-mesh screen,	10.04	per cent.
On a	80-mesh screen,	2.00	per cent.
On a	100-mesh screen,	11.20	per cent.
Through a	100-mesh screen,	68.88	per cent.

Cupels should be as uniform as possible as regards density, and for this reason are best made by machine, in which a constant pressure may be obtained, rather than by hand molds. Fig. 38 shows a good type of cupel machine. Considerable pressure may be used, and the cupels made quite firm. It is not possible to specify the proper condition in definite terms, but a batch of

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[1] W. Bettel, "Jour. Chem. and Met. Soc. of S. A.," Vol. II, p. 599.

cupels, after being made up and carefully dried for at least three weeks or a month, should be tested by cupeling a weighed quantity (200 mgs.) of c. p. silver with 20 grams of lead at the proper temperature, 700° C., and the loss noted. It should not exceed from 1.5 to 1.8 per cent.

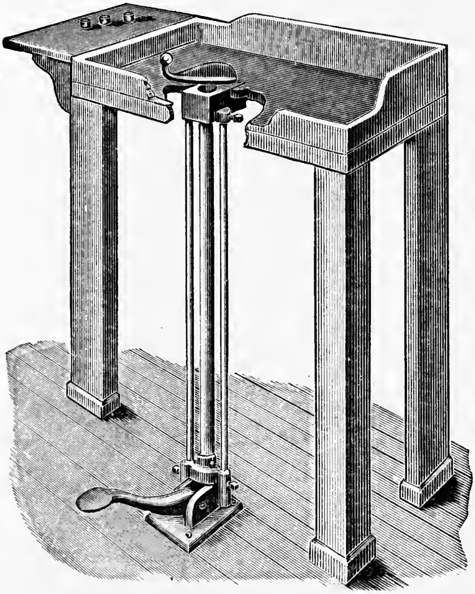

Fig. 38. — Cupel Machine

The bone-ash to be made into cupels is mixed with from 8 to 12 per cent. of water, in which is dissolved a little K_2CO_3, or to which has been added a little molasses or stale beer. After making, the cupels should be carefully and slowly dried. If possible, cupels should be several months old before using. In the Royal British Mint no cupels less than two years old are used for bullion assays.

If cupels are too rapidly dried, or have been made up too wet, they crack and check when placed in the furnace and make the assays conducted in them unreliable.

The importance of good cupels cannot be overestimated. Very frequently, inaccuracies in the assays are due chiefly to the cupel. The shape of the cupel has some influence on the loss of precious metals by absorption. If the cupel is very flat and shallow, so that the molten lead covers a large area and has little depth, the time of cupellation is decreased as the surface exposed to oxidation is increased, but as the absorption of precious metals is probably a function of the area exposed, it will be large in shallow cupels.[1]

Cupellation. — When ready to cupel lead buttons, the cupels are placed, empty, in the red-hot muffle and allowed to remain there for about 10 minutes in order to expel any moisture, or organic matter present (if molasses water has been used in making them up). If the buttons were placed into the cold cupel, the lead would melt before all the remaining moisture is expelled, which would then pass up violently through the molten lead, causing what is termed "spitting," *i.e.*, the projection of small lead particles, carrying values from the cupel. Some cupels, made from bone-ash containing $CaCO_3$, will commence to spit after the cupellation has proceeded for some time and the temperature has risen to above 700° C. This can be stopped by pulling the cupel to the cooler (front) part of the muffle, although the cupellation, after spitting, is to be considered unreliable When a piece of wood or coal is placed in the muffle to "open up" lead buttons, the cupels absorb gases at times, which later on, when the temperature rises, are again expelled, with a spitting of the lead.

When the lead button is put into the hot cupel, the lead melts (326° C.) and is covered by a gray-black scum. If the lead button is practically pure, as it should be, this black scum disappears when the lead reaches a temperature of 675° C.[2] This is called the "opening up" or "uncovering" of the lead button. The molten lead then appears bright, begins to "drive," and active and rapid oxidation commences. Lead buttons should uncover as soon as possible in the muffle. If other and more difficultly fusible metals, such as Cu, Fe, etc., are present, the temperature of uncovering is higher and the temperature required for cupellation is higher. These foreign metals should, however, as a general rule, be absent.

Little flakes of PbO form on the surface of the molten lead

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[1] H. K. Edmands, in "Eng. and Min. Journ.," LXXX, 245.

[2] T. K. Rose, in "Journ. Chem. Met. and Min. Soc. of S. A.," Jan., 1905.

and slide down the convex surface of the button, and are absorbed by the porous mass of the cupel. If the temperature of the cupellation is between 700° and 750° C., as it should be, this litharge is solid, as the litharge melts at 906° C. The temperature of the lead itself during cupellation is probably higher than that indicated by the pyrometer couple near it, owing to the rapid oxidation of the Pb. This is indicated by the brighter color of the lead.

Any foreign metals, as Cu, Sb, Fe, Zn, etc., which are present are oxidized (some by the PbO formed), and absorbed by the cupel, if not present in too large amounts.

$$\mathrm{Zn} + \mathrm{PbO} = \mathrm{Pb} + \mathrm{ZnO}.$$

Such elements as Sb, As, and Zn, when present in the button, are in part volatilized as oxides, and in part absorbed. When cupellation for silver is carried on, the temperature should not be above 700° C., in which case crystals of litharge (feathers) form on the side of the cupel toward the muffle mouth. If the temperature is getting too low for the cupel to successfully absorb practically all of the PbO, these feathers form low down in the cupel. When the temperature is about right, they form near the upper rim of the cupel. It is, however, to be noted that the draft through the muffle influences the formation of feather litharge; *i.e.*, if the draft is strong, feathers will form, although the temperature is somewhat above 700° C. During cupellation, the door of the muffle should never be left wide open, but should be set slightly ajar, so that the cold air will not strike directly upon the cupels. When silver and gold are cupeled for, owing to the higher melting-point of the silver-gold alloy, the finishing temperature will have to be 750° C. at least.

As the cupellation proceeds, the percentage of lead in the alloy decreases and that of Ag and Au increases. The litharge thrown off from the center of the button is in larger specks, and brilliant, and the button assumes a more rounded form. When this phenomenon appears, the button should be pushed back into the hotter part of the furnace or the temperature of the furnace raised somewhat. When the last of the Pb goes off, large buttons are covered with a brilliant film of colors (interference colors) and the button appears to revolve axially. The colors then disappear, the bead becomes dull, and then again takes on a silvery tinge.

If now the temperature of the muffle is below that of the melting-point of silver (962° C.), or below that of the gold-silver alloy constituting the bead, or if the cupel be withdrawn from the furnace, the "blick" or "brightening" or "flash" of the bead takes place; *i.e.*, the bead suddenly becomes very bright, at the moment of solidification, owing to the release of the latent heat of fusion, which raises the temperature of the bead very much for a short time. The bead has been in a state of surfusion, *i.e.*, in a state of fusion below its true freezing-point, toward the last of the cupeling operation; and if it be lightly jarred or the temperature allowed to drop still lower (by taking it out of the muffle), it suddenly congeals and assumes a state normal (solid) to the temperature existing.[1] The release of the latent heat, raising the temperature of the bead, causes the brightening. The "brightening" of very small beads is rarely noticeable. Silver and gold beads still containing small amounts of Pb or Cu do not brighten so noticeably. If even minute quantities of rhodium, iridium, ruthenium, osmium, or osmium-iridium, are present, buttons will not flash. Platinum and palladium are excepted.

Silver beads after cupellation, and at the moment of solidification, also "sprout." Just before the silver bead becomes solid it absorbs oxygen from the air, the maximum absorption being about 22 volumes. This oxygen is suddenly expelled when the bead solidifies, causing a cauliflower-like growth on the bead. Small particles of silver may even be projected from it and cause a serious loss. When gold is present in the silver bead to the extent of 33 per cent. or more, sprouting does not take place. Silver beads containing small quantities of Pb, Cu, Zn, Bi, etc., will not sprout, so that if a button does sprout it is a sign of purity.

Buttons below 5 mgs. in weight do not sprout readily; large buttons, however, do. Sprouting can be prevented by slow cooling in the muffle, or by having ready a hot cupel which can be set, inverted, over the one holding the bead, and withdrawing both from the muffle, thus cooling the bead slowly. Sprouted beads are to be rejected as an assay.

When cupeling for silver alone, or for silver and gold, it is

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[1] Rose, "Metallurgy of Gold."

necessary to watch the end of the cupellation carefully, and to promptly remove the cupel about 30 seconds to 1 minute after the bead has become dull. A heavy loss of silver commences if the silver buttons are kept beyond that time in the furnace. If silver is not to be determined, but gold only, the buttons may be left in for 5 to 10 minutes without loss of gold. Gold beads will retain minute amounts of lead which cannot be removed by permitting the bead to stay in the muffle.

The bead, when cold, is taken from the cupel with a pair of pliers, and cleaned of bone-ash by flattening somewhat with a hammer. It should be examined with a glass to make sure that no bone-ash adheres to it.

The bead should be either white or yellow, depending on the amount of gold present, round and not flat (the latter indicating the presence of foreign metals), and should possess a crystalline surface where it adhered to the bone-ash. It should be firmly attached to the bone-ash of the cupel. If it is not, this fact indicates that lead is still present. It should also have no rootlets extending into the cupel. The cupel, after cupellation, should be smooth and firm, not fissured and cracked, and of a light yellow color when cold. Other colors indicate the presence of foreign metals.

The freezing-point curve of lead-silver (Fig. 39) will give some idea of the proper temperature of cupellation. A lead button is to be considered as an alloy of lead and silver (or gold) which in the process of cupellation undergoes the change from practically pure lead to that of pure silver (or gold).

A 20-gram button containing 200 mgs. of silver contains 1 per cent. of Ag. An alloy of lead and silver containing 4 per cent. of Ag is of "eutectic composition" and melts at 303° C., the melting-point of pure lead being 327° C. Most assay buttons will contain very much less than 1 per cent. of silver and will melt practically at the melting-point of lead. Leaving out of consideration for the moment that lead "uncovers" at 675° C. in an oxidizing atmosphere, and the proper temperature required to cause a ready absorption of PbO by the cupel, it is evident that for a lead button weighing 20 grams and containing 20 mgs. of silver (0.1 per cent.), the temperature required to keep the button molten ranges from 327° C. to 303° C., until the button

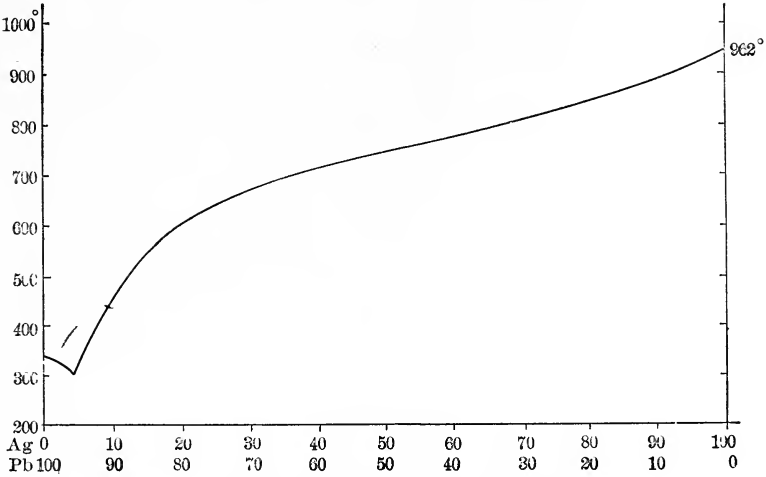

Fig. 39 - Freezing point Curve, Lead - Silver

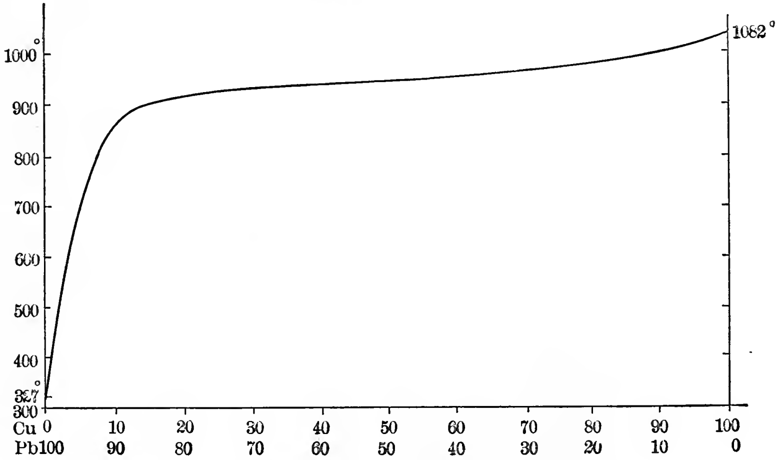

Fig. 40 - Freezing point Curve, Lead - Copper

has decreased $\frac{39}{40}$ in weight by the loss of Pb, practically the entire time of cupellation.

When the button has reached $\frac{1}{40}$ of its original weight, the temperature required to keep it molten will rapidly increase, according to the curve, as more lead is oxidized, until, in order to prevent freezing and get pure silver, a temperature of 926° C. and slightly above must finally be reached. In order, however, to cause a rapid formation of PbO and its ready absorption by the cupel, and not have heavy losses of Au and Ag, it is found that a temperature of about 700° C. is best for the main part of the cupellation. It is evident, however, that, in order to finish the cupellation, the heat must be raised toward the end, otherwise the alloy of lead and silver, as it increases in silver percentage, will tend to freeze, *i.e.*, to solidify. It is also to be noted, however, that this tendency, with most lead buttons of ordinary silver contents, is not reached until very near the end of the cupellation. It is an old saying amongst assayers that "a cool drive and a hot blick" are essential to a good cupellation. In the cupellation for silver it would seem at first sight that a final temperature of 962° C. is necessary in order to prevent freezing and to obtain a silver bead free from lead. However, the phenomenon of the "surfusion" of the silver, *i.e.*, silver in a molten state below its true melting-point, due probably to its formation from its lead alloy by the oxidation of the lead, appears to indicate that this temperature is not necessary. It is true, nevertheless, that the finishing temperature, depending somewhat upon the amount of silver present, may not fall much below 750° C.[1]

It is plain that buttons may be cupeled at temperatures much above those stated, but the loss of silver and gold, both by absorption and volatilization, is very much increased with the higher temperatures.

The reasoning outlined for silver applies also to gold, except that, owing to the somewhat higher melting-point of gold (1063° C.), the finishing temperature should be a little higher.

When the lead buttons are contaminated with base metals, such as copper, the temperature of cupellation must be higher in order to prevent freezing. The reason for this is readily apparent when the freezing-point curve (see Fig. 40) of the lead-copper series of alloys is inspected. The freezing-point of an alloy containing 10 per cent. Cu and 90 per cent. Pb is 900° C.

While the original copper percentage in the lead button may

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[1] The subject of cupellation offers a field for investigation. The actual temperature of cupellation has never been determined. Due to the active oxidation of the lead in the cupel, it is higher than that of the muffle, where the cupel stands. A determination of the temperature of the cupeling lead will, in the author's opinion, very much modify the present theory.

be quite small, the copper does not oxidize as readily as the lead, and tends to concentrate in the button, rapidly raising the melting-point of the alloy.

For the removal of copper in cupellation the ratio of Pb to Cu should be at least 200 to 1 or more. Even then Cu will be retained by the silver and gold in small amounts. If it is less than this, considerable copper is very apt to be retained with the silver and gold. In order to cupel at all, the ratio of Pb to Cu must be at least 20 to 1. In general, buttons to be cupeled should be free from base metal impurities. If they are unavoidably present in the button from the crucible assay, the base metals should be removed by scorification before cupellation.

Impurities in lead buttons are detected by the behavior of the button. Zn, As, Sb, and S tend to make the button brittle when hammered; iron and copper, etc., tend to make it hard. PbO in the lead button makes it brittle. PbO is often found in lead buttons that have been produced at too low a temperature. Where the gold and silver contents of the lead button approach 30 per cent. of its weight, it is brittle.

However, impurities in the lead button will not always be indicated by brittleness or hardness; without these characteristics, impurities may still be present in sufficient amount to cause loss. All impurities do not cause like amounts of loss in cupellation. The loss due to the presence of impurities is chiefly in absorption by the cupel, and comparatively small by volatilization.

The accompanying table[1] shows the influence of impurities. Twenty-five-gram lead buttons were cupeled, containing 1 gram of the impurity specified, 4 mgs. of Ag, and 1 mg. of Au. The temperature of cupellation was 1000° C., in order to prevent freezing as a result of impurity.

The high losses are due in part to the high temperature employed. The table really gives the relative influence of the impurities. Bismuth has been used in place of lead for cupellation.

While in the table bismuth is stated to be the cause of a very heavy absorption, this is not substantiated by other researches.[2] When it is present in the lead button it tends to concentrate dur-

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[1] T. K. Rose, in "Journ. Chem. Met. and Min. Soc. of S. A.," Jan., 1905.

[2] K. Sander, "Berg und Huttenmnnisäche Zeitung," 1903, p. 81. See also "Min. Ind.," XII, p. 244

ing the cupellation, and is removed by oxidation toward the last of the operation. Some of it is very apt to be retained by the precious metal bead. Cupellation may be carried on with bismuth, but the absorption is much higher.[1] The presence of Bi in the cold cupel may be recognized by the fact that the place which the silver button occupies is brown and surrounded by concentric rings of a yellow and blackish-green color. Copper colors the cupel from a dirty green to a black color, dependent on the amount of copper.

TABLE XIII.—INFLUENCE OF IMPURITIES

IMPURITY	LOSS OF GOLD	LOSS OF SILVER	REMARKS
None	1.2 per cent.	11.8 per cent.	
Tin	2.0 per cent.	13.9 per cent.	
Arsenic	3.9 per cent.	16.3 per cent.	
Antimony	5.3 per cent.	13.3 per cent.	Most of this loss, even with Te and Se, is cupel absorption.
Zinc	9.3 per cent.	17.6 per cent.	
Cadmium	3.5 per cent.	13.1 per cent.	
Iron	4.0 per cent.	16.6 per cent.	
Manganese	13.6 per cent.	24.3 per cent.	
Molybdenum	11.0 per cent.	26.2 per cent.	
Vanadium	7.7 per cent.	21.7 per cent.	
Copper	10.0 per cent.	32.6 per cent.	
Bismuth[2]	21.8 per cent.	27.9 per cent.	
Thallium	23.1 per cent.	34.4 per cent.	
Tellurium	55.8 per cent.	67.9 per cent.	
Selenium	54.1 per cent.	64.5 per cent.	

Tin, arsenic, zinc, cadmium, iron, and manganese cause scoria to form on the cupel, due to the formation of oxides which are not readily absorbed. Iron causes a dark coloration of the cupel. Antimony in considerable quantity causes the cupel to check and crack. The same may be said of copper.

Copper.—This metal is oxidized with more difficulty than lead, the Cu_2O forming by aid of the action of PbO; however, Cu_2O, again coming into contact with metallic lead, is reduced to Cu, and in this way is persistent toward the end of the cupellation, although a large excess of Pb over Cu is present, and finally some remains with the Au and Ag. The loss of silver during the cupellation is due mainly to absorption, in large part as oxide. This

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[1] Smith, in "Journ. Chem. Soc.," 1894, p. 863.

[2] Doubtful.

oxidation of the silver in the presence of much lead is not to be ascribed to the action of atmospheric oxygen, but rather to "oxygen carriers," such as PbO, Cu_2O, etc. It is very probable that Cu_2O acts peculiarly in this manner, and the high absorption noticed when Cu is present is due to this fact. It is to be noted that losses in silver occur toward the end of the cupellation, and occur in great part just before finishing; the small dark black-green rings, surrounding the place where the silver bead rests, locates most of the silver. It is the concentration of the copper, silver, and gold that causes the high absorption. Lodge[1] shows the influence of small amounts of copper on the cupellation of silver and gold.

TABLE XIV. — COPPER IN CUPELLATION OF SILVER AND GOLD

SILVER MILLIGRAMS	LEAD GRAMS	COPPER GRAMS	PERCENTAGE OF COPPER IN LEAD	TEMPERATURE DEGREES CENTIGRADE	PERCENTAGE OF LOSS	RATIO PB TO CU
202	10	0.0101	0.1	775	1.05	1000 to 1
203	10	0.0202	0.2	775	1.08	500 to 1
202	10	0.0303	0.3	775	1.29	333 to 1
202	10	0.0404	0.4	775	1.45	250 to 1
204	10	0.0500	0.5	775	Cu retained	200 to 1

GOLD MILLIGRAMS	LEAD GRAMS	PERCENTAGE OF COPPER IN PB	TEMPERATURE DEGREES CENTIGRADE	PERCENTAGE OF LOSS	RATIO PB TO CU
202	10	no.	775	0.155	
202	10	0.1	775	0.19[2] All contained	1000 to 1
201	10	0.2	775	0.20 copper on	500 to 1
200	10	0.3	775	0.13 finishing.	250 to 1
201	10	0.4	775	0.165	250 to 1
202	10	0.5	775	0.250	200 to 1

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[1] "Notes on Assaying," p. 143 *et al.*

[2] Actual losses; copper retained, 0.16 per cent. Gold about the same weight as before cupellation.

Gold is more retentive of copper than silver. It is to be noted that even with a ratio of 200 Pb to 1 Cu, it is not possible to remove all copper, and beads obtained from mattes and heavy copper ores should be examined for copper; otherwise silver results may be high. Retained copper in these silver beads will compensate for loss of silver, but the amount retained is so variable that this error cannot be considered to compensate the loss.

Tellurium. — Tellurium has a great affinity for gold and silver, and if present in an ore in any appreciable amount, some of it will go into the lead button with the gold and silver, and thus have its influence on the cupellation. It tends to concentrate during the cupellation and is with difficulty removed by oxidation. When there is present in the lead button more than 15 per cent. of the gold and silver weight in tellurium, the beads resulting from cupellation have a dull and frosted appearance. Larger amounts than this cause the beads to divide and split up in the cupel. F. C. Smith[1] shows the influence of tellurium on the cupellation as follows, these results being confirmed by J. C. Bailar[2] and others.

TABLE XV. — TELLURIUM IN CUPELLATION OF GOLD AND SILVER

MGS. OF BULLION	CONTAINING		MGS. TE ADDED	LOSS BY ABSORPTION		LOSS BY VOLATILIZATION	
	Au	Ag		Au	Ag	Au	Ag
				per cent.	per cent.	per cent.	per cent.
29.8	24.76	5.04	5.0	13.44	27.08	5.65	0.69
28.45	23.64	4.81	15.0	34.22	35.78	5.28	1.75
22.17	18.42	3.75	15.0	29.85	32.01	11.92	17.95

CUPELED WITH 12 GRAMS OF LEAD

Note the similar effect of selenium.

Antimony. — The presence of antimony causes increased losses by absorption, although its effect is not as pronounced as that

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[1] "The Occurrence and Behavior of Tellurium in Gold Ores," etc., in *Trans.* A. I. M. E., XXVI, p. 495.

[2] "West. Chem. and Met.," I, p. 119.

[3] Selenium instead of tellurium.

of copper or tellurium. During the cupellation litharge and antimony combine to form antimoniate of lead, which, if present in considerable amount, may cause the formation of scoria on the cupel. Small amounts of antimony tend to remain with the gold and silver, as with copper and tellurium.

As a guide in cupellation, the following scale of color temperatures is given.[1]

	Degrees Centigrade
Lowest red visible in the dark	470
Dark blood-red or black-red	532
Dark red, blood-red, low red	566
Dark cherry-red	635
Cherry-red, full red	746
Light cherry, light red	843
Orange	900
Light orange	941
Yellow	1000
Light yellow	1080
White	1205

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[1] White and Taylor, in *Trans*. Am. Soc. Mch. Eng., XXI, p. 628. H. M. Howe, in "Eng. and Min. Journ.," LXIX, p. 75.

VIII

PARTING

PARTING is the separation of gold from silver by means of acid. In assaying, nitric acid is almost exclusively used, although sulphuric acid may be employed. In order to separate silver from gold by means of acid, it is essential that there be present at least twice as much silver as gold. When less silver is present, it is impossible to separate all of the silver from gold by means of acid (see assay of gold bullion, in Chapter XII). When the above-stated amount is present, it requires acid of not less than 1.26 specific gravity, boiling for at least 20 or 30 minutes, to separate the silver from gold. The ratio of 2 and 2.5 to 1 is used practically only in bullion assay.

In parting beads from ore assays, it is considered necessary to have at least five times as much silver as gold present. The addition of silver to gold or to the gold-silver alloy in order to prepare for parting is termed "inquartation," from the fact that at least 3 parts of silver to 1 part of gold were formerly considered necessary. The nitric acid used for parting must be free from hydrochloric acid and chlorine in order not to have a solvent action on the gold. Nitric acid should be examined for chlorides before being used for parting. In order to part silver from gold successfully, the following points must receive careful consideration: (1) The strength of the acid used; (2) The temperature of the acid; (3) The ratio of gold to silver in the bead to be parted.

1. The proper strength of acid is of great importance. Formerly, most authorities recommended that acids of 1.16 and 1.26 sp. gr. respectively — 2 parts water to 1 of acid (1.42 sp. gr.) and 1 of water to 1 of acid — be used, first the weak acid and then the stronger acid. T. K. Rose recommends 4 parts acid to 3 parts water, which strength, if the acid be heated, will not break up the gold in the bead into fine particles, even if 50 parts of

silver are present to 1 part of gold. Gold is less apt to break up when it is less than 0.10 mg. in weight. Keller[1] recommends acid of the following strength: 1 part acid (sp. gr. 1.42) to 9 parts distilled water. In this strength of acid the gold almost invariably remains in a coherent mass, even when the silver is 500 times as much as the gold. This is the strength of acid recommended for ordinary assay purposes. The beads should be boiled in the acid for at least 10 to 15 minutes in order to insure parting.

2. It is essential to have the acid at the boiling-point before dropping in it the bead to be parted. Putting the bead into cold acid and heating up gradually is almost certain to leave the gold, especially where the ratio of silver to gold is high, in a powdered, fine condition, very apt to cause losses in washing and subsequent handling of the gold. Cold acid should not be used.

3. While the best ratio of silver to gold, for parting ordinary beads, is 5 to 1, this ratio is not always under control, since the assayer must be content in many cases with the ratio that the ore furnishes him, when this is more than 5 to 1. If less than 5 to 1, silver should be added in order to bring it up to this ratio. The silver may be added directly to the crucible or scorification fusion, or to the lead button during cupellation when it is not essential to determine the silver in the ore.

Where it is essential to determine the silver, and inquartation is necessary, the bead from the cupellation is first weighed, the requisite amount of silver is added to the bead, both wrapped up in about 2 grams of sheet lead, and then it is recupeled and parted.

Beads which need inquartation may also be fused with silver, on a piece of charcoal, by means of the blowpipe; but this method is not to be recommended, as it frequently occasions loss.

Many assayers, where they suspect an ore to be deficient in silver for parting, add silver to the crucible, not determining the silver in this assay, but running a separate scorification assay for this purpose.

After parting, the acid is poured from the parting cup or flask in which the operation has been conducted, and the gold residue is washed, at least three times, with warm distilled water in order to remove all trace of silver nitrate. The black stain occurring in parting cups after heating for the annealing of the

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[1] Keller, *Trans.* A. I. M. E., XXXVI, p. 3.

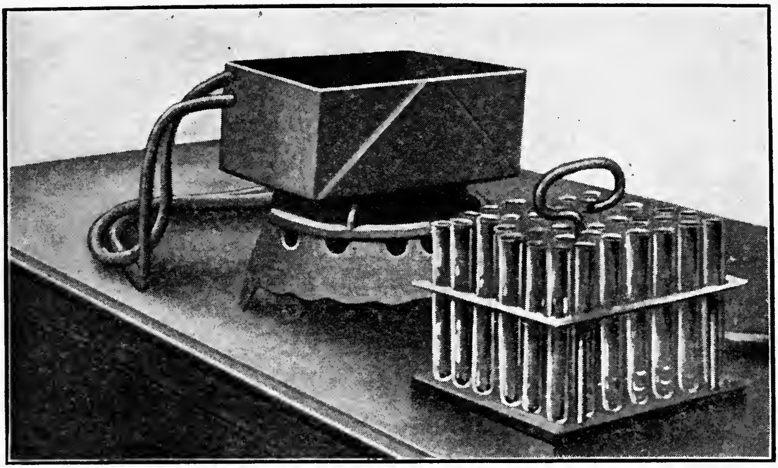

FIG. 41. — PARTING BATH

gold is due to metallic silver reduced from silver nitrate by the heat, showing insufficient washing. Parting may be carried on in small porcelain crucibles called "parting cups," or in test tubes, or in flasks similar to copper-assay flasks. In order to part in flasks or test tubes, it is essential to have the gold stay as a coherent mass, so as to prevent loss in transference. When parting cups are used, after washing, the gold is carefully dried and the gold annealed at a dull-red heat, either in the muffle or by means of the blowpipe. After acid treatment, the gold is left as a soft black mass, probably an allotropic condition of the gold; but upon heating this is changed to the normal yellow metallic state in which it is weighed. Fig. 41 shows a convenient parting bath with test tubes; Fig. 42 shows parting flasks commonly in use.

FIG. 42. — PARTING FLASKS

IX

THE ASSAY OF ORES CONTAINING IMPURITIES

IMPURITIES, from the assayer's point of view, are such substances, contained in ores, furnace products, or other material, as necessitate some particular method of assay or treatment, or the observing of special precautions not included in the ordinary crucible assay as already outlined.

Common impurities are sulphur, arsenic, tellurium, antimony, zinc, copper, etc. Of these sulphur is by far the most common.

In performing an assay it is usually the aim of the assayer, whenever this is possible, to produce by direct fusion, either by the crucible or scorification method, a pure lead button weighing approximately 20 grams. If the button is smaller than this, there is danger of not collecting the values; if larger, cupellation is too prolonged and losses are increased. The impurities mentioned affect either the size of the button, or the purity of the button, or both. To show the effect of sulphur the following definite example is taken.

Given an ore containing pyrite, which, in a charge yielding the ordinary type of monosilicate slag, gives a reducing power of 5 grams of lead per gram of ore. If the following charge,

15 grams of ore	70 grams of PbO
30 grams of Na_2CO_3	8 grams of SiO_2

Borax glass cover

be made up and fused, a 60-gram button (approximately) will be produced, on top of which will be a small quantity of "matte," *i.e.*, an artificial sulphide of the metals, in this case iron and lead. This matte is brittle and may contain some values. On hammering the button, it is lost. In general, it is an undesirable product to make. A small amount of matte is produced in this case, since the ore has the power to reduce 75 grams of lead from PbO, while only 70 grams of PbO are present, so that the excess sulphide of the ore not acted upon by the PbO remains in the charge, uniting with some of the lead to form a sulphide of iron and lead. The button is also much too large to cupel. If in the charge the PbO is materially increased, the ore will react to the extent of its full reducing power, a lead button of 75 grams will be produced, no matte will be found, and the slag will be improved, owing to the addition to it of the fusible base PbO. If the PbO in the charge be materially reduced, the lead button will be much smaller (owing to the dearth of PbO available for reduction), considerable matte will be formed, and the slag will be poor.

If the silica be increased, so that sufficient be present to form the higher silicates with all the bases present, practically no lead will be reduced, for the sulphide has not the power to reduce Pb from lead soda silicates unless a free base be present, *i.e.*,

$$(PbO.Na_2O)2SiO_2 + FeS_2 \text{ (no action)},$$

or possibly

$$(PbO.Na_2O)2SiO_2 + FeS_2 = (FeO.Na_2O)2SiO_2 + PbS + S.$$

In this way the sulphur remains in the charge in the form of sulphide sulphur.

Soda will cause the formation of SO_3, if PbO is present to furnish the oxygen, and if it can act as a free base, *i.e.*, if it is not combined with silica (see Chapter V, on Reduction and Oxidation Reactions). An increase of soda without an increase of PbO or SiO_2 will lessen the amount of matte, as sulphur will tend to combine to some extent with the Na_2O to form, with the FeS, a double sulphide of iron and soda, etc., which will be dissolved in the slag. The above outlines the effect of such impurities as sulphur and arsenic, and shows the necessity of special methods of assay directed toward the getting rid of impurities.

The impurities mentioned may be divided into two classes:

(*a*) Those which can be volatilized by oxidation or otherwise, *e.g.*, sulphur, arsenic, and antimony.

(*b*) Those which cannot be volatilized, *e.g.*, copper, zinc, etc.

Some of these may be partly volatilized, as antimony and zinc. For the removal of all of them, however, whether by volatilization or by slagging, oxidation is essential.

In one method employed on light sulphide or arsenic ores, the iron-nail method, sulphur and arsenic are carried into the slag as a double sulphide or arsenide of soda and iron, etc.

The following methods are standard methods for the assay of impure ores, and are discussed in detail:

Crucible Fusions.

1. The roasting method.
2. The niter method.
    - (*a*) The common niter method.
    - (*b*) Miller's oxide slag method.
    - (*c*) Perkins' excess-litharge method.
3. The iron-nail method.
    - (*a*) The niter-iron method.
4. The cyanide method (rarely used).
5. The scorification method.
6. The combination wet-and-dry method (removal of impurities by solution).

The Roasting Method. — It is usual to carefully weigh out 0.5 or 1 assay ton of the ore to be assayed, and place it in a roasting dish of sufficient size to permit of stirring without loss by spilling. The dish is placed in the muffle, the temperature of which is not above a "black red" and the firing of which is under good control, so that the temperature will not rise too rapidly. In the case of an ordinary sulphide ore, such as a pyrite, or, for example, a chalcopyrite and quartz, the following reactions take place, if the roasting is carried on slowly at a low heat:

$$3CuFeS_2 + 18O + \text{heat} = Cu_2S + 3FeSO_4 + CuSO_4 + SO_2$$

At 590° C. the ferrous sulphate decomposes spontaneously, sulphatizing the balance of the copper.

$$Cu_2S + 2FeSO_4 + 6O = 2CuSO_4 + Fe_2O_3 + SO_3$$

At 655° C. the copper sulphate decomposes into basic sulphate and SO_3, and at 700° C. into CuO and SO_3, as follows:

$$\begin{aligned} 2CuSO_4 &= CuO.CuSO_4 + SO_3, \\ CuO.CuSO_4 &= 2CuO + SO_3; \end{aligned}$$

so that the final products of the roast, when carried to above 700° C., are ferric and cupric oxide, with a complete removal of the sulphur. If the temperature is not carried above 700° C., sulphur remains in the charge as sulphate, which may again be reduced in the crucible to sulphides.

$$2CuSO_4 + 3C = Cu_2S + SO_2 + 3CO_2$$

If, for any reason, it is not desirable to carry the temperature as high as 700° C., the ore, after roasting until no further smell of SO_2 is discernible, is cooled and mixed with 5 to 10 grams of powdered $(NH_4)_2CO_3$, and reroasted at a low heat, the sulphuric anhydride (SO_3) being eliminated as volatile ammonium sulphate, $(NH_4)_2SO_4$.

$$CuSO_4 + (NH_4)_2CO_3 = CuO + (NH_4)_2SO_4 + CO_2$$

Any silver in the ore that has been roasted will be in the form of Ag_2SO_4, or if arsenic and antimony are present, partly in the form of arseniates and antimoniates. If the roasting temperature is carried to 870° C. and above, the silver sulphate will be decomposed, leaving the silver in the form of metallic silver. In order to avoid loss of silver it is best not to carry the temperature above 700° C.

In roasting plain pyrite ores, the reactions are similar, but simpler, and the temperature need not be carried above 600° C. During roasting, the ore should be stirred frequently in order to expose fresh surfaces to oxidation.

When ores contain arsenic and antimony, the roasting operation is more difficult and complex, and considerable care and skill are required to eliminate the greater part of these two volatile elements. The reason for this is that the arsenic and antimony pass by roasting, first to the state of the lower oxides As_2O_3, Sb_2O_3, which are volatile, and then to the state of the higher oxides As_2O_5, Sb_2O_5, forming arseniates and antimoniates of certain metals present in the ore, some of which are stable even at high temperatures, thus fixing the arsenic and antimony in the roasted ore, and not eliminating it. The arseniates (or antimoniates) which ordinarily form are those of copper, iron and silver. The best conditions for the elimination of arsenic and antimony are alternate oxidation and reduction at a low heat. The presence of sulphur tends to aid the elimination of arsenic and antimony by the formation of the volatile sulphides of these metals. The reducing action necessary for the elimination of arsenic and antimony is best obtained by mixing with the ore equal volumes of coal dust or charcoal, and roasting at a dark-red heat until the coal is burnt off, then cooling, adding more coal dust, and reroasting. In this way the greater part of the arsenic and antimony can be readily volatilized, except in very rich silver ores. When galena ores are to be roasted, the ore is best mixed with an equal volume of silica and roasted at a very low heat. In this roast $PbSO_4$ is formed to a considerable extent, which at a higher heat is decomposed by the SiO_2 present, as follows:

$$PbSO_4 + SiO_2 = PbSiO_3 + SO_3$$

Care must be taken with this roast as, at the formation point of lead silicate, silver losses are apt to occur. A successful roast will be indicated by a yellow color (lead silicate), and an unsuccessful one by a black or gray color (fused, undecomposed sulphides). In general, heavy sulphide ores that contain their chief value in gold may be roasted, when this is carefully done, without loss of gold; but silver ores, especially when of high grade, are apt to give low results.

In making up the charge for the roasted ore, it is to be noted that from a sulphide ore (pyrite, etc.) the product is frequently of an oxidizing nature and basic, which must be taken into account in adding the fluxes. In galena ores, when silica has been added, this must be accounted for.

The roasting method is frequently used for heavy sulphide ores, especially when they have a low value in gold and silver, as it permits of a large amount of ore being taken (1 assay ton and more), which after roasting presents no difficulty in making the proper fusion.

The Niter Method. — The first step in the niter method is the making of a preliminary assay according to the directions already given. The precautions concerning the reducing power of the sulphides in different types of charges must be carefully noted; it is best to have the preliminary charge of the same composition as the final assay charge. Or else the reducing power may be determined by the soda-litharge charge and this cut down by 25 per cent., 20 grams deducted for the lead button, and the remainder divided by 4 to get the amount of niter to add, in grams, if the monosilicate slag is to be made in the assay.

The amount of ore taken for the niter assay varies according to the grade of the ore in gold and silver and according to the amount of impurity present. It is rarely desirable to add more than 20 grams of niter to the charge, as larger amounts cause difficulty through the evolution of too much gas. One-half assay ton is the amount of ore most frequently taken. Sometimes, with ores containing much impurity, 0.10 to 0.25 assay ton is used. Twenty-gram crucibles (170 c.c. capacity) are used for amounts of 0.5 assay ton of ore and less, and 30-gram crucibles (240 c.c. capacity) for 1 assay ton of ore.

Miller's Oxide-Slag Method. — This method is a modified niter method applicable to such ores as contain practically no silica; *i.e.*, heavy sulphide ores, such as pyrites, arsenopyrite, mattes, etc. It is based on the fact that PbO has the power to hold in solution and in suspension oxides of such metals as copper, iron, etc. (see p. 95, where "scorification" is discussed), in certain amounts. Niter is added to oxidize the sulphides, etc., and Na_2CO_3 to aid in the complete oxidation of the sulphur by the formation of sulphates, in the manner already discussed. The first step, as in the ordinary niter method, is the preliminary assay, according to the following charge:

Ore	3 grams
PbO	50 grams
Na_2CO_3	8 grams

The final charge is as follows:

Ore	0.5 assay ton
PbO	70.0 grams
Na_2CO_3	12.0 grams
KNO_3	(calculated for a 20-gram button)

Quick fires, 1100° C., 30 minutes, are found to be best. The slags are usually dull black and pour readily, and the button separates easily from the slag. (In slags high in silica or containing much borax, the lead buttons are apt to adhere closely to the slag.) With the oxide-slag method, trouble is sometimes experienced through the lead refusing to collect and remaining shotted through the slag. The difficulty is usually due to too much soda (especially if considerable niter is used), although too low a temperature of fusion is also a factor.

The method gives reliable results on gold and silver, comparing well with the other standard methods.[1]

Perkins' Excess-Litharge Method.[2] — This method is based on the fact that PbO will dissolve oxides of other metals and, if present in very great excess, will prevent, to a large extent, the reduction of other metals, such as Cu and Sb. The presence of so much PbO also insures a strongly oxidizing tendency in the crucible, preventing impurities entering into the button.

It is desirable to add or have present SiO_2 in such an amount as will form a monosilicate with the bases present, including some litharge, but leaving much litharge uncombined in the charge.

The following table shows the proportion of PbO required to form fusible compounds with the principal metallic oxides:[3]

TABLE XVI. — PbO REQUIRED WITH METALLIC OXIDES

One part of	Cu_2O	CuO	ZnO	Fe_3O_4	Fe_2O_3	MnO	SnO_2	Sb_2O_3	As_2O_5
Requires parts of PbO .	1.5	1.8	8	4	10	10	13	5	1

In order to carry out the excess-litharge method intelligently, it is necessary to know the approximate composition of the ore, so as to provide the proper amount of PbO and SiO_2. The best fusion exhibits, in a section of the cone of the slag after breaking, silicates of lead, iron, etc., on the outer surface, gradually passing to crystalline litharge toward the center. The temperature of fusion should not exceed 1050° to 1100° C. It must be above 906° C. (melting-point of PbO). The first step is the making of a preliminary assay in order to determine the amount of niter to be added.[4]

The final charge most frequently used is:

Ore	0.25 to 0.5 assay ton	Na_2CO_3	12 grams
PbO	8 to 10 assay tons	SiO_2	10 grams

Niter to obtain 20-gram button

The button is generally clean, and separates easily from the

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[1] Miller, "The Reduction of Lead from Litharge," etc., in *Trans.* A. I. M. E., XXXIV, pp. 398, 399.

[2] W. G. Perkins, "The Litharge Process," *ibid.*, XXXI, p. 913.

[3] Hofman, "Metallurgy of Lead," p. 7.

[4] In place of niter, it may be necessary, in this method or in Miller's method, to add argol, if ore is not reducing.

slag. The method has been stated to give low results in silver, but this is contrary to the experience of the author.

The Iron-Nail Method. — This method does not attempt to oxidize impurities, but to carry sulphur, etc., into the slag. The ore is decomposed by the iron nails added to the charge and by the PbO present. As iron reduces PbO to Pb, the amount of litharge added to the charge is limited to 25 to 30 grams. The amount of soda needed is large, as this flux is depended upon to carry the sulphur into the slag. The slag should be below a monosilicate in degree, and high in soda, as basic slags have a high solvent power for sulphides.

A typical charge on an ore that has a reducing power of about 4 grams of Pb per gram of ore is.[1]

Ore	0.5 assay ton	SiO_2	2 grams
$NaHCO_3$	30 grams	borax	8 grams
PbO	30 grams	nails	17 grams

Salt cover

The soda should usually be twice the amount of ore in the charge. The reactions that take place are approximately as follows:

$$7PbO + FeS_2 + 4NaHCO_3 = 7Pb + 2Na_2SO_4 + FeO + 4CO_2 + 2H_2O$$

Part of the ore is decomposed by the PbO, and part of the S may go off as SO_2, as discussed in previous pages. The iron nails decompose the balance of the sulphides.

$FeS_2 + Fe = 2FeS$

$PbS + Fe = Pb + FeS$ (if galena is present or lead sulphide forms).

The iron sulphide (FeS) is dissolved by the alkaline slag, forming probably double sulphides of soda and iron.

To show the nature of the iron-nail fusion, the following results of two fusions on a pyrite ore containing 39.5 per cent. S — a reducing power equal to about 8 — are given:[2]

Charge 1		Charge 2
1 assay ton	ore	0.5 assay ton
30 grams	$NaHCO_3$	30 grams
30 grams	PbO	30 grams
4 grams	SiO_2	4 grams
4	nails	4
10 grams	borax glass cover	10 grams

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[1] Lodge, "Notes on Assaying," p. 99.

[2] Lodge, *ibid.*, p. 101.

The following results were obtained:

	No. 1		No. 2	
Slag	60	grams	65	grams
Matte	23.5	grams	none	
Lead	24.5	grams	26.5	grams
Crucible and charge before fusion	685	grams	662	grams
Crucible and charge after fusion	665	grams	642	grams
Loss in weight	20	grams	20	grams
Nails before fusion	64	grams	63	grams
Nails after fusion	43	grams	49	grams
Loss of iron	21	grams	14	grams
Per cent. of S in slag	6.73		7.63	
S in slag	4.03	grams	4.96	grams
S in ore	11.85	grams	5.92	grams
S passed off as SO_2	0.95	grams	0.96	grams
S in matte	6.87	grams	none	

It will be noted that the charges are identical as far as the fluxes are concerned, but that the amount of ore differs. It is desirable in heavy sulphide ores to keep the ore down to 0.5 assay ton and lower if necessary.

Care must be taken not to have the slag above a monosilicate in degree, for if higher in SiO_2 there will be particular danger in this charge of not having the sulphides oxidized by the PbO, more sulphide being retained in the charge than it can dissolve, and forming a matte, even with small amounts of ore.

The Niter-Iron Method. — This method is in principle the same as the iron-nail method. An amount of niter is added at random, sufficient to oxidize but a portion of the sulphides, the balance being decomposed by the nails.

The Cyanide Method. — Sometimes, when no other fluxes are at hand, or when a rapid assay is to be made in which accuracy is not essential, a fusion of ore with cyanide may be made, and the resultant button cupeled for silver and gold. The method is a rapid one and gives good malleable buttons, but is apt to be low in gold and silver, especially in silver. The cyanide used should be pure, free from carbonates or other impurities, and the fusion should be made at a low temperature. The following charge is used:

Ore	0.5 to 1 assay ton
PbO	25 grams
KCN	3 assay tons

When the ore contains copper and other base-metal impurities, these are reduced and enter the lead button. Sulphur is taken up by the slag as potassium-sulpho-cyanate (KCNS). In general, it is a method not to be recommended. The following results show the loss in silver which takes place in this method.[1]

TABLE XVII. — LOSS OF SILVER IN CYANIDE METHOD

	NITER METHOD	CYANIDE METHOD
Silver, by uncorrected assay	563.73 mgs.	525.5 mgs.
Silver in slag	4.10 mgs.	36.8 mgs.
Silver from cupel	7.81 mgs.	6.56 mgs.

The results are averages of duplicate assays. The loss of gold in the slag by cyanide fusion is not nearly so marked as that of silver.

A Comparison of the Different Crucible Methods of Assay for Impure Ores. — In very impure ores, containing large amounts of sulphur, arsenic, etc., the roasting method is applicable when gold only is to be determined, or when silver results need not be very accurate. The roasting method gives uniformly lower silver results than most of the other methods, although to a large extent this is due to roasting at too high a temperature.

The roasting method has the advantage that when ores are low grade large quantities of ore can be taken, which is not always possible with the other methods. Roasting, however, must be skilfully conducted in order to be successful.

The niter method is a desirable and clean method of assay giving accurate results. Where large quantities of niter are employed, the oxidizing action in the crucible is greatly increased, and it is probable that thereby losses in silver are apt to occur by the slagging of the silver.

There is no accumulated evidence on this subject, but many assayers hold this opinion. The niter method is desirable for such ores as do not contain amounts of sulphur requiring extraordinary amounts of niter. Usually, the limit of niter in a charge is placed at about 20 grams; if the ore should require more

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[1] E. H. Miller. "Corrected Assays," in "Sch. Mines Quart.," Vol. XIX, November, 1897.

than this, it is generally considered advisable to reduce the quantity of ore taken for the assay. This has the disadvantage of multiplying the error of the assay when finding the value per ton.

The modified niter methods discussed offer advantages in the slagging of base-metal impurities. This is particularly true of copper and zinc. It is very much easier to cause copper to enter the slag when an oxide slag is made than when a silicate is made. This is partly due to the oxidizing nature of the high litharge charges. The best method for the slagging of base-metal impurities is the excess-litharge method.

The iron-nail method is a standard method, which can be successfully applied to most sulphide ores and, with care, to arsenical ores. It is not applicable to ores containing base-metal impurities, such as copper, for, being essentially reducing in its nature, practically all of the base-metal impurities will be found in the lead button. When used with arsenical ores, the temperature employed should be low, not above 1050° C.; otherwise speiss (an artificial arsenide of iron) is apt to form, which may carry values. It also has the objection, in the case of very impure ores, that small quantities must be taken for assay, involving serious risk of multiplying an error of assay.

Scorification is the oxidizing fusion of ore with metallic lead in the muffle-furnace, producing, in the main, a litharge slag, *i.e.*, an oxide slag. It is a method of assay which requires no previous preparation of the ore or preliminary assay, and as practically only one flux is employed, it is both a cheap and a rapid method. It is also a thoroughly reliable method, when proper precautions are taken and when it is employed on material suitable for the purpose. The operation is performed in shallow fire-clay dishes, called scorifiers.

The sizes commonly used are:

1.5-in. scorifiers; cubic contents	15 c.c.
2.0-in. scorifiers; cubic contents	25 c.c.
2.5-in. scorifiers; cubic contents	37 c.c.
3.5-in. scorifiers; cubic contents	100 c.c.

The dimensions referred to are outside dimensions. The size most commonly employed is the 2.5-in. one. Before these dishes are used it is usual to line the inside with ferric oxide. This is done by preparing crushed iron ore or ochre, mixing with water, and painting the inside of the dishes. This gives them a basic lining, and to some extent prevents the oxide slag from attacking the silica in the clay.

Some scorifier slags, especially if they contain copper, are very corrosive. The amount of ore taken for scorification varies from 0.10 assay ton to 0.25 assay ton; but 0.10 assay ton is the amount most frequently taken. The larger amounts are rarely used, unless the ore contains practically no bases. Sometimes, for very impure material, as little as 0.05 assay ton is taken. The amount of test lead varies according to the nature of the ore. The more impure the ore the larger will be the ratio of lead to ore. With 0.10 assay ton the test lead will vary from 40 to 100 grams. A common charge is 40 to 50 grams of test lead for ordinary ores. As already pointed out, certain quantities of litharge are required in order to make fusible compounds with the metallic oxides. If the ore contains small amounts of the metallic oxide, the test lead will be small in amount; if it contains appreciable quantities of ferric oxide (Fe_2O_3) or Cu, etc., large amounts of test lead will be required. It is best to add a small amount of borax glass to the charge, from 1 to 1.5 grams, scattering it over the surface of the lead. This aids in the solution of the bases present. When the ore contains the basic oxides mentioned, borax glass up to 3 and 4 grams will materially aid in forming good slags, without infusible scoria. These infusible scoria often appears in ores containing large amounts of bases, and is very apt to give low results by entangling unfused portions of ore within itself. It is best to mix the weighed-out portion of ore with one-half of the test lead to be used, and then cover over with the balance.

The scorification may be divided into the following distinct steps:

1. Melting. In this stage the lead melts, and the ore, being of a lesser gravity, rises to the surface of the molten lead and floats there.

2. Roasting. The ore on the surface of the lead is attacked by the oxygen of the air and roasts in the same way as described under "Roasting of Ores."

3. Scorification Proper. The lead commences to oxidize, forming litharge. A small percentage (5), volatilizes and the

balance forms a fusible slag. This now absorbs the oxides formed by the roasting, dissolving them and forming an igneous solution. The silver and gold, liberated, are absorbed by the remaining metallic lead. The slag, as it forms, drops to the side, forming a slag ring, with the center of the lead bath open to the atmosphere. The reason for this is that the meniscus of molten lead is convex, thus causing the collecting of the slag on the rim of the scorifier. The scorification continues until the whole of the lead is covered over with slag. It is then considered finished and the assay is poured. Should the assay be left in the muffle, the lead will still continue to oxidize, although none is exposed to the air, the interchange of oxygen taking place by means of the litharge and other oxides present. The size of the lead button desired from this assay ranges from 15 to 20 grams. If the scorification is continued to produce smaller buttons, losses are apt to occur by oxidation of the silver, especially if this is present in considerable amounts, thus forming rich slags.

The temperature of scorification ranges from 1000° C. to 1100° C., although with pure ores higher temperatures may be employed.

When impure ores containing much base metal are scorified, the buttons from the scorification are very apt to be contaminated with base metal, especially copper, and will then have to be rescorified, with more test lead, in order to get a pure button for cupellation.

All metals are to some extent oxidized simultaneously, but a mixture of metals may be roughly separated by successive oxidation, each metal in turn partially protecting the metal next in order, while the latter may act as an oxygen carrier to the former.[1] The order of oxidation is as follows:

Fe to Fe_2O_3
Zn to ZnO
Pb to PbO
Ni to Ni_2O_3
Cu to Cu_2O
Pt to —
Ag to Ag_2O
Au to AuO

The order of oxidation of the following elements is not so certain:

Sb to Sb_2O_3
As to As_2O_3
C to CO_2
Bi to Bi_2O_3
Te to TeO_2
S to SO_2

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[1] T. K. Rose, "Refining Gold Bullion, etc., with Oxygen Gas," in *Trans. I. M. M.*, April, 1905.

The order given in the table shows the difficulty encountered in the removal of copper by scorification, as lead stands ahead of it in the order of removal, and it is very difficult and requires a number of re-scorifications, if the amount of copper is large, to reduce it to such an amount as to prevent loss in cupellation. Iron and zinc are very readily removed by scorification (oxidation). Certain elements, like Te and Se, are difficult to remove from the lead button, and may tend to concentrate with the Au and Ag in the final cupellation.

The slag from the scorification assay should be homogenous and glassy. If it has an earthy appearance, it is an indication of too low a temperature having been used, and the button is apt to be brittle, due to contained PbO. White patches of sulphate of lead on the slag after pouring also indicate rather too low a temperature of scorification, as this sulphate forms at a low temperature under slow oxidation.

The scorification method is a reliable one on most materials, with the exceptions enumerated below. As the usual quantity taken for assay is 0.1 to 0.2 assay ton, it is evidently not a suitable method for low-grade ores, especially low-grade gold ores, where at least 0.5 to 1.0 assay ton must be taken in order to get accurate results, and avoid the multiplication of the error of weighing. It is practically impossible to get reliable results on $5 to $10 gold ores by ordinary scorification. If, however, 10 assays of 0.1 assay ton are made, the buttons from these combined and re-scorified into one button, which is then cupeled, the results are reliable, but not so good as from the crucible assay on the same total amount, on account of the multiplicity of weighing and other operations, which occasion errors and losses. The method in this instance would also be more costly of time and materials.

For ordinary and rich silver ores, and very rich gold ores or furnace products, such as bullions, mattes, etc., the method is a desirable one. It requires no preliminary operations and thus saves valuable time. The slag loss is frequently somewhat higher than in the crucible assay. It is, as ordinarily performed (in duplicate), a cheap method as regards fluxes, etc. It does not give good results on very basic ores, *i.e.*, those containing hematite, manganese oxides, etc., as in this case, unless a great deal of lead is used, scoria are apt to form in the slag, which may entangle lead and undecomposed ore. Neither does it give good results on telluride ores, zinc precipitates, or ores that contain chloride of silver.

When basic material is to be scorified, small additions of SiO_2, up to 1 gram, may prove advantageous. In general, however, the addition of fluxes, except test lead, is not to be recommended. Scorification may be modified by the addition of considerable amounts of borax glass, litharge, silica, when it approaches the crucible assay in character with none of its advantages.

The Combination Method. — The trouble arising from the presence of considerable amounts of base metals, such as copper and zinc, has been fully discussed in previous pages, as well as the difficulty of their removal by fusion methods. For this reason the combination wet-and dry-method has been developed, to remove the objectionable impurities by solution. The method is used chiefly on copper-bearing material, such as heavy copper ores, copper mattes, blister copper, and to a lesser extent on zinc ores, and on cyanide precipitates produced by zinc, and has been advocated for telluride ores.

Van Liew's Method for Blister Copper. — This is the standard method for copper material. Weigh out duplicate samples of 1 assay ton each of copper borings, add 350 c.c. cold water and 100 c.c. HNO_3 (sp. gr. 1.42), and set in a cool place for 20 hours, stirring from time to time. Then, if the copper is not dissolved, add from 5 to 30 c.c. more of concentrated acid. At the end of 26 to 28 hours the solution of the copper is complete. Do not apply heat in order to minimize as much as possible the solution of small quantities of gold, by whatever action this may take place. The oxides of nitrogen in the solution are removed by blowing air into it for 20 to 30 minutes.

Salt solution (containing 5.4207 grams of NaCl per 1000 c.c.) is added in sufficient quantity to precipitate the Ag present as chloride. 1 c.c. of this solution will precipitate 1 mg. of Ag, and an excess of 4 to 8 c.c. above that required for the Ag should be added. If the amount of Ag in the copper is small, add 10 c.c. of a saturated solution of lead acetate and 2 c.c. of concentrated H_2SO_4 in order to form $PbSO_4$ to aid in settling the silver chloride. Let this stand for about 12 hours and filter the precipitate into the proper sized filter, and wash it well into the point of the filter paper. Dry the filter carefully in the air bath, and when dry, add 8 grams of test lead on top of the precipitate, and carefully transfer to a scorifier containing 2 grams of lead. This is placed in the muffle, heated just to incipient redness, and the filter papers burnt off, but only until the flame disappears, and not into ash. This takes only a minute or so, the precaution being taken to prevent loss of silver by volatilization as AgCl, the lead and carbon present reducing the AgCl to Ag. Then add 3 to 4 grams of PbO, and the same amount of borax glass, raise the heat until well molten, and pour. No scorification is necessary, as no impurities are present. The lead button will weigh 5 to 8 grams and is cupeled with feather litharge. The results should check within 0.2 to 0.3 oz. for Ag and very closely for gold.[1]

Combination Assay for Matte. — The above method of treating in the cold is rarely suitable for mattes, as heat is usually essential in order to insure a decomposition of the matte in a reasonable length of time. Take[2] duplicates of 1 assay ton each and treat in large beakers, provided with watch-glass covers, with 100 c.c. of distilled water and 50 c.c. HNO_3 (sp. gr. 1.42). After the violent chemical action subsides, add 50 c.c. more of concentrated acid, and warm the beakers on a hot-plate until everything soluble is dissolved: usually the residue is white or grayish. Next evaporate a considerable part of the acid by boiling, expelling all of the nitrous fumes, dilute to 500 c.c., add 3 c.c. of concentrated H_2SO_4, 10 c.c. of saturated lead acetate solution, and enough salt solution of the strength mentioned for blister copper to precipitate the silver; then stir briskly and let them stand over night. Next morning warm the solutions on a steam bath and filter through rather thick filter-paper.

Filtrates must be perfectly clear and free from suspended $PbSO_4$. Wash beakers and residue thoroughly with hot water, dry the filters in an air bath, and then wrap them up in about 8 grams of sheet lead and scorify with 40 grams of test lead and 1 gram of borax glass. Cupel the buttons with feather litharge. Re-assay the slag from the scorification and the cupel and add the resultant gold and silver to the assay.

[1] R. W. Van Liew, in "Eng. and Min. Journ.," LXIX, pp. 498 *et seq.*

[2] "Assay of Copper and Copper Matte," in *Trans.* A. I. M. E., XXV.

When heavy copper ores are to be assayed by this method, which are apt to leave large amounts of silicious residue, the general method for mattes is followed, except that the residues after filtering and drying are treated as follows:

Take a 20-gram crucible and place in it 1 assay ton of PbO; then put the filter-paper containing the residue on top of this, place the crucible in the mouth of the muffle at a low heat, burn off the filter-paper until the flame subsides, remove from the muffle, put a cover on the crucible, and allow to cool. When cold add 0.5 assay ton PbO, 15 grams of Na_2CO_3, 2 grams of argol, mix well with a spatula, and put on a cover of borax glass. Then proceed as in the ordinary assay.

General Precautions to be Observed in the Combination Assay. — The combination methods on copper material agree well with the standard scorification methods for the same material when correction for cupel loss is made for the latter method. The scorification methods will often seem to give higher results, but this is in most cases due to the fact that the silver beads frequently contain from 2.5 to 4 per cent. copper. The combination method gives in most cases (Van Liew's method possibly excepted) uniformly lower results in gold (4 per cent.) than the standard corrected scorification method. This is generally ascribed to the formation of nitrous acid (HNO_2) during solution, which, in connection with nitric acid, is said to have a solvent action on gold; but such authorities as W. F. Hillebrand[1] dispute this. The solution may be due to the formation of H_2SO_4 during solution, as the mixture of this acid and HNO_3 has a solvent action, or to the presence of impurities like chlorides or HCl, etc., or possibly to the presence of nitrates, particularly those of iron or copper. The fact that the combination method on copper-bearing material gives low results is, however, well established.

Owing to the number of manipulations in the combination assay, it is often apt to give low results in the hands of inexperienced chemists, mainly due to the mechanical losses in handling. The directions given should be carefully followed, especially those regarding amount of solution, strength of acid, temperature, time, etc. Neatness is indispensable. The HNO_3 must be pure.

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[1] W. F. Hillebrand and E. T. Allen, "Comparison of Wet and Crucible Fire Methods for Gold Telluride Ores," Bull. 253, U. S. G. Survey.

The directions regarding the burning off of the filter-paper must be closely followed. The amount and strength of the salt solution must be carefully adhered to and it must be added at the proper time. Some assayers, instead of adding salt solution at the same time as H_2SO_4 and $PbC_2H_3O_2$, filter off the residue containing the gold and make a separate precipitation for the silver, believing that the addition of a salt solution may cause a slight redissolving of the gold. At this point of the assay that is, however, hardly probable. A large amount of NaCl is to be avoided, as AgCl is very appreciably soluble in brine. C. Whitehead recommends NaBr instead of NaCl for this reason.

Combination Method for Precipitates from the Cyanide Process.[1] Where the troublesome base-metal impurity is zinc instead of copper, as in this case, sulphuric acid can be substituted with advantage for HNO_3. The method is as follows:

Of the precipitates 0.10 assay ton is taken, placed in a beaker, and 20 c.c. of sulphuric acid (concentrated) and 60 c.c. of water are added. This is heated on a hot plate for about one hour, or until zinc and zinc oxide are in complete solution. Add salt solution of the strength already mentioned in the paragraph on Van Liew's method for blister copper, in slight excess, to precipitate the silver present, remembering that 1 c.c. will precipitate 1 mg. of silver. Stir briskly with glass rod to agglomerate the silver-chloride formed.

The residues are then filtered through the proper sized filter, carefully washed with hot water into the point of the filter-paper, and dried in the air bath at a low heat. After drying, transfer to a 20-gram crucible containing 1 assay ton of litharge, and burn the filter-paper off in the manner already described. Then add 15 grams of soda and 2 grams of argol, mix thoroughly, and cover with a heavy cover of borax glass. Fuse and cupel the resultant lead button. Weigh the gold and silver bead, and from a preliminary assay determine the proper amount of silver necessary in order to inquart the bead. The amount of silver should be just about 2.5 times the amount of gold. Roll out the bead, after flattening with a hammer, until, after repeated rollings, the fillet will have about the thickness of a visiting card.

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[1] Fulton and Crawford, "Notes on Assay of Zinc Precipitates Obtained in the Cyanide Process," in "Sch. Mines Quart.," XXII, p. 153.

It is best to anneal the bead at a red heat between the various rollings, in order to prevent cracking on the edges. Then part in a parting flask in hot nitric acid having a specific gravity of 1.26. Boil twice for at least 20 minutes each time, in order to insure the complete removal of the silver. This method of parting leaves the gold in one coherent mass, termed a "cornet," and is identical with the method practised in the gold bullion assay.

X

SPECIAL METHODS OF ASSAY

Telluride Ores. — Gold ores carrying the values in the form of tellurides of gold and silver, mainly calaverite and sylvanite, are more difficult of assay than ordinary gold ores, and special methods are essential in order to get good results. The scorification assay is not reliable for telluride ores, giving almost uniformly low results. It is not used by assayers and chemists of the great telluride ore district in Colorado — Cripple Creek. It seems that in scorification the main cause of loss is volatilization, for while the slag loss is higher than for ordinary ores, slag and cupel corrections still leave the results from this assay far below those of the crucible assay when properly performed.

Tellurium is very tenacious in its hold on gold and silver, and if a high-grade telluride ore be assayed, even by special method, the beads from the cupellation will frequently still contain tellurium.[1] In the crucible assay the losses, which are somewhat greater than in ordinary ores, occur in the slag, and from the presence of the Te in the lead button, causing absorption of values by the cupel. The aim in the crucible assay is to remove the tellurium from the gold and silver and slag it. This is best accomplished by the presence of considerable litharge, and otherwise properly balancing the flux. The flux recommended quite generally by Cripple Creek assayers is made up as follows:

Potassium carbonate	7 parts
Sodium carbonate	6 parts
Borax glass	5.5 parts
Flour	1.0 parts
Litharge	30.0 parts

This is for the ordinary silicious Cripple Creek ores. About 75 grams of this flux is used with 0.5 assay ton of ore. This gives the following charge:

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[1] E. C. Woodward, "Cupel Losses in Telluride Ores," in "West. Chem. and Met.," I, p. 120.

Ore	0.5 assay ton	Borax glass	8.5 grams
PbO	45.5 grams	Na_2CO_3	9.0 grams
Flour	1.5 grams	K_2CO_3	10.5 grams

The heat recommended is such that a temperature of 1084° C., the melting-point of gold, is reached at the mouth of the muffle. Some assayers recommend a somewhat greater temperature to insure the decomposition of the tellurides. The time of fusion should be about 45 to 50 minutes. It is essential to recognize that the flux recommended above for tellurides does not make what can be strictly termed an "excess-litharge charge."

Hillebrand and Allen[1] recommend the following charge for Cripple Creek ores:

Ore	1 assay ton	Borax glass	10 grams
$NaHCO_3$	1 assay ton	Reducing agent (if necessary)	
PbO	6 assay tons	Salt cover	

This approaches more nearly the excess-litharge charge.

It is essential in telluride ores to have the sample crushed to 120- or, better, to 150-mesh. The reasons for this is that, owing to the irregular distribution of values in these ores, fine crushing is required to get a true sample, and also because the low melting-point of the charge usually employed makes this essential.

The precise behavior of tellurium in the crucible assay has not been completely investigated. It is probable that the greater part of it is oxidized to a tellurate, probably that of soda, under the oxidizing conditions which exist in the usual telluride ore charge. It is stated[2] that in the oxidizing roasting of Cripple Creek telluride ores, in their preparation for chlorination or cyanidation, the greater part of the tellurium in the raw ore is found in the roasted ore as a tellurite of iron. Some assayers add an iron nail to the assay, not so much to desulphurize as to provide an excess of iron for the purpose of combining the tellurium with it, as in the case of sulphur.

For the quantity of tellurium present, its influence on the assay is certainly profound. The following table gives an idea of the quantity present:

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[1] "A Comparison of a Wet and Crucible Fire Methods for the Assay of Gold Telluride Ores," Bull. No. 253, U. S. G. Survey.

[2] *Trans.* I. M. M., III, pp. 49, 50.

TABLE XVIII. — QUANTITY OF TELLURIUM IN ORES

Element	Cripple Creek Ore	Cripple creek Ore	Black Hills Cambrian	Black Hills Cambrian
Tellurium	0.0742 per cent.	0.092 per cent.	0.0033 per cent.	0.010 per cent.
Gold	0.0506 per cent.	0.060 per cent.	0.0026 per cent.	0.003 per cent.
Silver	0.0075 per cent.	0.0103 per cent.		

As already stated, tellurium is with difficulty separated from gold and silver, and in spite of an oxidizing charge is frequently carried down in the lead button. The loss then takes place in the cupel, tellurium causing a heavy absorption. Some loss, however, takes place by volatilization. There is also a somewhat higher slag loss in the telluride assay than in the assay of ordinary ores.[1] Hillebrand and Allen, already quoted, assayed telluride ores by the combination wet-and-dry assay, getting the gold and silver free from tellurium, but found that the crucible assay as ordinarily performed for telluride ores gave just as satisfactory, if not better, results.

A Study of the Assay of Black Hills Cambrian Ores. — These ores are probably complex tellurides. The ores were oxidized and of the following average composition:

SiO_2 = 71.5 per cent.; Fe_2O_3 = 16.3 per cent.; Al_2O_3 = 4.8 per cent.; CaO = 1.5 per cent.; Gold = 0.79 oz.; Ag = 0.10 oz.

Samples of this type of ore, representing controls on car-load lots, were assayed by assayers A and B in the same laboratory, with the same kind of cupels, and great regard to temperature of cupellation. Assayer A made fusions on 1 assay ton lots, in triplicate, with the following stock flux:

Na_2CO_3	3.25 parts	Borax glass	5.00 parts
K_2CO_3	2.25 parts	Argol	1.00 parts
PbO	18.00 parts		29.50 parts

The amount of flux used was 4 assay tons per assay ton of ore, with quite a heavy borax glass cover. Fusions made at 1100° C., approximately.

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[1] C. H. Fulton, "Sch. Mines Quart.," XIX. F. C. Smith, *Trans.* I. M. M., IX, p. 344. "Min. Rep." 51, p. 163. Hillebrand and Allen, Bull. No. 253, U. S. G. Survey, pp. 12, 14.

The stock flux is equivalent to the following charge:

Ore	1 assay ton	PbO	73.2 grams
Na_2CO_3	13.2 grams	Borax glass	20.3 grams
K_2CO_3	9.1 grams	Argol[1]	4.0 grams

On account of the negligible quantity of Ag present, every assay was salted with Ag. The beads were parted in acid 1 to 9, and were in each case required to check against each other in weight. The beads were then weighed together and the resultant weight divided by 3 to obtain the amount of gold.

Assayer B made assays on the same pulp samples with the following stock flux:

Na_2CO_3	3.25 parts	Borax glass	2.00 parts
K_2CO_3	2.25 parts	Argol	0.75 to 1.00 part
PbO	22.00 parts		30.25 parts

Three assay tons of flux were used to each 0.5 assay ton of ore, with a soda cover one-quarter inch thick. Assays were made in quadruple, all fusions being salted with Ag, parted in 1 to 4 acid, and the beads required to check against each other in weight and then weighed together, and the sum divided by 2 to get the value per ton.

The stock flux is equivalent to the following charge:

Ore	0.5 assay ton	PbO	67 grams
Na_2CO_3	9 grams	Borax glass	6 grams
K_2CO_3	6 grams	Argol	2.5 grams

The results of these series of assays were as follows:

Lot No.	Assayer A Oz. Au per ton	Assayer B Oz. Au per ton
88870	0.74	0.78
88832	0.80	0.83
88874	0.71	0.80
88823	0.82	0.98
88721	0.80	0.88
88851	0.85	0.89
88818	0.85	0.91
88940	0.79	0.84
3669	0.82	0.91
88853	0.85	0.91
88890	0.81	0.83

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[1] This amount of argol required because ores are oxidizing. The button produced usually 22 to 25 grams.

Lot No.	Assayer A Oz. Au per ton	Assayer B Oz. Au per ton
71957	0.79	0.82
88826	0.77	0.82
3843	0.77	0.81
88780	0.80	0.88
22522	0.66	0.73
98509	0.69	0.79
22050	0.50	0.58

Assayers A and B then exchanged fluxes, and as they checked each other's previous results closely, it became evident that the flux of assayer A was ill-balanced and would not give good results. Slag and cupel corrections were made by Assayer A on assays made with his flux, but even these corrections added failed to bring his results up to those of assayer B.

The question arises as to what is the specific trouble with flux A. On examination, it will be found to contain an excessive amount of borax glass, especially when the cover is considered. It is very probable that the acidity of the charge (although a good fluid slag is obtained) is so great, taking into account both the silica of the ore and the borax glass, that the ore is not completely decomposed by the basic ingredients of the charge; *i.e.*, the soda and litharge become saturated with borax and then do not completely decompose the silicious ore. The fact that re-assays of the slag do not bring the results up to the figures obtained by assayer B does not necessarily imply that the slag does not contain these values, as the charge used to flux the slags and cupels again contains much borax glass, so that practically the same conditions obtained as before.

The Assay of Copper-Bearing Material. — Copper-bearing material includes ores containing copper and furnace products, chiefly mattes, blister copper, etc. Copper, which in the assay has a strong tendency to go into the lead button, causes, when present in sufficient quantity, serious losses by cupel absorption. Therefore all methods of assay for this class of material endeavor to eliminate copper from the lead button to be cupeled. A standard method for the assay of material high in copper, especially for Ag, is the combination assay for blister copper and mattes, described in Chapter IX.

Another standard method, especially for gold, and one that is carried out frequently as a check to the above, is the scorification method. This is performed as follows:

Ten samples, of 0.10 assay ton each, are taken and placed in 3-inch scorifiers with 50 grams of test lead (the silver content of which is accurately known); 25 grams of the lead are mixed with the matte, or borings, etc., and the other 25 grams used as a cover. On top of the charge is placed 1 gram each of silica and borax glass. The scorification is carried on at a moderate temperature until the assays are just about to slag over, which takes usually about 25 minutes, and then they are poured. The resultant button will weigh about 15 to 16 grams and be quite hard with copper. The buttons, cleaned from slag, are scorified, test lead being added to make the total lead up to 40 grams. The second scorification will take about 30 minutes and the resultant buttons will weigh from 10 to 12 grams. These are cupeled in 10 separate cupels, placed so as to be subject to uniform temperature, *i.e.*, in one horizontal row across the muffle. Cupellation temperature should not exceed 750° C. (a full cherry-red) and should be finished with a hotter blick.

The beads are weighed separately and then together. They are then grouped in two lots of 5 each, which are parted in acid, strength 1 to 9, the beads being kept in this acid at nearly boiling temperature for 20 minutes and finished for 5 minutes with 1.42 sp. gr. acid (full strength). The ten cupels are taken in lots of two each (only the litharge-stained part is taken), crushed to pass 100-mesh and assayed by the following charge:

100 grams PbO
20 grams Na_2CO_3
45 grams borax glass
3 grams argol
Soda cover

The lead buttons are cupeled, and the silver and gold obtained added to the first weights. The scorification slags may also be reassayed and this correction added, but in practice the cupel correction is the only one usually allowed. Sometimes no correction is allowed. It is to be noted that, even with a rescorification of the first button of the assay, the final silver beads, from 55 per cent. Cu matte containing 180 oz. Ag per ton and 2.31 oz. gold, will contain from 2.5 to 4 per cent. copper, which must be deducted in order to get correct silver results. (For a further discussion of scorification slag losses and cupel absorption in assaying copper-bearing material, see Chapter XI.)

The scorification method is generally employed for the determination of gold in mattes, and the combination method for the determination of silver. Of recent years, special crucible methods for copper mattes and copper-bearing material have been developed with considerable success.[1]

A satisfactory method on copper mattes, up to 20 per cent. copper and high in gold and silver, is practised by the Standard Smelting Company, at Rapid City, S. Dak. The matte sample is put through a 120-mesh screen, and for controls 4 assays of 0.25 assay ton each are made, with the following stock flux:

Silica	11 parts	Sodium carbonate	25 parts
Litharge	70 parts	Niter	5 parts

An 0.25 assay ton matte is run with a 3.5 assay ton flux and a thin borax glass cover. The flux figured to the charge is as follows:

0.25 assay ton	matte	24.0 grams	Na_2CO_3
10.5 grams	SiO_2	5.0 grams	KNO_3
67.0 grams	PbO		

The heat used is high and the fusion short, giving a clean fluid slag and a bright button of approximately 20 grams. These buttons are cupeled directly for gold and silver. One cupel and one slag are then re-run in the same crucible that the original fusion was made in, and the result of the four corrections added to the sum of the original buttons. No scorification is made before cupellation. The average correction, on the usual grade of matte (5 oz. Au, 40 oz. Ag), is 2.5 per cent. gold and 5.5 per cent. silver. Below is a comparison of this method with the standard scorification assay, including cupel and slag correction. The copper content of this matte was 19.98 per cent.

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[1] "An All-Fire Method for the Assay of Gold and Silver in Blister Copper," in *Trans.* A. I. M. E., XXXII. Perkins, "The Litharge Process for the Assay of Copper Bearing Ores," *ibid.*, XXXI, p. 913.

TABLE XIX.—COMPARISON OF METHODS IN ASSAY

	Crucible Method		Scorification Method	
	Gold (oz.)	Silver (oz.)	Gold (oz.)	Silver (oz.)
Original assay	4.10	36.24	3.90	35.07
Correction	0.10	1.00	0.25	1.95
	4.20	37.24	4.15	37.02

The returns of this pulp by the refiner were: gold, 4.19 oz.; silver, 36.71 oz.

Matte No. 1545; copper content, 17.6 per cent.

TABLE XX.—COMPARISON OF METHODS IN ASSAY

	Crucible Method		Scorification Method	
	Gold (oz.)	Silver (oz.)	Gold (oz.)	Silver (oz.)
Original assay	3.42	31.94	3.40	31.86
Correction	0.10	1.85	0.11	1.93
	3.52	33.79	3.51	33.79

The following table shows results by this method with correction and refiners' results (by same method without correction):

Lot No.	Crucible Method: Standard Smelting Company		Crucible Method: Refiner		
	Gold	Silver	Gold	Silver	Copper
1391	17.73	75.4	17.67	74.13	7.2
1404	17.75	73.5	17.625	72.42	9.5
1412	11.35	45.7	11.145	42.95	10.3
1435	10.02	39.9	10.065	39.08	12.9
1450	9.10	44.6	9.02	43.01	13.2
1457	6.89	48.75	6.815	46.28	15.02
1458	9.95	58.37	9.935	52.31	19.9
1470	8.235	50.86	8.24	52.31	20.5
1471	4.845	40.52	4.87	39.48	18.4
1484	7.34	45.04	7.265	44.68	18.27
1489	6.45	47.98	6.83	46.67	19.4
1500	5.78	45.34	5.84	45.06	20.5
1503	4.61	27.11	4.58	26.51	18.8

Lot No.	Crucible Method: Standard Smelting Company		Crucible Method: Refiner		
	Gold	Silver	Gold	Silver	Copper
1513	3.815	32.75	3.80	31.55	11.8
1525	3.12	39.62	3.205	33.84	12.4
1529	3.10	33.00	3.36	31.14	18.7
1533	4.20	37.24	4.19	36.71	20.0

A typical sample of matte on which these assays were made analyzes as follows:

Gold	4.10 oz. per ton	Silica	3.3 per cent.
Silver	31.55 oz. per ton	Lime	0.5 per cent.
Copper	17.4 per cent.	Sulphur	29.1 per cent.
Iron	45.9 per cent.	Lead	trace
Zinc	2.5 per cent.		

The crucible charge employed can readily be modified to apply to mattes higher in copper or greater in reducing power.

Perkins' excess-litharge method has already been described. He states that for low-grade copper-bearing material (2 to 4 per cent.), 5 assay tons of PbO to 0.5 assay ton of ore will remove most of the copper, if the balance of the fluxes are properly proportioned, *i.e.*, if they have ample free PbO to dissolve copper oxides. For high-grade mattes, etc. — 48 to 60 per cent. copper — 8 assay tons of PbO to 0.1 assay ton of matte will remove most of the copper. Perkins also developed a crucible method for metallic copper, as follows:

Weigh out 0.25 assay ton of copper borings, divide it into 3 approximately equal parts, and place in 20-gram crucibles. In this way weigh out 4 sets, getting 12 assays. Into each crucible put 800 mgs. of powdered sulphur, mix thoroughly with the copper, and then on top of this put the following flux, being careful not to mix the flux with the copper:

Na_2CO_3	0.25 assay ton	PbO	8.0 assay ton
K_2CO_3	0.25 assay ton	SiO_2	0.5 assay ton

Salt cover

Place the crucibles into a dark-red muffle and gradually raise the temperature for 45 minutes to a yellow heat. The temperature regulation is important, and it is necessary to produce a neutral or reducing atmosphere in the muffle by the presence of coal or coke. The buttons, weighing about 18 grams each, are put together in lots of three, representing 0.25 assay ton, and scorified at a low heat. The resultant buttons should weigh 5 to 6 grams. Each of these buttons is now rescorified with 25 grams of lead at a low heat, until 6-gram buttons are obtained. These are cupeled with feathers. This method is stated to give results on gold equal to the all-scorification method, and on silver equal to the combination method.

The Assay of Zinciferous Ores and Metallurgic Products Containing Zinc. — Zinc most frequently occurs in ores as the sulphide, sphalerite, and, in certain metallurgical products, as the metal (zinc cyanide precipitates). Zinc boils at 940° C., and rapidly volatilizes. Zinc oxide volatilizes slowly at the melting-point of silver (962° C.), and rapidly at a white heat. Zinc silicates alone are difficultly fusible, but are readily so when mixed with borax or boric acid or ferrous silicate.[1] The presence of zinc in material to be assayed calls for certain precautions, and in general the assay is difficult. Metallic zinc has a great affinity for gold and silver, greater than lead, as is shown by the Parkes process for the desilverization of lead bullion. Under oxidizing influences [2] the formation of zinc oxide and its volatilization causes losses of gold and silver. That this loss is mechanical does not make it less serious. The boiling-point of zinc and the volatilization of its oxide occur at temperatures somewhat below the normal for ordinary scorification, and it is these general facts, coupled with the fact that the zinc oxide formed is with difficulty soluble in litharge, that make accurate assay-results hard to obtain, especially in scorification. Zinc containing gold and silver may be distilled off and volatilized with very little loss of gold and silver, if the conditions are reducing.[3]

Scorification is frequently employed for zinciferous ores, although it is not generally satisfactory. When used, it is best carried out in a way similar to that adopted for copper-bearing material, using from 0.05 to 0.10 assay ton of ore with from 50 to 80 grams of test lead, 2 grams of borax glass, and 1 gram of silica, the last being essential to flux the zinc oxide formed.

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[1] Rose, "Refining Gold Bullion, etc. in Oxygen Gas," in *Trans.* I. M. M, April, 1905.

[2] Williams, in Journ. Chem. Met. and Min. Soc. of South Africa, III, p. 132.

[3] Rose, *ibid.*, and references.

Otherwise insoluble scoria and crusts form on the scorifier. Slag and cupel corrections are generally necessary and from 5 to 10 assays are made, the results being averaged. As zinc is readily oxidized, lead buttons contaminated with zinc are not to be feared and rescorification is rarely necessary. Among the most important zinciferous material presented for assay are the zinc-gold precipitates from the cyanide process. Scorification is not desirable for these.[1] They are best assayed by the crucible method or by one of the combination methods already described.

Crucible Method. — The crucible method best suited for unoxidized zinc ores is the niter method, with sufficient silica present to form at least the monosilicate with zinc. Borax glass and much litharge is also desirable. On a practically pure sphalerite the following charge will give good fusions at temperatures of about 1100° C.:

Ore	0.5 assay ton	SiO_2	8 grams
Na_2CO_3	15 grams	KNO_3	22 grams
PbO	150 grams	Heavy borax glass cover.[2]	

This charge can be modified, as regards niter and silica, to suit any sphalerite ore.

A good crucible charge for cyanide precipitates, containing up to 50 per cent. zinc, is:

Precipitates	0.1 assay ton	SiO_2	5 grams
Na_2CO_3	5 grams	$Na_2B_4O_7$	2 grams
PbO	70 grams	Flour	1 gram

Light borax glass cover

Assay of Plumbago Crucibles for Gold and Silver. — Graphite or plumbago crucibles are extensively used in the smelting of cyanide zinc precipitates, and the old discarded ones are usually sold in lots to some smelter; they often contain considerable gold and silver. These pots present difficulty in assaying, chiefly on account of the graphite and zinc contained. From a given weight of sample, the metallics and scales are separated by passing the material through a 150-mesh screen, and a regular

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[1] "Notes on the Assay of Zinc Precipitates, etc.," in "Sch. Mines Quart.," XXII, p. 153.

[2] A similar charge is recommended by Lay, for complex zinc-lead concentrate; see "Min. Ind.," XIII, p. 287.

scale assay is made as outlined at the end of this chapter. The pulp is assayed as follows:[1]

From 0.05 to 0.10 assay ton is taken and mixed with a little more than one-half its weight of niter and 30 grams of litharge, placed in a 2.5-inch scorifier, covered with 30 grams of litharge and afterward with a thin cover of borax glass, placed in a muffle, and fused finally at a yellow heat. The buttons are cupeled, weighed, and parted as usual. Crucible assays may also be made on this material by the niter excess-litharge fusion, with a charge as follows:

0.1 assay ton, graphite
70 grams PbO
5 grams SiO_2
5 grams, Na_2CO_3
5 to 11 grams KNO_3 (according to carbon contents of pulp)
Borax glass cover

In both methods it is essential that the amount of pulp, usually, should not exceed 0.1 assay ton, the carbon giving difficulties with greater amounts than this.

The Assay of Residues from Zinc Distillation (containing considerable carbon) for Silver and Gold.[2] — From 0.10 to 0.5 assay ton of the powdered residue is mixed with 35 grams of niter and 10 grams of Na_2O_2 (sodium peroxide), and dropped, in lots of 5 grams each, into a red-hot crucible which can be readily covered, and the oxidation reactions permitted to complete themselves. The flux then added consists of 70 grams of litharge, 10 grams of borax glass, 10 grams silica, 2 grams argol and a light borax glass cover. The fusion is carried out at a yellow heat and the buttons cupeled as usual.

The Assay of Antimonial Ores for Gold and Silver. — Gold- and silver-bearing antimonial ores, such as stibnite, jamesonite, etc., are usually assayed by the niter method,[3] in the presence of considerable soda and niter, to induce the formation of the antimoniate of soda. A preliminary assay to determine the amount of niter is essential. The following charge is recommended for nearly pure stibnite:[4]

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[1] A modification of T. L. Carter's method; see "Eng. and Min. Journ.," LXVIII, p. 155.

[2] K. Sander, in "Eng. and Min. Journ.," LXXIII, p. 380.

[3] William Kitto, "The Assay of Antimonial Gold Ores," in *Trans.* I. M. M., 1906, Nov. 8 and Dec. 13.

[4] Smith, "The Assay of Complex Gold Ores," in *Trans.* I. M. M., IX, p. 332.

Ore	0.5 assay ton	KNO_3	18 grams
PbO	120 grams	Borax glass	6 grams
Na_2CO_3	10 grams	SiO_2	10 grams

Salt cover

The fusion should be conducted slowly and at a low temperature. The button will usually contain very little antimony, the cupel not showing scoria or cracks. If it does contain enough to cause losses in cupellation, the buttons should be scorified. Smith[1] gives the following charge for ore containing approximately 75 per cent. stibnite. The niter, etc., can be varied for the ore as the gangue increases:

Ore	1 assay ton	Borax glass	8 grams
PbO	75 grams	KNO_3	20 to 25 grams
Na_2CO_3	25 grams	Salt cover.	

Another method, practically as good as the niter method, is the roasting with charcoal or coke-dust.[2] The sample of ore, usually 1 assay ton, is mixed with approximately its own volume of coke-dust or coal-dust, placed in a 5-in. roasting dish, covered with another dish, and roasted in the muffle with closed door, at a temperature not exceeding a dark cherry-red (635° C.), for about 35 to 40 minutes. This will cause the volatilization of 95 to 96 per cent. of the antimony as sulphide without appreciable loss of gold. The roast should have a yellow appearance when finished, and can be fused with the following charge:

Roasted ore		SiO_2	7 grams
PbO	70 grams	Argol	2 grams
Na_2CO_3	20 grams	Borax glass cover	

This method gives good results on jamesonite ores.

Arsenical ores are assayed by the same methods as the antimonial ores; also by the iron-nail method, although this last is not generally to be recommended. The subject of the best method of assay of antimonial and arsenical ores still lacks thorough investigation. The chief points may be outlined as follows:

1. In the roasting, unless great care is taken as regards temperature, mechanical loss of gold and silver takes place,

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[1] Smith, *Ibid.*

[2] Sulman, *Trans.* I. M. M., IX, p. 340.

owing to the rapid disengagement of the arsenic and antimony oxides, or sulphides of these metals. Unless the roast is conducted at a low heat and in the presence of considerable carbon, arseniates and antimoniates of base metals or silver may form, holding values which later on are not completely decomposed in the crucible, owing to their stability at a high temperature, the result being appreciable slag losses.

2. In the niter method, the presence of much niter, with its powerful oxidizing effect, may also induce the formation of arseniates and antimoniates, containing silver and possibly gold, which will remain in the slag.

3. In the iron-nail method, unless the fluxes are carefully adjusted and the temperature kept below 1100° C., speiss carrying values is very apt to form above the lead button, and thus necessitate a re-assay, or a treatment of this speiss.

The Assay of Sulphides, mainly Pyrite, but containing Small Amounts of Copper, Zinc Sulphides, etc. — Where gold only has to be determined in ores of this character, the roasting method is satisfactory. This, however, proves unreliable for silver, and in many cases (as at Leadville) the silver contents of these sulphides are the most important. The best method, after many trials, was found to be the niter fusion on comparatively small lots of ore. The ore has the following analyses:

Iron	33 to 44 per cent.	Zinc	4 to 8 per cent.
Sulphur	38 to 45 per cent.	Copper	0.5 to 3.5 per cent.
Insoluble	4 to 20 per cent.	Lead	0 to 0.4 per cent.

Four assays are made on 0.25 assay ton each, with 3 to 4 assay tons of the following flux, the amount depending on the reducing power; *i.e.*, on the amount of sulphides present:

PbO	8 parts	SiO_2	1.5 parts
KNO_3	1.5 parts	Borax glass	1.5 parts
Na_2CO_3	3.0 parts		

Either a salt or a soda cover is used. The temperature of fusion is brought up gradually to a yellow heat. With 4 assay tons this gives the following charge[1]:

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[1] See also W. G. Vail, "Niter Assay for Sulphide Ores," in "West. Chem. and Met.," II, p. 14.

Ore	0.25 assay ton	Na_2CO_3	24 grams
PbO	62 grams	Borax glass	11 grams
KNO_3	12 grams	SiO_2	11 grams

The buttons are usually clean, and separate well from the slag.

Another method which may be used on this type of ore is the niter-iron method. This has the advantage that no preliminary assay is necessary to determine the amount of niter for the proper size button, but that only sufficient niter is added to partially oxidize the sulphides, the iron nails being relied upon to decompose the balance of the ore. On ores of the class shown by the analysis, the following charge is successful:

Ore	0.5 assay ton	SiO_2	8 grams
Na_2CO_3	25 grams	Borax glass	8 grams
PbO	30 grams	Iron nails	2 to 3 tenpenny
KNO_3	15 grams	Thin borax glass cover	

If the ore has a lesser reducing power than shown by the analysis given, niter and silica should be decreased in the charge.

The Assay of Material Containing Metallic Scales. — Ores of this kind are difficult to assay and obtain correct results, as the metallic particles (usually gold) are so unevenly distributed as to make it practically impossible to obtain an accurate sample. Two methods of assay are available:

(*a*) Approximately 500 grams of ore (or less, if deemed advisable) are weighed out, crushed, and put through a 150- or 200-mesh screen, care being taken to separate out the scales as closely as possible. Screening and crushing should frequently succeed each other. When all the scales have been separated out, they are transferred to a parting cup and dissolved in 3 to 5 c.c. of nitro-hydrochloric acid, if gold, or in nitric acid if silver or copper. The pulp is then heaped up into a cone in a large porcelain dish, the gold, etc., solution poured on the apex of the cone, and the parting cup washed out thoroughly with warm distilled water, using no more than is necessary to completely wash it out. The bed of pulp should be thick enough to readily absorb all of the solution, and not permit it to penetrate to the dish. The pulp is then dried in an air bath at 120° C., thoroughly mixed on glazed paper, and put through the screen repeatedly. It is then assayed by the method suitable to it, like any other ore.

(*b*) From 200 to 500 grams of ore are weighed out, crushed and screened, and the scales separated, as described above. The scales and the pulp are then weighed and the loss in dusting noted. The scales are assayed by scorification; the lead button is cupeled, and the bead weighed and parted. Then 15 grams of the ore is weighed out in duplicate, fused with the proper charge, the lead buttons from these fusions cupeled, and the beads weighed and parted. From the results obtained, the total amount of gold and silver in the original ore is calculated, considering both pulp and scales. The gold and silver, respectively, found is multiplied by 29.166 and divided by the original weight of ore, taken in grams; this gives the value in ounces per ton.

The Assay of Ores Containing their Chief Value in Free Gold. — As already pointed out, these ores are difficult to get correct results from. Even though the free gold particles are very fine, it is impossible to distribute them uniformly throughout the bulk of the sample. The only proper way to assay material of this kind is to take from 3 to 5 lbs. of the ore, crushed through a 100-mesh screen, place in a large jar with a tight screw cover, mix to a thick pulp with water, add 1 to 2 oz. of pure mercury, and agitate the jar and contents for from 1 to 2 hours. Then carefully separate the mercury from the pulp by panning in a gold pan (it may be necessary to add more Hg to the pan in order to collect what has been used), saving all the panned pulp. This is dried, thoroughly mixed, and assayed by the proper method. The mercury, with 30 grams of lead, is placed in a 2.5-in. scorifier, which is covered with a second one turned upside down, into the bottom of which a small hole has been bored. The scorifiers are luted together with clay. The mercury is driven off by raising the temperature gradually to a bright red. The top scorifier is then removed, the lead scorified down to a 15-gram button, which is cupeled, and the gold bead weighed and parted. The proper calculation is then made for the value per assay ton.

The Assay of Slags and Cupels for the Correction Assay. — (*a*) Slags: The charge for these depends upon whether they are acid or basic. Particular care must be taken to get a charge that will completely decompose the original slag. If this is acid, the charge should aim to make a new slag more basic, and vice versa. The lead button should be from 20 to 25 grams in weight. Many assayers frequently add simply litharge and reducing agent to the slag in making the fusion. This is not always desirable, for if the slag already has much litharge in it, soda, etc., may with profit be added as the extra base in place of litharge.

(*b*) Cupels: The bone-ash of the cupel will not unite with fluxes to form slags, but remains suspended in the fusion. For this reason the cupel should be put through a 150- to 200-mesh screen before assaying, the litharge-stained portion only being taken. For one large cupel, or two small ones, the charge is as follows:

Cupel		Borax glass	45 grams
PbO	100 grams	Argol	2.5 grams
Na_2CO_3	25 grams	Salt cover	

Fluorspar is not desirable in the assay of cupels, as it merely adds another ingredient in suspension.

XI

ERRORS IN THE ASSAY FOR GOLD AND SILVER

Losses in the Cupellation of Pure Gold and Silver. — These losses may be divided into (1) losses by absorption, (2) losses by volatilization. The losses of gold and silver in the cupellation are functions of (*a*) the temperature of cupellation; (*b*) the amount of lead with which the gold and silver is cupeled; (*c*) the physical nature of the cupel; (*d*) the nature and amount of impurities present; (*e*) the influence which silver has on the gold loss, and vice versa.

There is considerable literature extant upon losses in cupellation of the two precious metals, but in the older researches the temperature influence is but vaguely defined, owing to the lack of means for ready and satisfactory temperature measurements, a deficiency which is now supplied by the Le Chatelier platinum-rhodium pyrometer. Losses are also expressed as percentages of the total amount of metal cupeled, and then the average percentage losses are indicated. That this is very deceptive is made evident by reference to the curve of losses accompanying this chapter.

It is for this reason that the statement of results given by Mason and Bowman,[1] that the average loss in cupellation of pure silver under normal conditions is 1.99 per cent. and for gold 0.296 per cent., does not convey any very definite idea, unless the amount of metal cupeled is accurately specified, as well as the temperature. This fact has been noted by other observers,[2] but no effort has been made to express results coordinately.

The following data show the losses which occur:

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[1] "Journ. Am. Chem. Soc.," XVI, p. 505.

[2] Kaufman, in "Eng. and Min. Journ.," LXXIII, p. 829. Miller and Fulton, in "Sch. Mines Quart.," XVII, p. 169.

TABLE XXI. — CUPELLATION OF PURE SILVER

(J. Eager and W. Welsh [1])

Amt. of Silver Milligrams	Amt. of Lead Grams	Temperature Deg. Cent.	Total Losses Per cent.
204.62	10	700	1.02 (average)
205.00	10	775	1.28
203	10	850	1.73
203	10	925	3.65
203	10	1000	4.87

TABLE XXII. — CUPELLATION OF PURE SILVER

(L. D. Godshall [2])

Amt. of Silver Mgs.	Amt. of Lead Grams	Temp. ° C. Front of Muffle	Total Loss in Per cent.
2	7.5	750°?	3.66
2	15.0	750	4.40
2	22.5	750	5.52
2	30.0	750	5.96
5	7.5	750	3.29
5	15.0	750	2.63
5	22.5	750	3.83
5	30.0	750	4.31
10	7.5	750	3.73
10	15.0	750	2.89
10	22.5	750	4.47
10	30.0	750	4.26
20	7.5	750	3.42
20	15.0	750	2.34
20	22.5	750	3.59
20	30.0	750	3.10
50	7.5	750	2.14
50	15.0	750	2.46
50	22.5	750	2.33
50	30.0	750	2.89
100	7.5	750	2.11
100	15.0	750	2.40
100	22.5	750	2.10
100	30.0	750	2.28
200	7.5	750	1.71
200	15.0	750	1.64
200	22.5	750	1.62
200	30.0	750	2.07

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[1] Lodge, "Notes on Assaying," p. 59.

[2] *Trans.* A. I. M. E., Vol. XXVI, p. 473.

TABLE XXIII.—CUPELLATION OF PURE SILVER

(KAUFMAN[1])

AMT. OF SILVER MGS.	AMT. OF LEAD GRAMS	TEMP. ° C. FEATHERS	TOTAL LOSS IN PER CENT.
25	5	750°?	2.14
25	10	750	2.63 (2.38, 2.43)
25	15	750	2.69
25	25	750	2.09 (2.48, 2.44)
50	5	750	1.43
50	10	750	2.23 (2.10, 1.96)
50	15	750	2.14
50	25	750	1.86 (2.25, 2.37)
100	5	750	1.30
100	10	750	1.61 (1.82, 1.42)
100	15	750	1.68
100	25	750	2.12 (1.93, 2.12)
200	5	750	0.86
200	10	750	1.24 (1.29, 1.17)
200	15	750	1.40
200	25	750	1.74 (1.46, 1.76)

Parentheses indicate different types of cupels, *e.g.*, bone-ash made up respectively with pearl-ash and stale beer. The main figures were obtained by bone-ash cupels made up with water. The results, viewed as a whole, indicate that all three types have equal merit. Godshall (Table XXII) experimented with different types of standard bone-ash cupels (some made at the mint), with the same result. Rose, cited further on, shows that magnesia cupels cause somewhat greater losses than good bone-ash cupels.

The agreement amongst the different writers is very close, when the fact is taken into consideration that in the last two cases no precise statement concerning temperature is made, and that the amounts of lead differ somewhat.

AUTHORITY	AMT. OF SILVER Mgs.	AMT. OF LEAD Grams	TEMPERATURE Degrees Cent.	TOTAL LOSS PER CENT.
Eager and Welch	205	10	775	1.28
Godshall	200	7.5	? (feathers)	1.71
Kaufman	200	10	? (feathers)	1.24

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[1] "Eng. and Min Journ.," LXXIII, p. 829.

The accompanying curves are constructed from figures in Mr. Godshall's paper. The general averages are taken, and while his losses are perhaps a trifle higher than the best work calls for at the present day (owing to a better recognition of the precise temperature required), they form the best and most complete data for the construction of curves showing the relation between amounts of silver cupeled and the percentage loss. I refrain from a mathematical discussion, but an equation covering the case is tentatively offered.[1]

The influence of the size of lead button is clearly discernible by the ordinates of the curves. The temperature variations will show in the same way.

TABLE XXIV. — CUPELLATION OF GOLD

(EAGER AND WELCH [2])

AMT. OF GOLD	AMT. OF LEAD	TEMP. C.	TOTAL LOSS PER CENT.
201	10	775°	0.155
201	10	850	0.430
204	10	925	0.460
201	10	1000	1.430
201	10	1075	3.000

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[1] I am indebted to Mr. C. C. Van Nuys, B. S., for the curves and the equations.

[2] Lodge, "Notes on Assaying," p. 142.

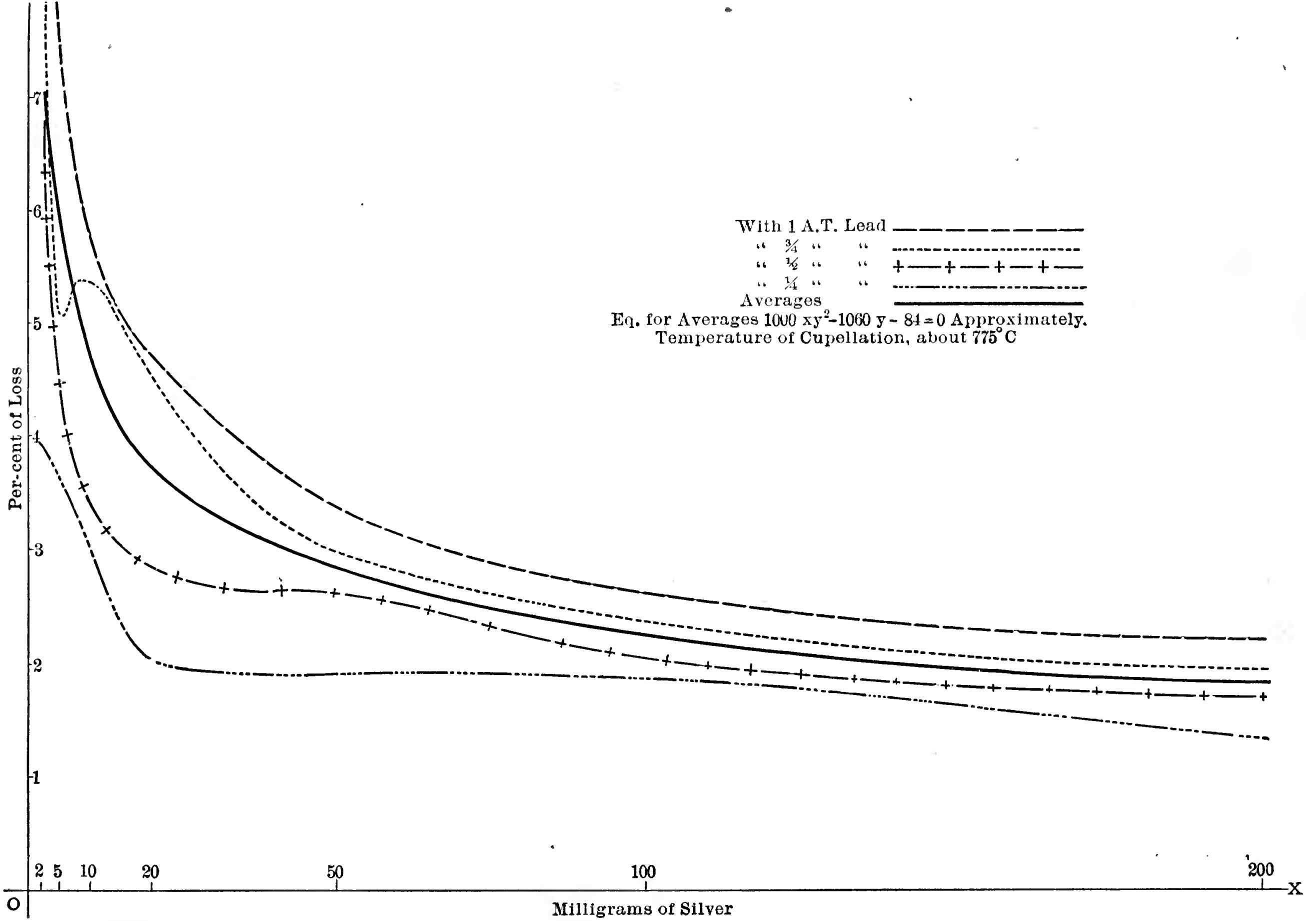
Per-cent of Loss
1
2
3
4
5
6
7
Milligrams of Silver
O
X
2
5
10
20
50
100
200
With 1 A.T. Lead
" ¾ " "
" ½ " "
" ¼ " "
Averages
Eq. for Averages 1000 xy²-1060 y - 84 = 0 Approximately.
Temperature of Cupellation, about 775° C

TABLE XXV. — CUPELLATION OF GOLD

(HILLEBRAND AND ALLEN[1])

AMT. OF GOLD MGS.	AMT. OF LEAD GRAMS.	TEMP. ° C.	TOTAL LOSS PER CENT.	TOTAL LOSS CUPEL ABSORPTION PER CENT.	TOTAL LOSS VOLATILIZED PER CENT.
30.58	25	750°? feathers	0.36		
30.32	25	increased	1.19	80	20
30.63	25	increased	1.76		
30.45	25	increased	3.78	77	23
30.16	25	increased	4.17	93	7
30.66	25	back of muffle	4.43	92	8
10.34	25	750°? front of muffle	0.29		
10.25	25	increased	4.68		
10.29	25	increased	1.36		
10.27	25	increased	10.42		
10.17	25	back of muffle	16.43		

The literature of gold losses is considerably less than that for silver. Rose[2] discusses them in the gold bullion assay. He gives the total loss on bullion 916.6 fine, under normal temperature conditions, as from 0.4 to 0.8 per 1000, of which 82 per cent. is cupel absorption, 10 per cent. volatilization (probably), and 8 per cent. solution in acid. This, calculated to percentage on actual gold, is equivalent to 0.0803 per cent. for the highest loss. (This is cupel loss only, not including solution loss.)

Hillebrand and Allen's results contain interesting data regarding the relative losses by absorption and volatilization, to which reference will be made again.

Cupellation of Gold-Silver Alloys. — The loss of gold and silver in cupellation is somewhat different when both gold and silver are present from the loss when either metal alone is present.

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[1] Bull. No. 253, U. S. G. Survey.

[2] "Metallurgy of Gold," 1902, p. 506.

TABLE XXVI. — CUPELLATION OF GOLD

(Rose [1])

Amt. of Gold Mgs.	Amt. of Silver Mgs.	Amt. of Pb Grams	Temp. of Cupellation ° C.	Total Loss Gold Per cent.
1	4	25	900°	1.2
1	6	25	900	1.05
1	8	10	900	0.90
1	10	25	900	0.80
1	6	25	700	0.45
1	10	25	700	0.39
500	1250	10	900	0.055

TABLE XXVII. — CUPELLATION OF GOLD-SILVER ALLOYS

(Hillebrand and Allen)

All Cupellations made with 25 Grams of Lead

Amount Gold Mgs.	Amount Silver Mgs.	Temp. ° C.	Total loss		Absorbed by Cupel		Volatilized	
			Gold Per cent.	Silver Per cent.	Gold Per cent.	Silver Per cent.	Gold Per cent.	Silver Per cent.
30.06	90.51	750?	0.50	1.70				
30.40	90.19	increased	1.22	3.73				
30.60	90.74	increased	2.32	5.51				
30.07	90.67	increased	3.76	7.66				
30.61	90.75	back of muffle	3.89	7.98				
15.56	45.06	front, 750?	0.19	1.91	67	81	33	19
15.14	45.19	increased	0.40	3.30	83	78	17	22
15.15	45.41	increased	1.52	4.14	52	63	48	37
15.44	45.30	increased	2.07	5.78	67	62	33	38
15.52	45.59	increased	2.59	6.55	67	70	33	30
15.39	45.05	back of muffle	2.40	6.61	73	71	27	29
10.67	30.33	front, 750?	0.47	2.17				
10.57	30.64	increased	1.61	5.68				
10.53	30.42	increased	5.13	10.19				
10.63	30.52	increased	10.63	15.99				
10.60	30.38	increased	12.46	18.34				
10.21	30.44	back of muffle	12.53	18.69				

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[1] "Eng. and Min. Journ.," LXXIX, p. 708.

Rose shows (Table XXVI) the protective action that silver exercises over gold, the total loss of gold decreasing as the amount of silver present increases. Hillebrand and Allen show how the total loss is distributed between absorption by the cupel and volatilization. It is evident that while the total loss of gold is increased by the presence of silver, the volatilization loss of gold is increased by the presence of silver (compare Tables XXV and XXVII). When gold and silver are present in the ratio of 1 to 2, the averages are as follows:

Of the total gold loss, 68 per cent. is absorbed, 32 per cent. is volatilized.

Of the total silver loss, 71 per cent. is absorbed, 29 per cent. is volatilized.

However, as the total loss is determined by the difference in weight between the proof gold and silver and the weights of the cupeled bead and parted gold, and the volatilization item by the difference between the total loss and the amount recovered by the re-assay of the cupel, it is evident that certain errors obtain which apparently make the volatilization loss appear greater than it really is. The error, however, cannot be very great. The data are inconclusive regarding the influence of the temperature on the relative losses by absorption and volatilization, but it seems indicated that the volatilization loss is proportionately greater with an increase of the temperature of cupellation.

Table XXVIII etc., show losses of gold and silver in the assay of ores, during fusion and cupellation, as influenced by the presence of certain impurities.

TABLE XXVIII. — TELLURIDE ORES

AMOUNT OF GOLD IN WEIGHT OF ORE TAKEN FOR ASSAY	WEIGHT OF LEAD BUTTON	METHOD OF FUSION	SLAG LOSS	CUPEL ABSORPTION
Milligrams	Grams.		Per cent.	Per cent.
(¹)493.83	20	Crucible[7]	0.51	1.56
95.57	20	Crucible	0.38	0.23 (⁵)
1.54	20	Crucible	1.30	0.40
1.95	20	Crucible	0.50	0.50
1.19	20	Crucible		0.40
1.17	20	Crucible		0.40
3.60	20	Crucible	2.14	0.80
6.20	20	Crucible	0.64	0.32
6.23	20	Crucible	0.50	0.64
1.38	20	Crucible	0.80	1.00
(²) 18.18	25	Crucible	0.49	
5.85	25	Crucible	1.03	0.12 (⁶)
(³) 34.0	27	Crucible	0.21	0.23
34.0	27	Crucible	0.56	
34.0	25	Crucible	0.15	0.41
68.0	25	Crucible	0.13	0.07
68.0	25	Crucible	0.16	0.22
(⁴) 15.5		Crucible[8]	0.25	0.19
15.49		Crucible	0.13	0.38
19.54		Crucible	0.20	0.23
19.63		Crucible	0.10	0.25

[1] Woodward, in "West. Chem. and Met." I, p. 12.

[2] Fulton, in "Sch. Mines Quart.," XIX, p. 419.

[3] Lodge, in "Tech. Quart.," 1899, XII, p. 171 (averages).

[4] Bull. No. 253, U. S. G. Survey (averages; Hillebrand and Allen).

[5] Average of 34 fusions, tellurium in all beads.

[6] Average of 10 fusions.

[7] Cripple Creek flux.

[8] Excess-litharge charge.

TABLE XXIX. — ZINCIFEROUS MATERIAL, ETC.

AMT. OF AU AND AG IN WEIGHT OF ORE TAKEN FOR ASSAY		WEIGHT OF LEAD BUTTON	METHOD OF ASSAY	SLAG LOSS		CUPEL ABSORPTION		REMARKS
Au Mgs.	Ag Mgs.	Grams		Au Per cent.	Ag Per cent.	Au Per cent.	Ag Per cent.	
[1] 232.0	287.0	18	Scorification after acid treatment	0.06	0.40	0.11	1.30	Zn. ppt. containing 42.3 per cent. Zn
232.0	284.0	18	Scorification after acid treatment	0.04	0.34	0.08	1.10	Figures represent averages
232.0	284.0	18	Direct crucible fusion	1.04	1.10	0.16	1.50	
[2] 233.0	197.0	20	Crucible fusion after acid treatment	0.06	0.51	0.18	1.18	Zn ppt. containing 14.3 per cent. Zn, 9.1 per cent. Cu.
233.0	202.0	20	Direct crucible fusion	0.15	2.73	0.16	1.29	Figures represent averages
[3]	561.0	20	Crucible fusion niter method		0.75		1.38	Galena
	567.0	20	Crucible fusion niter method		0.65		1.42	Galena
[3]	175.0	20	Crucible fusion niter method		0.23		1.90	Silicious ore containing some copper
	174.0	20			0.37		1.66	Silicious ore containing some copper

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[1] Fulton and Crawford, in "Sch. Mines Quart.," XXII, p. 153.

[2] Lodge, in *Trans.* A. I. M. E., XXXIV, p. 432.

[3] Miller, in "Sch. Mines Quart.," XIX, p. 43.

TABLE XXX.[1] — HIGH-GRADE CARBONATE AND SULPHIDE SILVER ORES[2]

Amt. of Au and Ag in Weight of Ore taken for Assay		Weight of Lead Button	Method of Assay	Slag Loss		Cupel Absorption		Second Correction from Fusion of Slags and Cupels of First Correction Per cent.
Au Mgs.	Ag Mgs.	Grams		Au Per cent.	Ag Per cent.	Au Per cent.	Ag Per cent.	
	1130	24	Crucible fusion		0.76		1.25	0.248
	1130	28	Crucible fusion		0.361		0.956	
	1130	28	Crucible fusion Double amt. of fluxes		0.511		0.88	0.15
	1130	32	Crucible fusion Double amt. of fluxes		0.736		1.02	0.15
	226	15	Scorification		2.8		1.40	0.559
24	1719	25	Crucible fusion	0.05	0.143	0.07	0.711	
12	860	20	Scorification	0.12	0.72	0.08	0.86	

TABLE XXXI. — CUPRIFEROUS MATERIAL

Amt. of Au and Ag in Weight of Ore taken for Assay		Weight of Lead Button	Method of Assay	Total Loss Recovered including Slag and Cupel		Remarks
Au Mgs.	Ag Mgs.	Grams		Au Per cent.	Ag Per cent.	
11.46	88.0	20	Crucible fusion	0.96	2.90	Mattes containing about 20 per cent. Cu
5.36	46.8	20	Crucible fusion	2.98	4.30	
4.20	37.24	20	Crucible fusion	2.38	2.70	
3.52	33.79	20	Crucible fusion	2.84	5.47	
4.20	37.24	20	Scorification	5.95	5.26	
3.52	33.79	20	Scorification	3.12	5.71	

The foregoing tables represent for the most part averages, and in every case the losses for the normal assay; *e.g.*, in the case of the fusion, the charge known to yield the best results, and the proper temperature for cupellation. The losses are therefore

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[1] First five results on lead carbonate ore, last two on silver sulphides. All results represent averages.

[2] Miller and Fulton, *ibid.*, XVII, p. 160.

to be ascribed to the nature of the material assayed, chiefly to the influence of certain elements present. In considering the percentage of loss, it must be recalled that this varies inversely with the amount of precious metal in the charge, *i.e.*, with the size of the gold-silver bead. The sum of the cupel absorption and the slag loss (which can, in part, be recovered) is not the total loss, as it does not include that by volatilization, which is small in most cases, but in some cases, again, may be quite appreciable, as in the case of telluride ores. What the loss is in slag, when no element like tellurium, copper, zinc, etc., is present, may be seen by reference to Table XXIX, to those assays fused after acid treatment, and to Table XXX, showing crucible fusions on lead carbonate ore. The slag loss in gold and silver for these ores is very small. In cases where the impurity present and causing loss is nearly all eliminated in the fusion, *e.g.*, zinc, antimony, etc., the cupel absorption is practically that for pure silver and gold under the same circumstances. Where the impurity is tellurium, or selenium, or copper, the cupel absorption is decidedly increased. One fact is to be noted, the fact that the slag losses present no regularity, even for the same material. This is probably due partly to differences of slag composition among different experimenters, and partly to difference of temperature of fusion; and also to the method of refusion of slag.

The high loss in scorification slags shown in Table XXX for lead carbonate ores containing silver is due to the general unsuitability of the ore for scorification, although scorification slags show higher losses than crucible slags. That, in spite of this, scorification assays on silver-bearing material show equally good and better results in many cases than the crucible assay, is due to the fact that the silver beads retain small quantities of lead and copper (see further on), and to the fact that in the multiplication of the weight of the silver bead by 5 or 10, or whatever the assay-ton factor may be, this error is multiplied, giving an apparently better result.

The amount of slag has comparatively little influence on the amount of precious metals retained, provided the amount of collecting lead is ample. Buttons of less than 18 to 20 grams should not be made, and if the amount of slag is great or the quantity of silver and gold in the charge is more than 500 mgs., 25- and 30-gram buttons are essential. In the case of large buttons which contain no impurity, it is also best to cupel direct, if possible, rather than rescorify to smaller size, as the rescorification causes greater loss than the direct cupellations.

During scorification there is also an appreciable loss of the precious metals by volatilization, which is absent in the crucible assay. This, in the case of telluride or zinciferous ores, may become so great as to put scorification out of the question.

Other Errors: Retention of Lead in Cupeled Beads. — Small quantities of lead are almost invariably retained in the gold and silver beads with ordinary temperatures of cupellation. Hillebrand and Allen,[1] in two careful experiments on sets of three beads, approximately together 90 mgs. gold, found that 0.30 per cent. and 0.37 per cent., respectively, of lead were retained. This retention of lead cannot be corrected by leaving the bead in the muffle for some length of time after the blick, as this is, of course, prohibitive in the case of silver, and in the case of gold seems to actually cause an increase of weight. It has already been stated that copper and tellurium are very apt to be present in the final bead, when in the ore in any appreciable quantity. The retention of base metal by the bead causes a plus error in silver, but will not effect the result on gold unless the parting is by H_2SO_4; and where the weight of the bead is multiplied by a factor to get results per ton, the final error in silver may be very appreciable. The presence of copper in the final bead practically insures the complete removal of the lead.

Retention of Silver by the Parted Gold. — Ordinary parted gold, after the proper treatment with weak and strong acid, retains from 0.05 to 0.10 per cent. of silver. In the assay of gold bullion, after the first acid treatment of the quartation alloy, the gold on the average retains 0.25 per cent. silver. After the second acid treatment, the final silver retention is from 0.06 to 0.09 per cent., depending on the time of boiling. If the amount of silver to gold in the quartation alloy is less than 2.5 to 1, somewhat more than the above amount of silver will be retained.[2]

Silver can, practically, be completely extracted by more than two treatments with acids, according to Hillebrand and Allen.[3]

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[1] Bull. No. 253, U. S. G. Survey.

[2] Rose, "Metallurgy of Gold," p. 453.

[3] Bull. 253, U. S. G. Survey.

In the ordinary assay for ores as usually carried out, it is safe to assume that some silver is invariably retained by the gold, and frequently much more than is supposed; however, with low-grade ores, this retention is negligible.

Solution of Gold by Acid. — It is essential that the nitric acid used for parting be free from impurities, especially from hydrochloric acid and chlorine; otherwise solution of gold is sure to follow. Gold is quite soluble in mixtures of hot sulphuric and nitric acid,[1] and is again precipitated by dilution.

According to Hillebrand and Allen,[2] nitrous acid (HNO_2) and mixtures of HNO_3 and HNO_2 do not dissolve gold, though there is much earlier literature to the contrary. Nitrous acid has frequently been considered in this connection, as it is formed to some extent by the action of HNO_3 on silver.

According to Rose,[3] some gold is dissolved by nitric acid on continued boiling to constant gravity of acid. This solution is placed in the bullion assay at 0.05 per cent. or 0.5 parts per 1000. Hillebrand and Allen state that the loss of gold by solution is very small and irregular. It may be disregarded in the ore assay.

Occluded Gases. — Parted gold beads and "cornets" retain about twice their volume in occluded gases after annealing. The principal gas is stated to be carbon monoxide. Two volumes amount to 0.02 per cent. by weight, which is already allowed for in the silver retention.

Errors in Weighing. — The best scales are accurate to 0.01 mg., and scales can be obtained weighing to 0.005 mg. This last is used in assay offices, where very great accuracy is required, on such material as bullions, rich mattes, etc. It is usually an unnecessary refinement in the ordinary ore assay, for the reason that the probable error in the assay is greater than this.

The errors in the assay for gold and silver may be summarized as follows:

1. Losses by absorption in the slag of the fusion.
2. Losses by volatilization during fusion.
3. Losses by absorption during cupellation.
4. Losses by volatilization during cupellation.

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[1] Lenher, in "Journ. Am. Chem. Soc.," XXVI, p. 552.

[2] *Ibid.*

[3] *Ibid.*, p. 507.

5. Errors by gain in weight of bead, due to retention of foreign elements. This affects results on silver chiefly.

6. Errors in weight of gold after parting by the retention of silver and occluded gases.

7. Losses of gold by solution in nitric acid.

8. Errors in weighing.

The chief losses are Nos. 1 and 3, which can be recovered by "corrected assay," *i.e.*, by re-assay of slag and cupel, to the extent of about 80 to 85 per cent. Wherever considerable accuracy is required, corrected assays should always be made. The losses by volatilization are usually slight, although from the foregoing data these are sometimes seen to be considerable. The retention of foreign metals by the bead is a plus error in favor of silver, and the retention of silver in the parted gold is a plus error in favor of gold. Silver losses are considerably greater in magnitude than gold losses. The total amount of precious metal recovered by the assay varies with the nature of the material. Designating the total amount of gold and silver in an ore or product as 100, the corrected assay will show from 99 to 99.8 per cent. of the gold, and from 98 to 100 + per cent. of the silver, the high silver result in some cases being due to retention of foreign metal.

In the bullion assay for gold, the algebraic sum of the errors outlined, the losses being designated minus and the gains plus, is called the "surcharge." In the gold bullion assay this will vary from +0.025 per cent. in very pure gold bullion, to 0.25 per cent. in base bullion, passing to zero for a bullion about 800 fine.

XII

THE ASSAY OF BULLION

General. — Bullion is classified as follows:

1. Lead bullion, usually the product of the lead blast-furnace; 95 per cent. and more lead, containing some copper, antimony, etc., silver and gold.
2. Base bullion, containing from 100 to 925 parts of silver per 1000, gold in varying amounts, and a large percentage of base metals, chiefly copper, zinc, lead, etc. Produced most frequently by cyanide mills.
3. Doré bullion, containing 925 to 990 parts of silver per 1000, some gold, and base metals, mostly copper, but also lead, antimony, zinc, etc.
4. Fine silver bullion, free from gold, containing 990 to 1000 parts silver per 1000, but some base metals, usually copper.
5. Silver bullion, containing little base metal and less than half its weight in gold.
6. Gold bullion, containing little base metal and more than half its weight in gold.
7. Fine gold bullion, free from silver, containing from 990 to 1000 parts gold per 1000.

Silver and gold in all bullions but lead bullion are estimated in parts per thousand, and bullion is said to be so many parts fine. Thus, if 1 gram (1000 mgs.) of bullion is taken for assay and it contains 925 mgs. gold, it is said to be 925 fine.

In the assay of gold bullion the "millieme" system of assay weights is used, a millieme being 0.5 mg., and the assay is reported in parts of 10,000, or the fineness with one decimal added. Thus the above bullion would be reported as 925.0 fine. In this system the 500-mg. weight is stamped 1000, the 250-mg. weight 500, etc. The scales used must therefore be sensitive to 0.05 mg., or 0.1 millieme. This presents no difficulty, as ordinary assay balances are sensitive to 0.01 mg. with a load of 0.5 gram.

Lead bullion is recorded in oz. per ton, in the same way as for ores.

The Assay of Lead Bullion.—The sample of bullion may be melted under charcoal and granulated in cold water, or it may be rolled out into a strip in the rolls, and the pieces cut at intervals from this for the sample. If lead bullion is free from copper, antimony, zinc, sulphur and arsenic, etc., it may be cupeled directly for gold and silver. In this case, 4 portions of 0.5 assay ton each are wrapped in about 7 grams of sheet lead, placed in the hot cupels, and cupeled with feathers. The cupels are fused with the following charge:

Stained part of cupel	45 grams borax glass
80 grams PbO	2 grams argol
15 grams Na_2CO_3	Thin litharge cover

The buttons from this fusion are cupeled and the weight of the gold and silver added to that obtained from the first cupellation.

If the bullion contains base metals which will influence the results of the cupellation, 4 portions of either 0.5 or 1.0 assay ton are weighed out and mixed with 30 to 50 grams of test lead; 1.5 grams of borax glass and 0.5 gram of silica are put on top of the lead and the charge scorified. The resultant buttons, which should weigh about 15 grams, are then cupeled. The scorifier slag and cupel are re-assayed by the above charge and the correction added.

The Assay of Silver Bullion[1] *(also applicable to Base Bullion, Doré Bullion, etc.). Cupellation Method.* — This method is used as an approximation for bullions in which silver is to be determined accurately, serving as a preliminary assay for the salt titration, mint, or Gay Lussac method.

(*a*) Preliminary Assay. — Exactly 500 mgs. of bullion are weighed out on an assay balance in order to save calculation, wrapped in 10 grams of sheet lead, and cupeled at 700° C., or with ample feathers of litharge. The silver bead is cleaned, weighed and parted in 1 to 9 HNO_3 for at least 20 minutes; then, if any gold shows, heated for 5 minutes more in concentrated acid, washed, and the gold dried, annealed and weighed. The

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[1] For sampling of silver bullion, see "The Assay of Gold Bullion," later in this chapter.

amount of gold found, subtracted from the weight of the bead, gives the approximate silver, and the weight of the bead, subtracted from the amount of bullion taken (500 mgs.), gives the base metal. This base metal is usually copper, and its presence may be detected by the coloring of the cupel.

(*b*) Making the Check Assay. — As the loss of silver and gold is a question of temperature, amount of precious metal present, amount of lead of cupellation, and amount and kind of base metal present, it is desirable to have the regular cupellation, accompanied by a check assay, made up as nearly as possible to the composition of the bullion to be assayed, and cupeled under the same conditions. The check assay is therefore made up from data obtained in the preliminary assay. As the silver determined in this preliminary assay is low, due to absorption and volatilization, a correction of 1.2 per cent. is added as an approximation or, rather, the amount of Ag found is considered as 98.8 per cent. of that present), and this amount of proof silver weighed out. To this is added, in proof gold, the amount of gold found in the preliminary assay. The difference between the sum of the corrected silver and the gold, and 500, is the amount of base metal to be weighed out for the check. As already stated, the base metal is usually copper, and in making up the check c.p. sheet copper is used. The check thus weighs 500 mgs. and approximates very closely the composition of the bullion. Duplicates of 500 mgs. of bullion are now weighed out, and these and the check each wrapped in the proper amount of sheet lead, as determined from the table below:

TABLE XXXII. — LEAD RATIO IN CUPELLATION

Fineness in Silver	Amount of Copper present	Amount of Lead for Cupellation	Ratio of Lead to Base Metal
Milliemes	Milliemes	Grams	
1000	0	3	——
900	100	7	70 to 1
800	200	12	60 to 1
500	500	18	36 to 1
300	700	21	30 to 1

(*c*) The Assay. — Three cupels are placed in a row across the muffle, so as to be exposed as nearly as possible to the same temperature, and three more cupels are placed near them to act as covers for the cupellation when finished, in order to prevent sprouting. When the cupels have had all volatile matter expelled, the assays are dropped into them, the check in the center one, and the cupellations carried on in the usual way, with feathers. After the blick, the cupels are drawn to the front of the muffle and covered with extra cupels. Sprouted buttons must be rejected. The beads are now cleaned, weighed, and rolled out, parted in flasks, with the acids as described for the preliminary assay, and the gold weighed.

The difference between the silver actually used in the check and that found by assay is the correction to be added to the mean silver result of the two bullion assays made, which should not differ by more than a millieme (0.5 point fineness). This correction may be plus or minus, according to the amount of copper in the bullion; for with much copper, some of this may be retained by the silver and give rise to a minus correction. The gold is corrected in the same way as the silver. The subtraction from 500 of the sum of the corrected silver and gold gives the amount of base metal. The individual results obtained, multiplied by two, express the assay results in fineness.

When metals of the platinum group are present, the method must be modified as outlined, in Chapter XIII, for the assay of platinum, etc.

Wet Methods: Gay-Lussac or Mint Method. — This method is a most accurate one and is based on the complete precipitation of Ag as AgCl in a nitric acid solution by means of sodium chloride. The reaction is as follows:

$$\begin{aligned} \mathrm{AgNO_3 + NaCl} &= \mathrm{AgCl + NaNO_3} \\ \text{1 part Ag} &= 0.54207\ \mathrm{NaCl} \end{aligned}$$

The standard solution of NaCl usually employed is of such strength that 100 c.c. precipitates 1 gram of Ag, so that 5.4207 grams of c.p. NaCl are dissolved per liter of distilled water to give the standard solution. This solution can also be made up by using a saturated salt solution at 60° F., and then adding 2.07 parts of this to 97.93 parts of distilled water. The last method of obtaining the solution is not as good as the first, owing to the difficulty of obtaining the precise temperature of 60° F. and keeping it there. Aside from the standard solution mentioned, there is required another of one-tenth its strength (obtained by taking 1 part of the standard NaCl solution and adding to it 9 parts of distilled water), and an acidulated solution of $AgNO_3$, obtained by dissolving 1 gram of proof silver in 15 c.c. of HNO_3, 1.26 sp. gr., and diluting with distilled water to 1000 c.c. It follows from the above that 1 c.c. of the one-tenth solution will just precipitate the Ag in 1 c.c. of the acidulated silver nitrate solution.

The standard NaCl solution is termed the "normal salt" solution in the assay, although not properly so; the weak solution is termed the "decimal salt solution," and the silver nitrate solution the "decimal silver" solution.

Standardizing Solutions. — The apparatus required is:

1. A large bottle or carboy, containing the normal salt solution, placed on an elevated shelf so that the solution may be siphoned by means of glass tubing and rubber hose to the main 100-c.c. pipette.
2. Liter bottles containing respectively the decimal salt and the decimal silver solutions.
3. An accurate 100-c.c. pipette, clamped to a suitable stand, and provided at the top with a glass overflow-cup containing a moistened sponge to catch the overflow of the normal salt solution.
4. Two small graduated 10-c.c. pipettes, one for the decimal salt and one for the decimal silver solution. Burettes may be used in place of these.
5. A number of strong 8- to 12-oz. bottles, similar to reagent bottles, provided with rubber corks.

The standardizing of solutions is carried out as follows: Two portions of exactly 1002 mgs. proof silver are dissolved in 15 c.c. of 1.26 sp. gr. HNO_3, the nitrous fumes are removed by boiling, the solution is transferred to the titration bottles and water added to bring up the amount of solution to 125 c.c. The 100-c.c. pipette is then filled with normal salt solution to the mark, after washing out with salt solution to prevent dilution. The filling is done by fastening the siphon hose to the bottom of the pipette, opening the clamp on the hose, and letting the pipette fill with a little overflow. The solution is then shut off by clamping the hose, a finger placed on the top opening of the pipette to prevent the solution running out, and the hose removed. The pipette is then permitted to drain to the 100-c.c. mark, and the solution held there by closing the top of the pipette with the finger. The bottle containing the dissolved proof silver is then placed under the pipette and the normal salt solution permitted to completely drain into it. The bottle is then violently shaken for three or four minutes, either by hand or a mechanical agitator, and the AgCl allowed to settle, leaving the supernatant liquid clear. If the normal solution is made up correctly, it will have precipitated just 1000 mgs. of silver, leaving 2 mgs. unprecipitated. One c.c. of decimal salt solution is now added to the bottle by means of one of the 10-c.c. pipettes or a burette, which, if the solution still contains Ag unprecipitated, gives rise to a white cloud of AgCl. The bottle is again shaken, the precipitate allowed to settle, and another c.c. of decimal salt solution added. If this fails to give a precipitate, then 100.1. c.c. of normal salt solution are equivalent to 1002 mgs. of silver (1 c.c. of decimal salt solution = 0.1 c.c. normal salt solution). If the second addition of decimal salt solution gives a precipitate, the shaking and settling are repeated, and a third and fourth, etc., addition made, until no further cloud appears. The assayer soon learns to judge by the density of the cloud whether only part of the c.c. has been used up. In this way he should be able to judge to the fourth of a c.c. or the half of a millieme. If the first addition of decimal salt solution fails to give a precipitate, the normal solution contains an excess of salt, and 2 c.c. of decimal silver solution are now added, one of which neutralizes or precipitates the 1 c.c. of decimal salt solution added, the other acting on the excess of salt in the solution. The decimal silver solution is added until no further cloud appears, in the same way as described for the decimal salt solution. In this way the exact strength of the normal salt solution is determined in duplicate. If it is incorrect to the extent of more than 2 points fineness either way (*i.e.*, either strong or weak), it is corrected by the addition of either water or salt, and restandardized, and, when correct, a new decimal salt solution made up from it. Its strength is finally recorded on the bottle as follows: 100 c.c. = 1000 mgs. Ag, or whatever it may actually be.

The Assay. — It is evident from the preceding that the amount of bullion to be taken for assay must contain as nearly as possible 1000 mgs. Ag in order to make the titration with solution as short as possible, and avoid undue additions of the decimal solutions. For this reason the bullion on which the silver determination is to be made is first assayed by the cupellation method, or at least a preliminary assay, described under this method, is made, and from these data the amount of bullion containing 1000 mgs. of silver calculated. For instance, suppose the cupellation method shows the bullion to be 900 fine in silver, then

$$\begin{array}{ccccccc} 900 & : & 1000 & :: & 1000 & : & x. \\ \text{fineness} & : & \text{amt. of bullion} & :: & \text{silver} & : & \text{amt. of bullion.} \end{array}$$

or 1111.11 mgs. bullion contains 1000 mgs. Ag. This amount of bullion is then weighed out in duplicate and dissolved in acid, placed in titration bottles, as described above, under "Standardization of Solutions," and titrated.

The calculation for fineness is as follows: Suppose the strength of the normal solution is 100 c.c. = 1001 mgs. Ag, and that 99.8 c.c. of normal solution were used in the titration (100 c.c. normal salt, and 2 c.c. decimal silver); then

$$100 : 1001 :: 99.8 : x$$

the x, or amount of silver in bullion, equaling 998.99 mgs.; and the fineness is

$$1111.11 : 998.99 :: 1000 : y$$

the y, or fineness, equaling 899.1.

The only metal interfering with the salt titration is mercury, which will be precipitated by the NaCl as Hg_2Cl_2; the addition of 20 c.c. sodium acetate and a little free acetic acid to the assay will prevent the precipitation of the mercury. Mercury can be detected in the titration if the AgCl has not turned dark as the result of exposure to sunlight. Mercury will be found sometimes in mill bullions which have been retorted at too low a temperature. The assay and standardization of the solution should be carried out where there is no sun, and where light is not too strong.

The Assay of Gold Bullion.—1 Sampling.—Bullion bars and retort sponge, as shipped to the United States assay offices and mints, is remelted into bars to make the deposit uniform. These are sampled by taking chips from diagonally opposite corners, each of which is rolled into a fillet and assayed by different assayers, who are required to check with each other within narrow limits; if they do not, the bar is remelted, stirred thoroughly, and recast; then sampled again and assayed. If base bullion, or one which liquates seriously on cooling, is to be assayed, dip-samples are taken from the molten bullion by means of a small graphite ladle, and the sample granulated in warm water. Silver bullion is sampled in the same manner.

2. Preliminary Assay.—This is made in the way described for silver bullion, except that in the assay of gold bullion no determination of silver is made by cupellation; but if this is to be determined, the mint wet method is used. Experienced assayers can judge the approximate fineness of gold bullion by the color, and add the proper amount of silver necessary to insure parting. In the San Francisco mint, 2 parts of Ag to 1 of Au are used.[1] The British royal mint formerly used 2.75 parts of Ag. to 1 of Au,[2] but now uses 2 to 1. More than 3 parts Ag to 1 of Au should not be used, otherwise the "cornet" of gold is apt to break up. With less than 2 parts of Ag, too much Ag is retained, although with continued boiling 1.75 parts Ag will part Au from Ag.[3] For the preliminary assay, 500 mgs. (1000 milliemes) are weighed out, silver added according to judgment to bring the ratio of silver to gold to 2 or 2.5 (allowing for silver in the alloy), and the bullion and silver wrapped in 10 grams sheet lead and cupeled at 775° C.

The resultant bead is cleaned, weighed, flattened and rolled out in jeweler's rolls to a fillet of the approximate thickness of a visiting card. If some copper is present in the bullion, enough is retained by the gold bead to toughen it, and it can be easily rolled without cracking, if, between reductions by the rolls, the fillet is annealed at a dull-red heat. The presence of copper in

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[1] John W. Pack, "Assaying of Gold and Silver in U. S. Mint," in "Min. and Sci. Press," Nov. 14, 1903.

[2] Rose, in "Eng. & Min. Journ.," LXXX, p. 492.

[3] Rose, "Metallurgy of Gold," p. 493.

the button aids in the total removal of lead during the cupellation.[1]

The fillet is then again annealed and rolled into a spiral, called a "cornet," and parted in a parting flask. This is filled with 30 c.c. of HNO_3 sp. gr. 1.20, free from Cl, H_2SO_4, H_2SO_3, or any sulphide, and heated to boiling (or at least 90° C.) for 20 minutes. The acid is then decanted off, and the cornet washed carefully several times with hot distilled water by decantation. Then 30 c.c. of boiling nitric acid, sp. gr. 1.30, are added to the

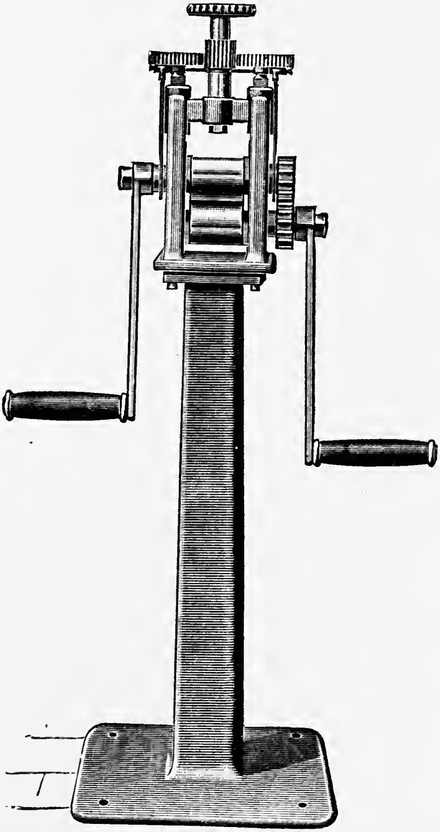

FIG. 43. — JEWELER'S ROLLS

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[1] Rose, "Refining Gold Bullion," in *Trans.* I. M. M., April 13, 1905.

flask, and the cornet boiled again for 20 minutes, after which the acid is decanted, and the washing with hot water repeated. During the boiling, a parched pea added to the flask prevents bumping. The flask is now filled to the very top with cold distilled water, a suitable sized porcelain parting-cup placed over the mouth, fitting reasonably tight, and the flask inverted. The cornet will settle into the parting-cup, and the flask is then gently tipped to permit the water to escape, the water is decanted from the parting-cup, and the cornet gently dried. When dry, the cornet is transferred to a clay annealing cup, the cover is put on, and the cup is placed in the muffle, and the cornet annealed at a full-red heat. It is then weighed. The weight of the gold plus that of the added silver, subtracted from the weight of the cupeled bead, gives the approximate amount of silver in the assay. This added to the weight of the gold and subtracted from 500 mgs. (the weight of bullion taken) gives the approximate amount of base metal. If the amount of silver added to part the gold has raised the ratio of Ag to Au over 3 to 1, the gold will probably have broken up, or at least parts will have broken from the edges of the cornet; care must, in this case, be taken to collect all of it in the washing. If the results show that the ratio of Ag to Au has been less than 2 to 1, the cornet must be recupeled with 2.5 parts Ag and parted as described.

The Assay. — The final assay is made up from data obtained in the preliminary assay. Duplicates on 1000 milliemes are run, with a check assay made up in composition as near to that of the bullion as possible, as described for the cupellation assay of silver. In making up the check, proof gold and proof silver are used, and c.p. copper foil. The United States mints use various proof alloys in the making up of check assays. For the assay of fine gold bars (990 fineness and above), a proof alloy of 1000 gold, 2000 silver, and 30 parts copper is used. For coin metal (900 parts fine), a proof alloy of gold 900 parts, silver 1800 parts, copper 100 parts is used. For the determination of base metal (the difference between the gold and silver, and the 500 mgs. taken for assay), a proof alloy of gold 900 parts, silver 90 parts, copper 10 parts is used.[1] In this last the gold need not be proof gold, but may be remelted cornets. It is to be noted

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[1] John Pack, *ibid.*

that these proof alloys are made up on the assumption that 2 parts of Ag to 1 of gold are used in parting. The British mint uses a proof alloy, or trial plate, 916.6 fine in gold.

For the assay of crude gold bullion, *i.e.*, mill bullion, the proof alloy for fine gold bars is generally used.

The amount of lead used in the cupellation is as follows [1]:

TABLE XXXIII. — LEAD RATIO IN CUPELLATION

Amount of Gold per 1000 Parts	Amount of Lead	Ratio of Lead to Copper (base metal present)
Milliemes	Grams	
916.6	8	96 to 1
366	9.15	64 to 1
770	14.75	64 to 1
666	16.00	48 to 1
546	17.50	38 to 1
333	18.0	27 to 1

To the duplicates of the 1000 milliemes of bullion, the proper amount of Ag is added, to bring the ratio of Ag to Au to 2 to 1, and then they are wrapped in the proper amount of c.p. sheet lead. The check is made up as indicated by the preliminary assay, and the three assays cupeled as described for the assay of silver bullion. The three beads are then treated and parted, as described for the preliminary assay. The two bullion assays should not differ by more than 0.25 part of a millieme. The correction as indicated by the check should then be applied, whether this be plus or minus. The difference between the fine gold in the check and that obtained by the assay of the check is the surcharge, which is more definitely defined in Chapter XI, on "Errors in the Assay for Gold and Silver." This surcharge will usually amount to about 0 for a bullion of about 700 to 800 fine; above that there will be a "plus surcharge," and below that a "minus surcharge." The plus surcharge will be added and the minus surcharge subtracted.

The Preparation of Proof Gold. — This is prepared by dissolving

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[1] Rose, "Metallurgy of Gold," 1902, p. 494.

practically pure gold (cornets) in nitro-hydrochloric acid, permitting the solution, after some dilution, to stand for four days to allow AgCl to settle out. It is then decanted very carefully by siphoning. The gold chloride solution is then evaporated almost to dryness, taken up with plenty of distilled water, a few c.c. of NaBr solution added, allowed to stand for some days, and again decanted by siphoning, after which operation it is slowly dropped from a burette into a beaker containing c.p. aluminum foil. When precipitation is complete, HCl is added to dissolve the excess of Al, and the residual gold is washed thoroughly with water by decantation, and then dried and melted into a bead in a fresh cupel (but not cupeled with Pb). The gold is then rolled into a thin strip for use.[1]

Proof silver is prepared by dissolving c.p. silver foil in HNO_3, and then precipitating with HCl after filtering. The AgCl is thoroughly washed with diluted HCl and converted into metallic silver by Al in the presence of HCl, all Al being dissolved out. The washed silver is then fused in a clean cupel, and rolled into strips.[2]

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[1] Consult also Rose, "Metallurgy of Gold," p. 12, and Pack, *ibid.*

[2] John Pack, *ibid.*

XIII

THE ASSAY OF ORES AND ALLOYS CONTAINING PLATINUM, IRIDIUM, GOLD, SILVER, ETC.

Materials containing some of the above elements are presented to the assayer for determination in the shape of sands containing chiefly platinum, alloys and jeweler's sweeps, and, more rarely, ores containing platinum in the form of the mineral sperrylite, etc.

The assay for platinum and associated metals is a difficult one, due to the fact that in the parting of the precious metal beads by acids, complex reactions take place, by which platinum, palladium, silver, etc., both go into solution and are retained in the residue, unless certain well established ratios of metals present are observed and the parting operation repeated several times. The alloys of platinum and silver have been most thoroughly investigated in this connection.[1] When the alloy is more complex, *i.e.*, contains also gold, palladium, iridium, rhodium, etc., the difficulties of the assay are increased; the data at present available are meager.

Platinum nuggets from the Urals contain:[2] Pt, 60 to 86.5 per cent.; Fe, up to 19.5 per cent.; Ir, up to 5 per cent.; Rh, up to 4 per cent.; Pd, up to 2 per cent.; also Os, Ru, Cu, Au, and iridosmium.

When material containing Au, Ag, Pt, Pd, Ir, Rh, Ru, Os, and IrOs is fused by the crucible assay or melted with lead, the Au, Ag, Pt, Pd, Ir, Rh, IrOs are collected by the lead and the Ru, and Os only partially so. If the resultant lead button is cupeled, the final bead will contain the Au, Ag,[3] Pt, Pd, Ir, Rh,

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[1] Thompson and Miller, in "Journ, Am. Chem. Soc.," XXVIII, p. 1115. See this paper for other references.

[2] Kemp, in "Eng. and Min. Journ.," LXXIII, p. 513 (Notes on Platinum and Associated Metals).

[3] Exclusive of losses by absorption and volatilization.

IrOs, and a comparatively small portion of the Os and Ru, the most of these two metals being lost by oxidation. The presence of any considerable amounts of Os and Ru in the lead button, owing to the fact that they will not alloy readily, causes them to appear as a black scum or as spots on the bead, near the end of the cupellation. The presence of the platinum group of metals, raising the melting-point of the gold-silver alloy, renders necessary a high temperature of cupellation in order to remove lead. Even then, when the ratio of Ag to Pt, etc., is less than 5 to 1, lead will be retained in varying proportions at the cupellation temperature of gold bullion. To get rid of the lead, the proportion should be 10 to 1.[1] The following points on the first cupellation of the lead buttons, resulting from the assay of material containing Pt, etc., will give the assayer an idea of what is present.

When Pt alone, or with very little silver, is present, the bead from the cupellation (at a comparatively high temperature) is rough, dull gray, flat, and contains lead.

If more silver is present, but less than 2 parts of Ag to 1 of Pt, the beads are rough, flat, and have a crystalline surface.

If more than 2 parts of Ag are present and not more than 15, the bead approaches more nearly the appearance of a normal silver bead, but has a more steely appearance and is flatter in proportion to the Pt, etc., contained.

Beads containing more platinum than 1 in 16 will not blick or flash.[2]

The effect on the appearance of the bead of Pd, Rh, Ir is similar to that of Pt, but not identical.

Owing to the difficulty in alloying iridium, this, when present, is apt to be found at the bottom of the bead, in the shape of fine black crystalline particles.[3]

The Action of Acid on the Alloy Beads. — A great deal of literature exists on this point; but most of it is very conflicting; some facts, however, have been definitely established.

Nitric Acid. — In an alloy of Pt and Ag treated by HNO_3, platinum goes into solution in various proportions, depending

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[1] Sharwood, "Cupellation on Platinum Alloys, containing Ag and Au," in "Chem. Ind.," Vol. XXIII, No. 8.

[2] Schiffner, in "Min. Ind.," VIII, p. 397.

[3] Rose, "Metallurgy of Gold," p. ~~514~~. 451

on the ratio of Ag to Pt, and probably to some extent on the strength of acid. It has been stated that when the ratio of Ag to Pt is 12 or 15 to 1, this solution of Pt is complete in one treatment, but this has been disproved by later investigation.[1] In order to accomplish the solution of Pt, the acid treatment must be repeated at least once or twice, with a possible recupellation of the residue with silver before the second treatment. It is even then doubtful if all of the Pt can be dissolved. The Pt goes into solution in the nitric acid in colloidal form, giving a brown to blackish color to the solution. The reason for this seems to be the presence of platinum-silver compounds in the alloy, some of which are insoluble, or only partially soluble, in HNO_3. When gold is present in the silver-platinum alloy, the solubility of the Pt seems to be decreased,[2] unless the ratio of Pt to Au to Ag is 1:2:15,[3] when most, but not all, of the Pt and all the Ag go into solution. Palladium goes into solution with nitric acid when at least 3 parts of Ag to 1 of Pd are present,[4] yielding an orange-colored solution; but double parting is necessary to insure complete solution. (This point is not sufficiently established.[5]) The orange-colored solution indicates colloidal palladium.

Iridium and Rhodium. — Iridium present in the beads is unacted upon by HNO_3 and remains with the gold.[6] Rhodium is slightly dissolved, but most of it remains with the gold. Iridosmium is not dissolved. Osmium is dissolved. Ruthenium is not dissolved.

Sulphuric Acid. — Platinum, alloyed with silver and gold, can be separated from the silver and remains with the gold, if concentrated sulphuric acid is used in parting. In order to insure thorough parting, at least 10 parts of silver to 1 part Pt and gold should be present, and double parting resorted to, otherwise silver will remain with the residue.[7] The parting in H_2SO_4 leaves the Pt and gold in a very fine state of division (but not as a colloid), some of which is very apt to be lost in decanting,

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[1] Thompson and Miller, in "Journ. Am. Chem. Soc.," XXVIII, p. 115.

[2] Sharwood, *ibid.*

[3] Lodge, "Notes on Assaying," p. 215.

[4] Rose, "Metallurgy of Gold," p. ~~514~~. 451

[5] Lodge, "Notes on Assaying," pp. 218, 219.

[6] Rose, *ibid.*

[7] Thompson and Miller, *ibid.*

so that it is best to separate by filtering through an ashless filter. It is also to be noted that lead may be present in consequence of too low a cupellation temperature, in which case residue should be treated with ammonium acetate, to remove lead sulphate.

Palladium. — In parting with H_2SO_4 this goes into solution with the silver, giving an orange-colored solution. Whether this solution is complete, has not as yet been demonstrated.[1]

Ir, IrOs, Rh, and Os and Ru in the bead are not dissolved.

Nitro-Hydrochloric Acid. — From the residue of the sulphuric acid parting, the Pt, Au, and any Pd left is dissolved by dilute aqua regia, 1 to 5, leaving Ir, IrOs, and Rh, and some Ru and Os, if present. This last residue, treated with strong aqua regia, removes Ir, leaving iridosmium and rhodium as a final residue.

Methods of Assay. — 1. Ores. — Rich ores, carrying Pt, etc., in grains, present difficulty in sampling, inherent to any ore containing "metallics." It is best to take from 30 to 50 grams of the sample and fuse it with 6 times its weight of lead in a crucible, fluxing the gangue. The lead is poured, and after cooling the slag is detached carefully, the lead platinum alloy being brittle, weighed and remelted under charcoal in order to insure a uniform alloy, and then granulated as fine as possible by pouring into a large volume of cold water from a considerable hight. The resultant sample is then dried and is ready for assay. An amount containing approximately 200 mgs. Pt. is weighed out and scorified with 50 grams Pb into a 20-gram button.

If, in the low-grade ores, the Pt, etc., is present as grains, a weighed quantity is concentrated by panning and the concentrates scorified with 20 to 25 times their weight of test lead, and the button treated according to method No. 1 or 2, as below. If the ore contains the rare metal in other form, crucible fusions are made on 1 assay ton, as with gold and silver ores, and if very low grade, the buttons from 4 to 5 fusions are scorified into one button, final duplicates being made as usual. The lead buttons are treated as below.

2. Alloys. — An amount of drillings or filings (representing a true sample of the alloy), containing, if possible, not to exceed 200 mgs. of Pt. etc., is weighed out and scorified, with 80 grams

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[1] Lodge holds the contrary, p. 219.

of test lead, to a button of about 18 to 20 grams. The lead buttons are treated as outlined below.

First Method. — The lead button obtained by any of the foregoing methods is cupeled at a temperature of at least 800° C., or, better, 850° C., and the resultant bead examined. If, from the foregoing description of the appearances of a bead, it is thought that the ratio Ag to Pt, Au, etc., is less than 10 to 1, the button is removed, the necessary silver added to bring it up to the above ratio, recupeled with 5 to 8 grams of lead at a temperature of 800° C., and weighed. The bead is then flattened and rolled out into a cornet, if large and not too brittle, and parted with 15 c.c. H_2SO_4 concentrated, boiling for 15 to 20 minutes. The acid is then decanted into a beaker and saved, the residue re-treated with 5 c.c. more of acid for 10 minutes, and the residue and acid washed into the beaker containing the previous acid. The acid is then diluted and the residue separated by filtration through a small ashless filter, and thoroughly washed with hot water to insure removal of Ag_2SO_4. The filter-paper is dried and carefully transferred to a porcelain parting-cup or an annealing cup, and the carbon burnt off in the muffle. The annealed residue is brushed out on the scale pan of the bead balance and weighed. It consists of gold, platinum, iridium, iridosmium, rhodium, and possibly osmium and Ru (if any escaped oxidation during the cupellation), and perhaps some palladium. Its color will be gray or black, if the rare metals are present to any extent. If not, the characteristic gold color will show. The palladium is largely in the filtrate. (It is questionable how complete this solution is.[1]) If it has been unnecessary to add Ag to the cupellation to get the 10 to 1 ratio, the difference in weight between the original bead and the weight of the residue represents the Ag. If silver had to be added and the bead recupeled, the weight of the added silver plus that of the residue, subtracted from the weight of the recupeled bead, gives the silver. Allowance must, however, be made for considerable loss of silver as a result of high cupellation temperature. If accurate silver results are required, a duplicate assay on the material must be run, and the silver requisite to bring the ratio

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[1] Ricketts and Miller, in "Notes on Assaying," state that the Pd dissolves with the Ag.

up to 10 to 1 is added at once to the lead button, one cupellation only being made. At the same time this is run, a check assay is run beside it, made up of the same weight of lead, and the proper weight of silver, *i.e.*, the amount added to the first cupellation plus the amount approximately known to be in the assay. The loss in this will give the correction to be added to the assay for Ag. It may be desirable to determine Ag in the wet way. (See "The Assay of Silver Bullion.")

The residue is now wrapped in 8 to 10 grams of lead foil with at least 20 times its weight in silver and cupeled again at a high temperature. The bead, if large, is rolled out and heated to boiling in a mattrass or flask for 20 minutes with HNO_3, sp. gr. 1.20, after which the acid is decanted into a beaker, and the treatment repeated with HNO_3 of 1.26 sp. gr. The residue, if finely divided, should now be filtered through an ashless filter and washed as already described. If not, the filtrate can be decanted and the residue washed. The residue consists of Au, Ir and iridosmium, and some Rh and Ru. If there is any suspicion that any platinum, etc., remains, the residue must be re-treated with acid until of constant weight. The platinum is in the filtrate, which will be colored brown or black.

The difference between the weights of the first and second residues is platinum, the result possibly being somewhat high if palladium is present in the material assayed. The second residue is now warmed in a mattrass with dilute aqua regia[1] (1 to 5) for 15 minutes. This dissolves the gold, some of the Ru and very little Rh, leaving the Ir, iridosmium and Rh, with some Ru. The residue is either filtered or decanted, as necessary, dried, annealed, and weighed. The difference in weight between the second and third residues represents gold, somewhat high, if the Ru has partly escaped oxidation and volatilization during cupellation. The gold can be recovered by precipitation with oxalic acid, as described in the second method.

If the third residue is treated with strong aqua regia, and boiled, it dissolves out the iridium, leaving as a residue the iridosmium and most of the Rh. This is dried, annealed, and weighed, the difference in weight between the third and fourth

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[1] Concentrated aqua regia is 1 part HNO_3, sp. gr. 1.42, and 3 parts HCl, sp. gr 1.20.

residues representing iridium, and the weight of the fourth residue representing iridosmium and Rh. The method determines Ag, Pt, Au, Ir, and iridosmium plus Rh. The probable errors in the determination have been pointed out. Palladium can be satisfactorily determined only by wet analysis.

Second Method.[1] — Take the lead button from the ore or alloy assay, and scorify at a high heat, with additional test lead, if necessary, to a weight of 8 to 10 grams. It should contain less than 5 per cent. Pt, etc., in order to be malleable. Roll out the button into a long thin fillet and place in a large beaker with 200 c.c. of HNO_3, sp. gr. 1.08,[2] and heat until all action ceases. Filter through a small ashless filter and wash the residue with hot water. Dry the residue and paper, transfer to a large-size parting-cup and ignite in the muffle, to burn off the carbon, and oxidize any Pb not dissolved. Then heat to boiling in the cup with HNO_3, 1.08 sp. gr., decant, wash thoroughly with hot water, dry, anneal, and weigh the residue. This consists of Au, Pt, Ir, iridosmium, and most of the Rh, as well as the Ru and Os which escaped oxidation and volatilization during the scorification. The filtrate contains the Ag and Pd and a little of the Rh.

Replace the residue in the capsule and warm (not boil) with dilute aqua regia (1 to 5) for 10 minutes. This dissolves the Au and Pt. Decant the solution into a small beaker, wash the residue, dry, anneal, and weigh. The second residue consists of Ir, IrOs, Rh, and a little Os and Ru. This residue is boiled with strong aqua regia, which dissolves the Ir and some Os and Ru, and leaves in the third residue the IrOs and Rh, with a little Os and Ru. This is washed, decanted, and weighed as before. The filtrate from the treatment of the first residue, which contains the gold, is evaporated just to dryness, but not baked, so as to prevent reduction to gold chloride, taken up with distilled water and a drop of HCl, and the gold in it precipitated by warming with crystals of oxalic acid for a half hour, filtering, and drying the yellow coherent precipitate of gold. This is transferred, filter-paper and all, to a piece of sheet lead, silver added to the weight of 3 times the gold present, approximately, and cupeled, the bead being parted in HNO_3 as usual and the

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[1] E. H. Miller, in "Sch. Mines Quart.," XVII, p. 26.

[2] 81 parts distilled H_2O to 19 parts HNO_3 conc. (sp. gr. 1.42).

gold annealed and weighed. The weight of the gold, subtracted from the difference in weight between the first and second residues, is the platinum. This last may also be estimated by destroying the oxalic acid in filtrate from the separation of gold, and precipitating as $(NH_4)PtCl_6$.[1]

It is to be noted that, by the assay as outlined, neither osmium nor ruthenium can be determined, owing to their volatility during part of the operation; that palladium cannot be readily determined, owing to its varying solubility; and that when rhodium or the above metals are present in any appreciable quantity, some of the results obtained are liable to error. Rhodium, osmium, and ruthenium are among the rarer of the group, and are frequently absent. The methods outlined will serve to determine reasonably well platinum, gold, silver, iridium, and iridosmium plus rhodium. When the other elements of the group are present, wet methods, not within the scope of this book, must be resorted to.

In the ordinary assay, as carried out for gold and silver, platinum and palladium may escape the assayer if present in only small quantities, for obvious reasons. Parting in sulphuric acid is therefore necessary to determine whether they are present.[2]

[1] Crookes, "Select Methods."

[2] An orange-colored solution indicates palladium.

XIV

THE ASSAY OF TIN, MERCURY, LEAD, BISMUTH AND ANTIMONY

THE assay of ores for base metal by fusion is still carried out in practice, especially for lead and tin. The fire assay gives, not the correct metal content, but the yield obtainable in smelting, although in metallurgic operations the yield may be greater or less. The smelter, therefore, purchases lead, tin, and copper ores on the basis of the "dry" or fire assay. The fire assay of copper is practically no longer in use, except in part of the Lake Superior district, on metallic copper concentrates, and in purchasing copper ores the assay is made by the standard electrolytic method, or a volumetric method, and a percentage of from 1 to 1.5 deducted to indicate dry assay. The usual deduction is 1.3 per cent. Thus the dry assay of copper on an ore is equivalent to the percentage obtained by the electrolytic method less 1.3 per cent.

While wet methods, with a deduction, will in all probability be employed eventually for all lead ores, as it is now for impure lead ores, pure lead ores are still assayed by the fire method. Tin ores are almost invariably assayed by the fire method, as the wet analysis of tin is long and tedious.

THE ASSAY OF TIN ORES

The fire assay of tin ores is applicable only to those ores in which tin exists as cassiterite, the oxide (SnO_2). The chief reasons for inaccuracies in the fire assay of tin are:

1. Some of the tin, reduced in the assay from the oxide, is apt to be volatilized at the temperatures necessarily employed.

2. Metallic tin may be slagged by alkaline carbonates used in some of the methods of assay, forming stannates.

3. Foreign metals present in the ore are apt to be reduced and enter the button.

4. Sulphides present carry tin into the slag. If sulphates are present, they are reduced to sulphides.

5. Silica and silicates, always present in the ore, even after very careful concentration, carry tin into the slag, as silicate, while the SnO_2 passes through the lower stage of oxidation in being reduced to metallic tin.

6. The cassiterite, before reduction, is apt to combine with basic fluxes present in the assay, and be carried into the slag as stannates.

From this, therefore, it is evident that the fire assay for tin is only approximation, although in many cases a very close one. If the result on a tin ore by the fire method checks that of the standard wet method (the modified Rose method[1]), it is to be ascribed to a balancing of errors, due to the presence of other metals in the ore, which have been reduced into the tin button.

Preparation of the Ore for Assay. — It is essential to remove all the gangue of the ore and have for the assay nothing but the cassiterite, as far as this is possible. The ore is roughly crushed on a buck board and put through a 40-mesh screen, crushings and screenings succeeding each other at frequent intervals in order to avoid the "sliming" of the cassiterite. If the ore is low-grade, *i.e.*, below 2 per cent. Sn, 1000 grams of the crushed ore is weighed out and carefully panned in a gold pan, the first pannings being saved for repanning. The ore is concentrated just as much as possible without incurring loss of cassiterite. The concentrates from the repanning of the tailings of the first treatment are added to the main lot of concentrates. Some or all of these will, unless the ore is very pure, contain probably garnets, feldspar, tourmaline, magnetite, zircons, wolframite, columbite, sulphides, quartz, etc. The concentrates are carefully transferred to a porcelain dish, dried, and roasted at a bright-red heat in order to decompose sulphides and sulphates. While the concentrates are still red-hot, they are transferred into a beaker containing water in order to make garnet and other silicates soluble (all except uvarovite), and after decanting water, treated with nitro-hydrochloric acid to remove most of the

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[1] Hofman, "The Dry Assay of Tin Ores," in *Trans.* A. I. M. E., XVIII, p. 1.

contaminating minerals, except quartz, wolframite, and some garnet. The concentrates are then filtered off and dried. If quartz is present, this can be removed by transferring the filtered concentrates to a platinum dish and treating with HF. This, however, will rarely be necessary. The concentrates are then crushed in an agate mortar to pass a 100-mesh screen and treated as described below.

The Assay. — The two best methods for assay are the cyanide fusion and the German method, with black flux substitute. Of these two, the cyanide fusion is generally to be preferred, as any minerals still left in the cassiterite have less influence on the assay, and the loss of tin by volatilization is reduced to a minimum, on account of the low temperature employed.

The Cyanide Fusion.[1] — It is essential to use only the purest cyanide obtainable — the best sodium or potassium cyanide on the market for use in the cyanide process. Such impurities as K_2CO_3 sulphates and sulphides in cyanide cause serious losses in the assay. In order that the fusion may be successful, it is essential to follow directions closely. It is best to use 10 grams of concentrates, or an amount near that; usually the amount of concentrates obtained from the concentration of the ore approximates this if the proper amount of ore is chosen for concentration. Two grams of powdered cyanide are firmly tamped into a 20-gram crucible, the concentrates are mixed with 30 grams more of cyanide, placed in the crucible, and covered with 5 grams more. The crucibles are placed in the muffle at a full-red heat (750° C.), and are kept at this temperature for about 15 to 20 minutes. The charge will become very liquid, and will be a brown-red. The temperature should not be so high as to cause the cyanide to boil and evolve heavy fumes. It may, however, be kept too low, in which case the chemical reactions will not complete themselves and the tin will fail to collect into a button. If the concentrates still contain some foreign minerals, the fusion takes longer than 20 minutes. The crucibles are then withdrawn, cooled, and the button recovered by breaking the crucible. There will be two distinct slags, the lower one, surrounding the button, usually light green, amorphous and subtranslucent, and the upper one, or fused cyanide, opaque, milk-white and coarsely

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[1] Hofman, *ibid.*

granular, soluble in water. The tin button should be white and soft; if not, it contains reduced impurities.

The German Method. — The German method is based on the fusion of the cassiterite concentrates with charcoal and black flux substitute, which has the composition, 2 parts K_2CO_3, 1 part flour. Five grams of the concentrates are intimately mixed with 1 gram of pure wood charcoal and put into a No. D lead crucible or an ordinary 20-gram crucible. On top of this are placed 15 grams of black flux substitute, with which 1.25 grams borax glass have been mixed. Finally a pure salt cover is added, and a piece of charcoal, the crucible covered with a clay cover, placed in the muffle, and heated at a moderate heat until boiling of the charge has ceased, and then for one-half to three-quarters of an hour more at a white heat. The crucible is then removed from the muffle, allowed to cool, and broken for the tin button. This should be white and soft, as in the cyanide fusion.

During the fusion, as the temperature rises, the charcoal reduces the stannic oxide to metallic tin, while any ferric oxide is reduced to ferrous oxide, if the heating is gradual, and is taken up by the slag. As the temperature rises, the flour in the black flux substitute partially decomposes, liberating carbon throughout the charge, which, as fusion takes place, prevents any stannic oxide not as yet reduced from uniting with the alkali of the flux. The slag, after cooling, should be crushed and panned for any prills of tin which have not entered the button. These are weighed and added to the weight of the button.

Results Obtainable. — Black Hills cassiterite concentrates, roasted, quenched, and treated with nitro-hydrochloric acid[1]

Wet method of Rose-Chauvenet
with K_2CO_3 .... = 67.84 per cent. Sn
German method .... = 67.58 per cent. Sn
Cyanide method .... = 67.49 per cent. Sn

Stream tin from Durango, Mexico,[2]

Wet method (Rose) .... = 65.62 per cent. Sn
German method .... = 63.92 per cent. Sn
Cyanide method .... = 65.19 per cent. Sn

It is to be noted that while the dry methods approach very

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[1] Hofman, *ibid.*

[2] E. H. Miller, "The Assay of Tin Ores," in "Sch. Mines Quart.," XIII, No. 4.

closely to the wet analysis, which gives the actual tin in the ore, the dry assay results are due more or less to a balancing of errors. Frequently dry assays will give higher results than the analysis; this is due usually to reduced iron.

Of the influence of foreign minerals left in the cassiterite concentrates, quartz has the worst, causing heavy losses. Feldspar and tourmaline have similar effect, but not to so marked a degree. Mica and garnet give high results, due to the reduction of iron, although tin is lost in the slag. Columbite acts in a similar manner. With the German method the result is much more seriously affected by these impurities than with the cyanide fusion.[1]

THE ASSAY OF MERCURY

Mercury occurs in ores chiefly as cinnabar (HgS), and may with accuracy be determined by Chism's method.[2] For low-grade ores, the method is especially satisfactory, and has the advantage of being rapid and short. It is based on the fact that mercury is distilled from HgS, etc., in the presence of iron filings, and can be caught on silver-foil. The difference in weight between the mercury-impregnated silver-foil and the foil before the assay gives the mercury. The apparatus required is as follows:

1. A small ring-stand.
2. A fire-clay annealing cup (No. B or C).
3. A piece of carefully annealed silver-foil 1.5 in. square, which is fitted and bent down to make a reasonably tight cover for the annealing cup.
4. A flat silver or copper dish, holding 20 to 25 c.c. of water. A silver crucible may be used in place of this.
5. A piece of asbestos board, 4 in. square and about 0.20 in. thick, in the center of which a circular hole has been carefully cut, into which the annealing cup will fit so as to project about 0.5 in. below the bottom of the board.
6. A small alcohol lamp, of about 60 c.c. capacity.
7. A wash-bottle with cold water, and a glass tube for a siphon. The silver-foil is carefully fitted over the top of the

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[1] Hofman, *ibid.*

[2] R. E. Chism, in *Trans.* A. I. M. E., XXVIII, p. 444.

annealing cup, the edges being bent down so as to make a close-fitting cover and prevent the escape of mercurial vapor. The silver dish should be polished on the bottom, and be in close contact with the foil, so that the cooling effect of the water will be fully transmitted.

The Assay. — For low-grade ores from 0.5 to 1 gram is taken and mixed with from 30 to 50 parts of iron filings. These filings should all pass a 40-mesh screen. A select lot of filings are best digested with alcohol for some time to remove oil and grease, then heated in a muffle to a dull-red heat for 10 minutes, cooled, and stored in a tight bottle. It is essential to have the filings free from oil and grease, else this will be deposited on the silver-foil with the mercury. The amount of mercury in the ore should not be so great as to cause too heavy a coat on the silver-foil. For high-grade ores, not more than 0.1 to 0.2 gram should be used. Very small amounts of mercury can be detected by this method.

The ore, mixed with filings, is placed in the annealing cup, which is set into the asbestos board on the ring-stand, the silver-foil weighed accurately, after igniting, to within 0.1 mg., and fitted to the cup, and the silver dish, filled with cold water, placed on the foil. The alcohol flame is then allowed to play just on the bottom of the cup, but not to spread around the sides. The flame should be about 1.25 in. high and is best shielded by a screen to steady it. The bottom of the crucible should not become more than a dull red, otherwise mercury will escape condensation. The time of heating should be from 10 to 15 minutes. It is best to heat for about 10 minutes, then cool, and reheat for 3 to 5 minutes. Longer heating than this causes loss of mercury. The degree and time of heat are very important.

During the heating the water in the dish should be replaced once or twice. It can easily be removed by a bent tube that has been filled with water, acting as a siphon. While the warm water is being removed, cold water is added from a wash-bottle. After the proper heating, the alcohol lamp is removed, the assay allowed to cool somewhat, the silver dish removed, and the silver-foil with the mercury transferred by forceps to a desiccator and then weighed. The difference in the weight of the foil after and before the assay is the weight of the mercury, from which the percentage is calculated. The foil can be used again after driving off the Hg at a red heat in the muffle, or with a Bunsen burner. A piece of foil can be used about six times. It should be weighed before each assay. The method also serves as a very sensitive and easily applied qualitative test on ores.

The following figures will serve to show the accuracy of the method:[1]

	By Electrolysis from Cyanide Solution	By Chism's Method
Ore No. 1	12.37 per cent.	12.44 per cent.
Ore No. 2	67.26 per cent.	67.23 per cent.

The accompanying illustration (Fig. 44) shows the apparatus employed.

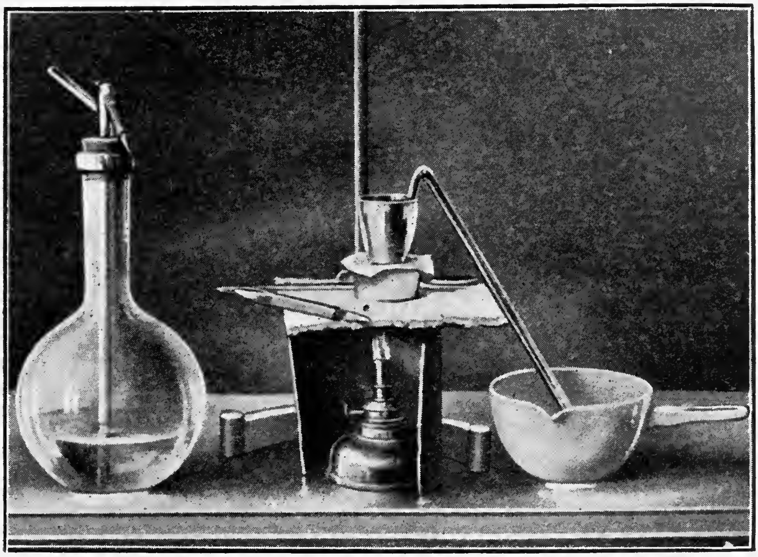

Fig. 44. — Apparatus Required for the Mercury Assay

The Assay of Lead Ores

The fire assay of lead ores will probably pass out of use in time, just as the fire assay of copper has done. At the present time it is still largely used, although for complex ores containing

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[1] G. N. Bachelder, in "Sch. Mines Quart.," XXIII, p. 98.

much copper or bismuth or antimony with the lead, it is not in vogue. It is, however, still the criterion in the purchase of pure sulphides and oxidized lead ores, and also such complex ores as furnished by the Leadville, Colorado, district. Unoxidized ores of this type contain pyrite, blende, galena, some little chalcopyrite and gangue. Oxidized ores contain cerrusite, anglesite, calamine, limonite, etc., and gangue. The object of the assay is to bring the lead of these ores down into a button, free from other base metals, such as Cu, Zn, Bi, Sb, Fe, and free also from S and As. The loss of lead by volatilization and slagging and the reduction of base metals should be kept to a minimum. As already stated, this is a difficult thing to do; so that pure ores will invariably give low results, and impure ones high.

There are three methods of assay, differing in the flux used; (1) the lead flux method; (2) the soda-argol method; (3) the cyanide fusion. Of these, the lead flux method is chiefly used throughout the West. The soda-argol method is a good one on ores not basic. The cyanide method is only applicable to pure ores. With impure ores it tends to reduce other base metals, due to its powerful reducing action. Various mixtures of lead flux are used, of which three are made up as follows:

No. 1	No. 2	No. 3
4 parts $NaHCO_3$	2 parts $NaHCO_3$	6.5 parts $NaHCO_3$
4 parts K_2CO_3	2 parts K_2CO_3	5 parts K_2CO_3
2 parts flour	1 part flour	2.5 parts flour
1 part borax glass	1 part borax glass	2.5 parts borax glass

Flux No. 3 is probably the best for most purposes, as determined on a series of ores, the results with it being slightly higher.[1] For assay, 10 grams of ore (100-mesh fine) are mixed with 30 grams of flux, placed in a No. 6 or D crucible, or in a 20-gram crucible, covered with 8 grams more of flux, and put into the muffle at a low heat, which is then raised to a light yellow (1080° C.). The fusion should take about 30 to 35 minutes. Nails are added to the charge, two tenpenny nails for heavy sulphides, one for light sulphides or oxidized ores. When the charge is taken from the muffle, the nails are removed from the crucible by a pair of short hand tongs, care being taken to wash off all

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[1] McElvenny and Izett, in "The Chemical and Fire Methods of Determining Lead Ores," "Min. Rep.," XLVIII, p. 26.

adhering lead globules. The crucible is then shaken and tapped thoroughly, and poured. The lead buttons are cleaned by hammering and weighed. The percentage is obtained by multiplying by 10.

The reactions in the crucible are as follows:

$$7PbS + 4K_2CO_3 = 4Pb + 3(K_2S, PbS) + K_2SO_4 + 4CO_2$$
$$K_2S, PbS + Fe = Pb + K_2S + FeS$$
$$2PbO + C = 2Pb + CO_2$$

The carbon liberated in finely divided particles from the flour on heating reduces any lead oxides or carbonates in the ore, while the iron reduces lead from its sulphides and sulphates. The assay should check (in triplicate) within 0.5 per cent.

The soda-argol method uses the following flux:

$NaHCO_3$	6 parts
Argol	1 part

For 10 grams of ore, 35 grams of flux are taken, with a light flux cover. The fusion is performed as described for the lead flux method. The method is good on ores containing some silica, but not on basic ores or pure galenas, as all acid is lacking in the flux. A borax glass cover is best where the method is employed on basic ores.

In the cyanide method, pure cyanide should be used, and the temperature should be kept much lower than for the other two methods. For the regulation of temperature, reference is made to the assay of tin by the cyanide fusion.

For the fusion, 10 grams of ore are mixed with 35 grams cyanide, and a light cyanide cover used. Concerning the accuracy of the method the following figures are appended:[1]

Ore	Fire Assay (lead flux) Per cent.	Gravimetric ($PbSO_4$) Per cent.
1. Galena	76	78.68
2. Galena	37	37.40
3. Cerrusite	9	10.60
4. Pyrite, Sphalerite, Galena	24.7	18.46
5. Galena and Stibnite	28.7	27.25
6. Cerrusite	37.8	38.60

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[1] Determination of Lead in Ores, I. T. Bull, S. of M. Quart., Vol. XXII, p. 348.

THE ASSAY OF ANTIMONY AND BISMUTH ORES

For accurate and satisfactory determinations on these ores, wet methods must be resorted to. Antimony occurs chiefly as the sulphide stibnite, although the oxides and some native metal are found as ore. Bismuth as an ore occurs chiefly as the native metal, but is found also in combination with oxygen, sulphur, etc. For the assay, the following charge is best:

Ore	10 grams
Cyanide	40 to 50 grams

Cover of cyanide.

Fuse at a full-red heat, as given for tin, for 30 minutes. The resultant buttons are brittle and cannot be hammered.

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