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METALLURGICAL TEXTS

FIRE ASSAYING

METALLURGICAL TEXTS

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FIRE ASSAYING

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PREFACE

The objectives of this book are to present the subject of fire assaying in such a manner as to serve the following needs: (1) as a self-study text of the practical art of assaying for individuals who may not have had a college course in chemistry; (2) as a text for technical institute students of assaying who do not intend to follow a complete academic curriculum in metallurgy; (3) as a reference for practicing assayers; and (4) as a college text for the student of metallurgy.

For the first and second of the above objectives, the book is arranged so that a working knowledge of the practice of fire assaying may be obtained without the need for a comprehensive understanding of the physicochemical principles involved; yet a sound foundation is laid for the intelligent application of scientific principles in such matters as crucible charge calculations, cupellation and scorification procedures, and other essential phases of the subject. For the practical assayer, Chap. VI, dealing with the more theoretical aspects of assay fusions, may be omitted entirely.

As a reference for practicing assayers, sufficient material is presented so that workable procedures can be evolved for the determination of gold and silver in almost any type of natural or artificial material. Complete schemes are given for the determination of the individual members of the platinum group in order to bring together many scattered references that are unlikely to be available except in the larger technical libraries. A brief résumé of the fire assay of base metals is also given. At the suggestion of assayers in the field, a short chapter on the preparation of bullion from amalgam and cyanide precipitates is presented, as well as appendixes listing assay equipment, assay supplies, and the location of assay supply houses.

A foundation for the correlation of fire assaying with the principles and processes of extractive pyrometallurgy is given in Chap. VI. This should prove of interest to college instructors who wish to utilize a course in fire assaying as a laboratory introduction to pyrometallurgy.

Every effort has been made to serve the interests of simplicity, clarity, and convenience. To this end the authors have introduced step procedures wherever possible and have prepared various tabular summaries to facilitate the selection of definite procedures and the readjustment of faulty techniques to avoid abnormalities.

The authors and their respective students have verified and demonstrated the workability of all the important procedures recommended in the book and furthermore have done a considerable amount of research to eliminate ambiguous and indefinite statements that have appeared in earlier works on fire assaying.

In addition to specific acknowledgments throughout the book, the authors wish to express their appreciation for the generous cooperation of many practicing assayers, who have been consulted from time to time by one or the other of the authors, and for the assistance of Miss Mabel E. Clark in the preparation of the manuscript.

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STANFORD UNIVERSITY, CALIF.;
SACRAMENTO, CALIF.;
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FIRE ASSAYING

CHAPTER I

THE SCOPE OF FIRE ASSAYING

The term "fire assaying" is applied to quantitative determinations in which a metal or metals are separated from impurities by fusion processes and weighed in order to determine the amount present in the original sample. The metals recovered are those which emerge from the fusions in the metallic state. For this reason, fire assaying is especially adapted to the determination of the noble metals: gold, silver, and the platinum group. Except for silver-rich alloys, fire assaying is the only method in common use for the determination of the noble metals. The method can also be used for the determination of metals that are comparatively easy to reduce, such as copper, tin, lead, bismuth, and antimony; but wet analytical methods for these metals are more accurate and are generally preferred.

The materials that are subjected to fire assay originate in a prospect, mine, or a metallurgical process, or in the recovery of scrap metal. These materials may be received in gross form in large lots, and the first consideration is to obtain a small sample that will be representative of the entire lot. For brittle materials, this is accomplished by a series of progressive particle-size reductions accompanied by the rejection of a part of the original volume of material at each stage, according to the principles discussed in Chap. II. The final assay sample, or pulp, consists of ¼ lb. or more which is ground sufficiently fine so that small portions can be weighed out for assay without introducing errors. The sampling of solid metals and alloys is done by a systematic method of drilling or sawing, conducted in such a manner as to obtain a representative sample.

Objectives of Assaying.—The most important outcomes of assay results are as follows:

1. Valuation of mining property.
2. Basis for buying or selling ores and metallurgical products.
3. Guide to prospecting and development of ore bodies.
4. Delimitation of boundaries of marginal ore.
5. Check against waste dilution in mining operations.
6. Control of average grade of ore mined and milled.
7. Investigation and control of metallurgical processes.
8. Accounting for all metals in process.

The degree of accuracy required in assaying depends upon which of the above purposes is involved; and the assayer should make a study of the permissible limits of error for each class of assay and devise methods that are as rapid as possible for each degree of accuracy required.

The highest degree of accuracy on individual samples is necessary in buying and selling ores and metallurgical products. On such materials most control assayers, acting for the buyer or seller, take the average of two—or preferably three—determinations. If the control assayers for buyer and seller do not agree within predetermined limits, a duplicate pulp is submitted to an umpire who usually reports the average of four or more separate determinations (see Chap. XIV).

Samples for mine valuation require rigid precautions to avoid gross or constant positive errors attributable to intentional or accidental salting; but the individual assays do not require a high degree of precision, since the final value of an ore body is determined by the average of a large number of assays, and the error involved in taking an individual sample is greater than the normal errors of assaying. Hence, single assays of valuation samples usually suffice and, as a precaution against the introduction of serious errors in individual assays, composite assays should be made of suitable groups of samples (see Chap. XIV).

In order to guard against salting,[1] the assayer should frequently check the precious-metal content of fluxes and reagents and should insert blanks or previously assayed samples at irregular positions in the sequence of valuation samples. All valuation samples should be kept under constant surveillance by a responsible party during their progress through the assay office.

Some forms of salting can be detected by a study of the samples. Valuation samples should be regularly tested by: (1)

[1] The extraneous introduction of precious metals.

panning and examination of the concentrate for unusual substances such as gold filings or amalgam, and (2) leaching with water followed by an assay of the water to find soluble precious metal salts.

The other purposes of assaying as outlined above do not generally require a high degree of precision. Single determinations, with ordinary precautions against errors, are usually adequate—particularly if periodical composites of important assays are made or if a metallurgical check is available, as by checking the metal content of the products against the feed to a metallurgical process. Mill-tailings samples or smelter slags require special care in assaying, since a small error will seriously affect the metallurgical balance sheet on account of the tonnage involved.

General Methods of Fire Assaying.—Figure 1 is an idealized flow sheet of the fire assay for gold and silver, with references to the chapters in this text where detailed descriptions of each part of the process are given.

The fire assay of ores and metallurgical products for noble metals generally starts with a crucible fusion or a scorification to slag the impurities and to collect the precious metals into a lead button. In the crucible fusion, fluxes are added to form with impurities in the ore a slag whose essential constituents are soda (Na_2O) or litharge (PbO), or both, and silica (SiO_2). Boric oxide (B_2O_3), in the form of borax glass ($Na_2B_4O_7$), is usually added to replace or supplement the silica. In scorification the amount of added fluxes is very small, the major flux being litharge derived from the oxidation of lead which is mixed with the ore at the outset. The size of the lead button is controlled in the crucible process by control of the oxidation-reduction reactions, so that just the right amount of lead is reduced from the added litharge in the charge. In scorification the button size is determined by the relationship between the size of scorifying dish (scorifier) used and the amount of granulated lead added. The crucible fusion allows the use of a larger sample of ore and is applicable to a wider range of materials than scorification and hence is the most generally used.

Prior to a fusion process, some materials—such as those containing metallic zinc or copper—require a preliminary acid treatment for removing undesirable impurities. Materials

high in oxidizable impurities are sometimes given a preliminary roast.

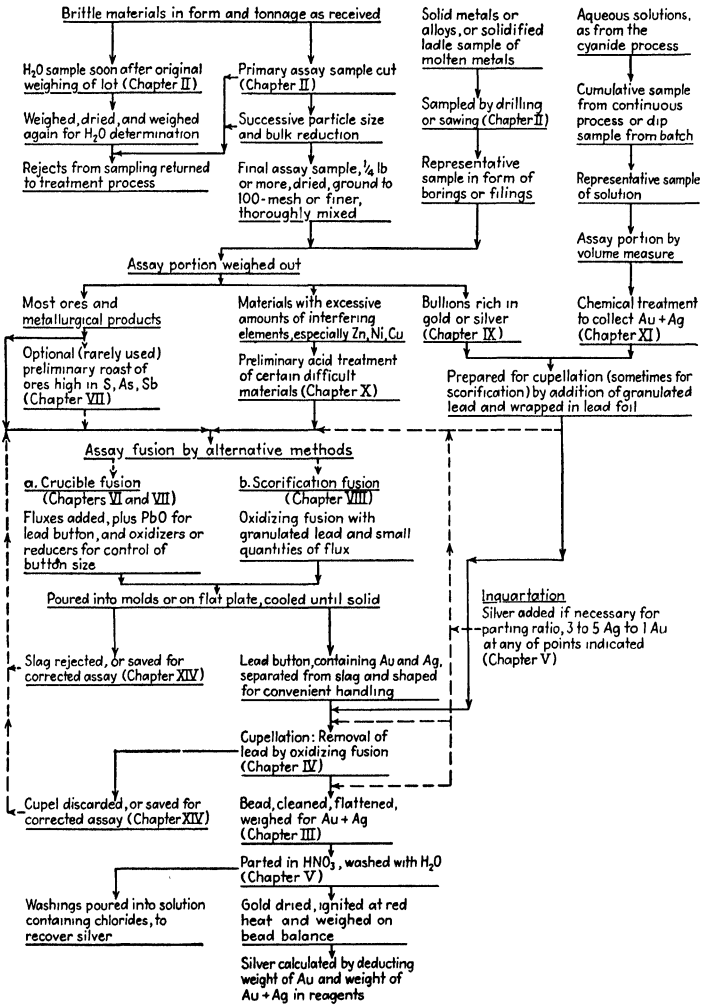


FIG. 1.—Idealized flow sheet of fire assay for gold and silver.

After the lead button is obtained, the lead is removed by an oxidizing fusion during which the lead oxide is partly volatilized

but is mainly absorbed by the vessel in which the process is conducted. This is known as "cupellation," and the vessel is known as a "cupel."

The end product of cupellation is a bead containing the noble metals. It is weighed on a bead balance, in order to obtain the gross weight of the noble metals present, and is then treated with acids which separate the metals from each other. This operation is known as "parting." In the absence of members of the platinum group, parting involves a solution of the silver in nitric acid, leaving the gold unattacked. The gold is then washed, dried, and weighed; and the weight of silver is calculated by subtracting the weight of gold from the combined weight.

A minimum ratio of three to five times as much silver as gold is necessary for parting. If this proportion of silver is not present in the original sample it must be added at one of the alternative points in the process indicated on Fig. 1. This procedure is known as "inquartation." The separation of members of the platinum group involves special chemical methods that are described in Chap. XII.

Bullions rich in noble metals but containing minor amounts of base-metal impurities are subjected directly to the cupellation process. Silver in silver-rich alloys is frequently determined by volumetric chemical methods, which are more accurate for this type of material than are fire methods.

Assay Equipment and Supplies.—The choice of equipment for an assay office is dependent upon the scale, scope, and permanence of operations. At some small mines the assayer may have numerous other duties and may devote only a few hours each week to the actual assaying, yet a well-equipped assay office may be justified for handling emergency assays and peak loads.

All the equipment and supplies for assaying can be purchased from assay supply houses, and the first step in establishing an assay laboratory is to send to one or more of the nearest supply houses for illustrated catalogues describing and quoting the equipment. A list of the leading distributors of assay equipment and supplies throughout the world is given in Appendix *C*.

The equipment for an assay laboratory is divided into the following categories:

1. Crushing, grinding, screening, and sampling equipment (Chap. II).

2. Assay furnace and accessory equipment (Chap. XVI).
3. Weighing equipment (Chap. III).
4. Parting equipment (Chap. V).
5. Chemical equipment, for special methods.

As an aid to the selection of equipment and to the local fabrication of certain items, brief descriptions of typical equipment are given in Chap. XVI and throughout the text. A representative list of complete assay-office equipment, with cost estimates, is given in Appendix *A*.

The supplies used in assaying, in relation to their applications, are discussed throughout the text; a check list of the essential supplies is given in Appendix *B*.

The layout of an assay office should be planned with a view to convenience, efficiency, and safety. The building should be located as far as possible from heavy machinery and railroad lines, to avoid the effect of vibrations on delicate weighing operations. Assay bead balances should be mounted on rigid foundations separated from the building structure, and a separate balance room is desirable. The sampling room, with its crushers and other equipment, should be, if possible, in a room separate from the rest of the laboratory, thus avoiding the possibility of dust contamination of assay reagents and dust damage to delicate balances. In large assay offices it is customary to provide a separate room for parting and other chemical work, an office, and separate storerooms for samples and for supplies. If the assayer is responsible for the retorting of amalgam and bullion melting, a separate room should be provided for that purpose. The handling of rich materials in the assay office requires great care to avoid salting.

Duties of Assayer.—The primary duty of an assayer is to assume responsibility for the accurate and prompt determination of valuable metals in samples submitted to him. At plants producing bullion he also is frequently charged with the duty of preparing the bullion from amalgam or cyanide precipitates and of ascertaining the weight and fineness of the bullion that is shipped. In addition to these fundamental responsibilities, the assayer at small mines may devote a part of his time to other engineering activities such as surveying, mapping, mechanical drafting, sampling, metallurgical calculations, metallurgical

testing, etc. In large organizations the assayer's duties are more narrowly confined to assaying only.

It is important that the limits of the assayer's responsibility be clearly defined with respect to the responsibilities of other persons in the organization who have any connection with the source of samples submitted to the assayer, and with the interpretation and use of the assayer's reports.

Part of the organization chart of a highly specialized mine and mill staff is given in Fig. 2, upon which the origin of assay samples is superimposed. In this example the chief sampler at the mine and the metallurgist at the mill are charged with the primary responsibility of organizing the scope and methods of all necessary routine sampling for the purpose of supplying data

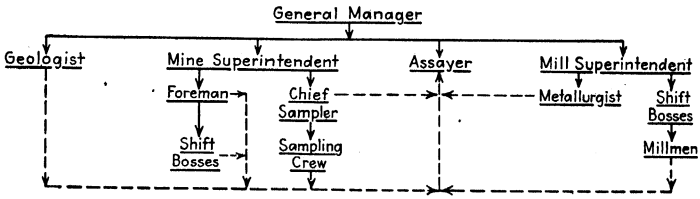


FIG. 2.—Partial organization chart of a typical mining and milling company.

for the effective operation of the mine and mill. Their work is subject to direct supervision by the mine and mill superintendents, respectively, who may desire more or fewer samples or special samples from time to time. At some properties the chief sampler and the metallurgist—particularly the latter—are staff officers responsible directly to the general manager. This arrangement is satisfactory if the company is operating a number of different mines and is conducting a campaign to acquire new properties, but in any event the mine superintendent of each mine and the mill superintendent of each separate milling unit should have the authority to demand such sampling as they may require.

The geologist, unless also serving as engineer in charge of development, generally has no responsibility for routine samples but is usually given blanket approval to submit to the assayer

within specified limits any samples that he needs for his geological studies. He may also suggest to the chief sampler, through the mine superintendent, that the regular sampling crew take certain samples. When new properties are under investigation, the geologist or the examining engineer (who may be the chief engineer, the chief sampler, or a subordinate) decides upon the samples to be assayed.

The foreman and shift bosses in the mine are usually permitted to take supplementary grab samples from newly blasted development headings or from chutes that deliver ore to the main haulage levels. These samples are usually transferred to the chief sampler, who includes them with his regular samples. At mines not employing a separate sampling crew, such samples by foremen and bosses may be the only ones used to guide mine development and operation.

The routine mill sampling is usually carried out by automatic devices or by the millmen, under the immediate supervision of the shift boss acting upon the metallurgist's advice, as approved by the mill superintendent. Millmen and mill shift bosses are seldom permitted to take and submit assays without the express approval of the superintendent or metallurgist.

At custom mills and smelters, in buying ores and concentrates, the sampling procedure of shipments purchased is of vital importance and is usually placed under the direction of a separate official who is responsible directly to the manager.

The general manager is always in a position to order a revision of the sampling and assaying procedure or to obtain special samples personally or through subordinates. The mine and mill superintendents are in a similar relationship to their respective divisions.

It is customary for the assayer to submit a complete copy of all assays to the general manager, mine superintendent, and mill superintendent. Another copy may be divided so that the chief sampler obtains a record of mine samples and the metallurgist a copy of the mill data; or the offices may be arranged so that these officials refer to the superintendent's copies. The geologist and others are generally given a separate record for such assays as they have personally submitted. Confidential reports to the general manager only are sometimes requested. In some organizations the routine reports for the manager are transmitted

to the chief clerk, who prepares such tabulations and summaries as the general manager may require.

In the organization under discussion the assayer assumes no responsibility whatsoever for the validity of the samples that he receives. Most of this responsibility is divided between the chief sampler and the metallurgist, each of whom has independent means of testing the general reliability of the assayer's work. On the other hand, serious sampling errors, in either the mine or mill, will be disclosed by reliable assay results if the actual mine or mill production does not check the calculated estimates. The principal disadvantage of divided authority over sampling and assaying is that the assayer has little opportunity to understudy for more important positions and tends to become technically narrowed to his specific duties.

The status of the assayer at small mines and properties in the development stage merits some discussion. At some properties he combines the functions of assayer with those of one or more of the following: engineer, sampler, geologist, and metallurgist. If he is in charge of all the sampling and engineering work, he is placed in a position where his integrity is of paramount importance, since the management has no satisfactory independent check of his reliability. In such a capacity, the assayer must use exceptional precautions to ensure the honesty and accuracy of his work; and he is justified in keeping a personal file of all relevant data so as to safeguard himself against becoming involved in fraudulent promotions.

One of the commonest tricks of fraudulent promotion involves the appointment of a dishonest mine superintendent, who personally takes all samples from development headings and is in a position to falsify ore-reserve estimates and other critical data. Even in legitimate promotions the superintendent or other responsible official may prolong his tenure by falsely encouraging reports of new development work. If the assayer suspects chicanery, he owes it to his future professional status to ascertain the facts.

Organization of Assaying Routine.—It is essential that the assayer organize every step in his daily routine to the end that maximum efficiency and acceptable accuracy are ensured. The general principle to be applied in the development of an efficient routine is that every effort be made to keep the assays in active

progress throughout the entire procedure, from the time the samples are received until the final results are reported. The principal details to observe are that the furnaces be hot when needed, that equipment and supplies be ready for use, that accidental delays or interruptions be avoided, and that the laboratory be neat and orderly. Since some of the individual steps in the assay process are cyclic and involve waiting periods, certain operations may be dovetailed together, and much of the incidental work of preparing flux mixtures and of keeping the laboratory in order may be done during these waiting periods. For example, a set of fusions remains in the furnace for from 15 to 20 min. If another set is to follow, the preparation of the second set can be made while the first set is in the furnace. If only a single furnace is available, it should be loaded with cupels immediately after the last set of fusions is poured, in order that the cupels will be hot when the buttons are ready for them. Cupellation requires from 25 to 30 min., and the experienced assayer learns how to control the furnace so that little attention is required except at the beginning and end of the process; he is therefore free to perform other duties during the greater part of the cupellation period. An interval, varying from 5 to 15 min., is also available during parting.

Assay Sequence.—It is of utmost importance that the assayer devise, and strictly adhere to, a good system of arranging and handling the daily assays in a predetermined order throughout the entire process, from the time the samples are received until the final report is made. Errors caused by misplacement of a sample, crucible, cupel, or parting cup are undetectable by ordinary means, with the result that high-grade samples might be reported in place of low-grade samples, and vice versa. To avoid such errors, every assayer should follow a system by which the order of samples is automatically maintained. If one man carries through all operations himself, his system may be devised to suit his own peculiarities; but, if helpers are employed, the system must be such that neither the assayer nor the helpers can confuse the sequence of assays without detection.

It is impracticable to use permanent marks on crucibles, because this practice is time consuming and becomes confusing when crucibles are reused. Cupels cannot be marked satisfactorily. Even if crucibles and cupels were marked, this would

be no guaranty in itself that the buttons would be placed in the proper cupel. Parting cups may be marked permanently, but time is lost in arranging them in the proper sequence. Thus a satisfactory routine should be developed that is independent of numbered marks on the assay receptacles.

When the day's set of pulverized and mixed samples has been assembled, the assayer arranges them in suitable order and records the sample numbers or description on his report form or notebook. From then on, until the final report is prepared, the assays are handled in the same sequence and may be assigned serial numbers from 1 upward.

Ruled lines may be provided in the notebook to separate each furnace load of crucibles, each set of cupellations, and each tray of parting cups. The number of assays in each of these units is usually different, but if special parting-cup trays are made they should hold the same number of parting cups and be in the same arrangement as a set of cupels in the furnace.

All carrying trays for crucibles, buttons, cupels, and parting cups should be designed so that the two ends are distinctive, thus avoiding the danger of reversing the entire set. The arrangement of assays in rows in the carrying tray should read from left to right, as printed matter is read, not zigzagged as in section numbering in a township. If assistants of uncertain reliability are employed, the assayer may insert a blank assay of known silver and gold content in a key position in each furnace set. If this assay appears in its proper place when the doré beads are weighed it is reasonable assurance that no misplacements have been made in the previous operations. For controlling the fusion and cupellation sequence a small quantity of some element may be added to one or more of the assays, that will give a stain on the cupel that is not present in any of the other assays. Copper or nickel is suggested for this purpose and may be added to any of the regular assays if the amount is just sufficient to give a distinctive cupel stain but not enough to cause cupellation loss or freezing of the button.

Records.—The principal technical records needed in an assay office are a suitable laboratory notebook, or work sheet, and a report form. The laboratory work sheet is used for keeping a record of the sequence of assays, the weight of ore taken, the amount of silver added for inquartation (if any), and the respec-

tive weights of the doré and gold beads, together with the calculated gold and silver content of the samples. For beginners a ruled form on which to enter the amount of fluxes used for each sample is helpful. Such a form is illustrated in Fig. 3. Experienced assayers do not need to keep details of flux charges, but a column for remarks on the work sheet should be provided for recording abnormalities.

The report form gives only the original description or number of the sample and the gold and silver content in weight units, or in monetary value, or both. In the United States, gold and

ASSAY LABORATORY

ASSAY REPORT

GOLD AT $35.00 PER OZ. TROY
SILVER AT $ PER OZ. TROY

LITHARGE CORRECTION { MG. Ag PER 2 A.T. PbO / MG Au " " "

SAMPLE NO.	DESCRIPTION	FLUXING DATA								WT. OF BUTTON G.	WT. BEAD IN MG.			ASSAY, OZ PERT.		VALUE IN $ PER TON		
		ORE A.T.	PbO A.T.	SODA A.T.	BORAX A.T.	B G A.T.	SiO_2 A.T.	FLOUR G.	NITER G.		DORÉ	CORR'D DORÉ	Au	Ag	Au	Ag	Au	TOTAL

REMARKS:

DATE
ASSAYER

FIG. 3.—Form for detailed record of assays.

silver are reported in troy ounces per avoirdupois short ton (2,000 lb.) and, for convenience, a special system of weights is used in which the assay ton (A.T.), weighing 29.166 g., bears the same relation to a milligram as the avoirdupois short ton bears to the troy ounce. Hence, when a 1-A.T. sample is weighed out, the weight of gold or silver in milligrams is the content of gold or silver in troy ounces per avoirdupois ton. In some British countries, gold and silver are reported in pennyweight (dwt.) per long ton (2,240 lb.); and in countries using the metric system, gold and silver are reported in grams per metric ton.

At assay offices connected with a mine, mill, or smelter a printed report form is usually prepared on which the daily results of all routine assays, as well as additional special assays, may be

recorded. Also, small report forms are needed for reporting the results of individual assays or special groups of assays to staff members, shippers of ore for treatment, and others. It is usually necessary to provide several copies of assay reports, and one copy should always be retained in the assay office. Any specially printed forms, therefore, should be assembled in convenient form for duplicating, and the use of distinctively colored paper for each copy is desirable.

CHAPTER II

SAMPLING

When a metal-content determination of a large amount of material is required, a sample is taken and sent to the assay office, where, by further sampling operations, a small portion is obtained for the assay process.

The proportion of the required metal that is found in the assay portion is attributed to the material from which the sample was taken. For example, if an assay portion of 1 assay ton (29.166 g.) is used in the assay of an ore, and if 0.23 mg. of gold are recovered, the ore is said to assay 0.23 oz. of gold per ton of ore. In order that the assay may be accurate the assay portion must contain the same relative amount of gold as the average of all the material from which the sample was taken. The difficulty of obtaining an assay portion small enough to be economically treated in the assay process and yet representative of the average of several tons of a heterogeneous material varying in grade from barren rock to particles of native metal is often greater than the difficulties encountered in the actual assay process.

Types of Samples.—There are three types of samples: the spot sample, the random sample, and the stratified sample. A spot or grab sample is taken from one place in the material to be sampled and tends to be less reliable than a random sample. The random sample consists of portions taken at random from various places in the material to be sampled. The stratified sample consists of portions taken at regular intervals throughout the material to be sampled. Stratified samples tend to be more reliable than random samples, and, for that reason, they are frequently used.

The Accuracy of Samples

Random and stratified samples are made up of a number of cuts or portions taken from different parts of the material to be sampled. Each cut consists of a number of individual fragments

of material. Either or both of these sampling units, cut and fragments, may vary individually in grade from the average of the material being sampled. Accuracy of sampling can be investigated from the standpoint of the sample cuts or from the standpoint of the individual fragments. With either point of view the factors influencing the reliability of a sample are: (1) the dispersion, or the variation in grade of the units in the material to be sampled, and (2) the size of the sample, or the number of units taken into the sample. In general the reliability of a sample is improved by increasing its weight, in order to increase the number of units, or by crushing and mixing the material before sampling, to decrease the dispersion per unit of weight. Increases in either the number of units taken into the sample or the amount of crushing and mixing increases the cost of sampling, and, furthermore, any increase in the size of the final assay portion increases the cost of assaying. The balance between cost and accuracy that has been found suitable at the average mine has resulted in customary sampling procedures. These should not be followed blindly; all important sampling operations should be planned to suit the material to be sampled and to produce the accuracy desired.

Limit of Error.—In any sample taken from a heterogeneous material there is the possibility of some chance variation; consequently a precise limit of error cannot be established for a particular sampling process. If a considerable number of samples were taken in the same way from the same material, and the assay results arranged according to the frequency of occurrence of results in various ranges, it would be found that the intermediate result would occur most frequently and there would be less and less of both higher and lower results.

Another sample taken in exactly the same way from the same material might deviate from the true result by a greater amount than any of the previous samples; but the probability of its doing so is small.

There is increasingly less chance of obtaining a sample with an increasingly greater error, but there is no limit to the possible error except the richest or poorest part of the material to be sampled. In lieu of a definite limit of error an artificial or practical limit may be taken at some point where the probability of greater error is considered so small that it may be disregarded.

The probability of error is conveniently expressed by the standard deviation σ, which is the square root of the mean of the squares of the individual deviations from the average and expresses in one figure the scattering of individual results.

With random sampling the distribution of results of duplicate samples should approximate the "normal curve." Two-thirds of the results will be within one standard deviation from the average, 19 out of 20 will be within two standard deviations from the average, 369 out of 370 will be within three standard deviations from the average, and 16,666 out of 16,667 will be within four standard deviations from the average. In most statistical work, three times the standard deviation is taken as the practical limit of error, or the greatest extent to which a result is liable to be in error due to chance variation.[1] Greater error is possible, but the chance of its occurrence (1 in 370) is so small that it may usually be disregarded.

The sampling error considered here is that due to chance variation in an honest random sample. If the sampling method is unfair the error cannot be decreased by increasing the size of sample or by averaging a large number of incorrect samples.

Standard Deviation.—The standard deviation of a sample may be determined by

1. Calculation from the individual deviations of a large number of duplicate samples.

2. Assaying the individual units or portions that go to make up the sample and, from the standard deviation of the individual units, calculating the standard deviation of the average of all the units.

3. Estimating the assay of the sample and the metal content of the pieces of rich ore, from which can be calculated the standard deviation of a sample composed of a very large number of fragments and containing only a comparatively few rich fragments.

The standard deviation is defined as the square root of the mean of the squares of the deviation of individual samples from the average of a number of duplicate samples. The first method of calculation is expressed by the relation

[1] EZEKIEL, M., "Methods of Correlation Analysis," p. 23, John Wiley & Sons, Inc., New York, 1930.

$$\sigma_x = \sqrt{\frac{\Sigma_x^2}{n}} \tag{1}$$

where σ_x = the standard deviation of the sample (milligrams per assay ton).

x = the deviation of each individual sample from the average (milligrams per assay ton).

n = the number of duplicate samples investigated.*

The second method is derived from the first by considering the sample to consist of the average of a number of units, where each unit has the standard deviation of σ_x. The reliability of this sample is expressed by the standard deviation of the mean (of the units in the sample) σ_m. The relation between the standard deviation of the mean σ_m, the standard deviation of the individual unit σ_x, and the number of units included in the average n', is

$$\sigma_m = \frac{\sigma_x}{\sqrt{n' - 1}} \tag{2}[1]$$

The third method of calculating the standard deviation of a sample depends upon the standard deviation of the number of rich particles (σ_p) where there is the chance of success (p) and the chance of failure (q) in obtaining rich particles that are present in the proportion p in a sample of n'' particles,

$$\sigma_p = \sqrt{n''pq} \tag{3}[2]$$

The chance of success plus the chance of failure is equal to one, so that $(1 - p)$ may be substituted for q and the equation becomes

$$\sigma_p = \sqrt{n''p - n''p^2} \tag{4}$$

In almost any ore sample the number of rich particles is very small in proportion to the total number of particles; consequently p is very small and $n''p^2$ may be neglected. The average number of rich particles in the sample M is equal to the total number of particles in the sample n'' multiplied by the proportion of rich

* The chance of error is somewhat greater than normal, when calculated from a standard deviation based on less than 30 samples.

[1] EZEKIEL, *op. cit.*, p. 25.

[2] YULE, G. U., "An Introduction to the Theory of Statistics," 7th ed., p. 257, Charles Griffin & Company, Ltd., London, 1924.

particles p. Substituting M for $n''p$ and neglecting $n''p^2$ give the Poisson relationship

$$\sigma_p = \sqrt{M} \tag{5}$$

The standard deviation in the number of rich particles in a sample of n'' particles σ_p, multiplied by the average metal content of the rich particles in milligrams C, is the deviation in milligrams, which also equals the standard deviation in milligrams per assay ton σ_x, multiplied by the weight of sample in assay tons W.

$$\sigma_p C = \sigma_x W$$

Therefore

$$\sigma_p = \sigma_x \frac{W}{C} \tag{6}$$

The average number of rich particles in the sample M is equal to the assay of the ore (in milligrams per assay ton) A, multiplied by the weight of the sample in assay tons W, and divided by the average metal content of the rich particles in milligrams C.

$$M = \frac{AW}{C} \tag{7}$$

Substituting (7) and (6) in Eq. (5) and simplifying give

$$\sigma_x = \sqrt{\frac{AC}{W}} \tag{8}$$

Examples of the Determination and Use of the Standard Deviation.—As an illustration of the methods for determining the standard deviation of a sample and its use in estimating the limit of error of a sample, or the minimum weight of sample to achieve any required reliability, consider the selection of the assay portion from a gold-ore pulp that has been pulverized to pass a 100-mesh sieve. Usually no detectable sampling error is found in this operation, but with some gold ores an alarming variation is found between duplicate assay portions. At the Alaska Juneau mine, for example, 10 separate assay portions from the same samples gave the results shown in Table I.[1] It

[1] BRADLEY, P. R., Mining Methods in the Alaska Juneau Mine, *Trans. A.I.M.E.*, vol. 72, p. 106, 1925.

is obvious that with this material any single assay portion of 1 assay ton is liable to deviate from the true result by more than can be allowed. By calculating the standard deviation of these samples, the practical limit of error in an individual assay ton can be determined; if it is more than permissible the size of the sample necessary to give the desired accuracy can be calculated. The computation of the standard deviation of a 1-assay-ton portion taken from sample 1 is given in Table II.

TABLE I.—RESULTS OF 10 ASSAYS ON SAMPLES FROM ALASKA JUNEAU MILL

Assay number	Assay results, ounces of gold per ton of ore			
	Sample 1	Sample 2	Sample 3	Sample 4
1	0.02	0.04	0.03	0.09
2	0.02	0.01	0.07	0.06
3	0.06	0.05	0.08	0.11
4	0.07	0.07	0.26	0.06
5	0.00	0.04	0.26	0.14
6	0.02	0.04	0.06	0.06
7	0.06	0.00	0.10	0.03
8	0.01	0.04	0.24	0.08
9	0.02	0.03	0.19	0.04
10	0.01	0.02	0.19	0.08
Average	0.029	0.034	0.148	0.075

The standard deviation of a single assay-ton portion as taken from sample 1 is shown to be 0.0236. On the average of two times out of three, any single assay-ton portion may be expected to give an assay between 0.006 and 0.053 oz. per ton. Only once in 370 times will the error exceed three standard deviations or 0.07 oz. per ton. Therefore, 0.07 may be taken as the practical limit of error in a single sample of 1 assay ton. If greater accuracy is desired, it can be obtained only by increasing the size of the sample, as the gold particles cannot be crushed to reduce the dispersion. The size of sample n' necessary to give a result within E ounces per ton of the true value is calculated by substituting $E/3$ for σ_m in Eq. (2), and solving for n'. Thus, to find the required number of assay tons of sample 1 to give an assay portion accurate to within 0.02 oz. per ton, substitute 0.02/3 for σ_m and 0.0236 for σ_z.

TABLE II.—STANDARD DEVIATION OF A 1-ASSAY-TON PORTION FROM SAMPLE 1

Assay number	Assay result, ounces of gold per ton	Deviation X	X^2
1	0.02	0.009	0.000081
2	0.02	0.009	0.000081
3	0.06	0.031	0.000961
4	0.07	0.041	0.001681
5	0.00	0.029	0.000841
6	0.02	0.009	0.000081
7	0.06	0.031	0.000961
8	0.01	0 019	0.000361
9	0.02	0.009	0.000081
10	0.01	0.019	0.000361
Average.....	0.029		$\Sigma X^2 = 0.005490$

$$\sigma_x = \sqrt{\frac{\Sigma X^2}{n}} = \sqrt{\frac{.005490}{10}} = 0.0234$$

From Eq. (2),

$$n' = \frac{(\sigma_m)^2 + (\sigma_x)^2}{(\sigma_m)^2} \tag{9}$$

Substituting,

$$n' = \frac{0.000043 + 0.000549}{0.000043} = 14 \text{ assay tons}$$

According to the calculation, an assay portion of at least 14 assay tons is required from this material, in order that the sample be accurate to 0.02 oz. per ton of ore. In practice this is usually accomplished by making seven separate fusions of 2 assay tons each.

Frequently it is desirable to know the standard deviation of a sample without going to the trouble and expense of taking a series of duplicate samples for assay. When the approximate assay of the ore is known and the average metal content of the rich particles can be estimated, the standard deviation can be roughly approximated by substituting in Eq. (8).

For example, the samples of Table I might have been known to assay about 0.07 oz. of gold per ton. A knowledge of the metal

content of the rich particles could have been obtained by panning a portion of the crushed ore and examining the gold. If a considerable number of the gold particles were of such a size as to weigh about 0.02 mg., the standard deviation of a 1 assay-ton sample would be:

$$\sigma_x = \sqrt{\frac{(0.07)(0.02)}{1}} = 0.038 \text{ oz. per ton}$$

This value for the standard deviation compares with 0.024 for sample 1, 0.019 for sample 2, 0.085 for sample 3, and 0.0311 for sample 4. Gold particles weighing 0.02 mg. are about the heaviest found in minus 100-mesh material, so that the examples have been of an unusually difficult ore. With many ores, even though an occasional large piece of gold is found, the majority of the gold particles are so small that duplicate assay portions of 1 assay ton will generally check to 0.01 oz. of gold per ton of ore.

If the sample is to be taken from material that has not been finely crushed, Eq. (8) can be used to estimate the minimum weight of sample to give any desired reliability. To illustrate, a calculation of the minimum weight of sample that may be taken from a certain silver ore is given below:

Calculation of Minimum Sample Weight

Conditions

1. The ore is expected to assay about 15 oz. of silver per ton of ore.
2. The ore has been crushed to 1-in. pieces, and an accuracy of 0.5 oz. of silver is desired.
3. Rich pieces of ore weighing about 50 g. and known to assay about 100 oz. of silver per ton of ore are observed in the material.

Solution

The silver in the rich pieces of ore is calculated from the assay-ton proportion and the weight of the pieces of ore to be about 171 mg.[1] The standard deviation allowed is 0.5/3 or 0.17. The grade of the ore is 15 oz.

[1] 1 A.T. = 29.166 g., in which quantity of ore 1 mg. of silver is equivalent to 1 oz. per ton. Hence, 29.166:50 = 100:(milligrams of silver), and milligrams of silver (in the rich pieces) = 171 mg.

Substituting in Eq. (8)

$$0.17 = \sqrt{\frac{15 \times 171}{W}}$$

Solving for W,

$$W = 89{,}000 \text{ A.T.}$$

or

$$W = 5{,}740 \text{ lb. minimum weight.}$$

The calculation just made indicates that a sample of at least 5,700 lb. must be taken from the silver ore described, in order not to exceed a practical limit of error of 0.5 ounce per ton.

Mine samples are frequently crushed to ¼ in. and divided on a Jones riffle to obtain a final assay sample of about 1 lb. The practical limit of error for an assay sample taken in this way from the above-mentioned silver ore is calculated below.

Calculation of Limit of Error

Conditions

1. The ore is expected to assay 15 oz. of silver per ton.
2. A final assay sample of about 1 lb. or 16 A.T. is to be split from a sufficiently representative portion of the ore that has been crushed to ¼ in.
3. Crushing finer than 1 in. has not released richer pieces of ore, so that the richest pieces still assay about 100 oz. per ton.

Solution

The weight of silver in the rich ¼-in. pieces is about 1/64 of that in the 1-in. pieces, or $^{171}/_{64} = 27$ mg.

Substituting in Eq. (8),

$$\sigma_x = \sqrt{\frac{15 \times 27}{16}}$$

$$\sigma_x = 5 \text{ oz. of silver per ton}$$

The practical limit of error $= 3\sigma_x = 15$ oz. of silver per ton.

The calculation shows that as often as one time in three, the assay sample taken by standard practice from this silver ore will be in error by more than 5 oz. of silver per ton. The practical limit of error is as great as the assay itself. This is an unusually large error, and would occur on an average of only one time in

370. In most cases a considerable amount of the rich silver particles are much smaller than ¼ in. but even if the average rich particle contained only 5 mg. of silver, the standard deviation would be 2 oz. of silver per ton of ore.

Probably most assayers do not realize the unreliability of a final assay sample, consisting of about 1 lb. of material when it is split from an ore, which has been crushed to about ¼ in. and consists of particles differing considerably in grade. After experimenting with some 136 triplicate assay samples split with the Jones riffle, from a gold ore crushed to ¼ in. and containing no visible free gold, Boericke[1] concluded that samples split from a gold ore of variable content show variations of as much as 25 or 30 per cent between assays, unless the original sample is crushed much finer than minus ¼ in. before splitting.

When such large errors are commonly present in single assay samples, one may wonder how assays can be used to evaluate ore bodies reliably or how assays can be used to obtain monthly metal balances in milling operations. Both of these operations are based upon the average of a considerable number of separate samples. Each separate sample may be regarded as a unit of a larger sample that is composed of the average of all the units. The accuracy of the average may then be expressed in terms of the standard deviation of the mean, from Eq. (2).

$$\sigma_m = \frac{\sigma_x}{\sqrt{n' - 1}}$$

where σ_m = the standard deviation of the mean.
σ_x = the standard deviation of the individual units.
n' = the number of units in the average.

For example, samples from a gold mine might individually have a standard deviation σ_x of about 0.03 oz. of gold per ton and a practical limit of error of 0.09 oz. of gold per ton, yet the average of 80 samples would have a limit of error of only 0.01 oz. of gold per ton. Similarly the feed sample of ore going to a mill for one day is likely to be considerably in error, but the monthly average of the daily assays is usually sufficiently reliable.

Effect of Particle Size on the Minimum Weight of Sample.—The minimum weight of sample may be decreased as the indi-

[1] BOERICKE, W. F., The Jones Riffle in Cutting Down Samples, *Eng. Min. Jour.*, vol. 140, No. 6, p. 55, 1939.

vidual particles in the material to be sampled are crushed smaller. The relation between particle size and minimum weight can be derived from Eq. (8)

$$\sigma_x = \sqrt{\frac{AC}{W}} \tag{8}$$

Consider sampling an ore of assay A, where a constant reliability of sample σ_x is desired. The weight of sample W must be proportional to C, the precious-metal content of the large rich pieces of ore. Disregarding the change in grade of the rich pieces of ore due to the liberation of pure valuable mineral on crushing, the metal content of the rich pieces of ore is proportional to their volume or to the cube of their diameters. Therefore

$$W = kd^3 \tag{10}$$

In Eq. (10), W is the minimum weight of sample when the ore contains large pieces of diameter d. The magnitude of the proportionality constant k depends upon the reliability of the sample and the units used for sample weight and diameter of particles.

Rich valuable minerals are usually broken free at a comparatively small size and increasingly larger pieces of rich ore contain a proportionately greater amount of gangue minerals, gradually approaching the average assay of the ore.

For this reason, the metal content of the rich pieces of ore is seldom proportional to the cube of their diameters but is approximately proportional to some power less than the cube of the diameter. Richards[1] found that the weights of samples used in practice varied approximately as the square of the diameter of the largest pieces. This gives the convenient and practical relation

$$W = kd^2 \tag{11}$$

The value of the proportionality constant can be found from the weight of sample that is satisfactory at some particular particle size. A 1-assay-ton sample is usually considered satisfactory for the final assay portion of ores that have been crushed to pass a 100-mesh sieve. Substituting 1 for W, and 0.0058 in.

[1] RICHARDS, R. H., "Ore Dressing," Vol. 2, p. 850, McGraw-Hill Book Company, Inc., New York, 1906.

(the aperture of the 100-mesh sieve) for d, gives 30,000 for the proportionality constant.

In Table III, minimum sample weights are given, which have been calculated from Eq. (11) with 30,000 substituted for k. This table should be used only for rough work on ordinary ores. The minimum weight of sample should be calculated by the method described on page 21 for important sampling operations.

TABLE III.—MINIMUM SAMPLE WEIGHTS*

Size of particles		Weight of samples	
Diameter, inches	Mesh	Assay tons	Pounds
4	...	240,000	15,432
2	...	120,000	7,716
1.5	...	67,500	4,340
1.0	...	30,000	1,929
0.5	...	7,500	482
0.25	...	1,875	120
0.065	10	127	8
0.0116	48	4	0.26
0.0058	100	1	0.06

* Minimum sample weights determined from the approximate relation $W = 30{,}000d^2$.

SAMPLING PRACTICE

The usual types of material to be sampled for assaying are listed in the following tabulation:

1. Brittle materials such as most ores and rocks:
   a. That can be crushed as fine as desired.
   b. Containing "metallics" or malleable scales that cannot be crushed.
2. Metals:
   a. Solid.
   b. Liquid.
3. Aqueous solutions such as cyanide solutions:
   a. Homogeneous.
   b. Mixed solids and solutions.

The Sampling of Brittle Materials

Practice in sampling brittle materials for assay is illustrated by the procedures used in sampling broken rock. The material to be sampled may comprise a large shipment of ore to a

smelter or a small sample from a mine or prospect. In either case the material is crushed and then divided into a sample portion and a rejected portion. The sample portion is again crushed and divided into repeated stages until the final assay sample is obtained. If malleable particles are encountered during the crushing operation the procedure for sampling material containing metallics (page 32) must be used.

Mine samples are usually comparatively small, and assay samples are prepared from them in a sampling room that is a part of the assay office. The sampling of large amounts of ore, such as the feed to a mill or a shipment to a smelter, is generally done outside the assay office.

Preparation of Mine Samples for Assay.—The sampling room at a mine assay office should be equipped with an adjustable crusher, either a disk pulverizer or a coffee-mill type of sample grinder, a Jones riffle, a sample drier, and pans and buckets for containing the samples during their preparation. An outline of the usual steps in the preparation of mine samples for assay is given in Fig. 4.

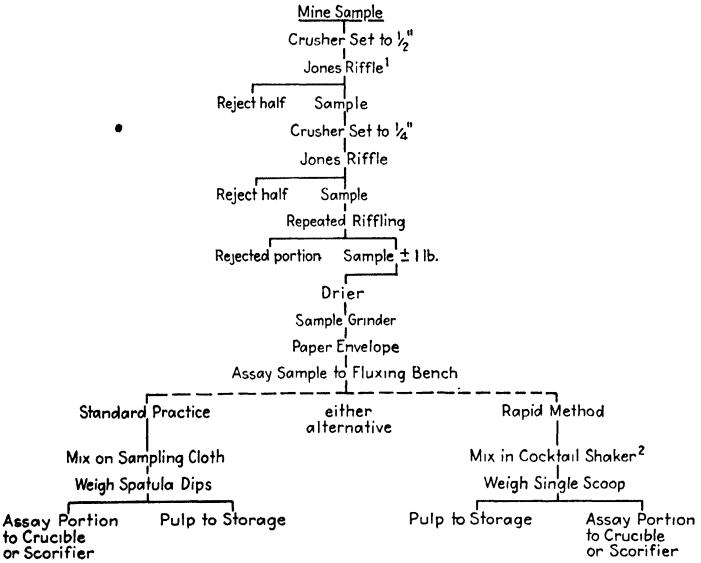
Mine samples are received in canvas bags, usually containing from 10 to 50 lb. of rock. One sample is opened at a time and dumped into a large pan or a bucket. The identifying number (on a piece of paper or a metal tag) is picked out from the material, and placed in the drying pan to be used for this sample. The sample is then fed with a hand scoop to a laboratory jaw crusher. If the sample is larger than about 30 lb. it is usually passed through a Jones riffle, and half of it is rejected and half taken into the sample.

The jaw crusher is then set to about ¼ in., and the sample portion, or all the material if it has not been split on the riffle, is crushed to ¼ in. or finer. Then, by repeated passes through the Jones riffle with half rejected at each pass, the sample is split until only about 1 lb. remains for the assay sample. This is placed in the drying pan containing the sample number, and the pan is placed in a drier heated to 105 to 110°C. It is desirable to have mine samples sent to the assay office in the afternoon, so that they can be brought to this stage and left to dry during the night.

After one sample has been crushed and split, the pans, riffle, and crusher should be cleaned before starting with the next

sample. When compressed air is available a pressure hose and valve may be arranged so that a blast of air can be used in cleaning. When air is not available the cleaning must be done with brushes. If the crushing room is not well ventilated the sampler should wear a respirator to avoid continual breathing of fine rock dust.

After the assay samples have dried they are passed through a pulverizer set so that the product will pass a 100-mesh screen.



1. Bypass 1st riffle with small samples
2. Use of cocktail shaker for mixing pulps suggested by H. R. Bramel

FIG. 4.—Typical preparation of mine samples for assay.

Then the dried and pulverized samples, called "assay pulps," are placed in heavy paper envelopes, each marked with the sample number.

Taking the Assay Portion.—The assay pulps are transported to the fluxing bench where the final assay portion is weighed. Two methods of taking the assay portion are available: the usual method with a sampling cloth and a rapid method with a cocktail shaker.

In the usual method of taking the assay portion the assay pulp is poured onto a square sheet of rubberized cloth and mixed by rolling the material back and forth from corner to corner of the cloth. At least 60 rolls are generally given; the material is then smoothed into a flat cake with a horizontal spatula stroke. From the mixed and flattened assay pulp, small dips are taken with a spatula at more or less regularly spaced intervals and placed on the pan of the pulp balance. When just a little more than the desired weight has been placed on the balance pan, a small portion is removed with the spatula and held immediately above the pan on the balance. Then the spatula is tapped with the finger to shake material, little by little, onto the pan until the desired weight is obtained. The remainder of the assay pulp is transferred back to its bag, and the sampling cloth is brushed clean before starting with the next sample.

When the rapid method of taking the assay portion is used, the assay pulp is poured into a cocktail shaker and given about 20 shakes. Then, with a single scoop just a little more than the desired assay portion is taken and placed on the balance pan. A small portion of the material is then removed from the pan and tapped back, little by little, onto the pan until the desired weight is obtained. The remainder of the assay pulp is then poured into its bag, and the shaker is brushed clean before starting with the next sample.

The rapid method is easier and takes about half the time of the usual method. Quicker and more thorough mixing of finely ground materials can be obtained in a cocktail shaker than on a rolling cloth, but taking the assay portion with a single scoop is theoretically not quite so reliable as taking it with 10 or 15 small spatula dips. In practice, no significant difference is found between assay portions taken by either method from ordinary samples.

Sampling of Large Amounts of Broken Rock.—The methods used for the sampling of large amounts of broken rock depend upon the material to be sampled and the expense justified by the importance of the sample. Highest accuracy is desired at custom smelters where rich ore and concentrates are purchased. Payment for a shipment is based upon the valuable metal contained in the shipment, and this is determined by (1) weighing, (2) taking a

moisture sample to find the moisture content, and (3) taking an assay sample to find the valuable-metal content.

A satisfactory moisture sample is difficult to obtain. Generally a grab sample of about 10 lb. is taken for the moisture sample, just after the shipment has been weighed and while it is being unloaded. The moisture sample is weighed soon after it is taken, after which it is dried at 110°C., and the moisture is considered to be the loss in weight. When the material contains large chunks of rock as well as fine material a sample as small as 10 lb. is not likely to represent accurately the moisture content.

This difficulty may be avoided by splitting the moisture sample from the crushed material during the preparation of the assay sample. When the moisture sample is taken from the crushed material a correction is made for the drying that takes place during the crushing and sampling operations. The average percentage loss of moisture during sampling is determined by experiment for different seasons of the year, and these corrections are arbitrarily applied to subsequent moisture determinations.

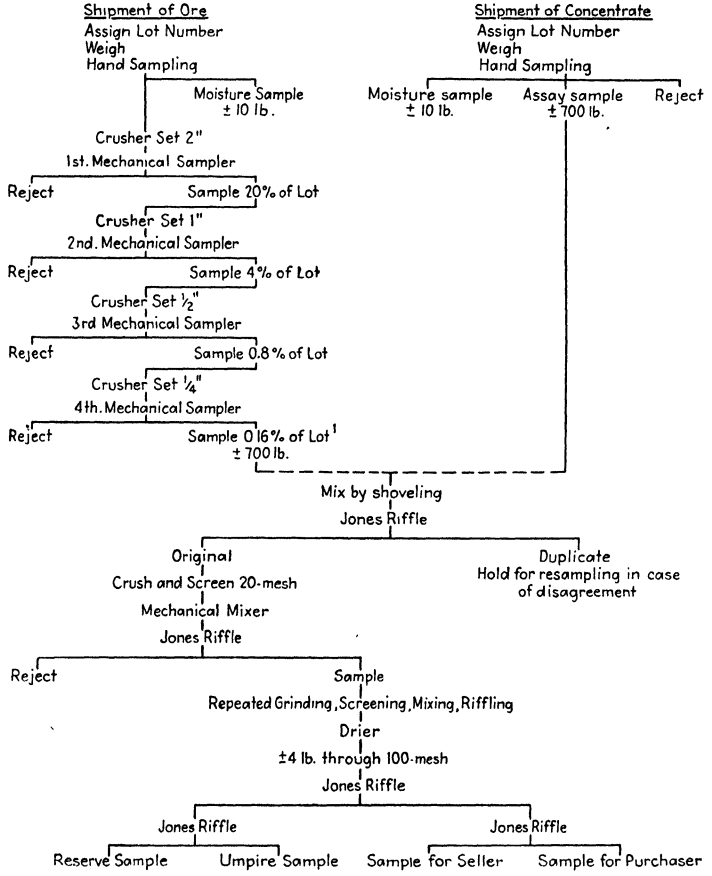
The assay sample is taken by hand sampling or machine sampling. Finely divided materials such as flotation concentrates are usually sampled by hand sampling methods, while ores containing coarse rock are passed through a sampling mill consisting of alternate crushers and mechanical samplers.

A diagram typical of the sampling operations at a Western lead smelter is given in Fig. 5. At mills or smelters where the sampling operation does not justify the expense of mechanical sampling equipment, hand sampling methods are used entirely.

Hand Sampling Methods.—The common methods of hand sampling are shovel sampling, coning and quartering, and pipe sampling.

Shovel sampling or fractional shoveling consists in taking for the sample a shovelful at regular intervals while the material to be sampled is being shoveled from one place to another. This is the best hand sampling method for lump ore and gives satisfactory results, if the material has been crushed to at least 2 in. and portions for the sample are taken at sufficiently close intervals, and provided that the operator does not deliberately select either rich or low-grade material for the sample.

Coning and quartering has been widely used for sampling small lots of crushed ore. It consists in shoveling the crushed ore into a conical pile, which is then flattened and divided into quarters.



[1] With small lots, bypass first samplers

FIG. 5.—Typical sampling at a custom smelter.

Opposite quarters are rejected, and the remaining quarters are taken for the sample.

When forming the cone it is essential that the apex of the cone be kept in a vertical line. A segregation of fine ore takes place

at the center of the cone, and, by drawing the cone to one side, it is possible for the operator deliberately to vary the grade of the sample. Coning and quartering is being replaced by shovel sampling, as shovel sampling requires less work and gives samples of greater reliability.

Pipe sampling is carried out by driving a pipe vertically down through the material to be sampled and withdrawing a core of material that clings to the inside of the pipe. The pipe is then tapped with a hammer to remove the sample from the pipe. This method can be used only for sampling finely crushed material, such as flotation concentrates, through which the pipe can be driven. The sample should be taken all the way from top to bottom of the material being sampled, and the sample of a large lot should be made up of material taken with the pipe driven at regularly spaced intervals through the material. Pipe sampling is a rapid and easy method of obtaining reliable samples of fine material.

Mechanical Sampling.—Mechanical sampling machines are either stationary or moving. Moving machine samplers, such as the Vezin or Brunton type, cut across a falling stream of ore at intervals, taking all the stream a portion of the time. The machines should be designed so that all parts of the ore stream are represented in their correct proportions. To avoid clogging, the width of the sample opening should be at least three times the size of the largest pieces of ore. Moving machine samplers give good results with materials that flow freely. They have a low cost of operation and are widely used for sampling large amounts of material.

Moving machine samplers are not suitable for sticky materials that will clog the opening. Consequently, concentrates are usually sampled by hand.

Stationary machine samplers have a fixed cutter and take a portion of the ore stream all the time. A falling ore stream is likely to have the coarse and fine material segregated so that one part of the stream may be richer or poorer than the rest.

The Jones riffle is the most widely used stationary mechanical sampler. It avoids the difficulty caused by segregation, by taking continuously small fractions from many parts of the ore stream. It is generally used for dividing samples that have been reduced to the point where they are handled by hand. The

openings in the Jones riffle should be large enough so that they do not become clogged and yet narrow enough so that many cuts enter the sample. Usually alternate cuts enter the sample and reject. There should be an even number of divisions so that the division at one end enters the sample and that at the other end enters the reject.

Sampling Material Containing Metallics.—Ores that contain coarse malleable particles should not be sampled and assayed in the ordinary manner. The malleable particles cannot be readily broken into small pieces, and the chance presence or absence of large fragments of valuable minerals in the assay portion causes serious variations in the assay result. Malleable particles likely to be encountered in ores are native gold, native silver, native copper, and cerargyrite. When large particles of any of these minerals are present, a "metallics assay" should be made.

Metallics Assay.—The metallics assay consists of the following steps:

1. Crush the ore sample to about the size of the malleable particles.
2. Take a metallics-assay portion so large that chance variation in distribution of valuable minerals will not disturb the reliability of the sample more than can be allowed.
3. Separate the coarse metallics from the bulk of the sample and weigh them.
4. Recover the gold and silver from the coarse metallics.
5. Assay the remaining bulk of the metallics-assay portion by ordinary methods.
6. Calculate the total gold and silver in the original metallics-assay portion.
7. From the total gold and silver in the metallics-assay portion calculate, by proportion, the amount per assay ton.

Crushing a Metallics Sample.—Materials containing metallics can be crushed by ordinary methods to about the size of the metallic particles. Further crushing by grinding between two rubbing surfaces, as in a disk pulverizer, causes the malleable particles to roll into cylindrical and spherical shapes, and part of the malleable minerals is rubbed into the grinding surfaces. Crushing by rolling action is much to be preferred, as there is less danger of salting the crushing equipment and because the malleable minerals are rolled into flat flakes, which can easily be

separated by screening. Roll crushers, or a grinding pan with a heavy iron roller, such as those used for working clays, are desirable for fine crushing samples containing metallics.

Taking the Metallics-assay Portion.—The minimum allowable weight of the metallics-assay portion depends upon the reliability desired, the metal content of the large metallics, and the grade of the ore. The relation of these factors to the weight of sample is expressed by Eq. (8). An example of its use is given below:

Conditions

1. One kilogram of the crushed ore is concentrated by panning. About 50 g. of concentrate is obtained, which consists of pyrite with some free gold.
2. Six comparatively large pieces of free gold are visible. The largest weighs close to 0.5 mg. and is estimated to be about 800 fine.
3. An assay accurate to 0.02 oz. of gold per ton of ore is desired.

Solution

Substitute values in the equation

$$\sigma_x = \sqrt{\frac{AC}{W}}$$

σ_x = one-third of the allowable error = 0.02/3 = 0.007
A = the assay of the ore due to coarse metallics
Gold in 1 kg. = (6 particles) (0.5 mg. weight) (0.8 fineness correction) = 2.4 mg.

$$\text{Gold per assay ton} = A = (2.4)\frac{29.166}{1{,}000} = 0.07 \text{ mg.}$$

C = gold in one large metallic particle = (0.5)(0.8) = 0.4 mg.

Substituting and solving for W,

$$0.007 = \sqrt{\frac{(0.07)(0.4)}{W}}$$

$$W = 571 \text{ A.T. or about } 37 \text{ lb.}$$

After the desired weight of the metallics-assay portion has been determined, a sample of about that weight is cut from the crushed

ore by standard sampling methods. This sample is then weighed and its weight recorded.

Separation of the Coarse Metallics.—Three processes are available for the separation of coarse metallic particles from the metallics-assay portion:

1. Screening.
2. Concentration.
3. Amalgamation.

Screening is ordinarily used to separate the malleable particles from the metallics-assay portion. It is carried out in stages, starting as soon as the malleable particles begin to interfere with crushing, and is continued during crushing, using increasingly finer screens until finally a pulp free from coarse metallics is obtained. The final screen size should be at least 100-mesh, and for accurate work should be 150- or 200-mesh. Some brittle minerals may be allowed to remain on the screen with the metallics, but the group of metallics must be of small enough bulk so that it can be put through the assay process. The weight of the metallics should be recorded.

Concentration is commonly used to separate metallics in the assay of placer gravels. It can also be used in the metallics assay of ores, but, when a large amount of sulfide minerals is present in the ore, the complete separation of the metallics by this method is difficult. The concentration separation is made with a gold pan or other gravity concentration device. With placer gravels the separation is frequently so complete that only the concentrate need be carried on through the assay process, and the tailings may be discarded. A considerable amount of black sand, however, often collects in the concentrate and makes it too bulky to be economically put through the assay process. In this case the concentrate itself may be given a metallics assay, using either screening or amalgamation to separate the coarse gold.

Amalgamation is particularly suited to the recovery of metallics from gold ores. It is carried out by grinding the metallics-assay portion in a grinding pan or an amalgamation barrel with water and mercury. The mercury, with the metallics that amalgamated, is then collected by panning or some other gravity concentration method and is assayed to determine the gold and silver that amalgamated. The tailings from amalgamation are dried and assayed by ordinary methods.

Recovering the Gold and Silver from the Coarse Metallics.—All the coarse-metallics fraction obtained from the metallics-assay portion must be treated to recover its gold and silver. That from screening or concentration is usually treated by the crucible assay (Chap. VII). Scorification (Chap. VIII) could be used, but this method is not suitable for handling more than about 2 g. of basic impurities.

The mercury with amalgamated metallics from the amalgamation separation can be assayed by the nitric acid method or by distillation in a crucible assay charge. If gold is the only metal sought, the nitric acid method is suitable. The mercury and amalgam are heated in a beaker with nitric acid until the mercury is dissolved. The residual gold is washed, dried, and weighed. Inquartation and parting (Chap. V) are not required unless large pieces of gold that did not amalgamate all the way to the center are present.

When silver as well as gold is to be determined in mercury and amalgam, distillation in a crucible assay charge is used for the method of assay. The mercury and amalgam are placed in the bottom of a 30-g. crucible and covered with a 1-assay-ton crucible charge corresponding to a crucible charge for a quartz ore, using assay silica and fluxes in accordance with the principles discussed in Chap. VII.

Liquid mercury dissolves about 1 mg. of gold per gram of mercury, so that even though the mercury used in the amalgamation assay has been squeezed through a chamois it cannot be assumed to be gold free. An assay should be made on another portion of the mercury used in the process, and the gold and silver found should be deducted from the amalgamation assay.

Calculating the Metallics Assay.—The weight of the metallics fraction is subtracted from the weight of the metallics-assay portion to obtain the weight of the pulp after separation of the metallics. The gold and silver content of this pulp is calculated from its weight and assay. To this amount of gold and silver is added that obtained from the metallics. The sum represents the total gold and silver content of the metallics-assay portion. The gold assay of the material is then found by dividing the gold in the metallics-assay portion (in milligrams) by the weight of the metallics-assay portion (in assay tons). An example is given below:

Conditions

1. Metallics-assay portion taken with a Jones riffle. Weight = 18.365 kg.
2. Weight of metallics = 11 g.
3. Gold in metallics = 56.12 mg.
4. Gold assay of pulp = 0.34 oz. per ton

Solution

Weight of pulp = 18,365 − 11 = 18,354 g.
Gold in pulp: 18,354 = 0.34:29.166
Gold in pulp = 213.96 mg.
Total gold = 213.96 + 56.12 = 270.08 mg.

$$\text{Assay-ton weight of metallics-assay portion} = \frac{18{,}365}{29.166} = 629.67$$

$$\text{Assay of the ore} = \frac{270.08}{629.67} = 0.43 \text{ oz. of gold per ton of ore}$$

Usually the weight of the metallics fraction is negligible in comparison with the weight of the metallics-assay portion. Then the assay of the pulp plus a proportional part of the gold or silver in the metallics equals the assay of the ore. The proportional part of the gold or silver in the metallics is the gold or silver in the metallics divided by the weight of the metallics-assay portion in assay tons. In the example just given, the proportional part of the gold in the metallics is 56.12/629.67 or 0.09 mg. of gold per assay ton. The gold assay of the pulp, 0.34, plus 0.09 equals 0.43 oz. of gold per assay ton—the gold assay of the ore.

Sampling Metals

Liquid metals are usually capable of dissolving other metals to form homogeneous liquid solutions. The precious metals are dissolved and collected in this way at a lead smelter by the blast-furnace lead, and at a copper smelter by blister copper. These bullions usually contain more lead or copper than the lowest melting alloy in their series of alloys with the precious metals. Consequently, as the bullions cool, the first solid to form is poorer and the last is richer than the original solution. When the liquid is cooled rapidly the constituents of different grade form in small grains and do not have time to segregate. With slow cooling,

as when the bullion is cast into a large bar or cake, segregation takes place and the precious metals are not uniformly distributed.

Sampling Solid Metals.—Solid metals are sampled by drilling, sawing, or punching. The samples should be taken in a manner that will secure representation of all parts of the metal, because solid metals are likely to be segregated.

With saw sampling, every fifth or tenth bar poured from one lot of molten metal is sawed across the middle. The sawdust is mixed and sampled similarly to a crushed ore.

When metals are sampled by drilling or punching, a template is used to distribute holes over the surface of the bars. The holes are drilled all the way through the bars. When a large number of bars are poured from a melt, one hole is drilled in each bar, following the order of the template. Thus the combined drillings represent all parts of the bars.

Sampling Liquid Metals.—Liquid metals are sampled by taking a dip from the molten bath with a ladle or by batting shot from a stream of metal as it is being poured. If a ladle is used it should be preheated so that the sample will not start to solidify until it is poured in water to granulate and cool it quickly. In the method of batting shot from a stream of molten metal a wooden paddle is used, and the shot is batted into a pan of water.

Shot produced by either method is fairly homogeneous because it has been poured from a melt and quickly cooled. Low-grade bullions require comparatively large assay portions, and the assay portion is weighed directly from the dried shot. The assay portion required in the assay of gold and silver bullion is comparatively small. Generally a few shot are rolled into thin strips with bullion rolls, and the assay portion is snipped from the strips with shears.

Sampling Aqueous Solutions

Sampling and assaying of aqueous solutions are required for the control of hydrometallurgical processes. Solutions are homogeneous with regard to dissolved constituents, and segregation does not take place in the liquid to be sampled except when it contains suspended solids. Two types of fluids are sampled at hydrometallurgical plants: (1) homogeneous solutions free from solid particles that will settle, and (2) pulps consisting of solid particles mixed with solutions.

Sampling Homogeneous Solutions.—Any portion taken from a homogeneous solution represents instantaneously the solution from which it was taken. Solutions in process may change in grade with time; consequently, fractions of sample should be taken at short time intervals to obtain a sample representative of a solution during a considerable interval of plant operation such as a shift or a day. Samples should be collected in containers that expose as little surface of liquid as possible to the atmosphere, in order to minimize enrichment due to evaporation.

Instantaneous samples, dipped out once a shift, are usually satisfactory for sampling large tanks of solution where the grade does not change rapidly.

An almost continuous sample can be taken from a falling stream of solution by a wire mounted so that it slants downward across the stream. Drops of solution run out along the wire and are caused to drop into a narrow-mouthed sample bottle by means of a string tied around the wire and hanging down into the bottle. When both rate of solution flow and grade of solution vary from time to time, the drip sample is not accurate, as it does not accumulate at a rate proportional to the flow being sampled.

Several types of moving machine samplers, which take samples proportional to the flow of a falling stream of solution or pulp, are on the market. These samplers move a sample cutter across the stream at regular intervals of time and remove a fraction of sample at each cut which is proportional to the stream.

Sampling Mixed Solids and Solutions.—A flowing stream of solution containing suspended solids, such as the tailings from a slime cyanide plant, is best sampled by means of a moving machine sampler. After the complete sample has been taken it is advisable to separate the solids and solution and to assay them separately.

Solids and solution are separated by settling and decantation or by filtration. A portion of the clean solution should be taken for the solution sample before dilution with wash water. The remaining solids should be washed before being dried for assay.

CHAPTER III

WEIGHING

In the fire assay of a material an assay portion is weighed from which the gold and silver are recovered and weighed. The proportion of weight of gold to that of ore and weight of silver to that of ore expresses the assay of the ore. Different units are used in different countries for the assay proportion.

Units Used in Assaying.—In the United States, Canada, and South Africa the assay proportion is expressed in troy ounces[1] of gold and silver per short or net ton (2,000 avoirdupois lb.) of ore.

A system of assay-ton weights is used in weighing the assay portion. The assay ton contains the same number of mg. (29,166⅔) as there are troy ounces in a short ton. Therefore, 1 assay ton : 1 mg. = 1 short ton : 1 troy oz. The milligrams of precious metals per assay ton indicates the assay in troy ounces per short ton.

In England and Australia the long or gross ton of 2,240 lb. is used, which has an equivalent assay long ton of 32.667 g. The gold assay in British countries is commonly reported in pennyweight (dwt.), a troy weight containing 1/20 troy oz.

In Mexico, South America, and other countries using the metric system the gold assay is reported in grams per metric ton, and the silver assay is reported in kilograms and grams per metric ton. The metric ton contains 1,000,000 g.; consequently, 1 mg. of gold from a 10-g. assay portion indicates 100 g. of gold per metric ton of ore. With larger assay portions the indicated assay per milligram is divided by the coefficient used to increase the assay portion, in order to find the assay per milligram of gold. For example, 1 mg. from a 30-g. assay portion indicates $\frac{1000}{30}$ or 33⅓ g. per ton of ore.

A comparison of assay proportion units is given in Table IV.

[1] The troy ounce contains 31.1035 g., and should not be confused with the avoirdupois ounce of 28.3495 g.

Assays of lead and copper bullion are reported in the same units used for ores. Gold and silver bullion assays are universally reported in fineness or parts per thousand. For example, sterling silver contains 92.5 per cent silver and, consequently, is 925 fine. The fineness of gold jewelry is reported in carats or twenty-fourth parts. Twenty-four carat gold is pure gold, and eighteen-carat gold is $^{18}/_{24}$ or 75 per cent gold. The term "carat" is also used as a unit of weight for precious stones. An international weight carat contains 200 mg.

TABLE IV.—COMPARISON OF ASSAY PROPORTION UNITS

Ounces per short ton	Ounces per long ton	Pennyweight per long ton	Grams per metric ton
1.00	1.12	22.40	34.23
0.89	1.00	20.00	30.61
0.04	0.05	1.00	1.53
0.026	0.033	0.65	1.00

Size of the Assay Portion.—The size of the portion of ore weighed for the assay process ranges from $^1/_{20}$ assay ton to 3 assay tons. As the size of the assay portion is increased, the cost of the assay increases because of a reduction in furnace capacity and an increase in the fluxes required. On the other hand the larger the assay portion the more reliably it represents the material from which it was taken and the smaller the percentage of error in weighing the metal obtained from the process. The gold and silver recovered from the assay portion are weighed on an assay balance, the best of which are sensitive only to about 0.002 mg. Therefore, if an accuracy of 1 per cent is required, the assay portion should be large enough to produce at least 0.2 mg. of metal. Most silver ores assay more than 5 oz. of silver per ton; consequently, assay portions as small as $^1/_{10}$ assay ton are satisfactory from a weighing standpoint. Low-grade gold ores require large assay portions, and frequently more than 3 assay tons should be used. This can be accomplished by scorifying together the lead buttons from two or more fusions of separate assay portions.

Weighing the Assay Portion.—The balance used to weigh the assay portion is called a "pulp balance." An unenclosed balance, sensitive to 1 mg. and having a pan that will hold 60 g. of pulp, is satisfactory. High accuracy is seldom required. The gold

obtained from an assay is weighed to the nearest 0.005 mg. and a variation of less than 0.002 mg. can scarcely be detected. If, for example, an ore contains less than 3 oz. of gold per ton, a deviation of 20 mg. in weighing a 1-assay-ton portion does not affect the assay result by a weighable amount. This is shown by the following proportion:

Assay portion : gold recovered = variation in assay portion : minimum weighable gold

29,167 mg. : 3 mg. = 20 mg. : 0.002 mg.

Aside from the minimum-weighable-bead consideration a variation of 20 mg. in a 1-assay-ton portion amounts to less than 0.07 per cent, an amount well below the other errors in an ordinary assay. Rich materials, from which accurate assay portions of less than ½ assay ton may be taken, should be weighed on a balance of greater sensitivity than the ordinary pulp balance. Large assay offices usually have an "analytical" balance available for this purpose. Assay portions of gold or silver bullion are commonly weighed on the balance used for weighing the final gold and silver.

The methods of taking the assay portion from crushed ore pulps are described on page 27. Taking an exact assay portion from samples of metals causes difficulty, particularly when the individual pieces of metal in the sample are comparatively large. Occasionally time can be saved by taking a portion approximating the desired assay portion, weighing this portion exactly, and then calculating each assay on the basis of the particular assay portion used.

Weighing the Gold and Silver.—The gold and silver recovered in the fire assay are weighed on a sensitive balance known as the "assay" or "button" balance. When both gold and silver are to be determined, the doré bead from cupellation is weighed. It is then parted, and the gold is weighed. Silver is determined by subtracting the weight of gold from the weight of the doré bead. The doré bead weight is used only for the determination of silver, and the weighing need be no more accurate than that required for the silver assay. For most work a variation in the silver assay of as much as $\frac{1}{10}$ oz. per ton is allowable; consequently, with ½-assay-ton portions of ore the doré bead need be weighed only to the nearest 0.05 mg. The gold is always weighed at least

to the nearest 0.005 mg., which is about the limit of accuracy of the assay balance.

Assay Balance.—The assay balance consists of a light trussed beam supported by a fulcrum knife-edge in the center and carrying a knife-edge bearing on each end, from which hang small pans by light short stirrups. The horizontal top of the beam is graduated with 100 divisions on both the left-hand and right-hand side for riders. Near the center, small star wheels are provided on both sides for equilibrium adjustment, and, extending downward from the center of the beam, a short threaded shaft carries a threaded weight, which can be screwed up or down to change the center of gravity of the balance. The pointer usually extends vertically upward from the center of the beam and terminates in front of a fixed scale for observing the oscillations of the beam. A mechanism is provided for raising the beam to arrest its motion. This mechanism also separates the knife-edge bearings and supports the pans. The beam arrest is released by turning a knurled knob at the front of the balance, which lowers the beam and pans onto the knife-edges, allowing the beam to swing.

The balance is enclosed in a glass-paneled case equipped with level bubbles and supported by leveling screws. Usually the front panel or door of the balance must be raised to place the bead on the pan or to change weights, beyond the 1-mg. variation possible with the rider. Multiple-weight attachments, having a keyboard arrangement for adding or subtracting weights without opening the balance door, are available. One make of balance can be purchased with a mechanical pan extractor for carrying the weighing pan out through a crystal shutter in the balance door. The mechanical pan extractor, together with the multiple-rider attachment, facilitates weighing but nearly doubles the cost of the balance.

Assay balances are built with maximum load capacities of 1, 2, and 5 g. The largest loads commonly used are 500-mg. assay portions of gold or silver bullion, so that a capacity of 1 g. is sufficient for all ordinary work.

The sensitivity of a balance is expressed in terms of the smallest weight that causes a measurable deflection in the point of rest, or in terms of the angle of deflection of the point of rest caused by a unit of unbalanced load. Assay balances are rated by the first

method, and balances can be obtained sensitive to $\frac{1}{200}$ mg., $\frac{1}{300}$ mg., or $\frac{1}{500}$ mg. The time of oscillation increases with the sensitivity; a good $\frac{1}{200}$-mg. balance will swing to one side and back in about 4 or 5 sec., while a $\frac{1}{500}$-mg. balance requires 7 or 8 sec. The sensitivity of a balance can be decreased below its rated value, and at the same time faster weighing is obtained by lowering the center of gravity. Raising the center of gravity to increase the sensitivity of the balance beyond the manufacturer's rating causes the balance to become unstable. It is desirable to have two assay balances: (1) a balance of comparatively low sensitivity for rapidly weighing doré beads, and (2) a balance of high sensitivity for weighing gold. Assay balances are constructed with the three knife-edges in one plane so that the center of gravity is not changed with increase of weight on the pans. Increased load decreases the sensitivity slightly, owing to the increased mass of the loaded beam assembly.

Assay balances are very delicate and should be installed in a room that is as free as possible from dust, vibration, and rapid temperature changes. The balance should be mounted on a rigid bench having a top about 26 in. from the floor. This height of bench places the balance in a convenient position for an operator sitting on a stool of ordinary chair height. If 2-in. planks are used for the bench top, side support is not required and the operator can place his knees under the bench. It is advisable to support the balance bench on concrete columns extending down through the floor to the ground. The effect of vibration on the balance can be reduced by placing rubber cushions under the balance rests that support the leveling screws of the balance. Sunlight causes rapid temperature changes in the balance room and should be excluded. In moist climates it is desirable to keep a small vessel containing desiccant in the balance case. Some assayers ground the rider carrier to discharge any static electricity that might accumulate on the beam.

Operating the Assay Balance.—Each time it is used the assay balance should be tested for adjustment by the following operations:

1. Brush the balance free from dust.

2. Pick up the balance pans with ivory-tipped forceps and brush them with a small brush to make sure they are empty.

3. See that the balance is level and that the balance beam, hanger, stirrups, and pans are in their proper positions.

4. Move the right or weighing rider to zero on the right-hand side of the balance beam.

5. Release the balance beam and adjust to "equal swings" by moving the left or equilibrium rider along the left-hand side of the balance beam. The balance door should always be closed to exclude air currents when testing for equilibrium.

The beam arrest should be released only for testing equilibrium; it should be up to support the beam and stirrups whenever changing weights or doing anything that will jar the balance. Care should be taken to raise the beam arrest slowly, particularly when the beam is tipped to one side.

Beads to be weighed are placed in the left or weighing pan of the balance. Large doré beads may be picked up with forceps and dropped on the pan while it is in place on the balance. Gold and small doré beads are best added from a parting or annealing cup. This is done by moving the weighing pan to the front of the balance case.[1] Then tip the parting cup, tapping it gently to cause the bead to slide from the cup to the pan. Particles of gold sometimes stick in the parting cup and must be dislodged by gently poking them with the forceps or by brushing with a feather. The pan containing the bead to be weighed is then placed in position on the balance.

An estimate of the weight of the bead is made, and the estimated weight is added to the right-hand side of the balance. The beam is then released to test for equilibrium. A practiced assayer can estimate, from the rate at which the beam moves when released, the amount of weight to add or subtract to bring about equilibrium. After the weight correction has been made, the beam is again released. If the beam does not swing, or if it swings only a short distance, the weight is close enough for doré and silver beads. This is known as weighing by "no deflection."

When weighing gold the balance equilibrium should always be checked by the method of "equal swings." To determine equilibrium by equal swings, start the beam swinging by raising the balance door and gently fanning one pan with the hand or,

[1] Ivory-tipped forceps should be used to handle the balance pans as well as for the manipulation of weights.

with the door closed, raise one rider from the beam for an instant. Then, with the balance door closed, observe the movement of the pointer as it oscillates from side to side. The amplitude of swing slowly decreases, but at equilibrium the pointer swings nearly the same amount on either side. When it swings consistently farther to one side than the other, shift the weighing rider in the required direction and again test for equal swings. The process is continued until equilibrium is reached. Most beginners have difficulty in estimating the amount of unbalanced load by the way in which the balance swings and, consequently, many trials are required to reach final equilibrium.

Facility in the use of the assay balance can be quickly acquired by using the "deflection method" of weighing. For this method of weighing, the beam release mechanism of the balance must be adjusted so that it does not start the beam swinging when released in balance. Then when released with a small unbalanced load the beam will swing to the side of the unbalanced load, and the amount of deflection is proportional to the unbalanced load. The balance can be calibrated, and a chart of unbalanced load for various amounts of deflection prepared for use in weighing. To weigh by the deflection method the operator proceeds by estimation and cut and try until within the maximum deflection of the balance. The first deflection after release is measured, and from the chart the corresponding unbalanced load is read. The correction (positive if the swing is to the left and negative if the swing is to the right) may be made arithmetically and the result considered the true weight, but it is safer actually to make the weight change and test for equilibrium by the method of equal swings.

CHAPTER IV

CUPELLATION

Cupellation is an oxidizing fusion of an alloy of lead, gold, and silver in an absorbent vessel known as a "cupel." During cupellation the lead is oxidized to litharge (PbO), most of which is absorbed by the cupel, leaving at the finish a bead of gold, silver, and most of the platinum and associated metals that may be present. The bead is subsequently treated to determine its precious-metal content.

Cupellation is a fundamental part of all fire assay procedures, whether the lead–precious-metal alloy is the button from a crucible or scorification fusion of an ore sample, a sample of lead bullion, or a synthetic mixture produced by adding lead to gold or silver bullion or to chemical precipitates high in gold and silver.

The process of cupellation is responsible for the greatest normal errors in the fire-assaying process, and in order to obtain consistently reliable results all factors in the cupellation process must be controlled in such a manner as to favor low losses of gold and silver.

The chief source of error in cupellation is the loss of silver and, to a lesser extent, of gold by absorption into the cupel. This loss is increased by increased cupellation temperature, especially toward the end of the process, or by the presence of impurities, some of them in minute amounts that either lower the surface tension of precious metals or necessitate increased cupellation temperature. The properties of the cupel also exert an influence on cupel absorption. Unless cupellation temperatures are abnormally high the loss of precious metals by volatilization is negligibly small.

Cupels.—A cupel is a porous cylinder or inverted-cone frustum of refractory material with a cupped depression in the upper end for retaining the lead button. In modern practice, cupels are made of bone ash, cement, bone-ash–cement mixtures, or mag-

nesia. Magnesia cupels are purchased as a finished product, but the others are usually made at the assay office.

Manufactured cupels and cupel-machine dies are available in a number of sizes, the commonest of which are 1¼ in. and 1½ in. in diameter and hold, respectively, a maximum of approximately 32 and 45 g. of lead. The height of the cupel must be such that the total volume of the cupel material is sufficient to absorb most of the litharge produced in cupellation, as nearly 98.5 per cent of the total litharge that is formed is absorbed by the cupel. Bone-ash cupels absorb a weight of litharge about equal to their own, cement cupels absorb slightly less than their weight, and magnesia cupels absorb three-fourths of their weight. Magnesia cupels are denser than bone-ash or cement cupels, hence a magnesia cupel of a given volume absorbs as much litharge as a bone-ash cupel of the same volume. A height of 1⅛ in. will provide approximately sufficient volume to absorb the litharge from buttons of the maximum size that can be handled in cupels 1¼ or 1½ in. in diameter. Cupellation losses vary slightly with cupel height, particularly if there is much height variation in a given row in the cupellation furnace. Hence it is preferable to standardize the cupel height and to keep within a maximum tolerance of ±1/16 in. from the standard.

The shape of the cupel cup has been thoroughly investigated by King,[1] who recommends either of the compound shapes shown in Fig. 6, in preference to the continuously concave, approximately spherical shapes in common use. King states the advantages of the improved cups as follows:

a. The small deep finishing cup protects the alloy near the bead stage from air draught, giving a slow oxidation rate and a consequent lower temperature. This protection gives lower losses where the loss rate is highest (at the finish), and reduces the hazards of sprouting.

b. The rapid cupellation at the start is due to the general convex shape or elevation of the main upper areas. The higher temperature thus produced materially assists in the elimination of impurities if present, at a time when lead is sufficient to protect silver from heavy loss.

c. The effective air draught is relatively automatically controlled; this advantage held at different temperatures and with various amounts of lead.

[1] KING, J. T., The Influence of Cupels on Silver Loss, *Univ. Toronto Bull.* 147, pp. 50–66, 1934.

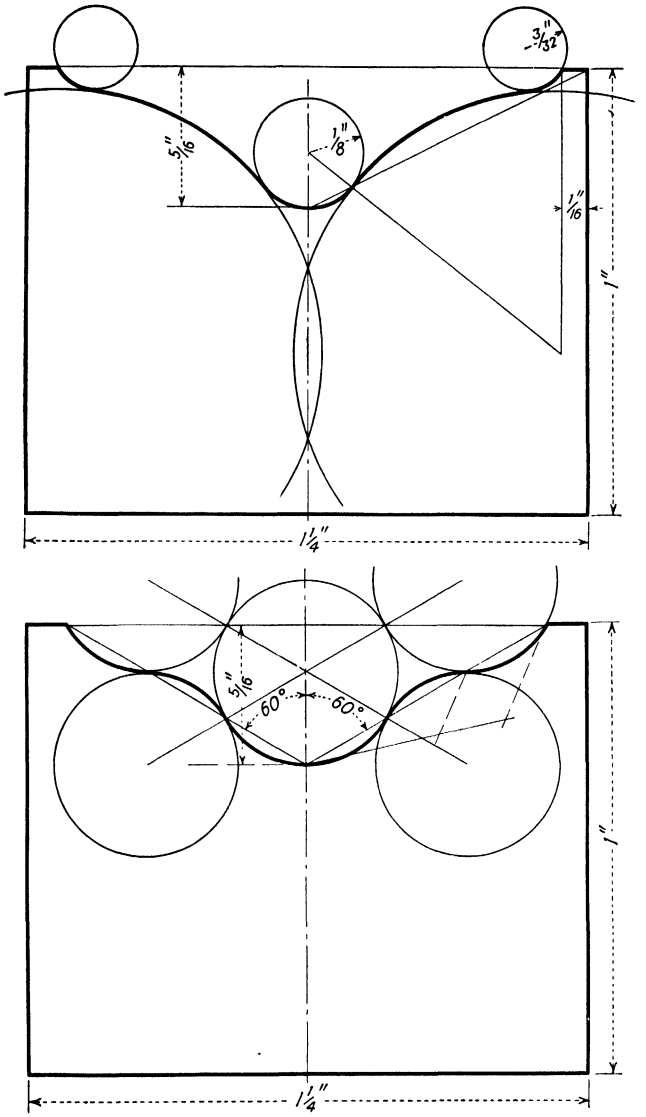


FIG. 6.—Cupel cup shapes recommended by J. T. King. (*Reproduced by permission from Univ. Toronto Bull.* 147.)

d. Since the loss is reduced, the bead more nearly represents the original quantity of silver present.

With a standard 1¼-in. bone-ash cupel having a simple spherical cup 0.201 in. deep, the cupellation loss with the improved cups was 1.65 per cent on 100 mg. of silver, compared to 2.13 per cent with the standard cupel. Similar results were obtained with 1½-in. cupels. King's work on cupel-cup shapes was done with 100 per cent bone-ash cupels, and it is not conclusive that his improved shape will show equal advantages with cupels of other materials, particularly of magnesia, which has very different thermal properties from bone ash or cement.

Bone-ash Cupels.—Bone ash is made by the calcination of animal bones and varies in composition according to the type of bones and the care taken in the manufacturing process. Clean, properly burned sheep bones contain approximately 90 per cent tricalcium phosphate, 5 per cent calcium oxide, 1 per cent magnesium oxide, and 3 per cent calcium fluoride. Commercial bone ash may contain some silica, from incomplete cleaning of the bones, and some carbon from incomplete calcination. Alkali sulfates and carbonates may also be present, owing to insufficient removal of organic matter before burning the bones. Calcium nitrate may be formed by the combination of free CaO in the bone ash with nitrous fumes in the laboratory. Calcium carbonate may also be formed in the same manner by prolonged exposure to the CO_2 of the atmosphere. The presence of organic matter and of carbonates, nitrates, and other salts that decompose at cupellation temperature (850 to 900°C.) or lower is undesirable, as the evolution of gases during cupellation causes loss by "spitting" of the lead.

Commercial bone ash is supplied in various grades, based upon the particle fineness. The grades marketed by the Denver Fire Clay Company are designated X, XX, XXX, and XXXX, in the order of increasing fineness. The average screen analyses of these four grades as reported by King[1] are given in Table V. King was unable to detect any appreciable variations in silver loss with cupels made from any of these grades, but he did find that a gradation of particle size and the absence of particles larger than 35-mesh were essential to low cupellation loss,[2]

[1] *Ibid.*, p. 12.

[2] *Ibid.*, pp. 31–38.

and that smooth cups are preferable to roughened cups. Coarse particles should be avoided, as they cause high erratic losses and adherence of the bead to particles of the cupel, making it difficult to clean the bead.

TABLE V.—AVERAGE SCREEN ANALYSES OF FOUR BONE-ASH GRADES*

Mesh	Grade of bone ash							
	X		XX		XXX		XXXX	
	Per cent	Per cent cumulative	Per cent	Per cent cumulative	Per cent	Per cent cumulative	Per cent	Per cent cumulative
35	0.17	0.17						
48	11.5	11.7	1.9	1.9	0.1–	0.1	0.02	0 02
65	13.7	25.4	10.8	12.7	0.8	0.9	0.33	0.39
100	18.3	43.6	21.0	33.6	18.1	19.0	14.6	15.0
150	13.7	57.4	15.3	48.9	18 7	37.7	22.3	37.3
200	5.6	63.1	5.2	54.1	6.9	44.5	7 0	44 3
270	7.1	70.0	7.2	61.3	9.8	54.3	7.9	52.2
−270	29.9	.....	38.6	....	45.6	....	47 9	
Total...	100.0	.....	100.0	....	100.0	...	100.0	

* KING, J. T., The Influence of Cupels on Silver Loss, *Univ. Toronto Bull.* 147, p. 12, 1934. Reproduced by permission.

The cost of bone ash in 1940 ranged from $9.50 to $10.75 per 100 lb., f.o.b. San Francisco. Cupels 1¼ in. in diameter and 1 in. high require 30 g. of bone ash, which is equivalent to 15 cupels per pound.

Cement or Composite Bone-ash–cement Cupels.—Portland cement alone is sometimes used for assay cupels; it is more commonly used with various percentages of bone ash. Cement contains approximately 62 per cent CaO, 22 per cent SiO_2, 10 per cent $Al_2O_3 + Fe_2O_3$ and minor amounts of MgO, SO_3, and other impurities. When moistened with water and allowed to dry, various aluminates and silicates are formed, which cause the cement to harden or "set." The internal bonding of cement gives cement cupels greater strength than pure bone ash. When cement is used as all or part of the cupel composition the amount of mixing water should be approximately 8 to 12 per cent. With

less than 5 or more than 15 per cent of water, cement cupels may crack on drying and will usually crack or check on heating.

Pure cement cupels give higher cupellation loss than do bone-ash cupels, but mixtures of cement and bone ash, up to 75 per cent cement, give as low percentage of losses as those made of pure bone ash.[1] A cupel containing 70 per cent cement and 30 per cent bone ash costs about one-third as much for materials as a pure bone-ash cupel; also, it has much greater strength and hence is less liable to breakage in handling. However, the recovery of materials from damaged unused cupels is impracticable if the cement content is high. This is due to the fact that the setting reactions are not reversible, whereas damaged bone-ash cupels can be pulverized easily and the bone ash used to make new cupels.

The cost of cement, in less-than-carload lots, f.o.b. shipping points in the United States, seldom exceeds $1 per 94-lb. bag or $3 per 376-lb. barrel.

Magnesia Cupels.—A number of manufactured cupels with a magnesia base are on the market under various trade names, such as Calmix, DFC Basic, Mabor, Morganite, and others. Most of these are formed under high pressure and use a special bond to increase their strength. Magnesia cupels have a higher heat capacity and thermal conductivity than bone-ash or cement cupels, and hence the heat of oxidation of the cupelling lead is abstracted more rapidly. The alloy is therefore maintained at a lower temperature than with bone-ash or cement cupels, but higher muffle temperatures must be maintained throughout the cupellation cycle. Largely on account of lower alloy temperature near the finish of cupellation the loss of silver by cupel absorption is greatly decreased and is usually less than half of the loss obtained with bone-ash cupels, under analogous cupellation conditions. The gold loss with magnesia cupels is the same as with bone-ash cupels.

In 1940 the price of one of the well-known brands of magnesia cupels, f.o.b. San Francisco, Calif., was $2 per hundred for the 1¼-in. size and $2.40 per hundred for the 1½-in. size. The cost of bone ash for one hundred 1¼-in. cupels is approximately $0.70; for 30 bone-ash–70 cement cupels, the cost per hundred is $0.25. Even if extra labor were employed to make them, the

[1] *Ibid.*, pp. 66–68.

total cost of officemade bone-ash cupels should not exceed $1 per hundred. On account of superior uniformity and lower and more constant silver losses, magnesia cupels are preferred by many assayers despite the higher cost.

Making Cupels.—At present, suitable raw materials for making magnesia cupels are not readily available to assayers; consequently, few attempt to make this type of cupel at the assay office. On the other hand, practically all bone-ash, or bone-ash–cement or cement, cupels in use are made by the assayer or his assistant.

Various types of cupel-making machines are on the market. The simplest and least expensive is a ring and plunger. The ring is set upon an anvil and filled with the cupel mixture, then the plunger or die is inserted, and the head of the plunger is struck sharply several times with a wooden mallet or a hammer, slightly turning the plunger within the ring after each blow. Considerable experience is needed to make cupels efficiently with this device. Bugbee[1] states that 100 cupels per hour can be made by this method. Fulton and Sharwood[2] state that "200 cupels an hour is a fair rate." Aside from limited production capacity the chief objection to the hand mold is that it is difficult to apply uniform pressure, with the result that the cupels are of uneven density, which causes variations in silver absorption.

For greater capacity and uniformity a lever-type cupel machine is used. A foot-lever machine is preferred to a hand-lever machine, as it has greater potential capacity and requires less physical exertion. An average operator should make at least 200 cupels per hour with the hand-lever type, and 400 per hour with the foot-lever type. Exceptionally efficient workmen can double these rates. In addition to molding time, allowance must be made for the preparation of the batch.

The effect of variations in molding pressure on silver losses was studied by King,[3] who recommended that, for bone-ash cupels, pressures of from 800 to 1,600 lb. per square inch be used, with mixing water from 10 to 12 per cent, and that, whatever pres-

[1] BUGBEE, E. E., "Textbook of Fire Assaying," 2d ed., p. 92, John Wiley & Sons, Inc., New York, 1933.

[2] FULTON, C. H., and SHARWOOD, W. J., "A Manual of Fire Assaying," 3d ed., p. 101, McGraw-Hill Book Company, Inc., New York, 1929.

[3] *Op. cit.*, pp. 43–50.

sure-moisture combination is used, it should be kept constant. The order of magnitude of the silver-loss variations, determined by King for various pressure-moisture combinations, is not large —it ranges from a low of 1.65 per cent loss on 100 mg. of silver with 4,000 lb. per square inch pressure and 15 per cent moisture, to a high of 1.98 per cent loss with 400 lb. pressure and the same moisture content. If desired, uniformity of pressure can be attained in making cupels in foot- or hand-lever machines, by providing an extension of the operating lever that may be weighted with a known weight, such as a bar of lead or a bucket of shot.

The amount of water used in mixing cupel materials should be just sufficient so that the mixture will cohere when firmly pressed in the hands. The optimum amount of water for any of the bone-ash or cement cupel mixtures, or of either alone, is from 10 to 12 per cent, but a slightly larger amount may be preferred for pure bone ash, and cement will set better if the water content is approximately 8 per cent.

If bone-ash–cement cupels are to be made, the dry ingredients are mixed thoroughly on a mixing cloth, or in a mixing box or barrel, and then sifted through a 10-mesh or finer screen.

To avoid puddling, water is added to the dry cupel batch in small increments, and the batch is kneaded slightly after each water addition. After all the water has been added, the entire batch is thoroughly kneaded with the hands and passed through a 10-mesh or other suitable screen to break up lumps and obtain more uniform diffusion of the water. The batch should then be covered with a damp cloth to prevent loss of moisture before being used, and mixtures containing cement should be used as soon as possible after adding water, in order to prevent premature setting of the cement.

Finished cupels are placed in an air drying rack and are ready for use whenever the free moisture has evaporated. Accelerated drying, as with hot air, should be avoided, as this may cause checking or cracking. Seasoning of cupels for longer periods is entirely unnecessary, although the literature of assaying since the days of Agricola (1556)[1] is replete with statements that several weeks' to several months' aging of cupels is essential to

[1] Agricola, Georgius, "De Re Metallica" (1556). Translated by H. C. and Lou Henry Hoover, *The Mining Magazine*, London, 1912.

good assay practice. Whatever free moisture may be present in an air-dried cupel is expelled when the cupels are preheated in the muffle just before using, a practice which is necessary in all cases in order to remove combined water, CO_2, and other volatile matter that would cause spitting and to avoid delayed opening of the buttons if placed in cold cupels.

Cupellation Process

The furnace operations involved in cupellation are divided into the following stages:

1. Preheating of cupels.
2. Charging of buttons.
3. Opening of buttons.
4. Driving of lead.
5. Finish of cupellation.
6. Removal from muffle.

For the proper conduct of each of these operations the control of temperature is of primary importance. Accurate temperature measurements in cupellation are difficult to make, and much of the literature of cupellation is confusing because of variations in the technique of temperature measurement among different investigators. The actual temperature of the button throughout the entire process, culminating in the bead, cannot possibly be measured with accuracy. An estimate of the most probable value of button or bead temperature at any given time can be made only by interpolation from the known melting-point data of the metals and alloys involved, as checked against optical pyrometers or by a correlation with temperatures measured at some point in the cupel or muffle near the button. Temperature measurements with a thermocouple pyrometer embedded in a blank cupel are subject to error because of serious lag behind temperature changes in the muffle and also because the heat of oxidation of lead is not available to contribute heat to a blank cupel, whereas it is an important factor in an active cupel. The air temperature within a muffle, for example, at a point 2 or 3 in. above the active cupels is subject to variations that depend upon draft velocity and furnace characteristics and is greatly different from the button temperature at all stages of the cycle. Probably the most satisfactory method of temperature measurement for the control of cupellation is by means of a thermocouple placed at

a point ½ in. above and just behind the central cupel in the row of cupels under control. This is the method used by King[1] in an extensive series of experiments on the cupellation of silver and is referred to by him as the "muffle temperature." In King's experiments, another thermocouple was placed 2 in. above the top of the central cupel in the row, and the readings of this pyrometer were called the "air temperature," which was from 30 to 40°C. less than the muffle temperature.

When muffle temperatures are measured in the manner used by King, the actual temperature of the button will be practically the same as the observed muffle temperature when no heat is being evolved by the button, but during the active period of oxidation of the lead ("driving") the temperature of the button rises and reaches a temperature above that of its surroundings. In this chapter, unless otherwise stated, "muffle temperature" refers to the temperature as measured by King that is, by a thermocouple placed ½ in. above and just behind the cupel under observation.

Few assay offices afford the luxury of a pyrometer for measuring the muffle temperature during cupellation. Consequently, experienced assayers become skilled in estimating and controlling muffle temperature and furnace draft at various stages of the cupellation process. This is accomplished by observing the temperature color of the muffle, the appearance or absence of crystals of litharge—"feathers"—surrounding the cupeling lead, the manner in which the litharge fumes are carried by the draft current, and by various other observable phenomena. As a guide to the beginner a color-temperature scale[2] is given in Table VI, but the application of this scale is subject to considerable uncertainty, depending upon the color sensitivity of the individual, the conditions of illumination, and the emissivity of the heated object.

Cupellation is usually performed in a muffle furnace, in which the products of combustion of the flame do not come in contact with the cupeling lead. A separate muffle draft, operated in conjunction with the muffle door, is used to control the amount of air passing over the cupels. The desirable temperature of

[1] *Op. cit.*, pp. 3–4 and Fig. 3, p. 5.

[2] HOWE, H. M., *Eng. Min. Jour.*, vol. 69, p. 75, 1900; WHITE, M., and TAYLOR, F. W.: *Trans. Amer. Soc. Mech. Eng.*, vol. 21, p. 628, 1900.

TABLE VI.—COLOR-TEMPERATURE SCALE

	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

cupellation is not constant throughout the cycle; hence the furnace must be designed so that a change of temperature may be made quickly. This consideration, combined with the desire for economy of design, has led to the development of furnaces fired with a liquid or gaseous fuel in which uniformity of temperature throughout the muffle is sacrificed to rapid heating or cooling. Liquid or gaseous fuels are better adapted to this requirement than is coal, coke, or charcoal. On account of the considerable temperature gradient from front to rear of the muffle it is not possible to utilize the entire floor area of the muffle for cupellation, and usually only the central third or the second fourth of the muffle from the front can be held at a satisfactory cupellation temperature. Thus, from two to four, or at the most five, rows of cupels can be cupeled at one time without overheating the rear rows. A baffle brick occupying the unused rear of the furnace is an aid to temperature uniformity. The unused front part of the muffle may be filled with blank cupels, which are useful to cover large beads before removing them from the furnace, or for the next batch of cupellations. The judicious use of hot and cold cupels, or pieces of brick moved to desired positions in the muffle, will aid in heating or cooling front or rear rows of cupels in emergencies. If the practice of covering finished cupels with hot cupels is not followed, a refractory baffle may be used in front of the cupels.

Preheating of Cupels.—Before cupellation the set of cupels should be charged into the furnace and heated at 850 to 900°C. for 10 min., with the draft slightly open to provide an oxidizing atmosphere. This will drive off free and combined water,

organic matter, carbon dioxide, and other volatile constituents that would otherwise rise through the lead during cupellation and cause the ejection of particles of lead. This phenomenon is known as "spitting" and is a source of loss to the assay in question, as well as the cause of salting other samples into which the globules of lead may fall.

The common form of cupel tongs is made to handle one cupel at a time. For loading blank cupels into large muffles, much time is saved by the use of the loading device illustrated in Fig. 21, which consists of a tray and a retaining bar. The tray is of suitable dimensions to hold the desired number of cupels. After setting the cupels on the tray the retaining bar is placed in position at the handle end of the tray, and the two are inserted into the muffle. When the cupels are in the desired position the retaining bar is held stationary while the tray is slid out from under the cupels.

Charging of Buttons.—After preheating the cupels the buttons are charged. Although some assayers make a practice of charging the largest buttons first, in order that all may finish at nearly the same time, this practice is unnecessary, and it is more efficient to charge them in the same systematic order in which the assays have been carried up to that point. Multiple-button-charging devices have been designed for charging an entire set of buttons at a single operation, but they have not been widely adopted. With practice, more than 30 buttons can be charged in 1 min. with a single pair of cupel tongs.

Opening of Buttons.—After the buttons are charged, the muffle draft and door should be closed. The lead melts and is covered with a dark crust composed partly of litharge. The draft is shut at this stage, to prevent oxidation, which would form a heavier crust of litharge. As the temperature rises, the crust melts, and the litharge is absorbed by the cupel. This should occur within 1 or 2 min. after charging and is the phenomenon known as "opening." The melting point of litharge is 888°C., and the actual temperature of the cupel must reach this point before cupel absorption of litharge begins. The muffle temperature required for reasonably rapid opening of the buttons is approximately 900°C.

If the opening of buttons is delayed beyond 2 or 3 min. it is evident that the muffle temperature is too low, that the muffle

atmosphere is strongly oxidizing, that the cupels were not sufficiently preheated, or that the buttons contain an excessive amount of copper, nickel, or other impurity of high melting point. Buttons containing too much impurity for normal opening should be rejected, as they can be cupeled only at abnormally high temperature that would increase the loss of silver and gold. If pure buttons fail to open promptly, even though the furnace temperature is correct, a small splinter of wood may be placed in front of the recalcitrant buttons and just enough air admitted to burn the wood briskly, causing the flame to pass over the unopened cupels. This reduces the litharge film and permits the buttons to open.

Driving of Lead.—When all the buttons have opened, as observed through the muffle peephole or through a slight opening of the door, the door is opened just sufficiently so that the buttons may be observed, and the draft is adjusted so that there is a positive current of air passing through the muffle. This is the beginning of the "driving" stage of cupellation, during which the lead is oxidizing rapidly.

The heat of oxidation of the lead causes the temperature of the button to rise considerably above that of the cupel and the muffle, in the case of bone-ash or cement cupels, but only slightly above the cupel temperature with magnesia cupels. Therefore with bone-ash or cement cupels the muffle temperature should be lowered during the driving period in order to keep the lead temperature from rising more than the minimum necessary for the reaction to proceed. The muffle temperature may drop to 840 to 850°C. without danger of "freezing," which is caused by the solidification of a litharge film over the lead surface and stops further cupellation. With large buttons and small beads in bone-ash cupels the minimum muffle temperature may drop to 790 to 800°C. for a brief period during the peak of the driving stage. The actual lead temperature probably must be in excess of 900°C., in order that cupellation may continue. The cupel temperature will be between that of the lead and the muffle. Under such conditions the lead will have a much higher temperature-color than the surroundings.

With magnesia cupels the temperature gradient from lead to cupel to furnace is not so great as with bone-ash or cement cupels, because of the greater heat capacity of magnesia compared with

the other materials. The button will appear slightly hotter than the cupel, but the observable difference is by no means so great as with the bone-ash or cement cupels. Since the minimum lead temperature must be the same in all cases the muffle temperature with magnesia cupels must be higher during the driving period than with other types. Muffle temperatures of 870 to 880°C., as measured ½ in. above the muffle floor behind the cupel, are recommended for the driving stage of cupellation in magnesia cupels, and temperatures as low as 830°C. may often be successfully used during the period of most active driving.

If temperature and draft conditions are correct during driving, a fringe of litharge crystals, known as "feathers," will appear around the upper edge of a bone-ash cupel. This is due to the condensation of that small part of the litharge which is volatilized at the surface of the lead. If the temperature is too high the volatilized litharge is carried away in the furnace gases or is deposited on cooler projecting surfaces in the path of the air stream as it passes through the furnace. If the air draft is too strong, feathers may appear only on the side of the cupel toward the draft, or may not form. As cupellation proceeds and the lead button becomes smaller, concentric rings of feathers are deposited within the original ring, but at all times the temperature should be high enough so that there is a clear area between the button and the feathers, otherwise there is danger that a pool of litharge will form immediately around the button, which will instantly prevent further absorption of litharge by the cupel, and the litharge will soon completely cover the lead and solidify, which will cause the button to freeze. Even though the assayer fails to note the encroachment of feathers toward the button, or the decrease in color temperature of the lead, the onset of freezing is plainly evident in the oily appearance of the ring of molten litharge at the outer periphery of the button, and the temperature should be raised immediately to avoid freezing. Individual cupels that show signs of incipient freezing may be saved by placing a hot cupel or brick near or over them. This is removed when the average furnace temperature has been increased sufficiently; or they may be moved to a hotter part of the furnace, although this latter operation must be conducted with care to avoid spilling, and to avoid chilling of the cupel still more by contact with cold tongs.

Buttons that freeze after driving has once been started should be rejected. To reopen them by raising furnace temperature, closing the draft temporarily, and perhaps by using a wood flame disturbs the normal cupellation of other buttons in the muffle, and results on the reopened buttons themselves are usually low. If wood is used for opening one or two frozen buttons in a muffle filled with others that are cupeling normally, freezing of the entire lot may ensue. The freezing would be due to retardation of the rate of oxidation in the reducing atmosphere, which then fails to supply sufficient heat for cupellation to continue. Only by raising the muffle temperature well above the melting point of litharge before applying a reducing atmosphere can the frozen buttons be opened without freezing others, and this practice must be avoided as it will increase silver losses on the entire set.

It is seldom possible to obtain feathers on all cupels in more than the first two rows in the furnace, unless exceptional precautions are taken and considerable personal attention is given to each button. To increase furnace capacity, two practices may be employed:

1. Use bone-ash or bone-ash–cement cupels in the first two or three rows, then magnesia cupels in an additional two or three rows. A little experimentation will indicate the proper spacing of the two types of cupels that will obtain satisfactory cupellation temperature for all.

2. At the outset of a day's assaying the samples may be arranged so that all low-silver samples, or samples in which silver is not to be determined, will fall in such positions that they will be cupeled in the rear row of the muffle. The losses of gold are not of so great magnitude as the silver losses; if muffle temperatures do not greatly exceed 900°C. the gold loss will not be excessive.

Among the criteria for proper cupellation temperature and draft control are the appearance of the lead and of the fume. The lead, when driving, shows active motion, from which the term "driving" was derived. This effect is caused by the rapid formation of molten litharge at the lead surface, which creates motion by sliding off the high meniscus of the lead to be absorbed in the cupel. When the temperature is too high, the motion, although still present, is less perceptible because the eye is less sensitive to the difference in temperature color between the lead

and the molten litharge upon it. The litharge film is thinner, owing to its greater fluidity. If the temperature is too low the motion becomes sluggish, and at the same time the button temperature color becomes progressively duller and less in contrast to the cupel, which indicates that oxidation is not sufficiently rapid to maintain the temperature of the lead. The fume effects are less easily identified by the inexperienced assayer. Under proper cupeling conditions as to temperature and draft the fume rises sluggishly from the button, curls lazily above the lead, and is wafted gently toward the rear of the muffle. If the draft is too weak the fumes are not carried away positively; if too strong they stream back from the cupels in a straight line.[1]

Finish of Cupellation.—Toward the end of cupellation the proportion of lead in the button decreases rapidly, and the melting point of the alloy rises toward that of the finished bead. At the same time the rate of oxidation of the lead decreases so that considerably less heat is being supplied to the button, and its temperature will drop unless additional heat is supplied from the furnace. The melting point of pure silver is 961°C.; of gold, 1063°C.; of platinum, 1773°C. The melting point of an alloy of these metals is approximately the mean of the melting points of the components. The melting points of lead-silver and of lead-gold alloys are given in Fig. 7. Down to approximately 20 per cent lead, the melting point of lead-silver-gold buttons is below the melting point of litharge (888°C.); but with less than 20 per cent lead the melting point of the alloy increases toward that of the gold-silver bead. If the platinum group of metals is present in excess over gold and silver the melting point of the alloy with lead rises above that of litharge at a higher percentage of lead than with gold and silver.

It is not necessary that the muffle temperature be increased at the finish to the actual melting point of the bead, as the phenomenon of *surfusion* keeps the alloy in a molten state at a temperature somewhat below the melting point. A maximum of 76°C. surfusion has been observed,[2] corresponding to a bead temperature at the finish of 885°C. To finish cupellation without

[1] KING, J. T., The Effect of Air on Cupellation Losses, *Univ. Toronto Bull.* 6, 1926.

[2] FULTON and SHARWOOD, *op. cit.*, pp. 117–121.

danger of freezing or of retention of lead in the bead the muffle temperature should be 860°C. for silver beads up to 100-mg. weight and in bone-ash or bone-ash–cement cupels. For larger beads a higher muffle temperature is needed on account of the greater mass of metal to be kept in a state of surfusion for a greater length of time. The finishing temperature for silver beads of the order of 500 mg. or larger should be 900 to 910°C. In magnesia cupels the bead temperature and muffle temperature are closer together, and a minimum muffle temperature of 890 to 900°C. is necessary for completion of the cupellation. Finishing temperatures should be higher than the foregoing minima whenever the bead is exceptionally high in gold or platinum.

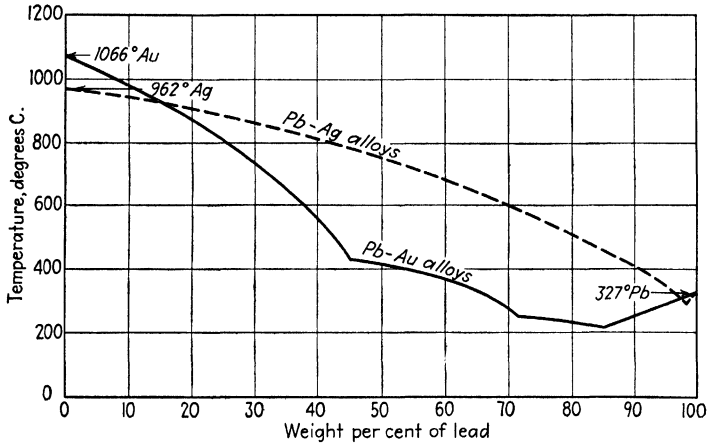


FIG. 7.—Melting points of lead-silver and lead-gold alloys.

The visual phenomena that appear near, and at the finish of, cupellation are of considerable aid to the assayer. Since both silver and gold have a higher surface tension than lead the button becomes more rounded as the percentage of lead decreases; this effect becomes pronounced as the proportion of precious metals increases beyond 50 per cent. When the cupellation of large beads approaches completion, oily-appearing drops of litharge can be seen to collect on the surface of the bead. These particles appear to move, and the movement becomes increasingly more rapid until just before the finish, when the molten litharge forms a thin film of variable thickness and creates interference colors.

The rainbow color bands move swiftly over the surface of the button and give the illusion that the button is revolving about a shifting axis. This is known as the "play of colors" and is strikingly developed with large beads. When the last trace of lead has been removed from the bead the play of colors disappears and the bead becomes dull for a brief period, after which it acquires a normal metallic luster. This change of luster is known as "brightening" and is not always observable.

If the bead was in a state of surfusion at the finish and consisted of nearly pure gold and silver it would solidify upon further cooling with the emission of a flash of light (known as the "blick" or "flash"). This flash is due to the sudden release of the latent heat of fusion of the alloy at the moment of solidification, which momentarily raises the temperature considerably. The blick is seldom perceptible in beads larger than 700 mg. Small amounts of lead or copper in the bead diminish the intensity of the blick. All the platinum group of metals, with the exception of platinum and palladium, suppress the blick entirely. If the blick is observable, it is a useful guide to the completion of cupellation, but the assayer need not waste time trying to observe the blick, as the end of cupellation is easily ascertained by other observations. The beads may be left in the furnace for a sufficiently long time thereafter to avoid the consequences of removing them prematurely.

Liquid silver has the peculiarity of dissolving a large volume of oxygen, which is expelled upon solidification. The solidification of large beads starts at the surface. When the center of silver beads solidifies, the oxygen is sometimes expelled violently, spewing forth some of the interior silver and forming a cauliflowerlike growth on the bead. This mechanism is known as "sprouting." Sprouted beads should be rejected if there is any reason to believe that any particles of metal have been lost. To avoid sprouting, all large beads should be cooled slowly, either by leaving them in the furnace after the blick, and until certain that they have cooled sufficiently, or by moving them to a slightly cooler zone in the furnace and then covering them with a very hot cupel before they have completely solidified. The hot cupel melts the outer crust and allows the bead to solidify slowly, so that the oxygen can escape from the interior without violence. When the bead contains more than one-third of its weight in

gold, it does not sprout; hence beads known to be of this composition may be removed from the furnace as rapidly as desired. Sprouting of silver beads is considered a sign of purity, but this indication is of no practical value to the assayer, as sprouting should always be avoided.

Removal from Muffle.—After the brightening, cupels may be removed from the muffle if precautions are taken to avoid sprouting. In the past, many assayers have thought that beads should be removed from the muffle within 1 or 2 min. after the blick in order to avoid loss. King[1] found that the increased loss, due to leaving cupels with 100-mg. silver beads in the muffle for 1 hr. at the finishing temperature of 870°C., was only 0.01 per cent compared with a total cupellation loss of 2.07 per cent under identical conditions when buttons were removed immediately after the blick. Since other investigators have already agreed that no loss of gold occurs by leaving beads in the muffle after finishing, it is evident that all beads may be left in the furnace for any reasonable time after the finish of cupellation, provided that the muffle temperature is not increased greatly above the proper finishing point. Presumably, if the temperature were raised above the melting point of the bead, increased cupel absorption and a slight volatilization loss would occur.

The lack of necessity for prompt removal of the cupels is a great convenience to the assayer, because all cupels may be left in their original position in the muffle until the last one has finished, and their subsequent cooling and removal can be done systematically and efficiently without danger of misplacing the sequence of the assays or of interfering with the final stages of the cupellation of unfinished beads. If desired, a scraper may be used to pull the cupels forward, a row at a time, where they will cool slowly without danger of sprouting—thus dispensing with the nuisance of covering them with a hot cupel. With this procedure a refractory baffle brick may be used in place of blank cupels in front of the muffle. This is removed in a single motion before drawing the finished cupel forward and is replaced before the next batch of cupellations is started. While waiting for the finished cupels to cool in the front of the muffle, fresh cupels may be loaded in position for the next set.

[1] KING, J. T., The Influence of Cupels on Silver Loss, *Univ. Toronto Bull.* 147, pp. 40–41, 1934.

When the finished beads have cooled sufficiently, the cupels are transferred in the established order to the cupel trays.

After the bead is cool enough to permit handling, it is gripped with a curved-nose pliers and pulled away from the cupel, to which it should adhere firmly. The under surface should appear frosted but free from roots that extend into cracks in the cupel. Particles of cupel material adhere to the frosted surface and are removed first, by squeezing the bead strongly with the pliers in a direction at right angles to the bottom surface or by flattening large buttons slightly with a hammer and then brushing the bead vigorously with a stiff bristle brush. The bead is then flattened on a small clean anvil with a mineralogist's hammer and is transferred to a clean parting cup. The flattening of large beads, as in the bullion assay, is usually done in hardened steel rolls, with frequent annealing to prevent cracking caused by work hardening.

During the operation of cleaning and flattening the bead the assayer must exercise extreme vigilance to avoid losing the bead. In order to minimize the risk of loss the work should be done on a clean smooth bench top or on a sheet of glazed paper in which the anvil is centered. A protecting shield or flange around the working space is desirable. The cupel should be placed close to the anvil to avoid carrying the bead in the pliers any farther than necessary. When the bead is brushed, the convex side of the pliers should be steadied against the anvil, and only a downward brushing movement should be employed. To flatten the bead the blows of the hammer must fall squarely upon the bead, which will eliminate the danger of projecting it away from the anvil. When the bead is flattened, the parting cup is placed alongside the anvil, the anvil is lifted and tilted over the cup, and the bead is gently slid into the cup with the aid of the pliers.

Pure silver-gold beads, if properly cupeled, will have the characteristic color of silver-gold alloys in which the gold color is not easily apparent until at least 50 per cent of gold is present. Since both gold and silver have a high surface tension the beads will be well rounded, and the small beads will be nearly spherical in shape. The bottom surface of the bead will be rough, and the bead will adhere firmly to the cupel. Any deviation from these conditions, particularly a dull luster, flattening, smooth bottom surface, or lack of adherence to the cupel, may indicate the presence of lead, showing that the cupellation temperature at the

finish was too low. The same abnormalities may, however, be caused by the presence of other impurities. Therefore, at the time the buttons are removed from the cupel and prepared for weighing and parting, the bead and the cupel should be examined for evidence of impurities or for detection of the possible presence of metals of the platinum group.

Summary of Cupellation-temperature Cycle.—Characteristic temperature cycles in cupellation are shown on Fig. 8, based on measurements taken with a pyrometer ½ in. above the muffle floor just behind the front row of cupels. These curves apply particularly to buttons from 20 to 25 g. in weight and with beads

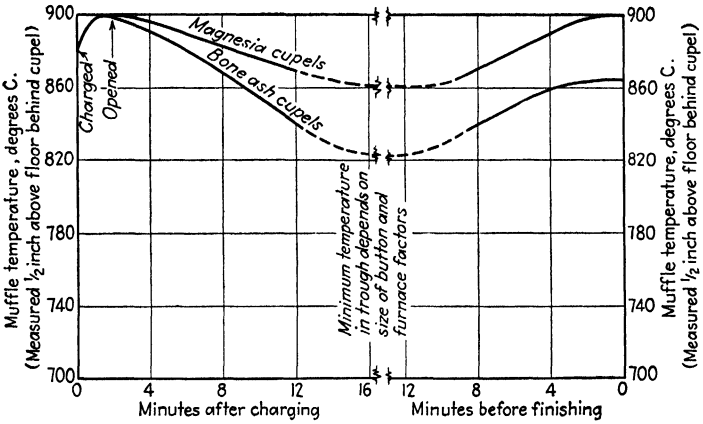


FIG. 8.—Characteristic cupellation-temperature cycles.

weighing 50 mg. or more, cupeled with feathers. The indicated temperatures are subject to corrections based on the furnace draft, heating and cooling lag, and the pyrometer position. The minimum temperature allowable during the driving depends also upon the type of cupel used and the size of the button and bead. Large buttons that are cupeled rapidly in bone-ash cupels with the ordinary shallow cup frequently permit minimum muffle temperatures as low as 790°C. and will finish at 820°C. if the beads are small. Magnesia cupels under similar conditions require minima of 830°C. in the driving trough, and 840° to 850°C. to finish. The formation of feathers of litharge can be observed readily with bone-ash or bone-ash–cement cupels and serves to indicate proper driving temperature, but when copious

feathers form on magnesia cupels the temperature is dangerously near the freezing point.

Finishing temperatures greatly in excess of 900°C., as measured in the manner indicated above, should be avoided in all cases, as higher temperatures cause greatly increased losses of gold and silver with all types of cupels and all variations in button and bead weight.

Evidence of Impurities.—The presence of impurities in lead buttons usually influences adversely the accuracy of assaying. In general the errors caused by impurities in cupellation may be either positive, due to retention of impurities in the bead, or negative, due to increased cupel absorption and to a slight extent to increased vaporization loss. Increased absorption and volatilization losses are usually due to the necessity for higher cupellation temperature to finish the process, but increased absorption of gold and silver may be caused by lowered surface tension of the button (as with tellurium and selenium), and increased volatilization loss may be caused by lowered vapor pressure of the precious metals or by mechanical losses if the impurity burns violently.

Elements below lead in the electromotive series, such as bismuth, copper, and tellurium, tend to become concentrated in the lead during cupellation and to be retained to a certain extent by the bead. Elements such as copper, nickel, tin, and zinc, whose oxides are infusible at cupellation temperature and are not greatly soluble in litharge, tend to form a crust over the cupeling bead and inhibit the driving. Even if the buttons can be finished without freezing, the higher cupellation temperature required to finish such buttons increases the loss of silver and gold.

The observable cupellation phenomena that indicate impurities in lead buttons are abnormal fumes and cupel stains, scoriae, and bead peculiarities. Exceptionally dense fumes may be observed from buttons containing antimony, arsenic, or zinc, each of which burns during cupellation and forms an oxide that condenses in the fume.

Any buttons that are hard or brittle may contain impurities that are detrimental to cupellation, but not all such impurities cause perceptible hardness or brittleness. Some of the embrittling impurities, such as PbO or PbS, do not hinder successful cupellation.

The identification of the nature of impurities in lead buttons can sometimes be made by observation of the slag obtained from the assay fusion or may be deduced from the recognition of minerals in the ore that are known to be a potential source of button impurity. When the assayer fails to identify the interfering element in the ore, slag, or button, an ex post facto identification can sometimes be made by indications that appear during cupellation. In a normal cupellation of pure lead the cupel will be free from unabsorbed infusible residues (scoriae), and will be stained a brownish-yellow color that is nearly uniform throughout the entire stained portion of the cupel. The litharge feathers, if present, will have a typical yellow color that the assayer soon learns to recognize.

Abnormal cupel stains that persist throughout the entire stained portion of the cupel are caused by such impurities as copper, iron, and nickel, whose oxides, although infusible at cupellation temperatures, are partly soluble in litharge. Abnormal cupel or "feather" stains that appear mainly on the surface of the cupel—usually near the bead—are caused by bismuth or tellurium, which concentrate in the button toward the end of cupellation, and hence their oxides do not have an opportunity to penetrate far below the surface of the cupel. Scoriae are formed whenever more of an infusible oxide is produced than can be dissolved by the litharge, leaving partly fused crusts on the cupel surface. Practically all the interfering metals, with the exception of bismuth, will form scoriae when in excess.

The impurities likely to be found in lead buttons are antimony, arsenic, bismuth, copper, nickel, selenium, and tellurium. Cobalt, iron, manganese, and zinc are not likely to be found in beads resulting from an assay fusion, as they are easily removed in the slag. Metallic aluminum or zinc may be present in cyanide precipitates that are cupeled directly, but if present in appreciable amounts they should be removed by a prior fusion or acid treatment.

Antimony is indicated by dense fumes of antimony trioxide in the early driving stage, and by yellow scoria of lead antimonate, which appear if more than 2 per cent antimony is present. The lead antimonate expands upon solidification and causes cupel cracking, which may result in leakage of lead from the button. The effect of antimony on accuracy is to increase the absorption loss of gold and silver. The increased loss is not

serious if the cupellation is conducted at normal temperature and if scoriae and cupel cracking are absent.

Arsenic exhibits the same cupellation phenomena as antimony, but the fumes are less perceptible and the scoriae are light yellow. The effect on accuracy is nearly the same as with antimony. Arsenic is seldom present in interfering proportions in lead buttons, as most of it is easily eliminated during the fusion process.

Bismuth acts like lead in cupellation, and cupels at a slightly lower temperature. It is indicated by orange-yellow or blackish-green feathers and by a brown stain on the cupel. If both lead and bismuth are present the bismuth concentrates in the button during cupellation, and the brown stain from bismuth will be more intense near the bead. Gold and silver losses are not excessive when cupellation is conducted in the presence of bismuth, but some bismuth is retained in the bead, requiring a correction to the silver result if high accuracy is desired.

Copper is one of the commonest impurities in assay buttons. Copper oxide is infusible at cupellation temperatures, but it has considerable solubility in molten litharge, and some copper is therefore removed with the lead. Small amounts of copper give a dirty greenish cupel stain, larger amounts give a dull-black stain, and still larger amounts leave scoriae and cause freezing. Cupel cracking is commonly observed if enough copper is present to give a black stain. If the ratio of lead to copper is greater than 500 to 1, cupellation losses of gold and silver are nominal, although some copper may be retained by the bead. Smaller ratios of lead to copper cause noticeably increased absorption loss, accompanied by increased retention of copper in the bead. Most assayers accept cupellations from copper-bearing buttons if the buttons finish at normal temperature without scoriae and the cupel has a greenish, rather than a black, stain.

Nickel is similar in its cupellation action to copper, but its effects are apparent at a much lower percentage. The stains are greenish, and the scoriae are dark green. Comparatively small amounts cause freezing at safe cupellation temperatures. Nickel increases absorption losses in cupellation, and some nickel is retained in the bead.

Tellurium and *selenium* are extremely detrimental to the accurate recovery of gold and silver in cupellation, when present in amounts greater than 1 per cent in lead buttons. Both elements lower the surface tension of the lead button and allow

some of the alloy to be absorbed by the cupel; the rest of the alloy may divide into separate particles, giving a number of individual beads. This effect is minimized by the use of fine-textured hard-finished cupels. Comparatively small amounts of tellurium leave a pink stain on the hot cupel, which disappears on cooling. If more than 15 per cent of tellurium is present in the bead, it is dull and frosted. Gold losses in the cupellation of buttons containing tellurium are much higher than with other impurities mentioned herein, which affect silver far more than gold. Selenium probably increases the volatilization loss of gold and silver,[1] but tellurium does not cause abnormal volatilization loss when the cupellation is carefully conducted. The total loss of gold in the cupellation of buttons containing selenium and tellurium is decreased by the presence of silver; it is therefore advisable to add silver, if necessary, to ensure at least three times as much silver as gold being present, which ratio is necessary for parting in any event.

Evidence of Platinum-group Metals.—The metals of the platinum group of metals are ruthenium, rhodium, palladium, osmium, iridium, and platinum. Each of these metals produces distinctive effects on the structure and appearance of the cupellation bead, and a few cause characteristic phenomena during the latter stages of cupellation. Since all the metals of the group are rare and have a considerable market value the assayer should seek evidence of their presence in order to aid the development of hitherto unknown sources of supply.

One of the significant effects of the presence of very small quantities of ruthenium, rhodium, osmium, and iridium—but not of palladium or platinum—is that flashing is prevented.

J. L. Byers[2] has amplified earlier observations by Lodge,[3] Bannister,[4] Bannister and Patchin,[5] and Bugbee,[6] by systema-

[1] FULTON and SHARWOOD, *op. cit.*, pp. 125–126.

[2] BYERS, J. L., Surface Effects on Assay Beads Caused by Metals of the Platinum Group, *A.I.M.E. Preprint*, 1932.

[3] LODGE, R. W., "Notes on Assaying," 3d ed., pp. 239*ff.*, John Wiley & Sons, Inc., New York, 1915.

[4] BANNISTER, C. O., *Trans. A.I.M.E.*, vol. 23, pp. 163–173, 1894.

[5] BANNISTER, C. O., and PATCHIN, G., *Jour. Chem., Met. Min. Soc. South Africa*, vol. 14, p. 478, 1913.

[6] BUGBEE, E. E., "Textbook of Fire Assaying," 2d ed., pp. 112–114, John Wiley & Sons, Inc., New York, 1933.

tizing the evidence of platinum metals in gold and silver beads and establishing a rapid approximate quantitative method of determination, dependent upon bead surface effects. For each of the six metals of the group alloyed with silver and with gold, Byers presents photomicrographs at 15 diameters of beads containing four different amounts of rare metals.

Ruthenium.—Ruthenium has a more marked effect on the appearance of gold or silver beads than any other member of the group. A blue-black encrustation of crystals of ruthenium dioxide appears at the lower edge of the bead, but not on the bottom, with as little as 0.004 per cent Ru; it spreads from that region with increased amounts of ruthenium until the entire bead is encrusted. Byers states that the encrusted area approximates 1 per cent of the surface of the bead not in contact with the cupel, in the 0.1 per cent Ru-Au or Ru-Ag bead, 100 per cent in the 2 per cent Ru-Au bead, and 100 per cent in the 2½ per cent Ru-Ag bead. The area covered is a direct function of the ruthenium content. The unencrusted surface of Ru-Au beads is scaly or platy, and the surfaces of the plated crystals are striated, with a faint dendritic pattern. The gold grains are moderately pitted. The unencrusted surface of Ru-Ag beads has a silver luster, marked only by dendritic striations.

Rhodium.—Bugbee[1] states that as little as 0.004 per cent of rhodium in silver beads causes a distinct crystallization, which is more apparent at 0.01 per cent Rh, and that 0.03 per cent Rh causes unavoidable sprouting of silver beads. Byers does not report sprouting but emphasizes iridescent color films on Rh-Au beads and microscopic pits on Rh-Ag beads. The color film on Rh-Au beads changes from gold, with a reddish tinge at 0.1 per cent Rh to an iridescent purple at 2 per cent Rh. With Rh in excess of 0.1 per cent the surface structure of Rh-Au beads becomes distorted, and a polyhedral structure develops, which is strongly accentuated at 0.5 per cent Rh. At 1 per cent Rh the spherical surface entirely disappears and the bead surface is composed of conchoidal facets, up to 1 mm. in largest dimension. Beyond 1 per cent Rh the number of facets increases and the bead once more approaches the shape of a pure gold bead. In Rh-Ag beads, iridescent films are not distinctive, but beads in the range from 0.02 to 5 per cent Rh are covered with microscopic pits

[1] *Ibid.*

usually filled with a dark crystalline material, which entirely covers the surface of beads containing more than 2 per cent Rh. Rhodium-silver beads containing less than 2 per cent Rh also show a slight dimpling, and those containing more than 2 per cent Rh appear to be collapsed.

Palladium.—The principal effect of palladium on gold or silver beads is increasing lack of definition of grain boundaries, accompanied by a somewhat pebbled appearance with increasing amounts of palladium in the range from 0.1 per cent to 3 per cent Pd. The color of Pd-Au beads varies from a brilliant gold at 0.02 per cent to a silvery bronze at 5 per cent. Palladium-gold beads in the range from 3 to 5 per cent Pd lose their spherical smoothness and develop ridgelike grain boundaries, giving a polygonal appearance with slightly conchoidal facets. Palladium-silver beads retain their spherical surface, marked by slight dimpling on the sides and top of the bead. The presence of Pd in Au-Ag beads may be verified by an orange-colored solution, due to colloidal Pd, in the nitric or sulfuric acid parting of the bead.

Osmium and Iridium.—It is difficult to distinguish between osmium and iridium in assay beads without chemical tests. Both metals, which usually occur together in nature, decrease the surface tension of Au and Ag, which is first apparent in the formation of a creased dimple in the central portion of the bead surface. Dimpling appears in Os-Au beads containing as little as 0.02 per cent Os, and in Ir-Au beads at 0.1 per cent Ir. With 5 per cent Os or Ir in gold beads, and with 5 per cent Ir in silver beads, the shape of the bead becomes considerably flattened and irregular because of extreme dimpling. At 10 per cent Ir in Ir-Au beads the surface tension is so low that the deposit, after cupellation, resembles scattered pieces of foil. In Os-Au, Ir-Au, and Ir-Ag beads a lacy fretwork appears in and near the surface of the dimples, whereas the rest of the bead surface is platy. Osmium-silver beads do not exhibit marked differences from pure silver beads, except for a slight decrease in grain size, faint dendritic striations, gentle undulations of the bead surface, and a silken luster. Beads containing 5 per cent or more of Ir in gold, or 2 per cent or more in silver, contain a small amount of dark crystalline material scattered over the bead surface, particularly near the base. In beads containing 5 per cent Ir, or an alloy of

Os and Ir, vugs containing a pinkish-brown resinous material may be found near the bottom of the bead.

Platinum.—The general effect of Pt on gold and silver beads is to develop a frosted appearance and a dulling of the luster due to a decrease in the size of the surface grain, to a pitting of the exposed grain surface, and to well-developed striations on the grain face. These effects are not so well marked with Pt-Au as with Pt-Ag beads. As little as 0.1 per cent Pt can usually be detected under low-power magnification, even with comparatively small beads. At 5 per cent Pt in a Pt-Au bead, the surface of the bead is broken by intertwining ridges and valleys; and from 3 per cent Pt and upward in Pt-Ag beads, the crystalline surface is gradually replaced by a surface with a multitude of microscopic pits. Buttons containing a large amount of Pt flatten toward the end of cupellation and may freeze, leaving a gray, rough bead that sticks to the cupel.

CHAPTER V

PARTING

In the determination of gold and silver the beads from cupellation are weighed and recorded as the weight of gold-silver alloy, commonly called "doré." The silver is then dissolved in acid, an operation called "parting," and the gold is washed, dried, annealed, and weighed. The weight of silver is determined by subtracting the weight of the gold from the weight of the doré.

When an assay for silver is requested and gold is not to be determined, it is customary to report the total weight of the cupeled bead as silver and to omit parting. Parting cannot be omitted in the assay of a gold ore because all gold ores contain some silver, which would represent too great an error if it were reported as gold.

The objectives of parting are to dissolve rapidly and remove all the silver and any base metals that may be present in the bead, and to leave the gold in a form that can be manipulated without mechanical loss, preferably in a single piece. In order to attain these objectives, the following factors should be considered:

1. Preparation of the bead for parting.
   a. Ratio of silver to gold.
   b. Inquartation.
   c. Flattening the bead.
2. Choice of parting receptacles.
   a. Parting cups.
   b. Parting flasks and other glass receptacles.
   c. Platinum or fused-silica porous or slotted thimbles.
3. Conditions of solution.
   a. Kind of acid.
   b. Purity of acid and wash water.
   c. Acid temperature.
   d. Acid quantity.
   e. Acid concentration.
   f. Time of contact.
   g. Effect of base-metal impurities in the bead.
   h. Indications of metals of the platinum group.

4. Removal of silver-bearing acid from the gold.
   a. Decantation and washing.
   b. Floured gold from parting.
5. Preparation of gold for weighing.
   a. Drying.
   b. Annealing.

Ratio of Silver to Gold.—A high proportion of silver in the alloy to be parted increases the rate at which silver is dissolved, but too high a proportion of silver tends to cause the gold to break up. An alloy containing less than two times as much silver as gold will not part, even in strong acid, and a still higher proportion of silver is required for rapid parting in dilute acid. When parting beads that contain more than six times as much silver as gold, the gold may break up, particularly if the bead weighs more than 2 mg. The gold in small beads breaks up less readily and is usually obtained in a single piece when beads smaller than 2 mg. are parted, even though ten times as much silver as gold is present.

Inquartation.—In order to ensure complete parting without breaking up of the gold, assay beads containing too little silver must be inquarted with additional silver. Usually a total of four or five times as much silver as gold is required, except when masses of 200 mg. or more of gold are to be parted, as in the gold-bullion assay, when the ratio of silver to gold is 2:1 or 3:1. Early assayers believed that the best alloy for parting contained one-fourth gold and three-fourths silver. In fact the literal translation of the Latin word for parting, *quartatio*, is "fourthing."[1]

If the original sample is known in advance to contain too low a silver-gold ratio for parting, inquartation may be done in the assay fusion or in cupellation. If silver is not to be determined, the amount of silver required is estimated approximately and is usually added as silver foil to the assay fusion or to the lead button before cupellation. If the determination of silver is required, the amount of silver added for inquartation must be accurately known. In Western United States, Herman inquarts are commonly used for this purpose. These consist of small squares of sheet lead containing a known amount of silver. Another common method is to add a standard silver nitrate

[1] CRAMER, JOHN ANDREW, "Elements of the Art of Assaying Metals," 2d ed., p. 194, 1764.

solution to the crucible charge. It is convenient to prepare solutions of two different strengths, one for low-grade samples and one for concentrates and other high-grade samples, so that in either case not more than a few milliliters of solution are required. Some assayers make a separate fusion for silver and gold, adding sufficient silver at the outset for parting the gold assay.

In some cases, the need for inquartation may not be suspected until after the silver-gold bead is obtained, when the gold color of the bead or the failure to part in strong acid may indicate that the silver-gold ratio is too low. After the doré weighing, inquartation can be accomplished by cutting off a piece of silver foil approximately equal to three times the weight of the bead, wrapping the bead and silver together in a piece of lead foil, and cupeling. The resulting bead is parted directly without reweighing. Inquartation by fusion of the bead and added silver on charcoal with a blowpipe may be accomplished, but this method is slow, and it is difficult to obtain completely homogeneous alloys that will part without breaking up of the gold.

Although c.p. silver foil is generally free from gold, each lot should be tested when used for inquartation to be certain that there is not enough gold present to affect the gold assay. Five or ten grams of silver should be used for the gold determination. The silver is dissolved in nitric acid, diluted slightly, and the gold is then carried down by the precipitation of a small part of the silver with hydrochloric acid or sodium chloride. The precipitate is settled, filtered, dried, scorified with lead, cupeled, and parted.

Flattening of the Bead.—The thinner the silver-gold alloy the more rapid and complete is the parting and the more coherent the gold. Ordinary assay beads, up to perhaps 500 mg. weight, are flattened with a small hammer on a steel anvil. Larger beads, as in the bullion assay, are rolled thin in successive stages between hardened and polished steel rolls, then coiled into a spiral called a "cornet." Strain hardening of large beads, which might cause them to crack in rolling, is removed by annealing at a red heat at intervals between successive rollings.

In the gold-bullion assay the operation of flattening the bead should be standardized to ensure uniformity of parting. The United States mint method of preparing cornets is to place the cleaned bead on an anvil used only for that purpose and flatten

it by a middle blow and two end blows, then reduce to the approximate thickness of a visiting card, nearly 0.01 in., in two passes through the bullion roll. The cornet is then rolled so that a uniform space is left between all turns of the spiral.

Parting Cups.—Ordinary assay beads are usually parted in parting cups, although some assayers prefer glass flasks or test tubes, and platinum containers are used at United States mints for parting gold bullion.

Parting cups are glazed porcelain crucibles of about 10 or 15 ml. capacity. They are conveniently handled in groups by means of parting-cup trays, which keep the cups in order and hold them upright.

When using parting cups the doré beads are taken out of the cupels, cleaned, flattened, and placed in order in a tray of parting cups. The tray is then taken to the assay balance where the doré beads are weighed. Here the parting cups have an advantage over bead trays because the individual parting cups can be picked up and the bead dumped onto the balance pan. This operation is easier than picking up the beads with forceps, particularly when the beads are small. After each bead is weighed, it is dumped back into its parting cup and remains therein during the subsequent operations of parting, washing, drying, and annealing, until the final weighing of gold is made.

Parting Flasks or Test Tubes.—The parting operation is essentially the same in either glass flasks or test tubes, except that flasks are usually placed directly on a hot plate during parting, and test tubes are held in a rack placed in a vessel of boiling water during parting. The capacity of the flasks or test tubes generally used varies from 30 to 60 ml. They are especially desirable for parting large beads, particularly when the silver is near the minimum parting ratio, and prolonged heating at or near the boiling temperature is required to secure complete parting. The neck of the flask or test tube acts as a condenser and prevents rapid evaporation to dryness. Furthermore the danger of mechanical loss of gold by boiling over is minimized. The chief disadvantage of flasks and test tubes is that the gold must be transferred to another receptacle for annealing. Unglazed fireclay annealing cups are used for this operation. Such cups are porous and absorb the small amount of water remaining with the gold after decantation so that they can be heated rapidly to

the annealing temperature without danger of loss of gold by spattering.

To prevent bumping in glass or fused-silica parting receptacles a small fragment of charcoal, electric-arc carbon, graphite crucible, or other similar material is added with the cornet. Bumping is absent when platinum vessels are used.

To transfer the parted and washed cornet from a flask into an annealing cup, fill the flask with water, place the inverted annealing cup over the neck of the flask, and quickly invert the assembly. The cornet will settle into the annealing cup and the flask is then removed by quickly raising and inverting it. The water in the cup is decanted off, and the cornet is ready for annealing.

Platinum or Fused-silica Thimbles.—Perforated or slotted platinum thimbles for parting gold bullion are used in United States mints and at some refineries having a large number of daily bullion assays. A number of thimbles are carried in a suitable rack or frame of platinum, and the entire set is immersed in a parting-acid bath contained in a platinum dish. Perforations or slots in the bottoms of the thimbles permit the acid to enter and attack the beads. When parted, the entire set is lifted out of the acid, drained, and immersed in a second acid bath, followed by successive washings. The principle of this method of parting obviously could not be used if there were danger of any of the gold breaking up, and in any event few assay offices could afford the outlay for the large quantity of platinumware required. It is possible, however, to obtain fused silicaware of a similar character, at considerably less cost.

Kind of Acid.—Sulfuric acid is used in parting commercial quantities of bullion, but nitric acid is almost universally used in assaying because of the difficulty of handling hot sulfuric acid and because of the danger of spattering during dilution of hot sulfuric acid with water.

Purity of Acid and Wash Water.—Particular precautions must be taken to ensure that the acid, dilution water, and wash water used in parting are free from chlorine or chlorides. Chlorine and chlorides in the parting acid and wash water precipitate silver chloride, which may coat the bead and prevent parting or may precipitate in the pores of the parted gold and add to its weight. If there is not sufficient silver present to precipitate all the chlorine, some gold may be dissolved and lost.

To ensure freedom from chlorine, all new lots of parting acid should be tested, and the distilled water should be checked at frequent intervals. Chlorine is present if a white turbidity or precipitate of silver chloride is formed when a small amount of silver nitrate is added. In conducting the test, which is very delicate, the assayer should be sure that the containing vessels are thoroughly clean and that chlorine is not accidentally introduced by perspiration from the hands or other parts of the body.

To test for chlorates in nitric acid, take 200 ml. or other convenient quantity of the acid, add a few milliliters of 1 per cent silver nitrate and 4 g. of a metal such as zinc, aluminum, silver, or copper, heat nearly to boiling to dissolve the metal, and reduce the chlorate. The formation of a precipitate of silver chloride indicates the presence of chloric acid.

If it is necessary to use acid or water containing chlorides, the chlorine may be removed by precipitation with silver nitrate. For this purpose, add silver nitrate solution, little by little, just to the point where no more precipitate forms. Let the precipitate settle and remove the chloride-free solution by decantation or siphoning.

If nitric acid is used in parting, it should be free from sulfuric acid, and vice versa, as the two acids together dissolve some gold. The presence of sulfates in nitric acid is determined by the formation of a precipitate of barium sulfate when barium chloride is added.

Acid Concentration.—The stronger the acid the more rapid and complete is the parting, but the greater the tendency for the gold to disintegrate. Hence, strong acid is necessary for parting alloys having the minimum allowable ratio of silver to gold, and weaker acid is desirable to avoid breaking up of the gold in silver-rich alloys. For example, 200 to 1,000 mg. samples of bullion containing 3 parts of silver to 1 part of gold may be started in 1:2 nitric acid (1 part concentrated acid to 2 parts of water by volume, sp. gr. 1.17) and finished in 1:1 (sp. gr. 1.25) or stronger acid. Beads containing 10 mg. of gold and more than 6 parts of silver to 1 part of gold, part almost completely without breaking up of the gold in hot 1:6 acid (sp. gr. 1.07). For more complete removal of silver this should be followed by a 30-min. heating in 1:1 acid. Long-continued boiling in strong nitric acid will dissolve an appreciable amount of gold and should be avoided.

At most assay offices handling ordinary mine and mill products other than bullions the parting-acid strength is arbitrarily chosen to give good results on the majority of routine samples. The most frequent strengths in use are from 1:4 to 1:8. The convenience of using a stock acid solution offsets the occasional annoyance of broken gold partings, and if the acid proves insufficiently strong for certain beads, additional strong acid may be added, drop by drop, until parting starts.

The necessity for a double acid treatment is avoided by many assayers for all except large beads by ensuring that all samples contain enough silver for complete parting by a single treatment of 15 to 20 min. duration in the stock acid.

Temperature of Acid.—Best results are obtained as to speed, completeness of parting, and coherence of gold if the parting acid is heated before use and is kept just below boiling during contact with the alloy to be parted. Boiling is undesirable, as the bumping causes mechanical disintegration of the gold, and boiling over would cause actual loss. To save manipulative time by the use of convenient acid-dispensing devices, which are not available for handling hot acids, many assayers handling a large volume of routine work start with cold acid of somewhat greater strength than would be used with hot acid. Although parting with cold acid at the start requires at least twice as long as when hot acid is applied to the beads, this time is not lost when the assayer is occupied with other duties during the interim. The tendency of the gold to disintegrate may be accentuated when parting is started in cold acid, but there is no proof that this is necessarily true if the acid strength and silver-gold ratios are properly adjusted.

Acid Quantity.—The theoretical amount of silver that can be dissolved by 10 ml. of 1:6 nitric acid is 2.4 g., but in practice, on account of loss of volume by volatilization, a 10-ml. parting cup will not hold enough 1:6 acid to dissolve much more than 500 mg. of silver without replenishment of the acid. Hence for large beads a larger parting cup is needed, unless a double acid treatment is employed. Parting flasks are desirable if more than 1,000 mg. of silver is to be dissolved, as 30 to 40 ml. of acid may be used.

Time of Contact.—With high silver-gold ratios, parting is practically complete when the evolution of gas bubbles ceases,

provided the acid has not been consumed by then. The great majority of routine assays containing up to 20 mg. of gold and suitably high ratios of silver to gold will part with a sufficient degree of completeness in 15 to 20 min. in 10 ml. of hot 1:4 to 1:8 acid. If more gold is present, or if the silver-gold ratio approaches the critical minimum, it is necessary to decant off the first acid after visible action ceases, then digest with stronger acid for an additional 20 to 30 min. to dissolve the last removable silver.

Effect of Base-metal Impurities in the Bead.—The presence of lead in assay beads increases the tendency of the gold to break up in parting. In the gold-bullion assay, copper is added prior to cupellation, if not already present, to ensure that all lead will be removed during cupellation. It is possible that other base metals have an effect similar to that of lead, but specific data are lacking.

Indications of Metals of the Platinum Group.—Certain of the metals of the platinum group may be detected in parting, supplementing or verifying the evidence obtained during cupellation.

Nitric acid dissolves part of the platinum and palladium from precious-metal alloys having a high silver content. Of these, palladium is the most readily identified because the parting acid becomes orange colored even with as little as 0.05 mg. of palladium in a bead. Platinum imparts a brown or blackish color to the parting acid, and the undissolved platinum discolors the gold, making it steel gray. Platinum is also said[1] to have a disintegrating effect on the gold, when not more than 5 per cent of gold is present in the bead.

Iridium is not dissolved by nitric acid and appears in the partings as detached black specks that remain black when annealed and hence are difficult to distinguish from extraneous particles.

Decantation and Washing.—Most assayers remove the spent acid and washings after parting by decantation into a small receptacle from which may be recovered any gold particles that are accidentally decanted. Some assayers remove the acid and wash water by suction through a glass nozzle attached by a rubber tube to an aspirator bottle to which hydrochloric acid is added, which collects the washings and precipitates the silver for future recovery. This method is quicker and more complete

[1] RAWLINS, *Trans. Inst. Min. Met.*, vol. 23, p. 177, 1894.

than decantation, and the accidental loss of gold is less than by decantation. If desired, a small bottle could be inserted in the suction line ahead of the solution bottle, to act as a gold trap.

Whatever method of washing is used, extreme care must be employed to avoid loss of gold. When the gold is excessively powdered, some of the particles may be so small as to be invisible to the naked eye, and it is virtually impossible to wash such partings without loss. The recovery of extremely fine gold from washings may be accomplished by adding a few drops of hydrochloric acid to precipitate a small amount of silver chloride, which carries down the gold in settling. The precipitate is filtered, scorified with lead, cupeled, and parted.

After removal of the waste acid the parting vessel should be partly filled with warm distilled water, rinsing the sides of the vessel with a fine jet at the same time. The wash water is decanted, and washing repeated until at least three washes have been given. Incomplete washing is indicated if black stains of silver appear in the parting or annealing cup after annealing. Before using the cups again, such stains should be removed by boiling the cups in a saturated solution of potassium dichromate in sulfuric acid.

Drying.—After washing, parting cups are dried by placing them on a warm hot plate. Care must be taken to avoid too rapid heating during this operation, as the violent evolution of steam may project the gold from the cup. Fire-clay annealing cups may be dried more rapidly, as the surplus moisture is absorbed by the cup and is given off gradually when heated.

Annealing.—Unannealed gold from parting is black in color and cannot be distinguished readily from particles of dust, bone ash, or other contaminants that may be present. The natural gold color is developed by annealing the gold at a red heat. If the annealed gold has a silvery tint the parting has been incomplete, and the gold should be inquarted and reparted. As already noted, platinum causes discoloration of the gold and must be removed by the methods described in Chap. XII.

Annealing does not change the weight of gold but merely changes its allotropic form. Annealing would not be necessary if it were not desirable to verify the completeness of parting, to examine the gold for evidence of the platinum metals, and

to avoid weighing extraneous matter as gold. Furthermore, annealing destroys most of the porosity of the freshly parted gold and hence avoids the possible effect of absorbed gases on the weight.

One of the most convenient methods of annealing is to place an entire tray load of parting cups in a muffle furnace. Some assayers object to keeping the main assay furnace under fire after cupellation is finished and have installed small electric or gas-fired annealing furnaces. For small-scale work, annealing may be done individually over a single bunsen burner; or a battery of a number of burners closely spaced in a row, with a suitable rack for holding the cups, may be provided. Eight to twelve burners are sufficient to keep the annealing manipulations continuous, as by the time the last parting cup is in place, the first one will be annealed and may be removed from the flame. A similar annealing apparatus heated with electricity can be made from nichrome resistance wire.

Recovery of Silver from Waste Liquor.—The waste parting acid and washings should be recovered in a bottle to which hydrochloric acid or common salt has been added, to precipitate the silver as silver chloride from which silver can ultimately be recovered.

When it is desired to recover the silver from accumulated precipitates, let them settle until the supernatant liquid is clear, decant and wash two or three times by decantation with hot water, and then transfer the precipitate to a filter paper and wash until free from acid. The precipitate may then be transferred to a graphite crucible and heated to decompose the chloride, finally melting down the silver and pouring into a suitable mold. A light cover with a borax-soda flux is desirable to aid in the removal of impurities.

Summarized Procedure for Assay Bead Parting.—The following routinized procedure for parting in porcelain crucibles is satisfactory for most assay work, except for special products, such as precious-metal bullion and other rich materials producing large beads. For such cases, see Chap. IX.

1. Fill the parting cup with warm parting acid of the stock strength in use (usually 1:4 to 1:8 acid). Cold acid of greater strength may be used if the assayer's routine permits the additional parting time required.

2. Place on a hot plate. If any beads fail to react with the parting acid after the boiling point has been reached, add 1:1 acid drop by drop until action starts. Beads that do not start readily in hot 1:2 or stronger acid need inquartation and should be removed for that purpose.

3. Keep just below boiling for 15 to 20 min., by which time all visible action should have ceased, and the gold will appear as a spongy mass, considerably shrunken from the original size of the bead. If an exceptionally large (500 mg. or more) gold bead is now disclosed, remove the first acid and repeat the digestion with 1:2 or stronger acid.

4. Remove from the hot plate, remove the acid by decantation or aspiration, and wash three times with hot distilled water, saving the washings for ultimate recovery of silver.

5. Dry carefully on a warm hot plate.

6. Anneal at a red heat.

CHAPTER VI

THEORETICAL DISCUSSION OF ASSAY FUSIONS AND RELATED SMELTING PROCESSES

An assayer should have a general knowledge of pyrometallurgy so that he can understand the processes that he is using and be able to adapt them to the assay of unusual substances. The materials that he may be required to assay range from any of the rocks and minerals occurring in nature to all kinds of metallurgical products such as metals, artificial sulfides or arsenides, slag, flue dust, cyanide solution, and precipitates from the cyanide process. In fact, nearly every known element may be encountered either by itself or in chemical combination with others.

The elements may be divided into two main groups: the metals and the nonmetals. In some instances the distinction is not sharp but in general the oxides of members of each group have distinctive characteristics both in water solutions and in nonaqueous melts. In water solutions the metal oxides unite with water to form hydroxides. These furnish an excess of hydroxyl ions (OH) in the solution and make it basic. The oxides of the nonmetallic elements unite with water to form acids and give an excess of hydrogen ions in solution. There is also a strong tendency for acids and bases to combine, forming salts. In nonaqueous melts the metal oxides combine with the nonmetal oxides and, because of the similarity to the action in aqueous solutions, the metal oxides with a few exceptions are considered basic, and the nonmetal oxides are considered acidic. Assay and smelter slags are formed by the union of the acid nonmetallic oxide silica with bases that, in smelting, are mainly the metal oxides CaO and FeO. In assaying, Na_2O and PbO are also important bases; and borax glass is used as an acid to supplement silica.

In fire assaying as well as in smelting processes, increased temperature is used primarily to melt the charge. Melting the material has the advantage of releasing for possible recovery the

precious metals that occasionally are so intimately disseminated in the rock that they are only partially exposed by any practical degree of crushing and grinding. It is this complete exposure of valuable particles in a rock to the recovery process that gives fire assaying its outstanding advantage over wet chemical determinative methods for gold and silver. If refractories were available that would stand the temperature required to melt directly the materials to be assayed, and if a sufficiently high temperature could be economically produced, assay fusions might be carried out at high temperatures. Actually, practical considerations of refractories and fuel have limited the usual assay temperature to a maximum of about 1200°C. Substances having higher melting points are brought to a molten condition by the formation of low melting compounds and mixtures.

Phases.—In the melts used in assaying, smelting, and fire refining there is the possibility of producing a number of separate liquids that are not miscible with each other and, therefore, segregate into separate layers called "phases." Any or all of the phases—metal, speiss, matte, slag, and molten alkaline salts—may be formed. The metal phase has the highest density and forms the bottom layer; the other phases separate above the metal phase according to their densities, which are usually in the order given above. The rules governing the formation and composition of these phases furnish the guiding principles of assaying and many pyrometallurgical operations.

The metal phase in fire assaying is a lead button that collects the gold and silver. The lead button is the heaviest phase and forms the bottom layer of an assay fusion. Its size and purity are the chief concern of the assayer.

The speiss and matte phases are avoided in fire assaying by proper conduct of the assay. Speiss consists of the arsenides and antimonides of iron, cobalt, nickel, or copper; matte is a mixture of fused sulfides, usually of iron and copper. Speiss is heavier than matte but lighter than lead; hence it forms a layer between the lead and the matte, if all three are present.

The slag phase, consisting of metal oxides and silica or borax glass, lies above the matte layer or, if matte and speiss are absent —as should be the case in an assay fusion—the slag rests directly upon the lead. Metallurgical slags are classified according to the silicate degree, which is defined as the ratio of oxygen in the

acids to oxygen in the bases. This classification should not be confused with that of silicate minerals formerly used by mineralogists. They considered silicate minerals to be salts of various hypothetical silicic acids and used such terms as "orthosilicate," "metasilicate," "sesquisilicate" and "bisilicate." The metallurgical classification, which is followed in this text, is given in Table VII. The silicate degree is expressed by name or by the oxygen ratio. For example, a sesquisilicate is said to have a silicate degree of 1.5.

TABLE VII.—METALLURGICAL CLASSIFICATION OF SLAGS

Silicate degree	Oxygen ratio acid to base	Formula with SiO_2 and MO base*	Formula with $Na_2O.2B_2O_3$ and MO base*
Subsilicate	0.5	$4MO.SiO_2$	$11MO.Na_2O.2B_2O_3$
Monosilicate	1.0	$2MO.SiO_2$	$5MO.Na_2O.2B_2O_3$
Sesquisilicate	1.5	$4MO.3SiO_2$	$3MO.Na_2O.2B_2O_3$
Bisilicate	2.0	$MO.SiO_2$	$2MO.Na_2O.2B_2O_3$
Trisilicate	3.0	$2MO.3SiO_2$	$MO.Na_2O.2B_2O_3$

* In this book, slag formulas are written with the constituents separated. Writing the true formula (for example $FeSiO_4$ instead of $FeO.SiO_2$) makes the silicate degree classification difficult to use.

Alkaline salts, such as the chloride, sulfate or cyanide of the alkali metals, are occasionally either formed or used in assaying. These salts do not mix with molten silicate slags but appear as an extremely fluid top layer in a fusion. The sodium sulfate produced in the fusion of sulfide ores is the alkaline salt most frequently encountered in assaying. Sodium chloride has found some use as a cover for crucible fusions but is seldom used today. Cyanide salts are strong reducing agents and are used in the tin assay.

METAL PHASE

The entire object of smelting, refining, or an assay fusion is to produce a suitable metal phase that separates from the rest of the molten charge because of its high density and forms the bottom layer.

Whether a metal appears in the metal layer or in the slag depends upon whether or not it is combined with oxygen. The metal oxides are quite soluble in the slag and, in general, are

insoluble in the metal. Consequently, when two different metals are present, if one can be oxidized to metal oxide it will go into the slag layer, while if at the same time the other metal can be prevented from oxidizing it will appear in the metal layer, provided no speiss or matte is formed. This principle forms the basis of the separations made in fire assaying, smelting, and fire refining. Fortunately, there is a difference in the ease of oxidation of the various metals, so that separations can be made.

The relative ease of oxidation of the metals can be measured by their electrode potentials when immersed in solutions containing 1 g. equivalent weight of their ions per liter of solution. By these measurements the elements have been listed in an order called the "electromotive series of elements" (Table VIII).

TABLE VIII.—PARTIAL ELECTROMOTIVE SERIES OF THE ELEMENTS

Element	Oxidation product	Electrode potential*
K	K^+	2.92
Na	Na^+	2.71
Mg	Mg^{++}	2.34
Mn	Mn^{++}	1.05
Zn	Zn^{++}	0.76
Fe	Fe^{++}	0.44
Cd	Cd^{++}	0.40
Co	Co^{++}	0.28
Ni	Ni^{++}	0.25
Sn	Sn^{++}	0.14
Pb	Pb^{++}	0.13
H_2	H^+	0.00
Sb	Sb^{+++}	−0.10
Bi	Bi^{+++}	−0.23
As	As^{+++}	−0.30
Cu	Cu^+	−0.47
Te	Te^{++++}	−0.56
Ag	Ag^+	−0.80
Hg	Hg^{++}	−0.85
Pt	Pt^{++++}	−0.86
Au	Au^+	−1.50

* Values largely from W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, 1938.

The electromotive series furnishes the key to the possible separations by oxidation or reduction. The metals low in the

series are called the "noble metals" and are difficult to oxidize. Those above silver combine with oxygen when heated in the air, and the action becomes more energetic as the list is ascended. Considering the reduction of the metal oxides, it is found that metal oxides up to and including silver lose their oxygen when heated in the air; while if heated in a current of hydrogen, the oxygen is easily removed from all the oxides up to and including those of iron, leaving in each case the metal.

Actually the oxidation of a metal or the reduction of a metal oxide is controlled by the pressure of oxygen, produced by the tendency of the metal oxide to dissociate, compared with the external oxygen pressure. When the dissociation pressure of the metal oxide is lower than the external oxygen pressure, the metal tends to oxidize; but if the dissociation pressure is greater than the external oxygen pressure, the oxide is reduced to metal. The dissociation pressure of metal oxides increases with the temperature, but only the noble metals can be reduced by heat alone. For example, at room temperature the oxygen pressure due to dissociation of silver oxide is less than the pressure of the oxygen in a normal atmosphere, and silver oxide can exist. At a temperature of only 227°C. (Table IX) the oxygen pressure is much

TABLE IX.—OXYGEN PRESSURE DUE TO DISSOCIATION OF METAL OXIDES

Temperature		Oxygen pressure, atmospheres, at equilibrium*					
Degrees absolute	Degrees centigrade	Ag_2O	Cu_2O	PbO	NiO	Fe_3O	ZnO
300	27	8.4×10^{-5}					
500	227	24 9	0.56×10^{-30}	$3\ 1 \times 10^{-38}$	$1\ 8 \times 10^{-46}$	. . . . .	1.3×10^{-68}
1000	727	. . . . .	$1\ 5 \times 10^{-11}$	$1\ 1 \times 10^{-15}$	$8\ 4 \times 10^{-20}$	2.0×10^{-22}	7.1×10^{-31}
2000	1727	. . . . .	$4\ 4 \times 10^{-1}$	$3\ 7 \times 10^{-4}$	$3\ 3 \times 10^{-6}$	$1\ 6 \times 10^{-7}$	9.5×10^{-12}

* Values calculated by W. Stahl, *Metallurgie*, vol. 4, 682, 1907. Taken from table in R. S. Dean, "Theoretical Metallurgy," p. 159, John Wiley & Sons, Inc., New York, 1924, with the permission of the author and publisher.

greater than atmospheric pressure, and silver oxide spontaneously reduces to metal. To reduce base metals it is necessary to supply a reducing agent—something such as carbon, carbon monoxide, hydrogen, or a metal higher in the series. These reducing agents combine with oxygen and lower the external oxygen pressure below the dissociation pressure of the metal oxide to be reduced.

When the oxidation of a metal or the prevention of its reduction is desired, sufficient oxygen pressure must be supplied to exceed the dissociation pressure of the metal oxide. The oxygen can be supplied from the air as in cupellation and roasting, or from niter as in the crucible assay of sulfide ores, or from a metal oxide lower in the electromotive series as in the use of litharge as an oxidizing agent in the softening of crude lead.

In an assay fusion the metal layer is the sole useful product. It is possible to produce in one step a metal layer consisting of the precious metals alone. This is not practical in either smelting or assaying, because the unavoidable mechanical loss of small amounts of the metal layer represents a value loss that is greater than can be tolerated. To reduce the value loss in both smelting and assaying a relatively large amount of a less valuable material that will dissolve or alloy with the precious metals is provided, so that the same loss in quantity of material from the layer represents only a small value. Lead alloys readily with the precious metals and is the less valuable material used to collect gold and silver in both assaying and lead smelting. Lead is a particularly suitable collector for the precious metals in assaying, because it can readily be separated from the precious metals by the simple process of cupellation. The lead alloy from the metal layer of an assay fusion is known as the "lead button." It must be produced under conditions that give:

1. Limited amounts of base-metal impurities.
2. Good collection of the precious metals.
3. A button close to the desired size.

Impurities of the Lead Button

Base-metal impurities in the lead button vary in their effect. Most base metals, with the exception of bismuth, will cause trouble in cupellation if they are present in the lead button in sufficient amount (Chap. IV). Fortunately, only a few metals and metalloids are low enough in the electromotive series that they can be reduced in an assay fusion and have the opportunity of alloying with the lead. A glance at the electromotive series shows that, besides the precious metals, there are only antimony, bismuth, arsenic, copper, tellurium, and mercury below lead. It is to be expected that when any of these elements are present in an assay fusion, they will be at least partly reduced and may

contaminate the lead button. Mercury is reduced the easiest of all these impurities, but it does not contaminate the lead button because it boils at 356.9°C., and, consequently, in the assay fusion it vaporizes and leaves the assay charge as soon as it is reduced.

Bismuth.—Bismuth is difficult to separate from lead, as it behaves so nearly like lead. In the assaying or lead smelting of ores containing bismuth, most of the bismuth is always reduced and alloys with the metallic lead. The separation of bismuth from lead is a difficult refining operation[1] even at lead smelters, and the processes used cannot be adapted to fire assaying. Bismuth can be cupeled similarly to lead, and a bismuth-lead alloy cupels without difficulty, so that the presence of bismuth in an ore does not interfere with the actual mechanism of the assay process. The doré bead produced from high bismuth ores, however, contains some bismuth, because it is more difficult to oxidize than lead. This residual bismuth adds to the silver assay but does not affect the gold result. At the present time, there is no known variation of the fire assay process that will eliminate bismuth from the doré bead. Accurate silver results can be had only by correcting for its bismuth content.

Antimony, Arsenic, Copper, and Tellurium.—The other troublesome impurities, that is, antimony, arsenic, copper, and tellurium, are easier to oxidize than are bismuth and mercury. Their concentration in the lead button can be lowered by the use of an excess of litharge in the assay slag. In any event a certain fraction of the impurity present in the charge will be reduced and will contaminate the lead button. Hence, in assaying impure ores, large samples cause much more difficulty than do small samples. Occasionally a sample smaller than would ordinarily be used must be taken, in order to reduce the concentration of some impurity in the lead button.

Use of Excess Litharge.—The effect of excess litharge in helping to keep the impurities out of the lead button depends upon its ability to keep them oxidized while some lead remains reduced; the action on copper is typical. Lead has a greater tendency to combine with oxygen than has copper, and it is only by the mass

[1] BETTERTON, JESSE O., and LEBEDEFF, YURII E., Debismuthizing Lead with Alkaline Earth Metals, Including Magnesium, and with Antimony. *Trans. A.I.M.E.*, vol. 121, p. 205, 1936.

action of excess litharge that a lead button can be reduced without reducing nearly all the copper in the charge. In an assay fusion of a copper-bearing ore the equilibrium constant of the following reaction governs the amount of copper reduced.

$$PbO + 2Cu \rightleftharpoons Cu_2O + Pb \tag{1}$$

According to the laws of mass action, we may write

$$\frac{A[Pb]A[Cu_2O]}{A[PbO]A^2[Cu]} = K \tag{2}$$

where K is the equilibrium constant and A represents the activity. The activity of the metallic lead and copper in the reaction is not known, but with a constant amount of lead produced and with a definite amount of copper allowed in the lead their activities must be constant.

$$\frac{A[Pb]}{A^2[Cu]} = K_1 \tag{3}$$

Substituting (3) in (2),

$$\frac{A[Cu_2O]}{A[PbO]} K_1 = K \tag{4}$$

Then a new constant, K_2, can be introduced for $\frac{K}{K_1}$,

$$\frac{A[Cu_2O]}{A[PbO]} = K_2 \tag{5}$$

The activities of the cuprous oxide and the lead oxide in the charge are proportional to the concentrations present, and therefore

$$\frac{\text{Concentration Cu O}}{\text{Concentrat on PbO}} = K_2 \tag{6}$$

Equation (6) shows that the amount of copper retained in oxidized form, and therefore remaining in the slag, is in proportion to the concentration of free PbO in the slag. The activity of PbO, when combined with silica, is very low and is therefore not effective in oxidizing copper. Accordingly, with a constant amount of litharge in the charge an increase in silica decreases

the free PbO and consequently more copper enters the lead bullion.

The problem of softening lead bullion in the refining of crude lead by the removal of the hardening constituents—arsenic, antimony, copper, and tin—is similar to that of keeping these impurities out of the lead button in assaying. Of these metals, tin does not contaminate the assay button nearly to the extent that it enters the lead bullion in a blast furnace, because of the difference in amount of reduction in the two processes. In all but the uncontrolled reduction assay fusions, reduction and oxidation are so adjusted that at the end of the operation both lead and lead oxide exist together. In the lead blast furnace and in uncontrolled reduction methods of assaying, much more reduction is carried out in an effort to reduce all lead oxide to lead. For this reason these processes carry an excess of reducer, which reduces a considerable amount of the tin in the charge, even though tin is above lead in the electromotive series. In the controlled reduction assay charge, a deficient amount of reducer is used so that tin and other metals above lead in the series are not reduced and, consequently, cannot contaminate the lead button.

The other metals—arsenic, antimony, and copper—contaminate assay lead buttons as well as the smelter's lead bullion. Two processes are available for the softening of lead bullion: (1) softening in a reverberatory furnace with litharge and (2) softening in a kettle with soda salts (Harris process).

Softening in a reverberatory furnace with litharge depends upon the oxidation effect of excess litharge, and the principle is exactly the same as in the case where excess litharge is used in a crucible assay charge. The refiner can carry the separation further than can the assayer, as he continually removes the oxidized impurities by skimming, and so disturbs the equilibrium and allows the type reaction (1) to proceed in the direction of further oxidation of impurities. The assayer does not have available this method of changing equilibrium and can force the reaction in the desired direction only by adding more litharge.

Use of Soda Salts.—Softening in a kettle with soda salts depends upon the ease of oxidizing arsenic and antimony to form arsenates and antimonates in a molten alkaline salt environment. This process does not separate copper, and, consequently, when

the Harris process is used in lead refining, copper must be removed by an additional process.

The authors have tried crucible assays with very alkaline slags in the hope of obtaining some of the refining effect of the Harris process. On the whole the results were discouraging; normal crucible assay charges caused less trouble from boiling over and gave better slags. It should be remembered, however, that, in an ordinary crucible assay of sulfide ores, arsenic oxidizes to As_2O_5 and requires extra base to form arsenate. An additional amount of sodium carbonate is usually added for this purpose.

Separation of Impurities by Scorification.—Scorification consists of heating the material to be scorified, whether it is an impure lead button or an ore sample, with granulated lead in a shallow fire-clay dish which is exposed to an oxidizing atmosphere. In the process, oxidation proceeds rapidly and a large proportion of the lead present is oxidized to litharge. The scorification process has no greater ability to eliminate impurities, except volatile ones, than has the crucible assay. The amount of impurities remaining oxidized at the end of the fusion depends mainly upon the proportion of free PbO existing in the slag at the end of the operation. Whether the final state is reached by partial oxidation of lead (scorification) or by partial reduction of litharge (crucible assay) makes little difference. In the scorification operation, silica is taken up from the scorifying dish so that the slags do not contain so large an amount of free PbO as one would expect. For this reason it is usually better to treat impure lead buttons by melting them in a crucible with litharge and then swirling for a few minutes than it is to scorify them.

Collection of the Precious Metals

Complete collection of the precious metals by lead during an assay fusion is desired. Actually, recovery is never quite complete, and the ratio of loss to recovery is dependent upon one or more of the following factors: (1) mechanical release of the precious-metal particles by fusion of the surrounding material; (2) contact of the released precious-metal particles with molten lead; and (3) solubility of the precious metals in the various phases present at the end of the fusion.

Release by Fusion.—The material surrounding the precious-metal particles must be fused to a mobile liquid, in order to

release the precious-metal particles for collection. Loss due to incomplete fusion should not be tolerated, since lumpy and viscous melts can be avoided by the use of properly proportioned fluxes and a suitable temperature.

Contact with Lead.—In order to be collected by lead, each particle of precious metal must actually contact molten lead. The action is quite similar to the amalgamation of gold by liquid mercury at ordinary temperatures. Although granulated lead is used in the scorification assay and small lead droplets are reduced from litharge well distributed through the crucible assay charge, it seems impossible to have sufficient contact between the precious-metal particles and the lead particles by their position in the assay charge. More likely, only a few precious-metal particles find themselves actually in contact with lead particles immediately upon release. The larger of the precious-metal particles readily settle through the molten slag to the metal phase below; the remainder probably encounter particles of lead, or even the lead button itself, during their circulation in the slag. Moreover, after the reactions have become complete, circulation, probably due to convection currents, can be observed in the molten slag. The ease with which good collection of the precious metals is obtained in assay fusions is remarkable.

Even in a fusion without any lead to serve as a collector there is almost complete elimination of gold and silver from the slag. After pouring such a melt the greater part of the precious metals will be found in the crucible. They are distributed in many small specks adhering to the crucible wall, so that the simple addition of lead to the molten fusion does not suffice to collect all of them. A study of collection subsequent to fusions, made in the absence of metallic lead,[1] has shown that the reduction of litharge to lead in the charge, and the stirring action of the charge produced by the addition of litharge and iron filings, are necessary for good collection. When lead is present at the time that the fusion is made, good collection is easier to obtain. The assayer may be certain that he is not seriously in error because of lack of contact between the precious metals and molten lead when

[1] SHEPARD, O. C., and DIETRICH, W. F., Oxidation-collection Method of Assaying Sulphide Ores for Gold and Silver, in *A.I.M.E. Tech. Pub.* 997; *Metals Technology*, vol. 6, No. 2 (1939).

a fluid slag is produced, and when more than 15 g. of lead are reduced. When less than 10-g. buttons are reduced in crucible fusions, erratically low results are frequently obtained; obviously the loss is due to lack of contact with lead for collection. In scorification, good collection of gold and silver is obtained with smaller buttons than in the crucible assay, partly because of the smaller ore charge and partly because collection is nearly complete while the button is still relatively large, and the ensuing shrinkage of the button during scorification virtually does some of the work of cupellation. Hence, buttons weighing 10 to 15 g. are usually satisfactory, unless they are to be cupeled adjacent to larger buttons.

In the crucible assay, increasing the amount of lead reduced above 20 g. does not continue to reduce greatly the loss encountered in fusions. The fact that one fusion in which a 40-g. button is reduced does not give so low a slag loss as a 20-g. button fusion, followed by a reassay of the slag to produce an additional 20-g. button, points to solubility of precious metals in the slag as the major source of loss.

Whether the usual small loss in an assay fusion is due to uncollected values or to slag solubility is difficult to determine. Ravitz and Fisher[1] have studied the distribution of gold and silver between lead, speiss, matte, and slag, by fusing these products with gold chloride and silver nitrate in a crucible. With equal weights of lead, speiss, matte, and slag, definite ratios were found between the gold and silver dissolved in the lead and that dissolved in the speiss and matte. In general the amount of silver in the speiss was close to 1.2 times that in the lead, while the silver in the matte was about 0.54 times that in the lead. Gold showed greater solubility in the speiss and less solubility in the matte; the amount of gold in the speiss was close to 1.6 times that in the lead, and the amount of gold in the matte about 0.07 times that in the lead. The distribution of values between the slag and lead was erratic, and both the gold and silver content of the slag varied from 0.001 to 0.01 times that of the lead. This is roughly the order of magnitude of the slag loss in assaying; but in assay fusions with different compositions of phases and with different proportions of slag to lead,

[1] Ravitz, S. F., and Fisher, K. E., Equilibrium in Lead Smelting, *Trans. A.I.M.E.*, vol. 121, p. 118, 1936.

considerable difference in the distribution of gold and silver is to be expected.

These results do show, however, the comparatively high solubility of gold and silver in lead, matte, and speiss; and the comparatively low solubility in slag. The control of these phases to secure high recovery of the precious metals in the lead button is discussed at greater length in the paragraphs on each phase.

Size of the Lead Button

The assayer, by controlling the amount of metallic lead existing at the end of the assay fusion, controls the size of the lead button. A size is desired that is a compromise between the inconvenience and added cost of cupeling large buttons and the increased loss of values occasioned by small buttons. Although the loss of values increases markedly when lead buttons weighing much less than 15 g. are produced in crucible assays, the recovery does not increase greatly with increase in lead-button size above 25 grams. In most cases a lead button weighing about 25 g. is desired. This is small enough to be economical and large enough so that further increase in size, within practical limits, gives scarcely appreciable added recovery. If extremely high recovery is necessary it is better to re-treat the slag as in a corrected assay rather than to increase the button size. An important reason for desiring uniformity in the size of lead buttons is the increased convenience and accuracy of cupeling buttons of uniform size.

During an assay fusion the lead button is produced by either (1) starting with lead oxide in the charge and reducing just a sufficient amount of lead for the lead button, as in the crucible assay; or (2) starting with an excess of granulated lead in the charge and oxidizing all but the amount required for the lead button, as in the scorification assay. The production of a lead button and the control of its size in either case depend upon the reactions taking place during fusion.

Crucible Assay.—Some crucible assay methods use excess reduction and limit the amount of lead compounds in the charge, in order to control the size of the lead button. If harmful impurities are present, their reduction to metal in such uncontrolled reduction methods may cause button contamination or other

difficulties. In controlled reduction assay methods, more litharge is added to the charge than is required for the lead button. Lead oxide is always available for the slag. The size of the lead buttons in the controlled reduction methods depends upon production in the assay fusion of just sufficient reduction to reduce the required amount of lead. Reduction is affected by (1) minerals, some of which have an oxidizing or reducing effect, and by (2) oxidizing or reducing agents, one of which is usually required in the charge to regulate the amount of reduction. Ores or materials to be assayed may contain no important amounts of oxidizing or reducing minerals to cause either oxidation or reduction of lead. A knowledge of the amount of lead reduced by the reducing minerals, and the amount of lead that is prevented from being reduced by oxidizing minerals present in the ore, is essential in order to determine the amount of oxidizing or reducing agent that must be added to the charge to produce a lead button of suitable size. For convenience in calculations, all figures for oxidation or reduction are referred to the corresponding weight of lead, even though the oxidizing or reducing agent may not react directly with lead or litharge.

The *reducing power* (R.P.) of any substance is defined as the weight of lead, in grams, reduced by 1 g. of that substance. Power as used here refers only to the quantity of material. A high reducing power does not mean ability to reduce metals high in the electromotive series. The *reducing effect* (R.E.) of any substance is the weight of lead reduced by the total amount of that substance in the charge. The *oxidizing power* (O.P.) of any substance is defined as the weight of lead, in grams, that is prevented from being reduced by 1 g. of that substance. The *oxidizing effect* (O.E.) of any substance is the amount of lead prevented from being reduced by the total amount of that substance in the charge.

Reducing Agents.—Reducing agents are substances added to the charge to take up oxygen and reduce litharge to lead. They are used only when the ore has insufficient reducing effect to produce the size of lead button desired. Commonly used reducing agents are: flour, charcoal, argol, sulfur, and metallic iron; many other substances could be used.

Ordinary *flour* contains about 15 per cent moisture, 70 per cent starch, and smaller amounts of proteins, sugars, and other

organic compounds. Only a small error in reducing power is made by lumping all the organic compounds in flour together, and, considering flour to be 85 per cent starch, as represented by the formula $C_6H_{10}O_5$,

$$\begin{array}{rcl} 12PbO + C_6H_{10}O_5 & = & 12Pb + 6CO_2 \\ 162 & & 2{,}486 \end{array}$$

In the above equation, 12 atoms of lead or 2,486 parts by weight are reduced by 1 molecule of starch or 162 parts. The theoretical reducing power of pure starch is 2,486/162 or 15.3. If we consider flour to be 85 per cent starch, its theoretical reducing power would be 13.0. The actual reducing power varies somewhat with different types of flour. The reducing power of a typical wheat flour was found to vary from 12.2 to 11.0, depending upon the acidity of the slag. Reducing agents from which incompletely oxidized gaseous products may be formed give lower reducing power in charges producing acid slags than in basic charges. This occurs with all organic reducers, because carbon can escape from the charge as CO instead of CO_2, and occurs with sulfur, which may be lost as elemental sulfur or as SO_2 instead of forming sulfates. The actual reducing power in basic charges is frequently close to the theoretical value. In basic charges there is plenty of available litharge, so that even a gaseous reducer cannot escape from the charge without nearly complete reaction. In acid charges the litharge particles are nearly all in contact with acids, and incipient reaction to form borates and silicates reduces the amount of free PbO available for lead formation before the reducing agent has completed its work. When there is a deficiency of free PbO present the efficiency of reducers that can escape from the charge is lowered. On the other hand a reducer such as iron that cannot escape from the charge will produce its full quota of lead, even from acid charges and from lead silicate slags. Flour will not reduce lead from an acid slag containing lead silicate.

The reducing power of *charcoal* depends mainly upon its carbon content and varies with the purity.

$$\begin{array}{rcl} 2PbO + C & = & 2Pb + CO_2 \\ 12 & & 414 \end{array}$$

Theoretically, 1 g. of carbon will reduce 34.5 g. of lead. Most charcoal in use contains a considerable amount of ash, so that lower reducing powers are obtained in practice. If charcoal is added separately to each crucible, it is desirable to dilute it with an equal weight of silica, so that greater variation may be allowed in measuring out the amount required.

Argol consists of the crude potassium acid tartrate that is deposited in the process of making wine. The reducing reaction with pure potassium acid tartrate is given below:

$$\underset{}{10PbO} + \underset{376}{2KH(C_4H_4O_6)} = \underset{2{,}070}{10Pb} + 8CO_2 + 5H_2O + K_2O$$

According to the reaction the reducing power of potassium acid tartrate is 2,070/376 or 5.5. Impurities usually present in argol increase the reducing power considerably above that of the pure tartrate. The argol reducing reaction produces K_2O, which acts as a basic flux; but the amount produced is small and can have little effect.

The reducing power of *sulfur* not only varies with the acidity of the charge, but also with the sodium carbonate content of the charge. In a very basic charge with sufficient PbO but with no sodium carbonate present, sulfur is oxidized to SO_2.

$$\underset{}{2PbO} + \underset{32}{S} = \underset{414}{2Pb} + SO_2$$

In this reaction, sulfur has a reducing power of 12.9. With the addition of soda to the same charge the reducing power of sulfur increases to a maximum of 19.4 corresponding to the nearly complete oxidation of sulfur to SO_3. Sodium carbonate goes through a series of reactions in an assay fusion with sulfur and litharge, to produce finally sodium sulfate.

$$2PbO + S = 2Pb + SO_2 \quad (1)$$

$$SO_2 + Na_2CO_3 = Na_2SO_3 + CO_2 \quad (2)$$

Sodium sulfite is unstable at that temperature and forms sodium sulfide and sodium sulfate.

$$4Na_2SO_3 = 3Na_2SO_4 + Na_2S \quad (3)$$

Sodium sulfate is an end product, but sodium sulfide reduces more lead.

$$3PbO + Na_2S = 3Pb + Na_2SO_3 \qquad (4)$$

The sodium sulfite formed in reaction (4) follows the last two steps over and over until all the sulfur is converted to sulfate. The series of reactions may be represented by a single equation:

$$\underset{32}{3PbO + S + Na_2CO_3} = \underset{621}{3Pb + Na_2SO_4 + CO_2}$$

from which the reducing power of sulfur is 19.4.

It is desirable to dilute strong reducers, such as sulfur, by mixing them with a material having no oxidizing or reducing effect to permit easier measuring of the required amount. If sulfur is diluted with 3⅓ parts of sodium carbonate the soda required for the formation of sodium sulfate is automatically provided. One gram-molecule of Na_2CO_3 (106 g.) is required for each atom of sulfur (32 g.)—106 ÷ 32 = 3.34.

Iron, as a reducing agent, differs from carbon, hydrocarbon, or sulfur in that (1) it cannot escape from the charge as a gas at any stage of the process, (2) it cannot migrate through an unfused charge to meet and reduce lead compounds, and (3) it has sufficient density to sink through a molten slag where it contacts lead compounds and reduces them more effectively than do reagents of low density. These characteristics make iron a suitable reducing agent for the oxidation-collection method and for the soda-iron method. Carbon, hydrocarbon, or sulfur fails to give satisfactory results in either of the above processes. In the oxidation-collection method, flour fails to give good collection of the precious metals, even though a suitable-sized lead button is reduced. The poor result with flour may be due to a too rapid reaction, or to reduction from the surface instead of down in the liquid melt. Tests comparing the use of iron with that of other common reducing agents in the ordinary crucible assay should be made. Iron will reduce lead at a later stage in the process, which may or may not be an advantage. It has the disadvantage of contributing its oxide to the slag. The reducing power of iron in normal assay charges is about 3.7, as shown by the reaction:

$$\underset{56}{PbO.SiO_2 + Fe} = \underset{207}{Pb + FeO.SiO_2}$$

Reducing Minerals.—Reducing minerals are those minerals which, if present in a crucible assay charge, will reduce litharge to lead. Some ores contain graphite or sulfur, but the usual reducing minerals encountered in assaying are the metal sulfides. The reducing power (R.P.) of metal sulfide minerals may be considered to be made up of two parts: (1) reduction caused by oxidation of the metal and (2) reduction caused by oxidation of the sulfur.

Pyrite has a reducing power equal to the amount of lead reduced by the 0.466 g. of iron and 0.534 g. of sulfur contained in 1 g. of pyrite. The reducing power can be calculated from either a knowledge of the reducing power of iron and sulfur or the combining weights.

Calculations of the Reducing Power of Pyrite

1. Without sodium carbonate and with excess litharge, sulfur oxidized only to SO_2.

a. By the reducing power of the constituents.

0.466 g. of Fe × R.P. 3.7 = 1.7 g. of lead reduced
0.534 g. of S × R.P. 12.9 = 6.9 g. of lead reduced
1.000 g. of FeS_2 = 8.6 g. of lead reduced (R.P. of pyrite)

b. By the combining weights.

One gram-molecule of pyrite, 120 g., requires 5 oxygen atoms to form one FeO and two SO_2. Five gram-atoms of lead are reduced, 207 × 5 = 1,035 g.

The lead reduced by 1 g. of pyrite or the R.P. of pyrite is found from the proportion:

FeS_2 5Pb
120 : 1,035 : : 1 : R.P. of pyrite
R.P. of pyrite = 8.6

2. With excess sodium carbonate and litharge, sulfur oxidized to SO_3.

a. By the R.P. of the constituents.

0.466 g. of Fe × R.P. 3.7 = 1.7 g. of lead reduced
0.534 g. of S × R.P. 19.4 = 10.4 g. of lead reduced
1.000 g. of FeS_2 = 12.1 g. of lead reduced (R.P. of pyrite)

b. By the combining weights.

One gram-molecule of pyrite, 120 g., requires 7 oxygen atoms to form one FeO and two SO_3. Seven gram-atoms of lead are reduced, $207 \times 7 = 1{,}449$ g.

FeS_2 7Pb

120 : 1,449 : : 1 : R.P. of pyrite

R.P. of pyrite = 12.1

Sometimes chemical equations are written to express the reduction of litharge to lead by pyrite in an assay fusion.

Without sodium carbonate:

$$FeS_2 + 5PbO + SiO_2 = 5Pb + FeO.SiO_2 + 2SO_2\uparrow$$

With sodium carbonate in excess:

$$FeS_2 + 7PbO + 2Na_2CO_3 + SiO_2 = 7Pb + FeO.SiO_2 + 2Na_2SO_4 + 2CO_2$$

These reactions should be regarded as the net result of the complicated intermediate reactions that actually take place.

The general study of the reducing power of all sulfide minerals is simplified by considering separately the reduction caused by metal and sulfur.

Metal Effect.—Many metals form more than one oxide, so that in order to calculate the metal part of the reducing power of sulfide minerals, the final stage of oxidation of the metal should be known. This can be determined by experiment. Results indicating the state of oxidation of metals and metalloids from the reducing power of common sulfide minerals are given in Table X. The measured reducing power given in the table is the highest value found in very basic charges with excess sodium carbonate and litharge. When sulfur alone is used in such charges, the full reducing power of sulfur to SO_3 is obtained; therefore it is assumed that the observed maximum reducing power of the sulfide minus the theoretical maximum reducing power of the sulfur in the sulfide gives a measure of the reducing power of the metal in the sulfide. Basic charges favor the formation of the higher metal oxide, and yet the calculated reduction by most metals is less than the theoretical value for the lowest metal oxide. Where lower results are obtained, the difference is due to the assumption of complete sulfur oxidation in the calculations. Both arsenopyrite and pyrite, however, give higher values than the theo-

retical for the lowest oxide. This can be caused only by (at least a part of) the metal going to the higher oxide. This conclusion has been verified in the case of arsenic by the fact that arsenious oxide gives a reducing power of at least 1.7 in basic charges, which is close to the theoretical value of 2.09 for conversion of all of the trioxide to the pentoxide. Antimonious oxide has no reducing power, and the experimental value for the metal reducing power, as given in Table X, also verifies the conclusion that antimony does not oxidize beyond the trivalent form in assay charges.

TABLE X.—INDICATED OXIDATION STATE OF METALS

Metal "M"	Mineral investigated	Weight of lead reduced by the oxidation of "M" in 1 g. of mineral					Indicated oxide
		Theoretical				Measured*	
		M_2O	MO	M_2O_3	M_2O_5		
Copper.....	Chalcocite	1.3	2.6	...	...	1.0	Cu_2O
Iron.....	Pyrite	...	1.7	2.6	...	2.2	Fe_2O_3†
Lead.....	Galena	...	0.9	...	...	0.8	PbO
Zinc.....	Sphalerite	...	2.1	...	...	2.1	ZnO
Antimony.....	Stibnite	...	...	1.8	3.0	1.7	Sb_2O_3
Arsenic.....	Arsenopyrite	...	..	1 9	3.2	2.9	As_2O_5

* The values in this column were obtained by deducting the calculated reduction of lead, due to oxidation of sulfur to SO_3, from the maximum measured R.P. of minerals in very basic charges. For arsenic the calculated reduction due to oxidation of iron to FeO was also deducted from the measured R.P. of arsenopyrite.

† Oxidation of iron to Fe_2O_3 takes place only in the very basic charges that were used in this experiment in order to obtain nearly complete oxidation of sulfur to SO_3.

Sulfur Effect.—A large part of the reducing power of most sulfide minerals is due to sulfur, and the reducing power of sulfur is in general more variable than that of metals. Consequently the factors influencing the reducing power of sulfur are the critical variables affecting the reducing power of sulfide minerals. Within the range of practicable assay slags the most important of these factors are: (1) the molecular ratio of litharge to soda in the slag, (2) the silicate degree of the slag, (3) the extent to which silica is replaced by an equivalent of borax glass, and (4) the molecular ratio of total base fluxes to metal sulfides.

1. The optimum molecular ratio of litharge to soda is 1.0, which nearly corresponds to 2 parts of litharge and 1 part of sodium carbonate by weight. If this ratio is increased without increasing the total flux ratio the reducing power generally decreases and becomes sensitive to variations in the silicate degree of the slag. Decrease below 1 in the litharge-soda ratio, if not carried to an extreme, has little effect on reducing power, but in practice, too much sodium carbonate is avoided on account of its bulk and the evolution of CO_2.

2. If the slags are more acid than the monosilicate the reducing power of sulfides decreases with increased silicate degree and becomes sensitive to a number of factors that are difficult to control, thus giving erratic results.

3. All or part of the silica may be replaced by the silicate degree equivalent of borax glass in slags less acid than the monosilicate without significant effect on the reducing power of sulfides, but, in more acid slags, borax glass is a more potent depressant of the reducing power than silica.

4. The full theoretical reducing power of sulfides is not approached unless the ratio of base fluxes to sulfide is somewhat higher than is necessary or convenient for satisfactory slag formation and button purity. However, if the volume of fluxes is sufficient for satisfactory fluxing, and if the three foregoing conditions are satisfied, the reducing power will be sufficiently constant, although somewhat less than the theoretical value. This consideration usually implies the presence of soda for slag formation in amount at least equal to the weight of ore taken for assay.

Since any variations in the state of oxidation of the metal portion of a sulfide mineral has been shown to have a minor effect on reducing power, the chief effect of any variable tending to decrease reducing power is incomplete oxidation of the sulfur. Although the lack of complete oxidation is due mainly to escape of incompletely oxidized sulfur from the charge, it is usually necessary to proportion the constituents of an assay charge to ensure maximum oxidation of sulfur and its conversion to sodium sulfate, which forms an alkaline salt layer above the slag. If this is not done the buttons may be brittle from entrapped sulfide or from the presence of reduced metals other than lead; or a separate matte or speiss layer may be formed. Hence, condi-

tions that favor maximum reducing power also favor maximum button purity.

To illustrate the order of magnitude of the important factors affecting the reducing power of sulfides, the reducing power of stibnite (Sb_2S_3) under various conditions is shown graphically on Fig. 9.[1] It should be noted that for all the slag types illustrated the reducing power does not vary greatly in the sub- to monosilicate range; and where the litharge-soda ratio is 1.0 or less, the reducing power of the subsilicates approaches the

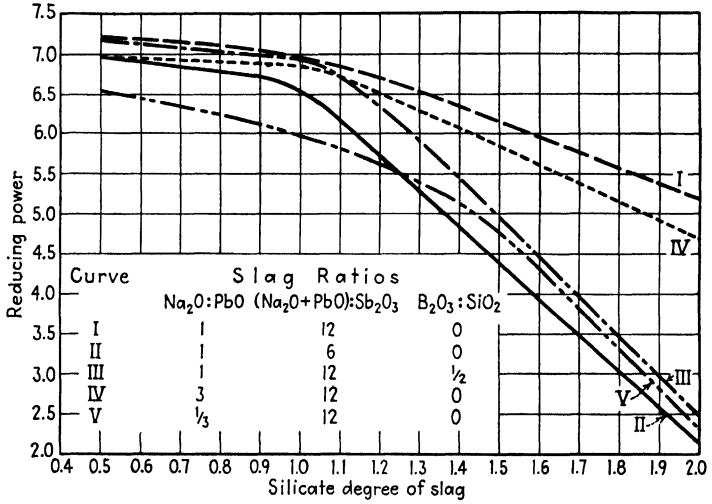


FIG. 9.—The reducing power of stibnite.

theoretical value of 7.3 for oxidation of the antimony to Sb_2O_3, and the sulfur to SO_3. With slags more acid than a monosilicate, however, the reducing power decreases notably with all slag types; and this effect is intensified by lower flux ratios, higher litharge-soda ratios, and by the substitution of borax glass for silica. In the series of tests illustrated by Fig. 9, all buttons produced under conditions that gave a reducing power much below 6.0 were brittle. Embrittlement or hardening of the buttons occurred in similar series of tests with galena, pyrite, arsenopyrite, and sphalerite whenever the reducing power was

[1] Unpublished investigation by the authors.

considerably below the theoretical value, which emphasized the necessity for nearly complete oxidation of sulfur in crucible fusions. With the copper minerals—chalcocite and chalcopyrite —a considerable excess of litharge is needed to keep copper from the button; therefore the litharge-soda ratio is much greater than is recommended for other sulfides, but this is compensated for by the considerably greater total flux ratio, and these sulfides, in very basic charges, give nearly their true theoretical reducing power.

In the crucible assay of sulfide ores, empirical rules are applied to flux proportioning in order to ensure satisfactory slags and buttons. These rules are developed more fully in a later section. The conditions to be met in order to satisfy the need for nearly complete oxidation of sulfides may be summarized as follows: (1) provide sodium carbonate for slag at least equal to the weight of the ore sample, (2) provide twice as much litharge for the slag as sodium carbonate, and (3) keep the silicate degree of the slag below 1.0. Additional sodium carbonate is needed for the formation of sodium sulfate, in the ratio of 3.34 sodium carbonate to 1 sulfur; and additional litharge must, of course, be provided for the button. Whether or not additional fluxes, or altered flux ratios, are required depends upon the nature of the metal portion of the sulfide and the difficulty of carrying the metal oxide in the slag.

Oxidizing Agents.—In the controlled reduction methods of assaying, oxidation is used to lower the reducing effect of sulfide ores that would otherwise produce too large a lead button. Oxidation can be produced by heating the ore when it is spread out in a thin layer, exposed to the air (roasting). The roasting process is slow and serves only to destroy the reducing power of the ore so that the size of the lead button can be controlled in a subsequent crucible fusion with a known reducing agent. This method is seldom used in modern assaying. Much time and effort can be saved by mixing an oxidizing agent with the ore in a crucible charge so that both oxidation and fusion can be carried out in the crucible. Either a single-stage or two-stage process may be used. In the single-stage, or ordinary niter, process just enough oxidizing agent is added to oxidize the excess reducing effect (R.E.) of the ore and to produce the desired size of lead button.

The two-stage process, known as the "oxidation-collection method," has the advantage that the amount of oxidizing agent does not need to be carefully proportioned to suit each individual ore. This is avoided by mixing an excess of oxidizing agent with the crucible charge.

Complete oxidation of the reducing minerals is accomplished in the early stages of the fusion, and the excess oxidizing agent is decomposed by heat. Near the end of the fusion, collection of the precious metals is brought about by the addition of a briquette containing litharge and sufficient iron filings to reduce a lead button of the desired size.

The oxidizing agent universally used in either the single-stage or two-stage process is niter (potassium nitrate). *Niter* decomposes when heated to over 400°C. The first step consists of the evolution of 1 atom of oxygen leaving potassium nitrite.

$$2KNO_3 = 2KNO_2 + O_2$$

With continued heating, KNO_2 decomposes, evolving more oxygen and nitrous oxide and leaving potassium oxide.[1]

$$2KNO_2 = K_2O + N_2O + O_2$$

According to these reactions, 1 gram-molecule of niter (102 g.) will furnish 1 gram-molecule of oxygen, which will oxidize 1 gram-molecule of carbon or equivalent reducer, and as a result will prevent the reduction of 2 gram-molecules of lead (414 g.). This gives a value of $414/102$, or 4.1 for the oxidizing power (O.P.) of niter in terms of lead. In the usual assay charge, an oxidizing power of about 4 is the value actually obtained. Fulton and Sharwood[2] obtained an oxidizing power value of 5.1 for niter in special charges containing only litharge, niter, and charcoal. This corresponds to a theoretical oxidizing power of 5.12, and was obtained by considering all the oxygen, except that required for K_2O, available for oxidation and that no oxides of nitrogen are evolved. Whether 4.1 or 5.1 is the theoretical oxidizing power of niter is of little importance, because the actual oxidizing power is

[1] PRESCOTT, A. B., and JOHNSON, J. C., "Qualitative Analysis," 7th ed., p. 288, D. Van Nostrand Company, Inc., New York, 1916.

[2] FULTON, C. H., and SHARWOOD, W. J., "A Manual of Fire Assaying," 3d ed., p. 78, McGraw-Hill Book Company, Inc., New York, 1929.

close to 4, and this value is satisfactory in the range of slag compositions required for sulphide ores.

Oxidizing Minerals.—Some ores contain minerals such as hematite, magnetite, and pyrolusite, which give up a part of their oxygen in the fire assay. The oxygen given up oxidizes reducing agents so that when a large amount of any of these oxidizing minerals is present in the charge, the amount of reducing agent must be increased.

The theoretical oxidizing power of *hematite* (Fe_2O_3) is derived from the equations

$$2Fe_2O_3 + C \rightarrow 4FeO + CO_2$$
$$2PbO + C \rightarrow 2Pb + CO_2$$

One gram-molecule of hematite combines with an amount of a reducing agent that is equivalent to 1 gram-molecule of lead; therefore the oxidizing power of hematite, in terms of lead, is $^{207}/_{160}$ or 1.31. Analogous calculations show that the theoretical oxidizing power of *pyrolusite* (MnO_2), when reduced to MnO, is 2.4; and the oxidizing power of *magnetite* (Fe_3O_4), when reduced to FeO, is 0.89. In practice, the full oxidizing power of oxidizing minerals is seldom attained, either on account of incomplete reduction or by loss of oxygen gas from the charge.

Summary. Size of Lead Button in the Crucible Assay.—In general the assayer desires to produce from a crucible assay fusion, a lead button that weighs about 25 g. If the ore contains no oxidizing or reducing minerals a reducing agent such as flour or charcoal is mixed with the charge. The weight, in grams of reducing agent required, is figured by dividing the weight of the lead button desired by the reducing power of the particular reducing agent used. When an ore contains either oxidizing or reducing minerals, or both, the net oxidizing or reducing effect of the ore must be determined if the ordinary single-stage assay is to be used. The oxidizing or reducing effect can be calculated from an estimate of the minerals present, and a knowledge of their oxidizing or reducing powers; or it can be determined by a preliminary assay. If the effect of the ore is oxidizing, a reducer is added to give the desired size of lead button with sufficient extra reducer to balance the oxidizing effect of the ore. If the effect of the ore is reducing but not sufficient to produce a large enough lead button, reducer is added to make up the difference.

If the reducing effect of the ore is just right, neither an oxidizing nor a reducing agent need be added. When the reducing effect of the ore is so great as to produce oversize buttons the weight desired is subtracted from the reducing effect of the ore, and the excess reducing effect is balanced by adding niter. The necessity for either an estimation or a preliminary fusion may be eliminated by the new oxidation-collection method (Chap. VII).

Scorification Assay.—In the scorification assay a small ore sample—usually 0.10 assay ton—is mixed with granulated lead in a shallow fire-clay dish (scorifier) and heated in an oxidizing atmosphere. A small amount of silica or borax glass is added if the ore is free from silica, and the slag obtains additional silica by attack upon the scorifier. Roasting reactions remove sulfur and other reducing agents. A part of the lead is oxidized progressively throughout the process, and the litharge produced forms the greater part of the slag. At first, a ring of slag forms at the outer periphery of the lead, which, on account of its high surface tension, assumes an ellipsoidal shape, whereas the slag surface is nearly flat. The process stops when sufficient slag has formed to cover completely the diminishing pool of lead. Hence, scorification is, in effect, a controlled oxidation method in which the final volume of the slag and the size of the lead button bear a geometrical relationship to each other; and the button size is dependent chiefly upon the following factors; (1) the amount of granulated lead added at the start, (2) the size and shape of the scorifier, and (3) the amount of ore and flux added. The character of the ore and minor variations in the furnace temperature do not seriously influence the size of the lead button.

The Speiss Phase

When arsenic or antimony is present in the lead smelter or in assay fusions it can appear in one or more of the three phases: slag, speiss, or metal. If arsenic and antimony are oxidized, they can neither form a speiss nor enter the metal phase. On the other hand, when they are reduced, they cannot enter the slag and consequently must appear in either the speiss or metal phase. Where they do appear, when reduced, depends upon the reduced metals present. If lead is the only metal present, reduced arsenic or antimony alloys with it and the lead is notice-

ably hardened. Speiss consists of compounds such as Fe_3As, NiAs, Cu_3As, and Cu_3Sb, formed by arsenic or antimony with one or more of the following metals: iron, nickel, cobalt, or copper. In lead smelting the speiss-forming metals are usually present, so that both speiss and hard lead are formed.

Speiss in Lead Smelting.—Speiss dissolves precious metals, and it is therefore undesirable in either an assay or a lead smelter. The assayer can and must avoid speiss formation, but the lead smelters are still troubled with this undesirable product. The amount of reduction necessary in the two processes accounts for its formation in one case and not in the other. In controlled reduction assaying, only part of the lead in the charge is reduced; while in the blast furnace of a lead smelter, strongly reducing conditions must be maintained in an effort to recover all the lead. The relatively strong reduction in a lead blast furnace not only prevents the oxidation of arsenic and antimony but also reduces part of the speiss-forming metals—iron, cobalt, nickel, and copper—some of which are always present in the blast-furnace charge. Under these conditions, speiss forms.

Speiss in Assaying.—In a controlled reduction assay fusion of materials high in antimony and arsenic there is little danger of speiss formation in the absence of copper. The other speiss-forming metals are too high in the electromotive series to be reduced in a normal controlled reduction assay. As a consequence, when copper is absent, arsenic and antimony—even though reduced—can only cause trouble by contaminating the lead button; no speiss phase will be formed. In the presence of copper, speiss will form in the assay fusion unless the charge is proportioned with sufficient excess of litharge and soda to keep the copper as well as the arsenic and antimony oxidized. Uncontrolled reduction methods should never be used for assaying materials containing large amounts of arsenic or antimony. The excess reduction used in uncontrolled reduction methods will reduce arsenic and antimony, as well as some of the speiss-forming metals, so that speiss is almost certain to form. When a speiss phase forms, it is found as a brittle substance just above the lead button. It can be distinguished from matte by its bright metallic luster. The danger of loss of precious metals in the presence of speiss occurs primarily through loss of small fragments of speiss when separating the lead button from the slag; but even though

all the speiss could be recovered, it cannot be cupeled satisfactorily.

The Matte Phase

Artificial sulfides of the heavy metals are called "matte." In general, mattes are almost completely insoluble in slag and have only slight solubility in metal or speiss phases, but they are soluble in molten alkaline salts such as sodium carbonate and, particularly, sodium sulfide.

Conditions of Matte Formation and Decomposition.—Matte can be formed by the fusion of metals with elemental sulfur, the reduction of metal sulfates, or simply by melting sulfide minerals.

In assaying, as well as in metallurgical work, natural sulfide minerals are usually present in the ore, and sulfur must be removed in order to produce metal. Oxidation is the process almost universally used for the separation of sulfur from metals. The oxidation reactions are similar, whether the process is an oxidizing roast (heating unmelted material in an excess of air), a niter crucible assay (in which oxygen is supplied by niter instead of air), or a copper converter operation (blowing molten matte with a limited amount of air).

In an oxidizing roast, sulfide minerals are heated to above their ignition temperatures, in the presence of air. The sulfur is burned to SO_2, and some is further oxidized to SO_3. Metals above silver in the electromotive series are oxidized, while the more noble metals are left in the reduced condition. If the temperature is held low, sulfates are formed by the combination of metal oxides with sulfur trioxide. Sulfates dissociate at higher temperatures, and, by heating to over 800°C., nearly all sulfate sulfur can be eliminated, provided that the SO_3 gas is carried away. A few typical reactions are given below:

Argentite:

$$Ag_2S + O_2 = 2Ag + SO_2$$

Pyrite:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

If pyrite is heated to about 500°C., in the absence of air, 1 atom of sulfur separates as elemental sulfur, leaving FeS. In the

presence of air, ignition takes place before the separation of the sulfur atom.

Galena:

$$2PbS + 3O_2 = 2PbO + 2SO_2$$

Sulfate Formation:

$$2SO_2 + O_2 \leftrightharpoons 2SO_3$$

Equilibrium depends upon the temperature and the partial pressure of the constituent gases.

$$PbO + SO_3 \leftrightharpoons PbSO_4$$

Equilibrium also depends upon the temperature and upon the pressure of the sulfur trioxide gas.

Except for a difference in the ignition temperature and temperature of decomposition of the sulfates, the other metal sulfides oxidize in a manner similar to the reactions given.

Sulfur has a tendency to combine with oxygen that, at smelting temperatures, is about the same as the tendency for lead to oxidize. Consequently, metals above lead in the electromotive series cannot be reduced by sulfur, but sulfur will take oxygen away from the oxides of metals below lead in the series. Roast-reaction and copper converting processes depend upon the use of sulfur as a reducing agent.

Roast-reaction Process.—The roast-reaction process can be used to recover, from sulfide ores, metals low in the electromotive series. The process consists of roasting the ore to produce metal oxides and sulfates, and the roasted material is then mixed with fresh sulfide ore and melted. The following reactions for the smelting of lead in the reverberatory furnace are typical:

Roast:

$$2PbS + 3O_2 = 2PbO + 2SO_2$$
$$PbS + 2O_2 = PbSO_4$$

Reaction:

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2$$

The roast-reaction process takes place in many smelting and assaying operations. Processes depending entirely upon its operation for metal production are now seldom used.

Converting.—Converting finds its important use in the production of copper and has no counterpart in assaying. The tendency of lead to combine with oxygen is too close to that of sulfur to allow selective oxidation of sulfur from PbS in a converter. In copper smelting, a matte consisting of cuprous sulfide and ferrous sulfide (Cu_2S, FeS) is produced. While still liquid, the matte is placed in a converter and blown with air. During the first stage of the blow, iron and sulfur are selectively oxidized and white metal, Cu_2S, is left. In the second stage, blowing is continued, selectively oxidizing sulfur and leaving blister copper. Metals such as lead, nickel, iron, and others above copper in the electromotive series are oxidized with the sulfur, and either go out in the converter gas or are found in the slag. The precious metals are collected by the copper matte and alloy with the metallic copper that was produced in the converter.

Matte in Assaying.—All processes of assaying sulfide ores, except for the soda-iron method, require the almost complete elimination of sulfide sulfur. If sulfide sulfur is not eliminated, matte will form with at least one of the metals present in the metallic state. The probable order of matte formation is given by Dean[1] as MnS (greatest tendency to form), Cu_2S, PbS, NiS, FeS, Ag_2S, and ZnS.

Matte in Uncontrolled Reduction.—In the uncontrolled reduction (soda-iron) assay method, an excess of iron is used in an attempt to replace all other metal sulfides with iron. Ferrous sulfide dissolves in the alkaline salt slag. The amount of the precious metals dissolved by ferrous sulfide and carried into the slag is low, but most other sulfides would cause excessive loss of precious metals.

The presence of copper-bearing minerals is particularly dangerous, as copper is reduced by the iron and will take sulfur from the iron to form Cu_2S—a good solvent for the precious metals. Other impurities such as nickel, cobalt, arsenic, antimony, bismuth, or tellurium, when present in an ore, are reduced by the excess iron

[1] DEAN, R. S., "Theoretical Metallurgy," p. 210, John Wiley & Sons, Inc., New York, 1924.

and cause trouble either by forming matte or speiss or by contaminating the lead button.

Matte in Controlled Reduction.—Lead is the only metal that should be present in the reduced condition and available for matte formation in controlled reduction methods of assaying. The precious metals do not form sulfides, because lead has a greater tendency to combine with sulfur, and there is always a large excess of lead present to take any sulfur available. When lead sulfide forms in an assay fusion it may not appear as a separate matte phase, as lead and lead sulfide are mutually soluble when liquid. A lead–lead sulfide alloy is formed in which the components are soluble when liquid and insoluble when solid.[1] Only when the lead button is cooled very slowly do the constituents have the opportunity to segregate according to their density. Usually the presence of lead sulfide in the button is evidenced only by the brittleness of the lead–lead sulfide alloy. Brittle buttons are to be avoided since it is almost impossible to separate them from the slag without loss.

Conditions Favoring Sulfide Elimination.—The elimination of sulfide sulfur is brought about by oxidation. In assaying, three sources of oxygen are used: (1) air, as in scorification; (2) niter, as in the niter crucible assay; and (3) litharge, as in all assay fusions to the extent that lead oxide is reduced to lead.

In the scorification assay, sulfur is eliminated in a manner similar to oxidizing roasting. In addition to the oxidizing-roast reactions, liquid lead oxide attacks sulfides by the roast-reaction process.

The amount of oxidation of sulfur and other substances that oxidize as easily as lead can be increased by increasing the diameter of the scorifying dish. Sufficient oxidation for a $\frac{1}{10}$-assay-ton sample of pure sulfide mineral is usually obtained in a 3-in. scorifier, which will allow the oxidation of about 40 g. of lead.

In the crucible assay, complete elimination of sulfide sulfur and the simultaneous reduction of a lead button are difficult, except in the presence of excess sodium carbonate and litharge. Niter can be used in the single-stage process only to oxidize sulfur above that required for the lead button. Complete elimination of sulfide sulfur depends upon the reaction between metal sulfides and lead oxide.

[1] *Ibid.*, p. 203.

$$PbS + 2PbO \leftrightharpoons 3Pb + SO_2$$

This reaction will reach equilibrium without completely eliminating sulfide sulfur unless plenty of PbO is readily available and unless the sulfur dioxide concentration of the environment is kept low.[1] Sodium carbonate is added to the crucible assay charge for the purpose of keeping the concentration of sulfur dioxide low. It does this by diluting the gas in the interstices of the charge with carbon dioxide and also by the removal of sulfur to the alkaline salt layer as sodium sulfate.

If either too small an amount of litharge or too little sodium carbonate or too large an amount of acid fluxes is added to a single-stage niter assay, the RP. of the sulfide minerals decreases. Sulfide sulfur is not completely eliminated, and brittle lead buttons are produced. The effect of acid fluxes is due to the slag-forming reactions, which reduce the amount of free soda and litharge available for desulfurization.

The Slag Phase

Slags, when liquid, consist of igneous solutions of basic and acidic oxides and the chemical compounds that form between them. Substances other than oxides are generally not miscible with slags and enter some other phase. The primary requirement of a slag is that it must take up the nonvolatile impurities from the ore and hold them in a liquid condition, which will allow the metal phase to separate completely at the furnace temperature available. Other generally desirable slag features are: (1) the slag should attack as little as possible the refractory with which it is in contact and (2) the cost of reagents (fluxes) required to impart the desired slag properties should be low. In certain particular cases it is necessary that the slag carry special reagents for their chemical effect on other phases. For example, in the crucible assay of a copper ore or in the softening of lead bullion an excess of litharge is carried in the slag for its oxidizing effect.

Smelter Slags.—Copper and lead smelter slags consist essentially of the basic oxides CaO and FeO and the acidic oxide SiO_2. The total of these three constituents usually amounts to over

[1] Maier, C. G., Thermodynamic Data on Some Metallurgically Important Compounds of Lead and the Antimony-group Metals and Their Applications; *U.S. Bur. Mines R.I.* 3262, p. 39, 1934.

80 per cent of the slag. The remainder of the slag consists of particular oxides taken up from the material smelted. Analyses of slags typical of lead blast-furnace smelting and copper reverberatory-furnace smelting are given below:

LEAD BLAST-FURNACE SLAG, MIDVALE 1935 AVERAGE*

Au, oz./ton	Ag, oz./ton	Cu, %	Pb, %	SiO_2, %	Al_2O_3, %	FeO& MnO, %	CaO, %	MnO, %	BaO, %	ZnO, %	S, %
0.00079	0.058	0.16	0.95	25.51	3.73	37.70	17.43	1.37	1.13	10.93	1.68

* CLEVENGER, G. H., Blast-furnace Practice at Midvale, Utah, *Trans. A.I.M.E.*, vol. 121, p. 57, 1936.

COPPER REVERBERATORY-FURNACE SLAG, GARFIELD*

Au, oz./ton	Ag, oz./ton	Cu, %	SiO_2, %	Al_2O_3, %	Fe & Mn, %	CaO, %	(MnO, BaO, ZnO not reported)	S, %
0.0016	0.25	0.39	40.3	6.7	31.5	8.7	.....	0.4

* HAYWARD, C. R., "An Outline of Metallurgical Practice," p. 63, D. Van Nostrand Company, Inc., New York, 1929.

Assay Slags.—Basic fluxes commonly used in assaying are sodium oxide (from sodium carbonate), and litharge. The principal acid flux is silica, supplemented by boric oxide, which is obtained by adding either borax or borax glass. Except for the particular use of litharge for oxidation, and of sodium carbonate for desulfurization, fluxes are added for the purpose of lowering the melting point and imparting a homogeneous fluidity to the melted oxide impurities. The oxide impurities most frequently encountered are silica (SiO_2) from quartz, lime (CaO) from calcite, and the various metal oxides such as FeO, Fe_2O_3, Cu_2O, PbO, ZnO, As_2O_5, Sb_2O_3, and Al_2O_3, which may be present as such in the ore or are formed during the process. Whether the constituents occur separately in the ore or are combined as a silicate mineral is immaterial in slag formation. In fact, artificial silicate minerals of microscopic size frequently separate from slowly cooled slags. The different artificial minerals or compounds formed in slags are generally mutually soluble when liquid and insoluble when solid. The melting point of mixtures of substances like these (soluble when liquid and insoluble when

solid) decreases according to Raoult's law, with the addition of one substance to the other, and there is one composition having the lowest melting point of the series. This is called the "eutectic."

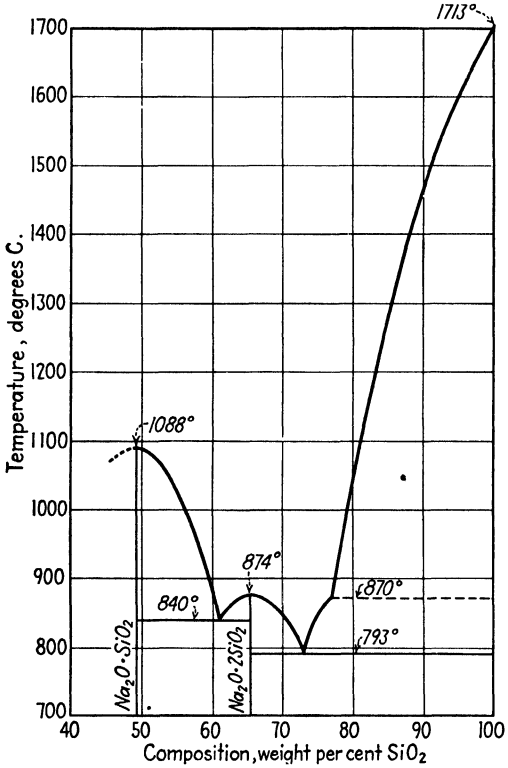


FIG. 10.—Constitutional diagram, system $Na_2O.SiO_2$–SiO_2. (*From International Critical Tables, Vol.* IV, *p.* 87, *McGraw-Hill Book Company, Inc.*, 1928.)

For an example of fluxing, consider an ore containing free gold and consisting almost entirely of quartz. Silica will not melt at a temperature that can be obtained in the assay furnace, so that a flux must be added to lower the melting point. Either sodium carbonate or litharge could be used. Sodium carbonate, when melted with silica, gives up carbon dioxide gas, and sodium oxide unites with silica. The constitutional diagram of the

sodium oxide-silica series (Fig. 10) shows two compounds: $Na_2O.SiO_2$ and $Na_2O.2SiO_2$. The eutectic between $Na_2O.2SiO_2$ and silica (containing 73.1 per cent SiO_2) melts at 793°C.

This slag composition might be considered desirable for the assay of a quartz ore, but it is unsatisfactory because, even though it melts at a low temperature, the melt is too viscous at assay-furnace temperatures to allow satisfactory separation of the

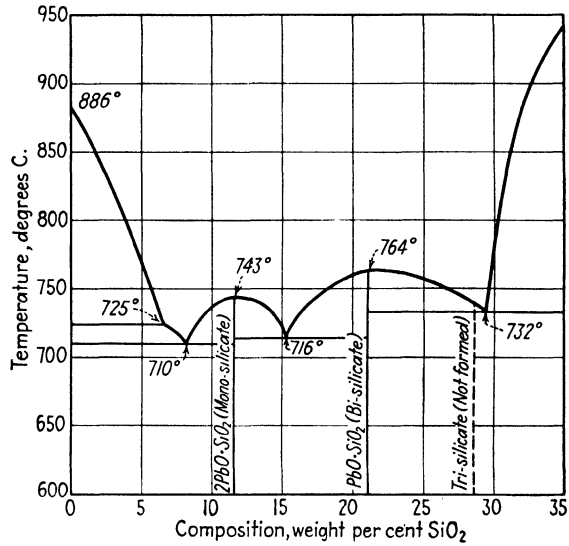


FIG. 11.—Constitutional diagram, system PbO-SiO_2. (*Melting points from Geller, Creamer, and Bunting, Bur. Standards, Jour. Research, vol.* 13, *p.* 243, 1934.)

metals. Litharge also produces low melting compounds and eutectics with silica (Fig. 11). Two compounds, $PbO.SiO_2$ and $2PbO.SiO_2$, are formed in this series. Either of these compounds, or the eutectic between them, melt at low temperatures, and the melts are sufficiently fluid for good separation of the metals.

Soda may be used to replace a part of the litharge and obtain equally satisfactory slags. The compounds and eutectic that form when three components are used become quite complex. In general, bisilicate or sesquisilicate slags are desired because they give good fusion of most basic impurities, and also because they scarcely attack the crucible. More basic slags are used only

to provide excess litharge for its oxidizing effect on sulfur, copper, arsenic, antimony, bismuth, or tellurium, and to provide excess sodium carbonate for its ability to replace a part of the more expensive litharge, and also for its desulfurizing effect. Many bisilicates, for example, $CaO.SiO_2$, are not sufficiently fluid in an assay charge without the presence of other constituents such as soda and litharge. These fluxes are used in nearly every crucible assay, even when the ore itself is essentially basic. In Chap. VII, practical rules are given for proportioning crucible assay charges.

The Alkaline Salt Phase

Slags are mainly composed of oxides, and, as a general rule, only oxides will dissolve in them. In fusions containing compounds such as chlorides, sulfates, or other similar metal salts, a separate layer or phase is formed. This layer occurs mainly as salts of the alkali metals, and, consequently, it is termed the "alkaline salt phase." The sodium sulfate layer that forms at the top of a crucible fusion of a sulfide ore is a typical example of this phase.

In the past, assayers added a cover of sodium chloride to crucible assay charges, to form, deliberately, an alkaline salt phase. Sodium chloride melts at a low temperature and is very liquid when heated slightly above its melting point. The use of a salt cover was thought to prevent dust loss, to prevent lead globules or unfused ore particles from sticking to the upper part of the crucible wall, to aid in preventing gas evolution from causing the charge to boil over, and to prevent either reducing or oxidizing furnace gases from acting on the charge so as to affect the size of the lead button. Ordinarily, no trouble is encountered from any of these causes, even without the use of a salt cover, and its use has been abandoned by most assayers because they wish to avoid any chance of losing precious metals through the formation of volatile chlorides. A few assayers continue the cover idea by adding some borax glass or sodium carbonate, or a mixture of the two on the top of the crucible charge. These substances enter the body of the charge and become a part of the slag as soon as boiling starts.

In smelting operations, alkaline salts are used in the Harris process of softening lead bullion, but otherwise they are seldom encountered.

CHAPTER VII

THE CRUCIBLE ASSAY

In the crucible assay a suitable portion of the sample is melted with fluxes in a fire-clay crucible, and oxidation-reduction reactions are controlled so as to produce a lead button by reduction of litharge. Gold and silver are collected by the lead button, which is subsequently cupeled and further treated to ascertain the precious-metal content of the sample.

The chief factors that must be controlled by the assayer in order to ensure reliable results are:

1. The weight taken for assay.
2. The fluxing of the ore constituents.
3. The control of lead reduction.

All types of ores and metallurgical products may be assayed for precious metals by the crucible assay, and for most materials this process is preferred, but certain substances, particularly alloys, may require preliminary acid treatment. The silver content of silver-rich alloys is usually determined by chemical methods. Some other materials may be assayed more conveniently by scorification (Chap. VIII).

With respect to fluxing requirements, ores may be broadly classified into acidic ores, high in silica; and basic ores, containing metallic compounds. With respect to oxidation-reduction reactions, ores may be classified as neutral, reducing, or oxidizing. In practice, any possible combination may be found: some of the minerals in an ore may be acidic, others basic, some may have a strong reducing power, others may be neutral or oxidizing. The assayer is concerned with the composite fluxing requirements of the sample and with the net oxidizing or reducing power.

Preliminary Investigation of Sample

The general nature of the sample submitted for assay must be known before the assayer can make an intelligent choice of reagents for lead-button control and for fluxing.

Visual observation of lump samples is the quickest and most reliable method of estimating the approximate mineralogical composition of a sample. If lump samples are not available, a simple concentration of the pulverized sample in a pan or vanning plaque may be applied, or the sample may be examined under water with a low-power microscope.

Vanning Test.—A 3- or 5-in. watch glass is quite suitable in place of a pan or vanning plaque. One or two grams of the sample is placed on the watch glass, covered with water, and then allowed to stand until wetting is complete. Extreme fines ("slimes") that do not settle readily are removed by successive shaking and decantation; the granular residue is then stratified by a gentle shaking motion, and the layers of different minerals are spread out for observation by causing an accelerated flow of water against one edge of the stratified sample. The heaviest minerals will be on the bottom, the lightest on top and, after fanning out, the heaviest minerals segregate at the apex of the fan toward the side from which the water current was directed.

To make percentage estimates from visual observations, it is necessary to take into consideration the relative specific gravity of the different mineral groups. For this purpose the light-colored gangue minerals, except barite and a few other minerals of lesser importance, may be taken as unity. Galena has approximately three times the specific gravity of quartz or limestone, other sulfides and the oxides of heavy metals have approximately twice the specific gravity of quartz.

Qualitative Tests.—Simple qualitative chemical tests on pulverized samples may be used by the assayer to aid in the classification of unknown samples. The following tests are useful in the identification of certain substances that are not readily identifiable by visual observation.

Effervescence and evolution of an odorless gas with cold dilute (1:1) hydrochloric acid indicate the presence of calcite ($CaCO_3$); a similar effect with warm dilute hydrochloric acid indicates dolomite [$(Ca, Mg)CO_3$]. This will serve to distinguish these important basic carbonates from silicates, all of which are comparatively inert with acids.

Sphalerite (ZnS) is attacked by warm hydrochloric acid with the evolution of hydrogen sulfide, which has a characteristic odor of spoiled eggs. The light-colored varieties of sphalerite are

difficult to determine by visual observation of the pulverized material.

All sulfides are attacked by warm concentrated (or dilute) nitric acid, especially with the aid of a few crystals of potassium chlorate. The rapidity of attack and the evolution of copious brown fumes are characteristic.

Copper and iron are easily detected by cooling and diluting a nitric acid solution, then neutralizing with ammonium hydroxide. Iron is precipitated as a flocculent brown precipitate of ferric hydroxide. Copper imparts to the solution an intense blue color.

The presence of nickel in ores can be confirmed by neutralizing an acid solution of the sample with ammonium hydroxide until the odor of ammonia faintly persists. Then filter and add an alcoholic solution of dimethylglyoxime. A brilliant red precipitate identifies nickel and forms in proportion to the amount of nickel present.

Slag Colors.—A preliminary assay fusion is often made to determine the reducing or oxidizing power of an ore. The color of the slag obtained from assay fusions frequently furnishes qualitative information as to the presence of some elements.

To most vitreous slags, copper imparts a green color that is particularly observable on the sides of the crucible or scorifier. In basic slags, high in litharge, copper gives a brick-red color.

Manganese gives a purple color to assay slags. In high proportions the color may be so deep as to appear black, but the purple color becomes apparent in thin sections or in pulverized samples of the slag. A black film may appear on the surface of basic slags containing manganese.

Cobalt is a strong coloring agent and imparts a blue color to slags of all types.

Antimony gives a greenish-yellow color to vitreous slags, but this color is easily masked by small amounts of more highly colored compounds.

Iron-bearing slags are yellow-brown, brown, or black, depending upon the amount present and the slag composition. Acid slags containing small amounts of iron are pale green and transparent. On account of the common occurrence of iron in ores, the iron color may mask all other colors; and only copper, manganese, and cobalt yield sufficiently strong colors to overcome the effect of an approximately equal amount of iron. When iron

and other strong coloring agents are absent, CaO, MgO, or ZnO may give a white color to the slag.

Weight Taken for Assay

The weight of sample to be taken for assay must be such that the cumulative errors of weighing and manipulation are within the desired limits of accuracy. The underlying principles involved in the determination of sample weight are considered in Chap. II on sampling.

For most mine samples, it is customary to use a ½-assay-ton sample. The errors in taking the original sample are such that extreme refinement of the assaying procedure is superfluous. For materials that are known to be low grade, such as tailings, at least 1 assay ton should be taken for assay; and 2 assay tons is the usual sample weight for low-grade tailings. For concentrates and high-grade samples, ¼-assay-ton samples are commonly employed, and even smaller portions may be used for exceptionally rich products.

If the sample is of material so complex that the required portion cannot be fluxed in a crucible of convenient size, two separate portions of one-half of the required total may be assayed and the results combined to give practically the same degree of accuracy as would a single assay of the same gross sample weight. This procedure should not be confused with check assays that may be required in addition.

Fluxing for the Crucible Assay

When sulfide ores are assayed by the crucible process, the metal originally combined with sulfur is converted to an oxide that, with a few exceptions, acts as a base in assay slags to combine with silica. Since carbonates are also converted to oxides in the assay crucible, and since the metallic oxides in complex silicates are already acting as base oxides, it is evident that the problems of fluxing are virtually independent of the problems of controlling the lead reduction.

As has been shown in Chap. VI, polybasic silicates or borosilicates containing sufficient soda or litharge or both satisfy most of the requirements of a good assay slag. Such slags may be successfully employed for practically all ores and metallurgical

TABLE XI.—FLUXING REQUIREMENTS OF VARIOUS ORE CONSTITUENTS

Dominant element	Common form of occurrence	Recommended slag composition					Remarks
		Silicate degree	Minimum ratio Na_2CO_3 to sample weight	Minimum ratio* by weight		Proportion of SiO_2 replaced by equiv. borax glass	
				PbO	To		
Aluminum	$Al_2O_3.xSiO_2$	1½–2†	1	2	Na_2CO_3	⅓	Add CaO or fluorides = Al_2O_3
Antimony	Sb_2S_3	½–1	1	2	Ore	⅓	
Arsenic	FeAsS	½–1‡	1	2	Ore	⅓	Add additional Na_2CO_3 = As
Barium	$BaSO_4$	1½–2	1	2	Ore	⅓	
Bismuth	.....	½–1	1	2	Ore	⅓	
Calcium	$CaCO_3$	1½–2	1	1	CaO	⅓	
Calcium	Bone ash	1½–2	1	2	Bone ash	⅔	Omit bone ash from silicate degree calculation
Chromium	$FeO.Cr_2O_3$	1 –1½	1½	½	Ore	½	For 40 per cent Cr_2O_3 in ore
Cobalt	.....	½–1	1	2	Ore	⅓	
Copper	Various	<½	1	30	Cu	None	Max. Cu in charge, 7.5 g.
Iron^{++}	FeS_2; FeO	½–1½	1	2	⅓	⅙	
Iron^{+++}	Fe_2O_3; Fe_3O_4	1½–2	1	2	Ore	⅓	Use more borax glass for Fe_3O_4
Lead	PbS	½–2	½	½	Ore	⅙	
Magnesium	$MgCO_3$	1½–2	1	1	MgO	⅓	
Manganese	MnO_2	1 –1½	1	2	Ore	⅓	
Nickel	.....	½–1	1	60	Ni	None	Max. Ni in charge, 4 g.
				100	Ni + Cu	None	Max. Ni + Cu in charge, 3 g.
Silicon	SiO_2	1½–2	1	.....	.....	⅙	
Selenium } Tellurium }	.....	½–1	1–2	500	Se or Te	⅓	Max. Se, Te in charge, 0.1–0.2 g. Slow fusion recommended
Tin	SnO_2	½–1	1	2	SnO_2	½	
Zinc	ZnS	1 –1½	1	2	Ore	⅓	

* If the uncontrolled reduction (soda-iron) method of assay is used, litharge in the slag is replaced by soda ash.

† Add lime or fluoride to flux the alumina and then disregard these constituents in proportioning the silicate degree of the rest of the slag.

‡ The arsenic is considered to form sodium arsenate with approximately its weight of Na_2CO_3. Disregard these constituents in the silicate degree calculation.

TABLE XII.—SLAG FACTORS, EQUIVALENT WEIGHTS PER UNIT OF SILICA

Dominant element	Compound	Original form	Combining form	Wt. orig. form per unit wt. SiO_2 — Silicate degree			
				Sub	Mono	Sesqui	Bi
Acid Fluxes							
Boron	Borax glass	$Na_2O.2B_2O_3$	$Na_2O.2B_2O_3$*	1.2	1 3	1 5	1 7
Boron	Borax	$Na_2O.2B_2O_3.10H_2O$	$Na_2O.2B_2O_3$*	2.2	2.4	2.8	3 1
Basic Fluxes							
Lead	Litharge	PbO	PbO	14 9	7.4	4 9	3.7
Sodium	Sodium carbonate	Na_2CO_3	Na_2O	7.1	3.5	2 4	1 8
Potassium	Potassium carbonate	K_2CO_3	K_2O	9.2	4.6	3 1	2 3
Basic Ore Constituents							
Antimony	Antimony trioxide	Sb_2O_3	Sb_2O_3	6.5	3.2	2 2	1 6
	Stibnite	Sb_2S_3	Sb_2O_3	7.5	3 8	2 5	1 9
Calcium	Calcium oxide (lime)	CaO	CaO	3 7	1.9	1 2	0.9
	Calcite or limestone	$CaCO_3$	CaO	6 7	3.3	2 2	1 7
Copper	Cuprous oxide	Cu_2O	Cu_2O	9 5	4 8	3 2	2 4
	Cupric oxide	CuO	Cu_2O	10.6	5 3	3 5	2.7
	Chalcocite	Cu_2S	Cu_2O	10 6	5 3	3 5	2 7
	Chalcopyrite	$CuFeS_2$	$Cu_2O.2FeO$	6 1	3 1	2 0	1 5
Iron	Ferrous oxide	FeO	FeO	4 8	2 4	1 6	1.2
	Hematite	Fe_2O_3	FeO	5 3	2.7	1 8	1.3
	Magnetite	Fe_3O_4	FeO	4 9	2.5	1.6	1 2
	Pyrite (marcasite)	FeS_2	FeO	8 0	4.0	2.7	2.0
Lead	Lead oxide (litharge)	PbO	PbO	14.9	7.4	4.9	3.7
	Galena	PbS	PbO	15.9	8 0	5.3	4.0
Magnesium	Magnesium oxide (magnesia)	MgO	MgO	2.7	1.3	0.9	0.7
	Magnesite	$MgCO_3$	MgO	5.6	2 8	1.9	1.4
Manganese	Manganous oxide	MnO	MnO	4.7	2.4	1.6	1.2
	Pyrolusite	MnO_2	MnO	5.8	2.9	1.9	1.4
Zinc	Zinc oxide	ZnO	ZnO	5.4	2.7	1.8	1.3
	Sphalerite	ZnS	ZnO	6.5	3 2	2.2	1.6

Note: The fluxing of aluminum and arsenic is explained in Table XI.

* The slag factors for borax and borax glass compensate the silicate degree for the base Na_2O in the borax or borax glass.

products; but for certain materials, notably those high in copper, oxide slags rich in litharge are preferable.

Although it is theoretically possible to calculate an ideal assay slag for any given ore, the exact analysis of an ore is seldom known to the assayer, and even if a complete analysis were available, the time required to calculate the ideal charge is not warranted unless a large number of assays are to be made on nearly similar material. Hence, for simplicity and convenience, assayers use an excess of fluxes and proportion these so that only minor variations are needed to flux any of the samples currently received for assay.

The fluxing requirements of various types of ores are summarized in Table XI.

Table XII gives slag factors for use in calculating charge compositions. For convenience in calculating the equivalents of compounds not listed in the table the first compound under each dominant element of the basic ore components is the oxide that combines with silica or borax in assay slags. The equivalents of compounds not listed can be found by first calculating the equivalent weight of the corresponding oxide and then dividing this value into the factor from the table.

The use of the slag-factor table is illustrated in the following examples:

Example 1: Find the amount of sodium carbonate and litharge in equal molecular proportions to form a sesquisilicate with 15 g. of silica.

Since half of the SiO_2 will be fluxed by each base, 7.5 g. of SiO_2 are to be combined with Na_2CO_3 and 7.5 g. with PbO.

From the slag-factor table the sesquisilicate factor for Na_2CO_3 is 2.4 and the factor for PbO is 4.9.

Therefore

$$(2.4)(7.5) = 18.0 \text{ g. of } Na_2CO_3 \text{ required}$$

and

$$(4.9)(7.5) = 36.8 \text{ g. of PbO required}$$

Example 2: Find the bisilicate silica equivalent of 15 g. of limestone and the amount of borax glass required to replace one-third of the required SiO_2.

From the slag-factor table, 1.7 g. of $CaCO_3$ combines with 1 g. of SiO_2 to form a bisilicate.

Hence

$$\frac{15 \text{ g. } CaCO_3}{1.7} = 8.8 \text{ g. of } SiO_2 \text{ required.}$$

The SiO_2 to be replaced by borax glass is $8.8/3 = 2.9$ g., leaving $8.8 - 2.9 = 5.9$ g. of SiO_2 to be added as such.

From the table, 1.7 g. of borax glass is required to replace 1 g. of SiO_2 in a bisilicate.

Hence $(1.7)(2.9) = 4.9$ g. of borax glass to be added.

Example 3: Find the monosilicate silica equivalent of the bases in 15 g. of an ore containing 20 per cent chalcopyrite and 10 per cent bornite ($FeS.2Cu_2S.CuS$).

From the table the monosilicate factor for chalcopyrite is found to be 3.1.

Therefore, the SiO_2 required to produce a monosilicate with the chalcopyrite in the sample is $[(0.2)(15)]/3.1 = 1.0$ g.

Bornite does not appear in the table, but the monosilicate factor for bornite may be calculated by either of the following methods:

a. Direct Calculation: For a monosilicate, $4(FeS.2Cu_2S.CuS)$ requires 14 oxygen atoms in the silica, or 7 moles of SiO_2 for 4 moles of bornite.

Therefore

$$\frac{\text{Molecular weight } 4(FeS.2Cu_2S.CuS)}{\text{Molecular weight } 7SiO_2} = \frac{4(501.93)}{7(60.06)}$$

$$= 4.77 \text{ g. bornite per g. } SiO_2$$

and the SiO_2 required to produce a monosilicate with the bornite in the sample is $[(0.1)(15)]/4.8 = 0.31$ g.

b. Indirect Calculation: The FeO equivalent of bornite is

$$\frac{\text{Molecular weight FeO}}{\text{Molecular weight } FeS.2Cu_2S.CuS} = \frac{71.84}{501.93} = 0.14$$

The Cu_2O equivalent of bornite is

$$\frac{\text{Molecular weight } 5Cu_2S}{\text{Molecular weight } 2(FeS.2Cu_2S.CuS)} = \frac{715.70}{1003.86} = 0.71$$

The monosilicate factor for FeO is 2.4, and for Cu_2O is 4.8. Hence the monosilicate silica equivalent of the FeO derived from the 10 per cent of bornite in 15 g. of ore is

$$[(0.1)(15)(0.14)]/2.4 = 0.09 \text{ g.}$$

SiO_2 for FeO, and the SiO_2 for the Cu_2O from the bornite is $[(0.1)(15)(0.71)]/4.8 = 0.22$ g. SiO_2 for Cu_2O. Hence the total SiO_2 for the bornite is $0.09 + 0.22 = 0.31$ g. SiO_2, which checks the value obtained by method *a*.

Control of Lead Reduction

Control of lead reduction involves consideration of the appropriate size of lead button, the estimation of the oxidizing or reducing power of ore minerals and of added reagents, and the proportioning of the assay charge to the end that buttons of suitable size are reduced in the crucible.

Size of Button.—The optimum size of the lead button obtained in the crucible assay is a compromise between convenience and the relative losses of precious metals in the slag and in the subsequent cupellation of the button. For convenience and accuracy of cupellation, the cupels in a single row in the furnace should be of uniform size, and the buttons should be of approximately the same weight. Nearly all assayers use cupels that are either 1¼ or 1½ in. in diameter. These hold a maximum of 32 and 45 g. of lead, respectively, and impose a practical upper limit to the button size. Larger cupels can be purchased or made but are rarely used. Buttons smaller than 10 g. usually fail to collect all the precious metals, so that 15 g. should be considered a safe minimum amount of lead. For ordinary work, most assayers aim for a 25-g. button and accept for cupellation all buttons larger than 15 g. and smaller than the maximum capacity of the cupels in use.

General Methods of Controlling Lead Reduction.—In the crucible assay, control of lead reduction is effected by one of the following general methods:

1. Controlled reduction, involving the use of litharge in excess of button requirements, and the addition of a controlled amount of a reducing or an oxidizing agent.

2. Uncontrolled reduction, involving the use of litharge (plus the PbO equivalent of lead in the original sample) for button requirements only, in the presence of an excess of reducing agents.

3. Oxidation of reducing agents in the ore by a preliminary treatment, followed by controlled reduction during the crucible fusion.

For the controlled reduction method, a reasonably accurate knowledge of the reducing power (R.P.) and the oxidizing power (O.P.) of ore minerals is required. For the two other methods, only a general approximation of the composite state of oxidation of the ore sample is needed. In all methods the reducing or oxidizing power of any added reducing or oxidizing agents must be known.

Oxidation-reduction Units.—The R.P. of a reducing substance is defined as the amount of lead reduced by a unit amount of the reducer. The reducing effect (R.E.) of a reducing substance is defined as the total amount of lead reduced by a given amount of the reducer.

The O.P. of an oxidizing substance is defined as the lead equivalent of a unit amount of the oxidizer, and the oxidizing effect (O.E.) is the total lead equivalent of a given amount of the oxidizer. It should be noted (page 109) that most oxidizing agents in crucible assaying do not react directly with lead but do react with reducing agents that would otherwise reduce lead from litharge in the charge.

Reducing Agents.—The effective R.P. of various reducing agents commonly used in assaying is given in Table XIII.

TABLE XIII.—EFFECTIVE REDUCING POWER (R.P.) OF REDUCING AGENTS

Substance	Effective R.P., Grams Pb per Gram Reducer*
Charcoal	25–30
Sulfur	13–19
Sugar	11–13
Flour	10–12
Starch	10–12
Argols	8–12
Cream of tartar	5– 6
Iron filings	4– 6

* The lower values apply to impure reducing agents and, to highly acid slags; the higher values apply to pure reducing agents and to slags having a silicate degree not greatly in excess of the monosilicate, except that impure argols have increased R.P.

The selection of a suitable reducing agent is largely a matter of convenience and cost. Flour is generally the cheapest reagent available and is widely used. If reducers are added separately to the charge, reagents having a distinctive color—such as argol (burgundy color), charcoal (black), or sulfur (yellow)—have the advantage that they indicate at a glance whether or not the

reducer has been added to a given crucible, thus minimizing the danger of adding it twice to one charge or omitting it entirely from another. Reducers having a high R.P., such as charcoal or sulfur, should be diluted with a neutral substance to permit rapid measuring of the required amount without the necessity for accurate weighing. Charcoal may be diluted with an equal or greater volume of silica or sodium carbonate. If sulfur is diluted with 3.34 parts of sodium carbonate by weight, the soda required for the formation of sodium sulfate is automatically included in the charge. It is obvious that diluted reducers should be thoroughly mixed, and their R.P. determined before use.

Iron nails are used as the reducing agent in the uncontrolled reduction method, and iron filings are used in the oxidation-collection method. Iron has the advantage over other reducing agents that no incompletely oxidized gases that might escape from the charge and give erratic results are formed. For this reason, iron deserves wider use as a reducer in the controlled reduction method with nonreducing ores, as the R.P. is not affected by the composition of the slag. Iron is undesirable as a reducer only in charges high in hematite or magnetite, which are not completely reduced to the ferrous oxide by metallic iron.

Determination of the Reducing Power of a Reducing Agent.—The R.P. of the common reducing agents has been so well established that the assayer seldom needs to determine it unless he proposes to use an unknown material to suit the convenience of local conditions. Since the R.P. varies to a certain extent with the composition of the slag and with the rate of heating, the R.P. determination should be made under conditions that correspond to normal assaying practice.

The following charge is similar to assay charges for silicate ores and may be used to determine the R.P. of a reducing agent:

Sodium carbonate	30 g.
Litharge	60 g.
Silica	15 g.
Borax glass	5 g.
Reducing agent	2 g. or as required.

Mix the reducing-power charge in a 15- or 20-g. crucible and fuse in a hot furnace at 1000 to 1150°C. As soon as the fusion is complete, which should be in from 15 to 20 min., pour the charge into a mold. When cool, separate the button from the slag and

weigh it to the nearest 0.1 g. The R.P. is the weight of the button divided by the weight of the reducing agent used.

In R.P. determinations the litharge entering the slag may vary from the possible maximum of all litharge present, as in the case of a material having no reducing power, to the possible minimum of no litharge entering the slag, as in the case of pure carbon. The extremes give slag compositions, with the above R.P. charge, ranging from a monosilicate to a bisilicate. This variation in slag composition would not change the R.P. of most reducers more than 10 per cent from the mean.

TABLE XIV.—REDUCING POWER OF CERTAIN SULFIDE MINERALS

Mineral	Formula	S, per cent	Normal slag-forming oxides	R.P., grams per gram of mineral		
				Computed R.P.	Actual R.P.	
				S to SO_3	Preliminary assays*	Niter charges†
Galena	PbS	13.4	PbO	3.46	2.9	2.9
Chalcocite	Cu_2S	20.2	Cu_2O	5.20	4.5	4.7
Arsenopyrite	FeAsS	19.7	FeO, As_2O_5	8.25	8.1	7.4
Stibnite	Sb_2S_3	28.6	Sb_2O_3	7.35	5.9	5.8
Chalcopyrite	$CuFeS_2$	34.9	Cu_2O, FeO	8.44	8.2	8.2
Sphalerite	ZnS	32.9	ZnO	8.51	8.2	8.1
Pyrite	FeS_2	53.4	FeO	12.07	11.6	11.0

* The charge in all cases was 3 g. sulfide, 45 g. PbO, 15 g. Na_2CO_3, 5 g. SiO_2.

† The values in this column were determined with monosilicate slags under normal assaying conditions with niter and excess litharge. U.S.P. niter was used which had an O.P. of 4.0.

Reducing Power of Sulfide Minerals.—The most important group of minerals with high R.P. are the sulfides, although some ores contain organic matter that may make them reducing. The theoretical reactions and the method of calculating the R.P. of sulfide minerals are given in Chap. VI in which it is pointed out that the actual R.P. varies with the conditions of the fusion, and that the R.P. of all sulfides decreases sharply as the silicate degree increases beyond the monosilicate.

The theoretical R.P. of sulfides is a maximum value that is seldom attained in actual fusions. Table XIV gives theoretical and actual R.P. values of the minerals as determined in the preliminary assay described in the following section, without control of button size by the addition of an oxidizing agent. The column headed "Actual R.P.—Niter charges" gives the values of reducing power normally obtained in controlled reduction fusions with mono- or subsilicate slags in which niter (KNO_3) is used to control button size.

With the aid of Table XIV the reducing effect (R.E.) of a given sample of ore can be estimated if the approximate mineralogical composition has been determined. Many assayers prefer to make a preliminary fusion to determine the reducing power of unknown sulfide ore samples, if the controlled reduction method of assay is to be used.

Determination of the Reducing Power of Sulfide Ores.—For the direct determination of R.P. it is convenient to prepare a universal charge that may be used on any materials that are suspected of having an appreciable R.P. Such a charge requires a high ratio of fluxes to ore, and sufficient litharge to provide an excess for the slag even with ores having the maximum possible R.P. Moreover the silica and borax glass content should be such that the slag composition, except for ores comparatively high in silica, should not be more acid than a monosilicate, as the R.P. of sulfides decreases rapidly with more acid slags, and correlation with the conditions to be used in the final assay would be impracticable.

A general flux recommended for the R.P. determination of ores is as follows:

Ore	3 g.
Sodium carbonate	10 g.
Litharge	45 g.
Silica	3 g.
Borax glass	1 g.

Use a 10-g. crucible and melt at normal operating temperatures. In general the fusion will be complete in 15 min. To save time the fusion may be poured on an iron plate so that the button may be recovered and weighed almost at once after pouring. The weight of button divided by the weight of ore taken is the R.P.,

in grams of lead reduced per gram of ore used. Reference to Table XIV may indicate the necessity for a slight correction in the estimated R.P. in calculating niter charges for a larger quantity of ore.

The above charge will yield buttons ranging from 10 g. in weight for pure galena to 33 g. for pure pyrite. Allowing for soda to form sodium sulfate and litharge for the button the calculated silicate degree will be 1.1 for pure pyrite, 0.5 for pure galena, 0.7 for pure sphalerite, 0.4 for pure limestone, and 0.8 for pure silica. In view of the relatively large proportion of fluxes to ore, any of the slags will be satisfactory, although in the regular assay a higher silicate degree would be preferred for some ore types. Crucible corrosion is an automatic corrective factor, as the more basic slags will increase their silica content at the expense of the crucible yet will not greatly exceed the monosilicate by that process.

Preliminary R.P. assays are unreliable if the button weight is too small. If the ore sample is suspected to have a R.P. less than 2 it is advisable to double the quantity of ore and to add approximately one-third more of the flux mixture.

Oxidizing Agents.—In two of the methods of crucible assaying to be described, an oxidizing agent is added to the charge in order to counteract the reducing effect of the ore. The only oxidizing agent commonly used by assayers for this purpose is niter (KNO_3). Sodium nitrate could be used, but is too deliquescent for convenience. Sodium peroxide is open to the same objection, although it has the advantage of minimizing the boiling of the charge, by not giving off inert gases, and of providing a concentrated source of Na_2O for slag formation.

One gram of niter should furnish sufficient oxygen to oxidize the equivalent of 5.12 g. of lead, provided all the oxygen was used in the process and nitrogen gas evolved. Actually the practical oxidizing power (O.P.) of commercial niter is 4.0, corresponding closely to a value of 4.1 for the theoretical decomposition of niter to N_2O, K_2O, and oxygen.

Oxidizing Minerals.—The higher oxides of certain multivalent metals are capable of reduction to a lower state of oxidation in an assay fusion, hence they possess an O.P. that must be taken into account in calculating the amount of reducing agent to be added for the desired lead fall.

The commonest ores of this type are those containing hematite (Fe_2O_3), magnetite (Fe_3O_4), or the higher oxides of manganese, as pyrolusite (MnO_2). More rarely, ores containing the higher oxides of copper, nickel, cobalt, arsenic, or antimony are encountered in practice; but the O.P. of these is seldom of importance. The theoretical O.P. of Fe_2O_3 is 1.3 g. of lead per gram, of Fe_3O_4 is 0.9, and of MnO_2 is 2.4. The actual O.P. of these oxides is somewhat less, and for the purpose of calculating assay charges the O.P. of pure hematite may be taken at 1.0, that of magnetite at 0.5, and that of pyrolusite at 2.0.

Determination of Oxidizing Power.—The O.P. of any mineral is not large, so that the oxidizing effect of an ore in an assay can usually be calculated with sufficient accuracy from a visual estimate of the amount of oxidizing minerals present. The estimate is easily made when a lump sample is available for inspection; pulverized ores should be vanned for observation.

An O.P. determination of an unknown ore sample or of an oxidizing agent can be made by fusion. The following charge is recommended:

Ore or oxidizer	5 g.
Sodium carbonate	10 g.
Litharge	45 g.
Silica	6 g.
Borax glass	2 g.
Reducer	To give reducing effect of 30 g.*

* For strong oxidizers such as niter, increase the reducing effect to 40 g.

With hematite or magnetite the above charge will be approximately a monosilicate. The oxidizing effect of the 5 g. of material investigated is equal to the reducing effect of the reducer minus the weight of lead actually obtained. The O.P. is found by dividing the oxidizing effect result by the amount of material tested, that is, 5 g.

Methods of Crucible Assaying

A. Single-stage processes.
1. Controlled reduction.
   a. Ores with deficient R.P.
   b. Ores with excess R.P.
2. Uncontrolled reduction. The soda-iron method.

B. Two-stage processes.
3. Oxidation-collection method.
4. Roasting-fusion method.
5. Acid-treatment–fusion methods (combination methods).

Before proceeding with any of the methods it is necessary to estimate the approximate mineralogical composition of the sample in order to decide upon the weight of sample to be used and to select a crucible of suitable size. Before actually adding ore and fluxes to the crucible and proceeding with the fusion, see Manipulative Procedures, pages 151ff.

A. Single-stage Processes

Single-stage processes of crucible assaying are those methods in which the charge components are adjusted so that fusion, lead reduction, and precious-metal collection take place entirely within the crucible with no further reagent additions prior to pouring.

1. Controlled Reduction Methods.—Controlled reduction methods are those in which the size of the lead button is regulated by adjusting the amount of reducing or oxidizing agents that are added to the charge. In these methods more litharge than that required for the lead button is always added to the charge.

Before proceeding with this method it is necessary not only to estimate the mineralogical composition of the sample but also to estimate the net reducing or oxidizing power, either by calculation or by direct determination.

a. Ores with Deficient Reducing Power

CHARGE CALCULATION FOR SILICEOUS ORES.—If the net R.P. of an ore sample is less than that required for producing a lead button of suitable size, an added reducing agent is required. If the sample is dominantly siliceous, use the following procedure in making the charge calculation:

1. Add sodium carbonate equal to the weight of ore.
2. Calculate the bisilicate silica equivalent of the sodium carbonate. From the slag-factor table,[1] it is seen that 1 part of silica combines with 1.8 parts of Na_2CO_3 to form a bisilicate; therefore the weight of Na_2CO_3 divided by 1.8 gives the bisilicate silica equivalent of the sodium carbonate.
3. Deduct step 2 from the estimated silica in the ore.
4. Calculate litharge to form bisilicate with the remaining silica: from the slag-factor table, 3.7 parts of litharge are required

[1] Table XII, p. 126; also inside rear cover.

for each part of silica; therefore, step 3 multiplied by 3.7 gives the litharge required for a bisilicate.

5. Add additional litharge for the button. For convenience, 30 g. is a suitable quantity.

6. Add reducer for the button: Multiply the R.P. or O.P. of the sample by the weight of sample in grams, to give the total reducing or oxidizing effect of the sample used. If the sample is reducing, *subtract* the total R.E. from the desired button weight and divide by the R.P. of the reducing agent to be used,[1] in order to get the weight of reducing agent required. If the sample is oxidizing, *add* the total O.P. to the desired button weight, and divide by the R.P. of the reducing agent.

7. Add from 3 to 5 g. of borax glass to the charge before mixing, or approximately twice the amount of borax as a cover.

Example: Assume that a ½-A.T. (nearly 15-g.) portion of a quartz-pyrite ore with a R.P. of 1.0 is to be assayed. Since the amount of pyrite present is small (less than 10 per cent), the base

Step	Item	Calculation, grams	Recommended charge in round numbers
1	Weight of ore (14.58 g.)	.....	½ A.T. ore
	Na_2CO_3 equal to weight of ore	.....	15 g. Na_2CO_3
2	Silica in ore	15.0	
	Bisilicate silica equivalent of Na_2CO_3: (Factor from slag table): (15) ÷ (1.8)	− 8.3	
3	Silica to be fluxed with PbO	6.7	
4	Litharge for bisilicate: (6.7)(3.7)	24.7	
5	Add litharge for 25-g. lead button	26.9	
	Total litharge required	51.6	50–60 g. PbO
6	Desired weight of button	25.0	
	Total R.E. of ore: (15)(1.0)	−15.0	
	Net R.E. to be supplied	10.0	
	Flour required at R.P. 12: (10) ÷ (12)	0.8	1 g. flour
7	Borax glass (maximum used to counteract basic effect of pyrite present)	.....	5 g. borax glass

[1] Table XIII, p. 130.

content of the ore may be ignored, and the charge calculated as though the sample were of pure quartz. The charge calculation is as shown on page 137.

CHARGE CALCULATION FOR BASIC ORES.—It is evident that samples which are dominantly basic yet deficient in R.P. will contain relatively small proportions of sulfides. Into this category fall the basic carbonates and sulfates, ores high in alumina, and the oxidized ores of the heavy metals. If lime, magnesia, alumina, or the higher oxides of iron are the principal bases, bisilicate slags should be used; if copper, nickel, or tellurium is present in interfering amounts, subsilicates with a large excess of litharge are required; and monosilicates would be preferred for most other bases, including antimony, arsenic, ferrous iron, lead, and zinc.

For basic ores requiring bisilicate slags, the following procedure is used, which may be modified suitably for sub- or monosilicates.

1. Add sodium carbonate equal to the weight of ore.
2. Add litharge for the slag equal to the weight of ore. If the ore is high in alumina, double the quantity of litharge.
3. Calculate the bases in the ore, other than alumina.
4. Calculate the bisilicate silica equivalent of the bases in steps 1, 2, and 3. Deduct the silica in the ore and replace one-third of the remaining silica with borax glass.
5. Add additional litharge for the button.
6. Add reducer for the button, calculating as in step 6 of the charge calculation for siliceous ores.
7. If the ore is high in alumina, estimate the Al_2O_3 content and provide (if not already present) an equal weight of CaO, or double the weight of $CaCO_3$. Sodium or calcium fluoride up to 1½ times the weight of Al_2O_3 may be used in place of CaO.

Note: If impurities are present that require monosilicate slags, the amount of litharge for the slag (step 2) should be double the weight of ore. If copper, nickel, or tellurium is present, refer to Table XI for the fluxing of these impurities, and to the example given on page 143 of a charge calculation for copper sulfide ores.

Example: Assume that a given ore sample contains approximately 50 per cent hematite (Fe_2O_3), 40 per cent limestone ($CaCO_3$), and 10 per cent quartz, and that ½ A.T. is to be used for assay. The charge calculation is as follows:

Step	Item	Calculation, grams	Recommended charge in round numbers
1	Weight of ore (14.58 g.)	....	½ A.T. ore
	Na_2CO_3 equal to weight of ore	15.0	15 g. Na_2CO_3
2	Litharge equal to weight of ore	15.0	
3	Estimated weight of bases in ore:		
	Fe_2O_3: 0.5(15)	7.5	
	$CaCO_3$: 0.4(15)	6.0	
4	Bisilicate silica equivalent of bases (refer to slag table):		
	Silica for Na_2CO_3: (15) ÷ (1.8)	8.3	
	Silica for litharge: (15) ÷ (3.7)	4.1	
	Silica for Fe_2O_3: (7.5) ÷ (1.3)	5.8	
	Silica for $CaCO_3$: (6.0) ÷ (1.7)	3.5	
	Total silica for bases	21.7	
	Deduct silica in ore: 0.1(15)	−1.5	
	Net silica required	20.2	
	⅔ of required silica as SiO_2	13.5	15 g. SiO_2
	⅓ of required silica as borax glass: $\frac{(20.2)(1.7)}{3} = 11.5$ g.	11.5	10 g. borax glass
5	Litharge for slag (step 2)	15	
	Add litharge for 25-g. button	26.9	
	Total litharge added	41.9	45 g. PbO
6	Desired weight of button	25.0	
	Estimated O.E. of ore:		
	7.5 g. Fe_2O_3 at 1.0	7.5	
	Total R.E. required	32.5	
	Flour needed at R.P. 12:		
	(32.5) ÷ (12)	2.7	3 g. flour
7	Step for alumina not required in this case		

b. Ores with Excess Reducing Power

If the net reducing power of an ore sample is greater than the reducing power required for producing a lead button of suitable size, an added oxidizing agent is required in the controlled reduction method, in order to prevent the reduction of

more lead than is needed for the button. It is evident that ores with deficient and with excess R.P. grade into each other. In fact a ½-A.T. portion of a given ore may have insufficient R.P., whereas a 1-A.T. portion of the same ore may have an excess R.P. As the R.P. of ores increases, the amount of added reducing agent decreases to zero. With further increase in R.P. an oxidizing agent, usually niter, is added. In no instance should both reducing and oxidizing agents be added to the same charge, as this is not only a waste of reagents but complicates unnecessarily the proper control of button size.

On account of the use of litharge in excess of button requirements, and the use of niter as an oxidizer, this method is frequently known as the "litharge-niter" method.

Most of the ores of the excess-R.P. class are sulfides, and the nature of the particular sulfides present influences the type of charge to be chosen. For the entire group, except for nonsulfides containing organic matter, the slags should not be more acid than a monosilicate, partly because of variable and uncertain R.P. in the presence of more acid slags, and partly because of the difficulty of fluxing some of the heavy metal oxides in highly acid slags. Ores containing copper, nickel, or tellurium in important amounts require subsilicate or oxide slags and are discussed separately. Charges for ores containing organic matter should be proportioned for the other constituents in the ore with an adjustment of the oxidizing or reducing agent, to allow for the reducing effect of the organic matter present in the ore.

CHARGE CALCULATION FOR ORES WITH EXCESS REDUCING POWER AND RELATIVELY FREE FROM COPPER, NICKEL, OR TELLURIUM.—The general method of calculating crucible charges for sulfide ores requiring monosilicate slags is as follows:

1. Add sodium carbonate for the slag equal to the weight of ore.
2. Add litharge for the slag equal to twice the weight of ore.
3. Calculate the bases in the ore.
4. Calculate the monosilicate silica equivalent of the bases in steps 1, 2, and 3. Deduct the silica in the ore and replace one-third of the remaining silica with borax glass.
5. Add additional litharge for the button.
6. Find the total reducing effect of the ore by multiplying the R.P. (as estimated or as determined in a preliminary fusion) by

the weight of ore in grams. Subtract the desired button weight from the reducing effect. Divide the result by the O.P. of niter, usually taken at 4.0. This gives the amount of niter to be added.

7. Add additional sodium carbonate for the sulfate layer equal to one-fourth of the weight of niter.

Example: Assume that ½ A.T. of an ore containing approxi-

Step	Item	Calculation, grams	Recommended charge in round numbers
1	Weight of ore (14.58 g.)	.....	½ A.T. ore
	Na_2CO_3 for slag, equal to wt. of ore	15.0	
2	Litharge for slag, 2 times wt. of ore	30.0	
3	Weight of bases in ore:		
	FeS_2: 0.4(15)	6.0	
	ZnS: 0.4(15)	6.0	
4	Monosilicate silica equiv. of bases:		
	Silica for Na_2CO_3: (15) ÷ (3.5)	4.3	
	Silica for litharge: (30) ÷ (7.4)	4.1	
	Silica for FeS_2 (to FeO): (6.0) ÷ (4.0)	1.5	
	Silica for ZnS (to ZnO): (6.0) ÷ (3.2)	1.9	
	Total silica required	11.8	
	Deduct SiO_2 in ore: (0.2)(15)	−3.0	
	Net silica needed	8.8	
	⅔ of silica as SiO_2	5.9	6 g. SiO_2
	Borax glass replacing ⅓ of silica: (8.8)(1.3) ÷ (3)	3.8	4 g. borax glass
5	Litharge for slag (step 2)	30.0	
	Litharge for 25-g. button	26.9	
	Total litharge needed	56.9	60 g. PbO
6	R.E. of ore: (15)(8.0)	120.0	
	Desired size of button	−25.0	
	Excess R.E. of ore	95.0	
	Grams of KNO_3 required: (95) ÷ (4)	23.8	24 g. KNO_3
7	Na_2CO_3 for slag (step 1)	15.0	
	Na_2CO_3 for sulfate: (24 g. KNO_3) ÷ (4)	6.0	
	Total Na_2CO_3 to be added	21.0	20 g. Na_2CO_3

mately 40 per cent pyrite (FeS_2), 40 per cent sphalerite (ZnS), and 20 per cent quartz is to be fluxed. By calculation the composite R.P. of the ore is approximately 8.0, which value will be used for the purpose of illustration. The charge calculation is as shown on page 141.

CHARGE CALCULATION FOR ORES WITH EXCESS REDUCING POWER AND RELATIVELY HIGH IN COPPER, NICKEL, OR TELLURIUM.—Ores that are high in Cu, Ni, or Te require subsilicate or oxide slags and a high ratio of litharge to the interfering element. To obtain buttons that are sufficiently pure to avoid difficulty in cupellation the minimum ratio of litharge to copper should be about 30 to 1 by weight. Nickel requires at least 60 parts of litharge to 1 of nickel, and, when associated with copper in approximately equal proportions, 100 parts of litharge to 1 part of combined nickel and copper are required to avoid cupel scoriae and retention of copper and nickel in the bead. The silicate degree of slags for fluxing copper-bearing samples should not exceed 0.5 (subsilicate), and in difficult cases may be as low as 0.25. For fluxing nickel-bearing materials the silicate degree may be increased to 1.0, thereby avoiding excessive crucible corrosion, but if much copper is also present a much lower silicate degree should be used. Borax should be omitted entirely if much copper is present and should be used sparingly, if at all, for nickeliferous materials. Increased sodium carbonate has no advantages for fluxing either copper or nickel-bearing materials and is best held within the usual limits, that is, equal to the weight of sample, to minimize boiling and to leave room in the crucible for the extra litharge.

The above considerations impose a practical maximum content of nickel or copper that can be fluxed in a 20-g. crucible. Unless a larger crucible is used, not more than about 7.5 g. of copper, 4 g. of nickel, or 3 g. of nickel and copper together should be present in the charge.

Tellurium seldom occurs in ores in amounts greater than a few hundredths of 1 per cent but may be present in metallurgical products in greater proportion.[1] Reliable data are lacking on the maximum limits of tellurium or selenium in the crucible assay, but in general not over 0.1 to 0.2 g. of tellurium or selenium should

[1] Ores sufficiently high in tellurium to cause assaying difficulty will give a deep-red solution when heated gently in concentrated sulfuric acid.

be present in a crucible assay charge, and the ratio of litharge to either of these elements should be at least 500 to 1. Increased sodium carbonate is desirable. The silicate degree should be between 0.5 and 1.0, and borax glass is useful. If trial cupellations of buttons from fusions that employed the maximum fluxes indicated the presence of tellurium in undesirable amounts, buttons from subsequent fusions should be purified by soaking under molten litharge for 10 or 15 min. In extreme cases a combination method may be preferable.

The general basis for charge calculations for ores containing copper, nickel, or tellurium is as follows:

1. Estimate the approximate percentage of copper, nickel, or tellurium in the sample. Calculate the weight of sample to be used, so that there will not be over 7.5 g. of copper, 4 g. of nickel, 3 g. of copper and nickel together, or from 0.1 to 0.2 g. of tellurium present in the assay. Add sodium carbonate equal to the weight of ore.

2. Add litharge for the slag equal to 30 times the weight of copper, 60 times the weight of nickel, 100 times the weight of nickel plus copper, and 500 times the weight of tellurium and selenium.

3. Calculate the bases in the ore. Nickel or tellurium need not be calculated, as the amount present can be omitted from the slag calculation.

4. Calculate the subsilicate silica equivalent of the bases in steps 1, 2, and 3. Deduct the silica in the ore. Omit borax glass for copper or nickel ores but replace one-third of the silica by borax glass for telluride ores.

5. Add additional litharge for the button.

6. Calculate the niter (or reducing agent in the case of some telluride ores) according to step 6 in previous examples.

7. Add additional sodium carbonate for the sulfate layer equal to one-fourth of the weight of niter required.

Note: It is particularly important in the case of copper and nickel ores to complete the fusion and pouring in the shortest possible time, not exceeding 20 min. in a 20-g. crucible or 30 min. in a 30-g. crucible. Authorities generally recommend slower fusions at lower finishing temperatures for telluride ores.

Example for Copper Sulfide Ores: Assume that a given sample of sulfide copper ore contains 80 per cent chalcopyrite ($CuFeS_2$)

and 20 per cent quartz, and that the precious-metal content is so low that the maximum weight of ore must be used, up to ½ A.T. Chalcopyrite contains 34.7 per cent copper, therefore the ore contains 27.8 per cent Cu. The following calculations apply:

Step	Item	Calculation, grams	Recommended charge in round numbers
1	Wt. of sample to contain not over 7.5 g. Cu. $\frac{7.5 \text{ g.} \times 100}{27.8} = 27$ g., hence ½ A.T. (14.68 g.) should be used, which will contain (14.68)(0.278) = 4.1 g. Cu.	.....	½ A.T. ore
	Na_2CO_3 for slag equal to wt. of ore	15.0	
2	Litharge for slag, 30 times wt. of Cu: 30(4.1)	122.0	
3	Wt. of bases in ore: $CuFeS_2$: 0.8(15)	12.0	
4	Subsilicate equivalent of bases:		
	Silica for Na_2CO_3: (15) ÷ (7.1)	2.1	
	Silica for litharge: (122) ÷ (14.9)	8.2	
	Silica for $CuFeS_2$ to $Cu_2O.2FeO$: (12) ÷ (6.1)	2.0	
	Total silica required	12.3	
	Deduct SiO_2 in ore: 0.2(15)	−3.0	
	Net SiO_2 to be added (omit borax glass)	9.3	9 g. SiO_2
5	Litharge for slag (step 2)	122.0	
	Litharge for 25-g. button	26.9	
	Total litharge added	148.9	150 g. PbO
6	R.E. of ore: 12 g. $CuFeS_2$ at R.P. 8.0	96.0	
	Desired size of button	−25.0	
	Excess R.E. of ore	71.0	
	Grams of KNO_3 required (71) ÷ 4	17.8	18 g. KNO_3
7	Na_2CO_3 for slag (step 1)	15.0	
	Na_2CO_3 for sulfate: (18 g. KNO_3) ÷ 4	4.5	
	Total Na_2CO_3 to be added	19.5	20 g. Na_2CO_3

Note: A 30-g. crucible will be required, and the fusion should be completed in 20 to 30 min. in a hot furnace.

2. Uncontrolled Reduction Methods.—In the uncontrolled reduction methods of crucible assaying the amount of added litharge plus PbO derived from the ore is limited to that required for the lead button, and an excess of reducing effect (R.E.) is permitted or is deliberately provided, so that practically all the lead is reduced to the button. Hence, soda (or potash) is the only basic flux available for the formation of low-formation-temperature slags.

The method has three chief applications: (1) to recover precious metals from slags or cupels containing litharge; (2) to assay certain classes of sulfide ores without the necessity for controlling the reducing effect of the charge with niter or by other means; and (3) to save litharge on quartz, galena, and other simple ores.

With respect to the first of these applications, many assayers feel that it is necessary to reduce completely all litharge in assay slags and cupels when making corrected assays. It is doubtful if this practice is either necessary or desirable. The evidence at present available indicates that, if litharge in an amount not more than double the sodium carbonate is provided for the slag, the precious-metal recovery is entirely satisfactory from such materials and—particularly in the case of the assay of cupels—it is much less difficult to ensure adequate fluxing when litharge is permitted as a slag constituent.

The uncontrolled reduction method of assaying sulfide ores by the soda-iron method had considerable vogue in the past but is seldom used in modern assay practice. The method consists of a reducing fusion in an alkaline flux, with an excess of metallic iron in the form of large nails or spikes as a reducing and desulfurizing agent. The sulfides react with the PbO present and with the iron nails. After all the lead in the charge is reduced to metal, the reactions with the remaining sulfides and iron produce matte, principally ferrous sulfide (FeS), which is suspended in the alkaline slag.

The soda-iron method is unsuitable for ores containing appreciable amounts of metals near or below lead in the electromotive force series, as these will be reduced with the lead and contaminate the button. Hence, ores containing antimony, arsenic, bismuth, cobalt, copper, nickel, tellurium, or tin should not be

assayed by this method; on the contrary, only those ores in which the principal sulfides are those of lead, iron, or zinc are amenable to the method.

Silver losses in the slag are higher with the soda-iron method than with the niter method, probably owing to the increased solubility of silver in the matte.

Best results are obtained with subsilicate slags in which approximately 75 per cent of the silica is replaced by borax glass. In no case should the slag be more acid than a monosilicate. The buttons should be larger than is customary with other methods, up to 35 g. for ores high in pyrite. The charge cannot be calculated accurately in advance of fusion, as a variable amount of iron is gained from the iron nails; consequently, the fluxes are estimated empirically.

Procedure.—The following procedure is recommended for the soda-iron method:

1. For heavy sulfides, the ore charge should not exceed ½ A.T. If the principal sulfide is galena, use twice as much sodium carbonate as ore; if large amounts of pyrite or sphalerite are present, use three times as much sodium carbonate as ore.
2. Add one-fourth as much borax glass as sodium carbonate.
3. Add one-fifth as much silica as borax glass, unless the ore contains sufficient silica.
4. Allow for lead in the ore and add sufficient litharge so that the total lead in the charge is from 30 to 35 g. (The factor Pb:PbS is 0.865, and the factor Pb:PbO is 0.928.)
5. Mix the charge in the crucible, and insert, point downward, four 20-penny nails or one 3½-in. track spike.
6. Heat gradually in a reducing atmosphere and finish in not less than 30 min. Slow heating aids sulfur elimination.
7. Fusion is complete when the nails can be freed from lead by gentle tapping and washing in the slag. Remove the nails and pour the fusion as usual.

B. Two-stage Processes

Two-stage processes of assaying are those in which lead reduction and precious-metal collection are effected in a separate stage following a preliminary treatment to destroy the reducing effect of the ore or to remove impurities that are difficult to

flux. The preliminary treatment may take place in the fusion crucible or may involve a separate roasting or acid treatment.

In all the two-stage processes the actual lead reduction and metal collection are accomplished by controlled reduction with added reducing agents. For this reason litharge is available as a flux, and the principles of slag formation are the same as those already discussed for the single-stage controlled reduction processes.

3. Oxidation-collection Method.—The oxidation-collection method[1] eliminates the necessity for niter estimation in the assay of sulfide ores yet obtains buttons of nearly uniform size. Complete oxidation of sulfur and other reducing agents is obtained during fusion by adding an excess of niter. After oxidation is complete, briquettes of iron filings and litharge are dropped into the crucible, in order to effect lead reduction and the consequent collection of gold and silver.

From the reaction between metallic iron and litharge,

$$Fe + PbO = FeO + Pb$$

the theoretical R.P. of iron is 3.7; hence 6.75 g. of iron are required for a 25-g. button. The actual R.P. is slightly higher than the theoretical R.P., probably owing to the formation of some Fe_2O_3: Consequently, not more than 6.0 g. of pure iron need be used for 25-g. buttons. Commercial grades of iron filings are of cast iron, which contains up to 4.5 per cent carbon and other impurities that increase the R.P. of the iron so that only 5 to 5.5 g. may be required instead of 6 g.

Present data on the method indicate that the litharge for the button should be added with the iron, although further investigation may prove this to be unnecessary. With some types of ores it is necessary to use two stages of collection in order to ensure complete recovery of gold and silver. It is convenient to use briquettes containing 2.5 g. of iron filings and 15 g. of litharge, bonded with sodium silicate.

For the oxidation-collection method the same slags may be made as in the single-stage litharge-niter controlled reduction method. If litharge for the button is to be added with the

[1] SHEPARD, O. C., and DIETRICH, W. F., The Oxidation-collection Method of Assaying Sulphide Ores for Gold and Silver, *A.I.M.E., Tech. Pub.* 997, 1938.

collector the amount added to the charge is decreased accordingly. For ½-A.T. charges, 30 g. of niter is sufficient for complete or nearly complete oxidation of heavy sulfide ores. In most cases, 25 g. is sufficient. With pure pyrite a small lead button is formed with 30 g. of niter, but the standard amount of collector may be used without increasing the size of button beyond acceptable limits. An excess of niter does no harm, as it is decomposed by heat according to the reaction:

$$2KNO_3 + \text{heat} = K_2O + N_2O + 2O_2$$

and the K_2O formed enters the slag as a desirable base. For economy, and to minimize boiling, less than 25 or 30 g. of niter may be used for ½ A.T. of ore if it is known that the reducing power of the ore is less than 8.

In view of the compensating effect of K_2O derived from that portion of the niter which is not used in oxidizing reactions to form potassium sulfate, it is possible to prepare a standardized charge for ½-A.T. samples, which, although wasteful of fluxes in some cases, can be applied to practically any combination of sulfides and siliceous gangue. With the following charge:

	½ A.T.
Ore	
Sodium carbonate	30 g.
Litharge	30 g.
Silica	10 g.
Borax glass	5 g.
Niter	30 g.

the calculated silicate degree of the slag is 0.70 for pure galena, 0.73 for chalcocite, 0.79 for sphalerite, 0.99 for pyrite, and 1.34 for pure quartz, all of which are satisfactory.

It is evident that if the character of the ore is known in advance, considerable saving in fluxes may be made and better slags can be produced if the fluxes are modified to favor the substances that are difficult to flux, so that in so far as is practicable the suggestions given in the section on fluxing should be applied to specifically known substances. For example, for best results with a high copper sulfide ore, an additional 30 g. of litharge should be added to the above standardized charge, and it is desirable to decrease the silica to 5 or 8 g. and the borax glass to 3 g. or less. Pure quartz or other neutral or oxidizing ores, if their character

is recognized in advance, would be assayed by the regular flour reduction method. Ores high in lime or magnesia will not be satisfactorily fluxed with the standard charge, as the silicate degree of the slag would be too low.

In order to minimize boiling and for convenience in preparing charges, large batches of the flux mixture, without niter, may be mixed and fritted in a suitable furnace, such as a bullion melting furnace.

General Procedure for Oxidation-collection Method.—After preparing the charge as described above, mixing and placing it in the crucible, heat for at least 15 min. in a hot furnace. Then add one collector briquette containing 2.5 g. of iron and 15 g. of litharge. After not less than 1 min., add a second collector briquette. Continue heating for at least 3 min. and pour as usual.

At the time of adding the first collector briquette, most of the oxidation reactions should be completed, although the charge does not need to be thoroughly liquid. Before pouring, the fusion should be quiet, and the slag fluid. If the temperature is sufficiently high and the flux charge is approximately correct the time factors given above will be sufficient. Shotting of the lead and other defective fusions result from the same causes as in the regular litharge-niter method and are corrected in the same manner.

4. Roasting Method.—The roasting method consists of heating a weighed amount of the material to be assayed in a shallow fireclay dish in the presence of air in order to oxidize the metals present and to eliminate certain impurities.

The impurities that can be eliminated by this oxidizing roast are carbon, sulfur, arsenic, antimony, and tellurium. After roasting, the roasted product (calcine) is treated in a crucible fusion in the same manner as an ore with no reducing power.

Roasting is a slow method of eliminating impurities, and there is considerable danger of mechanical or volatilization loss. Except for low-grade materials consisting mostly of carbon or hydrocarbon, such as charcoal cyanide precipitate, the roasting method has little to recommend its use. Other impurities can be handled either in the niter assay or, preferably, because they are better eliminated, by acid treatment. Should 2-assay-ton or larger fusions be desired for arsenical or antimonial sulfide ores,

without using acid treatment, the roasting method might prove useful.

Procedure.—Weigh out the ore and spread in a thin layer in a roasting dish that has been previously coated with chalk or silica. (Materials such as a charcoal cyanide precipitate, that leave a rich residue, should be diluted with an equal weight of silica before roasting.) Place the dish in a muffle at a barely perceptible dull-red heat. Keep covered until danger of decrepitation has passed. Gradually increase the temperature until fumes appear from the ore, then hold at that temperature with frequent stirring until reaction has nearly ceased. Gradually raise the temperature to a maximum of 650 to 700°C., stirring at 20-min. intervals, and hold at the final temperature for 30 min.

Sulfur, carbon, or tellurium can be eliminated in a straight oxidizing roast with an oxidizing atmosphere at the roasting dish. The only precautions are to avoid loss by violent reactions and to avoid fusion, which prevents complete reaction and may cause the material to stick to the dish. If at any stage of roasting the charge shows signs of becoming sticky from incipient fusion it should be removed from the furnace and mixed with silica. This is particularly necessary with galena ores, and silica, equal to the weight of the ore, should preferably be added at the outset. Sphalerite will require a higher roasting temperature than other sulfides, and a longer roasting time, but the maximum roasting temperature should not greatly exceed 700°C. in any case.

In order to secure the removal of arsenic and antimony, roasting must be modified to avoid the formation of arsenates and antimonates, which may form with strongly oxidizing conditions. The oxides of antimony boil above the range of roasting temperatures, so that reducing conditions must be maintained in order to drive off the volatile Sb_2S_3 before it is oxidized. Strongly reducing conditions should be maintained by adding sulfur to the ore and by heating in a reducing atmosphere. After sufficient antimony has been removed, finish with an oxidizing roast to remove carbon and sulfur. Arsenic is volatile as the sulfide and as the oxide As_2O_3. It is best removed by alternate oxidation and reduction with sulfur. Finish with an oxidizing roast.

An oxidizing roast converts most metals remaining in the calcine to their higher oxides. Thus the calcine from thoroughly

roasted pyritic ores will contain a high proportion of ferric oxide, the oxidizing power of which must be considered in the crucible fusion.

5. Acid-treatment Method.—The acid-treatment method consists of leaching a weighed amount of the material to be assayed with acids and other reagents, in order to dissolve impurities that cause difficulty in assaying. This process is commonly used for the assay of high copper materials such as blister and refined copper, but it can be used for the separation of any acid-soluble impurity. In most cases, acid combinations that might dissolve gold are avoided. If silver dissolves, it is precipitated as the chloride just before separation of the insoluble by filtration. The precious metals in the precipitate and insoluble are recovered by scorification, if the total insoluble is small; or by a crucible assay if it is large. Detailed procedures for the acid-treatment methods are given in Chap. X.

Manipulative Procedures in Crucible Assaying

In routine assaying practice it is important that the assayer strive for a high degree of efficiency so that the maximum number of reliable assays may be completed in the minimum time. Fire assaying is particularly amenable to systematization and the use of labor-saving devices where the volume of work is sufficiently great to justify the expense of the special equipment. The following paragraphs illustrate current manipulative practices.

Crucibles.—Most assay crucibles are made of fire clay. Crucible sizes are now generally designated in grams, which is an approximate index of the number of grams of a simple quartz ore that can be fluxed in the crucible. For example, a 15-g. crucible will hold the charge for ½ A.T. (nearly 15 g.) of an easily fluxed ore, but in most cases a 20-g. crucible would actually be required.

In any given laboratory it is desirable to use the minimum number of different crucible sizes. In general, to avoid boiling over, crucibles should not be more than two-thirds to three-fourths full before melting. For reducing-power determinations and for 0.1- to 0.2-A.T. ore charges, 10-g. crucibles are suitable. For most charges of ½ A.T., 20-g. crucibles are used. For larger charges, 30-g. crucibles are required; for fluxing 2 A.T.

of ores requiring more than the minimum fluxes it may be necessary to use 40-g. crucibles.

Fire-clay crucibles larger than 40 g. are impracticable for fire assaying because the severe thermal shock to which assay crucibles are subjected may cause failure of large crucibles, even during the first fusion. Dixon sand crucibles are satisfactory where larger crucibles are needed. When assaying low-grade tailings, it is sometimes necessary to use 3 or 4 A.T. of the sample. If it is not desired to use large crucibles, two separate fusions of 1½ or 2 A.T. each can be made, combining the buttons by scorification, by pouring them into a single mold, or by cupeling them together in a cupel of suitable size.

Crucibles should be kept dry in order to prevent cracking when placed in the furnace. In moist atmospheres it is advisable to store crucibles before use on a drying rack located close to the furnace.

Both fire-clay and sand crucibles are acid refractories and are quite resistant to corrosion by highly acid slags, such as the sesqui- or higher silicates. With such slags a crucible may be reused a number of times, until it finally cracks or becomes salted. Even with very basic slags the crucible wall is usually thick enough for more than one use. Basic refractories, such as magnesite, would be very suitable for highly basic slags but are thus far not available at a cost to compete with fire-clay crucibles.

A crucible that shows serious corrosion or a deep crack should never be reused because the loss in time, materials, and possible damage to the furnace caused by crucible failure greatly exceeds the cost of the crucible. Precious metals not recovered in a crucible fusion are partly left in the crucible, where they may be picked up to salt a subsequent charge. At some laboratories every crucible is discarded after a single use, thus avoiding the possibility of this source of salting.

When crucibles are to be reused, care should be taken to segregate those in which rich samples have been fused. These crucibles should be discarded or used only for the assay of similarly rich materials. Every crucible that has contained a viscous, lumpy, or shotted slag, or a fusion in which a small lead button was obtained, should be discarded.

Assay Sequence.—It is of extreme importance that the assayer devise, and strictly adhere to, a good system of arranging and

handling the daily assays in a predetermined order throughout the entire process from the time the samples are received until the final report is made. Errors caused by misplacement of a sample, crucible, cupel, or parting cup are undetectable by ordinary means, with the result that high-grade samples might be reported in place of low-grade samples, and vice versa. To avoid such errors every assayer should follow a system by which the order of samples is automatically maintained. If one man carries through all operations himself, his system may be devised to suit his own peculiarities; but, if helpers are employed, the system must be such that neither the assayer nor the helpers can confuse the sequence of assays without detection.

It is impracticable to use permanent marks on crucibles, because this practice is time consuming and becomes confusing when crucibles are reused. Cupels cannot be marked satisfactorily. Even if crucibles and cupels were marked, this would be no guaranty in itself that the buttons would be placed in the proper cupel. Parting cups can be marked permanently, but time is lost in arranging them in the proper sequence. Thus, a satisfactory routine should be developed that is independent of numbered marks on the assay receptacles.

When the day's set of pulverized and mixed samples has been assembled, the assayer arranges them in suitable order, then records the sample numbers or description on his report form or notebook. From then on, until the final report is prepared, the assays are handled in the same sequence and may be assigned serial numbers from 1 upward.

Ruled lines may be provided in the notebook to separate each furnace load of crucibles, each set of cupellations, and each tray of parting cups. The number of assays in each of these units is usually different, but if special parting cup trays are made they should hold the same number of parting cups and be in the same arrangement as a set of cupels in the furnace.

All carrying trays for crucibles, buttons, cupels, and parting cups should be designed so that the two ends are distinctive, thus avoiding the danger of reversing the entire set. The arrangement of assays in rows in the carrying tray should read from left to right, as printed matter is read, not zigzagged as in section numbering in a township. If assistants of uncertain reliability are employed, the assayer may insert a blank assay of known sil-

ver and gold content in a key position in each furnace set. If this assay appears in its proper place upon weighing the doré beads it is reasonable assurance that no misplacements have been made in the previous operations. For controlling the fusion and cupellation sequence a small quantity of some element may be added to one or more of the assays, which will give a stain on the cupel that is not present in any of the other assays. Copper or nickel is suggested for this purpose and may be added to any of the regular assays if the amount is just sufficient to give a distinctive cupel stain but not enough to cause cupellation loss or freezing of the button.

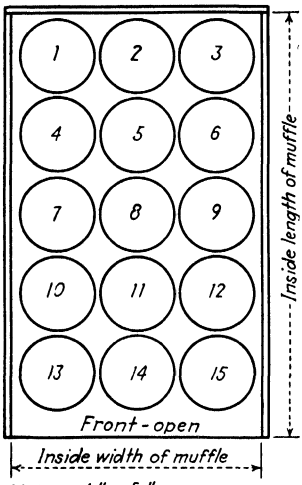


FIG. 12.—Crucible tray.

Handling Crucibles.—A carrying box or tray should be constructed with the same floor area as the muffle, to hold a complete set of crucibles for a furnace. A typical crucible tray for a muffle furnace, which holds five rows of three 20- or 30-g. crucibles, is illustrated in Fig. 12. The crucibles are arranged on the tray as shown and carried to the fluxing bench. When ready for the furnace, the tray is carried to a bench alongside the furnace, and the crucibles are transferred to the furnace by placing the front row (13-14-15, Fig. 12) of the tray in the rear of the muffle. When the furnace is loaded, the crucibles will be in reverse order, front to back, but in the same order left to right, compared with the original position on the crucible tray. In pouring from left to right in each successive row, the No. 1 crucible will be poured first, and the rest in numerical sequence.

Crucible Tongs.—For moving crucibles into and out of a pot furnace, tongs are used that grip a point on the upper rim of the crucible. For muffle furnaces the commonest form of tongs consists of a U-shaped fork on the lower arm that partly encircles the crucible near its mid-height, and a slightly longer tongue on the upper arm that is held down on top of the crucible.

Multiple forks as illustrated in Fig. 20, Chap XVI, permit more rapid handling of the crucibles than the usual type of implement. These are not on the market at present but can easily be constructed. The part holding the crucible is made by tapering the inside of an iron pipe of suitable size until it closely fits the crucible of given size about half-way up from its base. Then a ring $\pm \frac{3}{4}$ in. long is sawed from the pipe, and enough of the ring is sawed out to give an open end that will slip around the base of the crucible.

To make a pouring tongs, one of these rings is brazed to a $\frac{1}{8}$-in. pipe. A short crossarm may be brazed or fitted to the other end of the pipe, to form a handle. In pouring, the edge of the crucible is rested on the edge of the mold, which prevents the crucible from falling out of the tongs when inverted. The charging tongs are built to hold as many crucibles as will fit in a row across the muffle, by brazing the desired number of tapered rings to a reinforcing bar and to spreader blocks. At the Selby Smelter, of the American Smelting and Refining Company, six crucibles are charged into the furnace at a time by this implement.

Addition of Fluxes.—In most commercial assay offices it is common practice to prepare stock flux batches containing all the principal ingredients for fluxing ores of a given general type. By using an excess of fluxes on all samples it is possible to prepare a flux that will serve for practically all purposes, requiring only the addition of a reducer or oxidizer in the controlled reduction method, and minor additions of special reagents for difficult ores. Some assayers prepare one flux for nonreducing silicate ores in which the required reducer is incorporated, and another flux for sulfide ores and concentrates to which niter is added separately for each assay. Assayers having a daily routine of mine samples, concentrates, and tailings may prepare all-inclusive stock fluxes for each class of material.

Flux batches may be conveniently prepared by weighing out the various ingredients and mixing them in a suitable mixing box. A simple form of mixer is a small barrel with lifters on the inner surface. After weighing out the fluxes the barrel is closed and is rolled back and forth until the contents are thoroughly mixed.

Whether or not stock fluxes or individual fluxes are used it is entirely unnecessary to weigh out all the charge components for

each assay. Except for the ore and niter, a volume measurement gives sufficient accuracy. Even the weighing of niter is eliminated in the oxidation-collection method. Although special measuring devices can be made for any requirements it is possible to assemble and calibrate a set of measuring receptacles by using, for example, half-teaspoons, teaspoons, tablespoons, parting cups, 35- and 50-ml. iron crucibles, scorifying dishes, assay crucibles either whole or sawed off, and various other articles that are easily obtainable. The smaller measures may be used "level" or "heaping," as required. For example, a level half-teaspoon of flour is close to 1 g.; a level teaspoon is nearly 2 g. The usual amount desired, 2½ g., is easily obtained by scraping level about ¾ of the top from a heaping teaspoon.

If batch fluxes are used, it is convenient to store them in bins, barrels, or boxes at a bench where the crucibles are assembled on the trays. The assayer or his assistant adds a measure of the stock flux to each crucible, then carries the tray to the fluxing bench where the ore and additional reagents are added, and the charges are mixed.

At the fluxing bench a supply of all individual fluxes should be kept in a partitioned flux box, which is provided with a lid that can be closed while ore samples are being weighed out and the charges are being mixed. This precaution is advisable to prevent accidental salting of the fluxes. A metal strip mounted across the top of the compartments is a useful scraper for producing quickly leveled spoons of flux. In the controlled reduction method with niter the niter is weighed out to the nearest gram on a pulp balance. If desired, a set of 10-, 5-, 2-, and 1-g. measures can be used for niter, but their use will usually take more time than weighing.

Open-type pulp balances, accurate to 5 mg., are suitable for weighing out ore samples, except for very small charges (0.1 or 0.05 assay ton) of high-grade ores, in which case an analytical balance is preferable.

When preparing crucible charges it is customary to add a part or all of the fluxes before adding the ore, so that there will be less danger of particles of ore adhering to the crucible walls and possibly escaping the action of the fluxes. If the charges are to be mixed in the crucible, and if fluxes are added separately, the lighter fluxes are added first, and the heavier ones are placed on top.

Mixing.—After the ore and fluxes are placed in the crucible, they are thoroughly mixed with a spatula, in a cocktail shaker, or on a mixing cloth.

Mixing with a spatula is the commonest procedure. The spatula is inserted to the bottom of the crucible along the inside surface and then lifted with a motion that crowds the spatula tip toward the opposite side of the crucible, the blade finally being turned on edge at the completion of the stroke as the blade emerges from the charge. The crucible is rotated a few degrees with the holding hand, and the spatula stroke repeated The process is continued until the batch is homogeneous.

A 1-pt. aluminum cocktail shaker can be transformed into a suitable mixer by sealing the pouring cap (and sieve if any) from the inside so as to present a smooth interior surface to the charge batch. From 12 to 16 vigorous shakes are sufficient for mixing a crucible charge. There is some danger of salting if the charge is not tapped out carefully, but results are generally satisfactory, and the process is considerably faster than any other method of mixing charges.

Mixing the charge on a mixing cloth is slow and cumbersome and, unless carefully performed, may introduce mechanical losses.

Furnace Operations.—Although slow firing is necessary for the soda-iron method, best results will be obtained with other methods by charging the crucibles into a furnace or muffle that is maintained at a finishing heat, which ranges from 1050 to 1150°C. Upon loading the furnaces with cold crucibles the furnace temperature will drop but will soon increase and, in a properly fired furnace, the finishing temperature will again be reached in from 10 to 15 min. In general, if the fluxes are correctly proportioned, assays in 10-g. crucibles should be ready to pour in 15 min.; 20-g. crucibles require 20 min., and 30-g. crucibles require from 25 to 30 min. Excessive temperatures or prolonged heating cycles should be avoided, as such practices decrease crucible life and tend to cause abnormalities in button size and purity. A nearly neutral atmosphere during fusion also helps to prevent undue variation in the size of the lead button. This is accomplished by avoiding a large excess of air in the combustion chamber of a pot furnace, or by closing the muffle draft in a muffle furnace. If necessary a large piece of coke

may be used in the front of a muffle furnace, or crucible covers may be used in a pot furnace.

For the soda-iron method the furnace temperature should be below 600 to 700°C. immediately after charging, then should increase to a maximum of approximately 1050°C. in 30 to 45 min.

It is true that there is an optimum firing cycle for each distinctive type of crucible charge, but in practice it is not convenient to treat each crucible as an individual, and the above suggestions provide a standardized firing procedure that is generally satisfactory. Charges that are known in advance to require higher melting temperatures than others in the same set may be favored by arranging these so that they will be placed in the hottest part of the furnace.

Pouring.—Before pouring, a crucible may be removed from the furnace and inspected to see that fusion is complete, as shown by the homogeneity and fluidity of the slag, and the absence of floating pellets of lead or of scoriae of undecomposed ore.

Completed fusions are usually poured into conical iron molds. A few assayers prefer to pour on a flat iron plate because the lead cools rapidly and is more easily separated from slag. When molds are used, it is customary to coat them with chalk or ruddle and to warm them slightly before using. Molds must be dry, but, unless warming is required for drying, heating the molds is unnecessary. The chalk or ruddle coating is used to prevent the lead button and slag from sticking in the mold. If the inside surface of the mold is rusted, additional coating is not required. Some assayers deliberately rust their molds with a salt or acid solution. Such a coating lasts much longer than chalk or ruddle.

Just before pouring a crucible, many assayers swirl the contents slightly and gently tap the crucible down against a solid surface. This is supposed to aid in collecting all lead in a single pool at the bottom of the crucible. Such an operation may have some beneficial effect in rare instances, but in most cases equal results are obtained if it is omitted.

Crucibles should be poured in a smooth unbroken motion, turning them upside down and entirely over in a complete revolution. With this practice, the last slag drop runs back inside the crucible instead of down the outside. Slag on the outside of crucibles is a nuisance when they are reused. As the crucible is tipped, the

slag that floats on top of the lead pours out first. The stream of slag should be directed at a point in the mold slightly off-center toward the crucible so that the lead with its greater trajectory will fall as nearly as possible in the center of the mold. A skilled assayer pours the slag very rapidly and slows the motion slightly just before and during the time the lead pours. Assay charges larger than 1 assay ton usually have more slag than the mold will hold. No harm is done if the mold is filled to overflowing with slag before the lead starts to pour, but this can be avoided by pouring part of the slag to one side before pouring the rest of the fusion into the mold.

If two buttons are to be combined together in a single mold, a part of the slag from each crucible should be poured off into a separate mold or to one side, in order to provide room in the button mold for both buttons and a part of both slags. The second pour must follow quickly after the first, before the slag has become so viscous as to prevent the second button from settling.

After pouring into molds it is necessary to wait until certain that the lead has solidified before attempting to recover the buttons. Acid slags decrepitate on cooling, and with most types of molds, unless originally overheated, the lead will have solidified by the time the decrepitation of the slag begins.

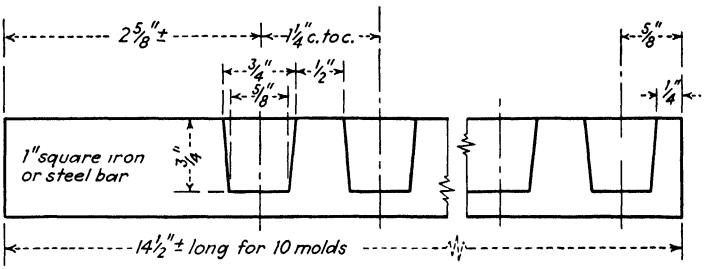
Most of the slag can usually be separated from the button by tilting the block of slag and lead on edge, so that the tip of the button rests against the upper edge of the mold, and then striking a sharp blow with the peen of a machinist's hammer at the junction of the slag and lead. If the slag adheres to the mold, it is necessary to shatter it with the peen until the lead is exposed, then pry out the lead with a sharp-pointed tool.

To complete the removal of slag from the button, and to facilitate charging into the cupel, pound it into an approximate cube and, if necessary, brush off adhered slag with a stiff brush.

Figure 13 illustrates a type of button mold that is favored by some assayers to obviate the necessity of separating slag from the button and hammering the button into shape for cupellation.[1] Each mold is an inverted truncated cone and is large enough to hold 50 to 55 g. of lead. As many molds as desired may be drilled in a bar of suitable length of 1-in. square iron or steel, leaving

[1] Details kindly supplied by H. H. Bein, assayer, Lava Cap Gold Mining Corporation, Grass Valley, California.

about 2 in. at one end as a handle. When pouring a crucible its lip is held just over the near edge of the mold, and a slow steady pouring motion is used so that the slag runs down the side of the crucible and collects on an iron table top. When the lead appears, the higher trajectory of the molten lead carries it into the button mold with little or no slag. Buttons are ready for cupellation immediately upon removal from the mold. Although the pouring operation is slightly slower than when regular molds are used, this is more than offset by the time saved in preparing buttons for cupellation. The contamination of the exterior of the crucible with slag is a disadvantage and tends to shorten the life of crucibles.



Note: With dimensions as above, each mold holds 50-55 g. of lead

FIG. 13.—Longitudinal cross-section of button mold.

Pouring on a flat plate is preferred by some assayers to pouring into molds. The plate should be of steel of sufficient thickness to avoid buckling and of large enough area to permit all the charges from a given furnace load to be poured in a continuous sequence. A plate 3/8 in. or 1/2 in. thick and 28 by 36 in. is suitable for pouring 12 assays. Preheating of the plate is unnecessary if it is dry. In pouring, the stream of slag is directed on the plate so as to form an elongated pool. When the lead appears, a slight deflection of the stream will produce a bay into which the lead can be poured in a compact globule, after which the remaining slag is poured in a continuation of the original pool. With practice this method is as rapid as mold pouring and saves much time in the subsequent cooling of the buttons and separation from slag. It is particularly convenient for reducing-power determinations, where at least 15 min. can be saved in obtaining a set of buttons to be weighed.

Trouble Shooting in Crucible Assaying.—When imperfect fusions, outsize or impure buttons, or other irregularities appear in crucible assaying the assayer is concerned with the correction of the defect when the repeat determination is made. The diagnosis of the source of trouble may sometimes require a more careful identification of interfering minerals than was made prior to the original assay. Frequently the cause of the difficulty can be detected from some peculiarity exhibited by the slag or button from the first fusion, or by the appearance of the cupel and bead during and after cupellation.

The distinction between acid and basic slags can be made by observing the viscosity of the slag as it cools, and by observing the appearance of the cooled slag. If an iron rod, or crucible tongs, is dipped into the molten slag and drawn slowly away from it, acid slags may be drawn out in thin threads, whereas basic slags will drip from the end of the rod. During cooling in the mold, acid slags tend to decrepitate with considerable violence as room temperature is approached. Fresh fractures of acid slags are vitreous, whereas basic slags are stony or crystalline.

With respect to slag colors, only the copper green or red, the cobalt blue, the manganese purple, and, in some cases, the antimony yellow, are sufficiently distinctive to be certain criteria of the presence of specific elements in the slags.[1] Other colors are less unique or are masked or altered by litharge or by iron, which alone imparts a wide range of colors including yellow-brown, brown, black, and yellow-green.

One of the commonest sources of error with beginners is the failure to estimate correctly the required amount of fluxes and oxidizing or reducing agents, and the failure actually to include the desired reagents in the charge. Before applying other remedies, the assayer should be certain that the difficulty is not due to a personal error of this type.

Table XV is presented as a guide to crucible assay difficulties and their correction. Good judgment is required to decide to just what degree a given defect may be permitted without influencing the final result. The term "excessive viscosity" implies that the slag is so viscous that it will not pour readily from the crucible, and that lead will not settle through it. If the slag is homogeneous, a relatively high viscosity may be

[1] See slag colors on p. 123.

TABLE XV.—CRUCIBLE ASSAY ABNORMALITIES AND THEIR CORRECTION

	Type of defect	Probable cause	Suggested remedy
Slag	Excessive viscosity	1. Insufficient finishing temperature	1. Increase furnace temperature, sometimes requiring longer fusion time
		2. Excess of acids (slags are vitreous)	2. Be sure that slag is not more acid than a bisilicate. Decrease acids or increase bases
		3. Insufficient total flux for difficult ores, especially for CaO, MgO, and Al_2O_3	3. Verify presence of interfering substance, and adjust charge accordingly
	Undecomposed or insoluble slag components	4. Insufficient fusion time	4. Heat until visible action ceases
		5. Deficiency of acid fluxes, especially with CaO, MgO, Fe_2O_3, Fe_3O_4, and Al_2O_3 (slags are nonvitreous or crystalline)	5. Add additional acid fluxes to ensure sesqui- or bisilicate slag
		6. Lack of suitable flux for a specific impurity, as Al_2O_3, bone ash, and others	6. Identify the impurity and provide required flux
	Shotting	7. Excessive slag viscosity	7. See 1, 2, and 3
		8. Unfused particles of Fe_3O_4 in a mushy layer between slag and lead, (may be derived from sulfides as well as from oxides of Fe)	8*a*. Repeat with bisilicate slag, or 8*b*. Add approximately 1 A.T. PbO to crucible before pouring.
		9. Spattering of lead in mold caused by pouring before fusion reactions are completed	9. Leave in furnace until fusion is quiet
	Excessive adhesion of slag to button	10. Slag too acid, generally with borax glass	10. If other conditions permit, decrease the acid fluxes or increase basic fluxes
	Excessive crucible corrosion or breakage	11. Excessively basic slag	11. Increase acid fluxes
		12. Furnace temperature too high	12. Decrease furnace temperature
		13. Poor crucible quality	13. Try other crucible brands under comparable conditions
		14. Crucibles contain moisture	14. Dry crucibles before using
		15. Slag on furnace floor	15. Keep furnace floor free from fusible slags. Use bone ash to absorb spills of slag, lead, or fluxes
	Matte or speiss layer	16. Insufficient PbO or Na_2CO_3 or both	16. Increase PbO or Na_2CO_3 or decrease weight of sample

TABLE XV.—CRUCIBLE ASSAY ABNORMALITIES AND THEIR CORRECTION.—(*Continued*)

	Type of defect	Probable cause	Suggested remedy
Button	Hard or brittle	17. Base metals, such as Cu, As, or Sb, or matte in button not caused by incorrect furnace operation	17. *a*. Increased PbO and Na_2CO_3 usually required, or charge reproportioned for specific impurity, or 17. *b*. Repeat with smaller ore charge, or 17. *c*. Treat slag as in 8*b*.
		18. PbO in button	18. Seldom serious, but usually corrected by higher temperature, or decreased PbO in slag
		19. Rejection of base metal, especially copper, from slag by change in composition by crucible attack	19. Use a quick, hot fusion cycle
		20. Very high gold in button	20. Decrease weight of ore or increase size of button or both
	Outsize	21. Erroneous estimate or weighing of reducer or oxidizer	21. Recalculate reducer or oxidizer and ensure correct addition
		22. Insufficient PbO for button	22. Add more PbO
		23. Excessive oxidizing (small button) or reducing (large button) atmosphere in furnace	23. Standardize furnace operations to obtain nearly neutral atmosphere
		24. Slag much more acid than in reducing-power determination (small button from niter assay charge)	24. Decrease silica or niter, and increase PbO for additional button weight expected

acceptable although it is more convenient, and generally more reliable, to use slags that are sufficiently fluid to pour cleanly from the crucible. "Shotting" refers to the presence of small shots or globules of lead distributed throughout the slag. The assayer should make a practice of inspecting the interior of the crucible just after pouring, to detect the existence of shotting. All shotted assays, as well as those containing undecomposed or insoluble slag components, should be rejected. The crucibles in which such assays were made should be discarded unless cleaned out by the use of a blank charge in which a normal button and slag are produced.

Hard or brittle buttons are unacceptable only if they indicate the presence of too much copper, antimony, arsenic, or other impurity that might cause loss or freezing during cupellation, or if they are so brittle as to cause loss when separated from the slag and hammered into shape for the cupel. Buttons containing copper usually have an exceptionally bright luster and separate easily from the slag, but unless they are notably hardened they may ordinarily be used without excessive cupellation loss. Buttons that show a faint copper color, especially on the upper surface, are generally discarded, as they contain too much copper for reliable results in cupellation. Antimony has a pronounced hardening effect on lead but does not cause brightening of the luster and hence may be distinguished from buttons hardened by copper. Arsenic, zinc, and a few other metallic impurities cause brittleness. For superior accuracy, buttons rendered appreciably hard or brittle by antimony, arsenic, or zinc, as well as by copper, should be discarded. Under certain conditions, particularly with low fusion temperatures and with excess litharge in the slag, some PbO may become mixed in the button, causing a form of brittleness that is seldom sufficient to cause loss in handling and does not cause cupellation loss.

Buttons from fusions in which a detectable layer of matte or speiss appears should be discarded.

The addition of litharge just before pouring helps to prevent shotting and also helps to produce soft lead buttons. Some assayers treat all important slags with approximately 1 assay ton of litharge, to which a small quantity of a reducer may be added in order to obtain a slag-washing effect.

CHAPTER VIII

THE SCORIFICATION ASSAY

The scorification assay is an oxidizing fusion in a shallow fire-clay dish, known as a "scorifier," of a relatively small quantity of ore and a minimum of acid fluxes with a comparatively large amount of granulated lead. Oxidizing conditions are maintained by admitting air to the muffle, which oxidizes a part of the lead and roasts the ore. The fused litharge combines with silica, borax glass, and the oxidized base metals of the ore to form a slag. Precious metals are collected by the molten lead and remain alloyed with the lead button. The buttons from the scorification are cupeled, weighed, and parted as in the crucible assay.

Applications and Limitations.—The scorification method is best adapted to the assay of ores (1) that are sufficiently rich in gold or silver so that weighable beads are obtained with ore samples not exceeding 0.2 assay ton, and usually 0.1 assay ton, in weight; (2) that are so homogeneous that a small sample is sufficiently reliable; (3) that are relatively free from basic oxides and from metals, other than mercury, below lead in the electromotive force series of elements; and (4) that contain oxidizable impurities but not any appreciable quantity of decrepitating compounds.

The above limitations restrict the ideal applications of the method to high-grade gangue-free or siliceous ores or metallurgic products containing oxidizable forms of zinc, tin, manganese, copper-free nickel, cobalt, or lead, particularly those in which silver, rather than gold, is the principal precious metal. For such materials, scorification is an acceptable, but not a necessary, alternative to the crucible assay.

Ores containing large proportions of basic oxides are unsuited to scorification because of the excessive quantity of acid fluxes required and because the method, being essentially an oxidizing process, does not favor the reduction of higher oxides to the lower forms that are more readily slagged. Hence, unfused scoriae of iron and manganese may be formed when hematite, magnetite,

pyrolusite, and similar minerals are scorified. Calcium and magnesium oxides are not fluxed in scorification without excessive additions of acid fluxes, as the normal scorification slags are too basic for the formation of fusible slags high in lime or magnesia.

Ores that decrepitate violently are troublesome in scorification because of "spitting," which is the violent projection of small particles of lead from the scorifier. Products such as zinc cyanide precipitates, containing considerable metallic zinc, may suffer loss during the intense combustion of zinc.

Ores containing antimony, arsenic, bismuth, copper, nickel-copper, tellurium, and other metals below lead in the electromotive force series can be more readily handled in the crucible assay, as a greater excess of litharge is available to help oxidize the impurities.

One of the useful applications of scorification is the retreatment of crucible assay buttons, either to remove certain impurities, to decrease their size, or to combine two or more crucible buttons in case the crucible charge is so large as to require distribution between two or more crucibles. The beginner is apt to overdo this application of scorification in the endeavor to avoid repetition of crucible assays in which a large or impure button was obtained. It must be kept in mind that the addition of a scorification step following the crucible fusion increases the slag loss of precious metals, and, furthermore, that scorification is less adapted to the removal of nonvolatile impurities than the crucible assay.

The principal advantages of scorification over crucible assaying are that the control of button size is independent of the nature of the ore, the cost of fluxes is low, less time is required to prepare the charges for melting, and the muffle capacity for scorifiers can be made greater by stacking a second layer of scorifiers on the rims of the first layer. These advantages are largely offset by the narrow limitations of the method with respect to the size and character of the sample, and by a longer heating cycle in the furnace. The cost of fire-clay ware is nearly equal for the two processes, because scorifying dishes, though cheaper, are ordinarily usable only once, whereas the average life of crucibles is 3 to 4 fusions. On ores of types suited to ideal scorification, the accuracy of scorification compares favorably with the crucible

assay for equal sample weights, but in general the error is greater since smaller samples are used.

Scorification has no chemical advantages over the crucible method for ores that are free from oxidizable compounds. Scorification has an advantage over the crucible assay only in the separation of impurities having volatile oxides that escape as a vapor more readily in scorification than in the crucible assay. On account of the simplicity of the scorification method, it is a suitable alternative for high-grade silver ores associated with lead.

Slag Characteristics.—The chief distinction between the slags formed in scorification and those formed in the crucible assay is that the scorification slags are free from alkalies unless present in the ore. The silica and borax-glass content of scorifier slags is kept at a minimum by adding very little of these reagents. Normally, only 1 to 3 g. of borax glass is added for 0.1 assay ton of ore charge. No silica is added unless it is entirely lacking in the ore, when 1 or 2 g. may be added to prevent excessive corrosion of the scorifier. Although most authorities[1] classify scorifier slags as oxide slags high in litharge, in which other metallic oxides are dissolved, actual scorifier slags increase their silica content at the expense of the scorifier and are distinctively glassy, corresponding closely in composition to lead sub- to monoborosilicates. Within this range the litharge of the slag is able to act as an active carrier of oxygen to aid in oxidizing metallic sulfides and to retain metallic oxides in the slag. Care must be taken to avoid excessive additions of acid fluxes, because in slags more acid than the monosilicate the litharge is so firmly combined in the slag that it fails to act as an oxidizer.

When it is necessary to add excessive quantities of silica, as in fluxing CaO or MgO, the operation becomes a miniature crucible assay with little or no true scorification, and an actual crucible assay is greatly to be preferred as the fluxes can be balanced more satisfactorily.

Control of Button Size.—The control of button size in scorification is fixed by the geometry of the scorifier and the surface

[1] BUGBEE, E. E., "Textbook of Fire Assaying," 2d ed., p. 127, and note 15, p. 133, John Wiley & Sons, Inc., New York, 1933. FULTON, C. H. and SHARWOOD, W. S., "Manual of Fire Assaying," 3d ed., p. 151, McGraw-Hill Book Company, Inc., New York, 1929.

tension of the lead and slag. Molten lead has a higher surface tension than molten slag. When the charge is first melted, the unfused ore floats on a bath of lead. As roasting and slagging reactions proceed, the slag forms a ring around the outside of the high meniscus of the lead. As more slag is produced at the expense of the lead the slag ring gradually rises over the lead meniscus until finally the slag completely covers the remaining lead, and the assay is ready to be poured.

Commercial scorifiers have an inside shape corresponding approximately to a spherical segment, and are available in two general shapes, shallow and deep, and in various sizes ranging from 2 to 4 in. inside diameter at the top. The sizes most commonly used are 2 in., 2½ in., or 3 in. diameter. For most routine work, scorification practice can be standardized so that only one size, or at the most, two sizes, of scorifier need be carried in stock.

For each scorifier size of a given shape, the size of button is fixed, for all practical purposes, by the amount of granulated lead used in the assay. Table XVI gives, for the deep form of scorifier used in American practice, the relation between scorifier size and granulated lead used to obtain buttons weighing 20 to 25 g.

TABLE XVI.—SIZE OF DEEP SCORIFIER VS. WEIGHT OF GRANULATED LEAD

Scorifier diameter, inches	2	2¼	2½	2¾	3	3½
Granulated lead required, grams	30	35	45	50	60	75

Weight of Ore Sample.—For mixtures composed largely of galena with quartz gangue, 0.5-assay-ton charges may be assayed in a 3- or 3½-in. scorifier with 75 g. of lead and 2.5 g. of borax glass, but this does not represent common practice, and the maximum weight of ore that is ordinarily assayed by scorification is 0.2 assay ton. This requires a 2½-in. deep-form scorifier and 45 g. of lead for simple galena or pyrite ores with quartz gangue. For more difficult ores, either a larger scorifier or a smaller sample weight or both must be used. For example, 0.1-assay-ton samples of difficult ores may require 60 g. of lead and 3-in. scorifiers. Samples as small as 0.05 assay ton may be used for very rich materials, such as cyanide precipitates.

On account of the small weight of ore taken for assay, exceptional care must be taken to ensure that the pulp is ground and mixed properly and that the portion taken for assay is weighed accurately. Samples of rich materials from which 0.05 or 0.1-assay-ton portions are to be obtained should be ground to 200-mesh or finer, and weighings should be accurate to 1 mg. or less. See Chap. III for the principles involved.

Scorification Procedure.—The general procedure for scorification is embodied in the following steps:

1. *Preparation of Charge.*—Decide upon the weight of ore and size of scorifier to be used, thus determining the weight of granulated lead required. Measure out one-half of the required amount of granulated lead and place it in a dry scorifier. Weigh out the ore and mix with the lead in the scorifier, cover with the second half of the lead, and sprinkle the required amount of borax glass over the surface.

2. *Fusion.*—Place the scorifier into a muffle at 500 to 600°C., close the door and muffle draft, and heat for 2 or 3 min. until the lead is melted and danger of decrepitation or spitting is past.

3. *Roasting.*—Open the door and draft to admit air and gradually raise the muffle temperature to 900°C. In a few minutes roast reactions are completed and patches of unfused ore should disappear, leaving a smooth-surfaced ring of slag surrounding the lead bath.

4. *Scorification.*—Continue heating in an oxidizing atmosphere until the slag covers the lead. The temperature may be raised to 1000°C. or more if necessary to scorify ores containing large amounts of base metals other than iron, lead, or copper, but excessive temperature should be avoided as it increases the amount of silica in the slag by scorifier attack and may increase the loss of silver by volatilization.

5. *Liquefaction.*—Toward the end of scorification, increase the muffle temperature to 1000 or 1050°C. to decrease the viscosity of the slag for clean pouring. This may be done conveniently by closing the muffle door and draft for a few minutes after the scorification stage is complete.

6. *Pouring.*—Pour the fusion in the usual manner, allow to cool, and separate the button from the slag. If the button is soft and malleable it is ready for cupellation in the usual manner. Buttons containing impurities could be rescorified with additional

TABLE XVII.—SCORIFICATION DIFFICULTIES AND THEIR CORRECTION

Phenomenon	Cause	Remedy
Spitting	1. Moisture in scorifier	1. Dry thoroughly before use
	2. Volatile matter in scorifier due to impure clays or underfiring in manufacture. (Ignition loss at 1000°C. should not exceed 2 per cent)	2. Try other brands under comparable conditions
	3. Decrepitating minerals in ore	3. Assay by crucible method, or heat very slowly at first
	4. Excessive rate of heating or oxidation in early stages	4. Decrease heating rate or air admission or both during melting and roasting stages
Cracked or leaky scorifiers	5. See 1, 2, and 4	5. See 1, 2, and 4
	6. Excessive amounts of corrosive constituents present, for example, copper	6. Crucible assay preferred
Scoriae	7. Deficiency of acid flux	7. Increase acid fluxes, but if more than 3–4 g. are needed, ore should be assayed by crucible method
	8. Insufficient temperature	8. Increase temperature
	9. Large amounts of Sb, As, Ni, Sn, or higher oxides of Fe or Mn	9. Crucible assay preferred
Shotting	10. Insufficient finishing temperature	10. Finish at higher temperature
	11. Deficiency of PbO in slag	11. Decrease acid fluxes, or increase Pb in charge
Impure buttons	12. Presence of impurities not readily removed by scorification, as Sb, As, Cu, Ni, Se, Te	12. Crucible or combination assay preferred
Outsize buttons	13. Incorrect proportions of lead to scorifier size	13. Adjust quantity of granulated lead (Table XVI)

lead, but this treatment is not entirely successful when much copper, nickel, or tellurium is present, and in any event the additional slag loss from the second scorification must be taken into consideration.

Trouble Shooting in Scorification.—As in the crucible assay, scorification slag colors often indicate the presence of specific metals in the ore. The slag colors may best be observed by the glaze on the cooled scorifier after pouring. In addition, scoriae and fumes may aid in the identification of impurities, as in cupellation.

The principal abnormalities that may occur in scorification are spitting, cracked or leaky scorifiers, scoriae, shotting, impure buttons, and outsize buttons. If any of these phenomena are pronounced, the accuracy of the assay is adversely affected.

The causes and remedies of scorification difficulties are given in Table XVII.

CHAPTER IX

THE ASSAY OF BULLION FOR GOLD AND SILVER

In assaying and metallurgy, "bullion" is a generic term referring to alloys containing sufficient of the precious metals so that their recovery or estimation is of economic significance.

Lead Bullion.—Lead bullion is a bullion in which lead is the dominant metal. At lead smelters the blast-furnace product is known as "base bullion" and usually contains in excess of 90 per cent of lead together with most of the gold and silver charged to the furnace and minor amounts of various base-metal impurities, chief among which are antimony, arsenic, and copper. The term "base bullion" is also used to refer to impure silver or gold bullion produced from zinc precipitates in the cyanide process, in which case the chief impurities are zinc, lead and copper, but since such bullions are predominantly silver and gold they should be classed as silver or gold bullions rather than as lead bullions.

At lead smelters, in addition to the blast-furnace lead, routine assays include the assay of refined lead and various intermediate products. The general methods described under the heading of lead bullion may be adapted to the assay of any such materials, provided that lead is the dominant metal present.

Copper bullion is defined as a bullion containing in excess of 50 per cent of copper, and not more than 10 per cent of base metals other than lead and copper. The most common copper bullions occurring in assay practice are the products of various stages of the copper smelting and refining processes. The product of the copper converting process is referred to as "blister copper" because the evolution of gases during the solidification of copper causes the surface of the cast copper to become blistered. Blister copper usually contains in excess of 98 per cent of copper, a small part of which is present as sulfide and as oxide. It commonly contains in excess of 50 oz. of silver and 0.5 oz. of gold per ton, but the content of precious metals depends upon the amount present with the copper in the materials being smelted. Blister

copper and other sources of crude copper to be refined electrolytically are given a preliminary furnace refining, then cast into anodes, in which form the copper is known as anode copper, and contains slightly more copper, gold, and silver than the original blister copper. The final product of the electrolytic refinery is called "refined copper" and usually contains less than 0.6 oz. of silver and 0.01 oz. of gold per ton.

Silver bullion is a bullion containing more than 50 per cent of precious metals of which more than half is silver, and with less than 10 per cent of base metals other than lead and copper. The term "doré bullion" literally means gold-bearing and is generally used to refer to bullion containing more than 90 per cent of combined silver and gold, in which silver is dominant. "Fine silver bullion" refers to bullion containing more than 99 per cent of silver and practically no gold.

Gold bullion is a bullion containing more than 50 per cent of precious metals of which more than half is gold, and with less than 10 per cent of base metals other than lead and copper. "Fine gold bullion" is bullion containing more than 99 per cent of gold and practically no silver. Free gold or retorted amalgam from lode or placer mining is a common source of gold bullion. Dental and jeweler's scrap gold is another source. Some of these materials may be so impure as to merit the classification of base bullion.

Fineness.—The assay of gold and silver bullion and of some of the richer base bullions is expressed in parts per thousand, known as the *fineness*. For example, a gold bullion containing 990 parts of gold per 1000 is 990 *fine*. A doré bullion containing 800 parts of silver and 150 parts of gold is 800 fine silver and 150 fine gold, and the total fineness is 950.

For convenience in bullion assaying the millième system of assay weights is frequently used. The millième is 0.5 mg. and 1,000 millièmes (0.5 g.) is the amount of bullion usually taken for assay. All weights are stamped in millièmes, and if a 5-mg. rider is used on the assay balance, the weights are read directly in fineness.

Sampling.—The sampling of bullion requires exceptional precautions, which are fully dealt with in Chap. II. Samples are obtained as chips, borings, granules, filings, or as sheet metal, depending upon the method of sampling employed.

Weight of Sample.—The weight of bullion to be taken for assay should be such that the combined weight of silver and gold in the assay is not greatly in excess of 1½ g. Larger beads are difficult to part, and no increase in accuracy is obtained. A 0.5-g. (1,000-millième) sample is satisfactory for all silver or gold bullions, that is, those that have a total fineness in excess of 500, unless the gold content is so low as to require a larger weight for accurate weighing of the gold, in which case a 1.0-g. sample may be used. For base bullions and for lead or copper bullion, if the assay is to be reported in ounces per ton, the assay-ton system of weights is used, using 0.05, 0.1, 0.2, or other suitable weight up to 1 assay ton for low-grade bullions.

On account of the difficulty of weighing out a predetermined quantity of bullion in the form of sheet, turnings, or chips, an approximate quantity is weighed out and the exact weight is determined and recorded. Experienced assayers, however, often learn to weigh out the exact desired quantity without undue loss of time, and it is not uncommon to make an average of one weighing per minute. If the sample is in the form of filings, the difficulty of obtaining a predetermined sample weight is decreased. An accuracy of 0.05 mg. is sufficient for bullion weighings as this is within the limits of variation of duplicate assays.

For control assays in buying and selling bullions it is best to make all assays in triplicate or quadruplicate.

Lead-bullion Assay

For ordinary lead-smelter bullions, comparatively free from interfering impurities, a simple cupellation of 0.5- or 1.0-assay-ton samples, wrapped in 5 to 8 g. of sheet lead, is satisfactory. A cupel correction may be used if a high degree of accuracy is required. If the bullion contains impurities that interfere with cupellation, then scorification, crucible fusion, or acid treatment should be used prior to cupellation.

Copper-bullion Assay

The assay of copper bullion or blister copper for gold and silver involves the removal of most of the copper prior to cupellation. This may be done by scorification, crucible assay, or by acid treatment. Acid-treatment methods, described in Chap. X, give the best results.

The scorification method, though at one time accepted as standard by smelters, is wasteful of time and materials and gives high silver losses unless slag and cupel corrections are made, because several successive scorifications are needed before the buttons are pure enough for cupellation.

Crucible Method.—The crucible method is rapid and is sufficiently accurate for preliminary estimates or for plant-control purposes. It is carried out by placing the assay portion of copper bullion, mixed with powdered sulfur, in the bottom of a 30-g. assay crucible. The copper-sulfur mixture is covered with a high litharge flux, and the charge is then melted. The sulfur reacts first with the copper to form a copper sulfide matte. Then the litharge reacts with the matte to oxidize both sulfur and copper and is itself partly reduced to form a lead button, in accordance with the principles discussed in Chaps. VI and VII. The copper-sulfur mixture is not mixed with the flux, in order to avoid reduction of lead before the copper is oxidized.

A maximum of ¼ assay ton of copper can be fluxed in a 30-g. crucible, and, with this amount of copper, 1.5 g. of sulfur will produce a lead button of approximately 25 g. The slag should be very high in litharge—a silicate degree of 0.25 gives better results than the subsilicate slag ordinarily recommended for ores high in copper. Using the method of charge calculation given in Chap. VII, the complete charge is as follows:

Copper bullion	0.25	A.T.
Sulfur	1.5	g.
Flux (Mix separately and place on top of the copper-sulfur mixture):		
Sodium carbonate	8	g.
Litharge	250	g.
Silica	9	g.

Fuse in a hot furnace and pour immediately upon completion, in 15 to 20 min. The buttons from two ¼-assay-ton charges of the same bullion may be scorified together to remove additional copper prior to cupellation and to increase the accuracy of weighing the beads.

Silver-bullion Assay

The assay for silver in silver or gold bullion may be carried out by either cupellation or volumetric methods. Cupellation

is used to obtain approximate results. For greater accuracy the volumetric methods are preferred.

Cupellation Method.—The errors in the cupellation assay for silver in silver-rich bullions are corrected by means of a check or "proof" assay of a synthetic sample of approximately the same weight and composition as the bullion sample. The check sample is cupeled alongside the bullion sample, and it is assumed that the losses as determined for the check apply to the bullion. Thus the cupellation method involves a preliminary assay to determine the approximate composition of the bullion before the check can be prepared. The entire procedure is as follows:

1. *Preliminary Cupellation.*—Weigh out nearly or exactly 500 mg. of bullion and record the exact weight. If it is known that extra silver is needed for parting, the estimated amount of proof silver should be weighed out and added to the bullion, recording the exact weight added. Fold a small square or rectangular strip of lead foil into a cone or box, add sufficient silver-free granulated lead[1] to make a total weight of 20 g., bury the weighed-out bullion sample and the inquarting silver, if any, in the granulated lead, and wrap into a compact shape. Cupel carefully with feathers and with precautions to prevent freezing or sprouting. Weigh the bead, part, and weigh the gold in the usual manner. If the bead does not part, the preliminary cupellation should be repeated with sufficient added silver, the exact weight of which is recorded.

2. *Preparation of the Check.—a.* Assume that approximately 1 per cent of the silver was lost in the preliminary assay but that the gold is approximately correct. The original weight of the preliminary bullion sample, plus the added silver, if any, minus 101 per cent of the weight of the bead is the estimated weight of base metal present. The usual base metal is copper and if this is verified by the cupel stain, use c.p. copper foil to make up the base-metal content of the check. If the base metal is not dominantly copper, ascertain by qualitative tests, spectrographic analysis, or other means what metals are present, and use those metals in preparing the check.

If the silver-gold ratio is so high as to cause serious disintegration of the gold in parting, it is desirable to add proof gold in

[1] It is advisable to use as little lead foil as possible, as it generally contains silver, whereas granulated lead may be obtained practically silver free. A correction should be applied if necessary.

sufficient amount so that the bead will not contain more than 3 or 4 parts of silver to 1 part of gold. With bullions low in gold, this procedure is impracticable, and the assayer must rely upon manipulative skill to recover all the gold in the floured partings.

b. Weigh out the ingredients for the check assay in the same proportions as were indicated in the preliminary bullion cupellation, using proof silver, proof gold, and c.p. base metal. If the final assay is to be made in duplicate, one check is sufficient; if in triplicate, two checks are required.

c. Wrap the ingredients of the check in the same amount of lead as for the bullion assay, as per section 3*a* following.

3*a*. *Lead Required.*—If the base impurity is copper, weigh out the amount of sheet and granulated lead for the cupellation of 500 mg. of bullion and for the synthetic checks in accordance with the recommendations in Table XVIII.

TABLE XVIII.—LEAD REQUIRED FOR CUPELLATION OF COPPER-BEARING SILVER BULLION
(500-mg. Bullion Sample)

Fineness of bullion, Au + Ag	Weight of copper		Weight of lead, grams	Ratio, Pb:Cu
	Milligrams	Millièmes		
1,000	0	0	3	
950	25	50	5	200
900	50	100	7	140
850	75	150	9	120
800	100	200	11	110
700	150	300	14	93
600	200	400	16	80
500	250	500	18	72

3*b*. *Preliminary Treatment of Bullions Containing Sb, Se, Te (and Bi).*—If the principal impurity is antimony, first scorify the bullion and checks in 2½-in. scorifiers with 30 g. of lead and make up the scorifier buttons to within 1 g. of the same weight by adding sheet lead to the lighter ones if necessary. It is not essential that the checks contain the same amount of antimony as the bullion because the antimony is removed by scorification, and the scorification losses are practically the same with or with-

out the small amount of antimony that might be introduced with a 500-mg. sample of bullion.

If the bullion contains selenium or tellurium in notable amounts, first scorify the bullion and checks in a 2½-in. scorifier with 40 g. of lead, then flatten the buttons into sheets about 3 in. square and proceed to remove the selenium and tellurium by the acid-treatment and scorification method given in Chap. X. It is not necessary that the checks contain the same amounts of selenium and tellurium as the bullion, but it is essential that no selenium or tellurium appear in the cupellation.

Bismuth may be removed by the same treatment as for selenium and tellurium, but if the amount of bismuth is known, and the checks are made up accordingly, direct cupellation will give good results, as the losses are not greatly different than when lead is the cupeling medium, and the results will be consistent between the bullion and the checks. Some bismuth may be retained in the beads.

4. *Final Assay.*—Arrange the cupels in the furnace so that the bullion buttons and the check buttons alternate in the same row. Cupel carefully with feathers with particular attention to uniformity of temperature across a row so that the checks and the bullion buttons they control receive equal treatment. Raise the temperature toward the finish to avoid freezing, and be careful to avoid sprouting. Weigh and part the beads in the usual manner. The preparation of a cornet for parting, as described for the assay of gold bullion, is desirable, especially if the silver-gold ratio approaches the minimum (2:1) for complete parting.

5. *Calculation of Results.*—The principle that applies to the calculation of the silver and gold is that the percentage of loss in the checks is applicable to the percentage of loss in the bullion samples adjoining the check in the muffle. If two or more checks are used in the same row, the average percentage of loss in the checks is applied to all the bullion assays in the row. The results are expressed in fineness (millièmes) of gold and silver and should check within 0.1 gold fineness and 0.5 silver fineness.

Volumetric Method.[1]—Chemical methods for the determination of silver are based on the insolubility on dilute nitric acid solutions

[1] For a more extended discussion, see standard treatises on quantitative analysis, such as W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley & Sons, Inc., New York, 1929.

of either the chloride or the thiocyanate. The volumetric thiocyanate, or Volhard's, method is generally the most convenient and is the one described here. Good results are obtained on ordinary silver bullions in which copper is the principal impurity. For impure alloys, ores, and metallurgical products, fire assay methods are generally more suitable, on account of the difficulty of removing interfering elements.

Principles.—The reactions on which Volhard's method is based are as follows:

$$AgNO_3 + KSCN = AgSCN + KNO_3 \quad (1)$$

$$3KSCN + Fe(NO_3)_3 = Fe(SCN)_3 + 3KNO_3 \quad (2)$$

Reaction (2) does not occur until (1) is completed, hence the addition of a small amount of a soluble ferric salt serves as an indicator by the formation of red ferric thiocyanate in the presence of an excess of thiocyanate.

If more than 70 per cent of copper is present, silver in known quantity must be added to prevent interference of copper in titration.

Chlorides interfere by reaction with the silver, hence all reagents and glassware must be free from chlorides.

Mercury reacts with thiocyanate in a manner similar to silver and hence must be absent. Amalgams and retort sponge must be given a preliminary fusion.

Palladium interferes but is rarely present. Other interfering elements and compounds are generally eliminated by the acid treatment of the sample.

Standard Thiocyanate Solution.—Either potassium or ammonium thiocyanate may be used as a standard solution. A 0.05 *N* solution is satisfactory, but many chemists prefer to use an empirical standard that is adjusted so that 1 ml. on a 0.5-g. sample of bullion is exactly equal to 1 or 2 per cent of silver. A solution equivalent to 1 per cent of silver per milliliter when a 0.5-g. sample is taken requires 9.01 g. of KSCN or 7.06 g. of NH_4SCN per liter. Standardize the solution against a weighed amount of pure silver, treated as in the procedure given below.

Ferric Alum Indicator.—Prepare a saturated solution of ferric alum in distilled water, then add sufficient (usually about 10 per cent) pure colorless nitric acid to bleach the brown color of the solution.

Procedure.—1. Weigh out 0.5 g. of bullion and transfer to a 200-ml. Erlenmeyer flask or a 250-ml. beaker.

2. Dissolve in 15 ml. of 1:1 nitric acid and boil until nitrous compounds (brown fumes) are expelled.

3. Cool, dilute to 50 to 75 ml.

4. Add 5 ml. of ferric alum indicator and titrate with standard thiocyanate solution to the appearance of a faint red color that persists on shaking or stirring.

5. Calculate the percentage (or fineness) of the bullion from the amount of thiocyanate used and its known strength as determined by standardization.

Gold-bullion Assay

The general method of assaying gold bullion for gold at mints and assay offices is by cupellation and parting accompanied by check assays on synthetic alloys corresponding in composition to the bullions. To ensure uniform parting without disintegration of the gold, the ratio of silver to gold must be adjusted within narrow limits, the bead must be rolled thin, and the parting procedure standardized carefully. To aid in the removal of lead during cupellation and to toughen the alloy to minimize cracking in rolling, approximately 3 per cent of copper should be present prior to cupellation. Some copper is retained in the bead but dissolves in the parting acid and does not affect the gold assay. The removal of lead is necessary to avoid error and to prevent breaking up of the gold in parting.

In the gold assay, small losses of gold occur by volatilization (approximately 0.0001 per cent), absorption (0.04 to 0.05 per cent), and solution (0.0005 per cent), but in assays exceeding 700 to 800 fine gold plus silver, these losses are more than offset by the retention of silver in the gold, so that the final weight of gold in such cases is usually from 0.02 to 0.1 per cent high. The algebraic sum of the errors is known as the "surcharge," and its exact value is determined by calculation from the check assay. A negative surcharge will usually occur in bullions less than 700 to 800 fine.

The procedure given herein is suitable for the determination of gold in copper-bearing bullions containing upward of 500 gold plus silver fineness. If the base metal is not copper or lead and is present in interfering amounts, see the suggestions given in

paragraph 3*b* of the cupellation method for the silver-bullion assay.

The method to be chosen for the determination of silver in gold bullion depends on the composition of the bullion and the degree of accuracy required. For most purposes the silver fineness as calculated from the data obtained from the gold assay is sufficiently accurate, but many assayers prefer to use a volumetric method.

1. *Preliminary Assay.*—Weigh out 500 mg. (1,000 millièmes) of bullion and cupel as in the preliminary cupellation of silver bullion. Weigh the resulting bead and subtract from the original weight to estimate the base metals present.

Experienced assayers judge the approximate fineness of the bead by color, but the touchstone method is more reliable. In the touchstone method the streak of the sample on a black jasper slab is compared with the streak of alloy strips ("needles") of known composition.[1] If no other means of estimating the silver-gold ratio is available the bead is inquarted with enough silver to make the silver-gold ratio from 2:1 to 3:1 and parted. Estimation of the gold fineness within 5 per cent by the preliminary assay is sufficiently accurate unless silver is to be determined in the same assay, when a closer estimate is desirable. In the gold assay, variations in composition and weight of the bead and in the conditions of cupellation do not affect the cupellation losses as much as with silver.

2. *Final Assay.*—Duplicate assays and a single check are usually sufficient. The check is made up as nearly like the bullion in weight and composition as possible. Since all beads will be calculated to contain a fixed ratio of silver to gold, and since all will contain a fixed minimum amount of copper, it is convenient to prepare a proof alloy of silver, gold, and copper that can be used as the foundation for preparing the checks, to which additional copper is added as needed. Pure or "proof" gold for making check assays can be purchased or may be prepared in the assay office.

The proper silver-gold ratio is established by each assayer within the limits of 2:1 to 3:1 and is coordinated with the parting

[1] Jeweler's test needles are used for standard jewelry alloys, in which copper is the principal alloying element with gold. Such needles read in carats, and 24 carats is 1,000 fine.

procedure. Once established, the same ratio is maintained on all subsequent assays. If less than 2:1 silver to gold is used, too much silver is retained in the gold when parted, unless the parting treatment is inconveniently prolonged. With more than 3 parts of silver to 1 of gold, the gold may break up in parting. The San Francisco mint uses a ratio of 3 silver to 1 gold, the Denver mint uses a 2½ to 1 ratio, and the New York mint uses a 2:1 ratio.

The lead for cupellation is ascertained from Table XVIII. Some authorities recommend slightly different ratios of lead for gold bullion than for silver bullion, but the distinction is unimportant. Some assayers prepare uniform squares of sheet lead weighing 5 or 6 g. and use as many as necessary to approximate the desired ratios, keeping the same proportions for the duplicates and checks of a given sample.

The description of the silver-bullion cupellation should be referred to for the manner in which the ingredients of the assay are wrapped together and cupeled. In the gold-bullion assay it is not so important to use strictly silver-free lead, hence all the lead may be supplied as lead foil if desired.

Since the melting point of a silver-gold alloy is higher than that of silver, the cupellation temperature at the finish should be higher than with silver bullions. Moreover, if gold only is being determined, more complete removal of lead and copper is obtained at higher cupellation temperatures without increased loss of gold, provided that temperatures in excess of 1050°C. are not employed. Hence, the entire cupellation may be conducted at a muffle temperature of 900 to 950°C. Any variation in the gold loss due to cupellation temperature will be compensated by the check if the temperature is uniform for the assays and checks in a set. At the finish of cupellation the blick will occur in the absence of platinum. It is desirable to leave the cupels in the furnace for 10 to 20 min. after finishing, to remove the last traces of lead, but many assayers remove the cupels at once, even while still fluid, as there is no danger of sprouting if the silver-gold ratio is less than 3 to 1, and if copper is present.

3. *Parting.*—The beads are removed from the cupels, flattened with a hammer, rolled into a fillet approximately 0.01 in. thick, and shaped into a spiral or cornet. Parting is commonly done in parting flasks. Two acid treatments of 15 to 20 min. each at or near the boiling point are generally necessary for com-

plete parting, using nitric acid of 1.17 to 1.22 sp. gr. for the first treatment, which is decanted off and replaced by strong acid, for example, of sp. gr. 1.2. Approximately 30 ml. of acid are used for each treatment. After the acid treatments the acid is decanted off, and the cornet is washed at least three times with hot distilled water, transferred to an annealing cup, annealed, and weighed. The gold is reported in fineness, and the correction from the check applied. Duplicate results should check within 0.1 fineness.

It is essential that the preparation of cornets and all subsequent parting operations be standardized because variations in the thickness reduction at each stage of hammering and rolling, in acid strength and time of contact, and in annealing practice affect the amount of surcharge.

Preparation of Fine Gold

Assayers sometimes have occasion to prepare small lots of fine gold. Several methods are available,[1] but the oxalic acid precipitation is usually the most convenient in modestly equipped laboratories. The procedure is as follows:

Dissolve the purest gold available, as from assay partings, in one part of c.p. nitric acid and 4.7 parts of c.p. hydrochloric acid by volume. Drive off the excess acid, cool, dilute to contain about 30 g. of gold per liter. Add a small excess of hydrochloric acid or salt to precipitate silver, let settle, and siphon off the clear solution. Dilute further, settle until clear, siphon the clear solution into a flask. Warm the solution, and precipitate gold with a solution of oxalic acid, using approximately as much acid as gold by weight. Shake vigorously and keep warm for several days until precipitation is nearly complete. Siphon off the clear solution, wash thoroughly with hot water, transfer to a porcelain dish, and evaporate to dryness. The gold may be used as a loose powder or melted and rolled into strips. For melting, transfer to a clay crucible that has been glazed with molten borax, using scraps of filter paper to clean the dish. Melt under a borax cover and then cast into an iron mold. After casting, clean the bar with fine sandpaper or with assay silica moistened with water, roll, and clean again. For highest purity, polish and heat to redness just before using.

[1] Rose, T. K., and Newman, W. A. C., "Metallurgy of Gold," 7th ed., p. 524, J. B. Lippincott Company, Philadelphia, 1937.

CHAPTER X

THE ASSAY OF MATERIALS REQUIRING PRELIMINARY ACID TREATMENT

Certain impurities in ores and metallurgical products are not readily eliminated by fusion and cupellation, and certain others, even though removable, introduce errors at one stage or another of the assay process. When present in harmful proportions it may be necessary to remove the greater part of such impurities by preliminary acid treatment before proceeding with the fire assay. The principal impurities that may require acid treatment for their removal are bismuth, copper, nickel, selenium, tellurium, and zinc.

Bismuth is rarely present in critical amounts and in general affects only the silver assay, by retention of some bismuth in the silver bead. The bismuth error is usually corrected by deducting the bismuth in the silver bead (determined by wet analysis). A correct silver assay could be made by volumetric determination of silver in the parting acid or by preliminary acid treatment to separate the bismuth before the assay is made. In the latter case, silver is also extracted and must be precipitated and added to the remainder of the ore before assaying.

The maximum tolerance for copper in an all-fire method is approximately 7.5 g. per charge, and the tolerance for nickel is 4 g. per charge. Beyond these limits it becomes necessary to remove copper and nickel by wet chemical methods. Preliminary acid treatment is the preferred method of assaying copper bullion for gold and silver.

Selenium and tellurium are the most potent of the interfering elements in their harmful effect on the recovery of gold in fire assaying, and as little as 0.1 g. of these elements in an assay charge may leave enough in the lead button to cause serious loss of gold in cupellation. Somewhat larger amounts of these elements may be removed in fire assaying by special methods, such as an oxidizing roast prior to fusion to form iron tellurite, which is removed in

the slag, or by a prolonged "soaking" of the lead buttons under a litharge flux, but in extreme cases it may become necessary to remove selenium and tellurium by acid treatment prior to fusion methods.

Zinc interferes only when present in metallic form, as in zinc box precipitates, especially "zinc shorts," consisting of undissolved zinc shavings containing more or less gold and silver. Although it is possible with such materials to obtain good results directly by fire assaying, it is sometimes more convenient to remove the zinc by acid treatment prior to scorification and cupellation.

The essential conditions to be observed in planning a combination assay method are to ensure reasonably complete attack and solution of the undesired impurities without dissolving gold and then to precipitate the silver with a slight excess of sodium chloride, followed by a prolonged period of settling. After filtering and washing, the residues are subjected to a crucible or scorification fusion, followed by cupellation of the resulting button.

Choice of Acids.—When considering the choice of an acid for the removal of impurities prior to a fusion assay, it should be remembered that it is not essential to dissolve and remove all the interfering elements, as the subsequent fire-assay step is still capable of removing small amounts of undesired impurities, within the usual limits of tolerance. Hence it is more important to avoid solution of gold than it is to secure complete decomposition of the sample.

Pure hydrochloric acid has no solvent action on gold, but in the presence of nitric or sulfuric acid, iron sulfates, cupric chloride and various other base-metal salts, the gold solubility in hydrochloric acid is such as to prohibit the use of this acid in most cases that occur in the practice of assaying, because of the danger of forming one or more of the above-mentioned compounds during the treatment of the sample. Hydrochloric acid is more effective than other acids in dissolving oxidized ores, such as those containing copper, nickel, and iron, and if either nitric or sulfuric acid fails to give satisfactory results, hydrochloric acid may sometimes be used successfully if care is taken to avoid high concentrations of acid at any stage of the procedure and to avoid a great excess of the acid over that required for the solution of impurities

and the conversion of silver to chloride. Hydrochloric acid is not effective in decomposing sulfides, hence incompletely oxidized ores may require a subsequent treatment with nitric acid *after* filtering and washing the residues free from hydrochloric acid. Under no circumstances should hydrochloric acid be used with either nitric or sulfuric acid simultaneously in contact with the sample, otherwise excessive solution of gold may result. One of the few safe applications of hydrochloric acid is for the treatment of metallurgical products containing metallic zinc. The zinc is readily dissolved in dilute hydrochloric acid and silver and gold are not attacked until all the zinc is dissolved. By avoiding an excess of hydrochloric acid and prolonged treatment, the zinc may be removed without danger of loss of gold. In this case, as in practically all others not amenable to the use of nitric acid, it is preferable to use sulfuric acid in spite of the prolonged treatment necessary in some cases to ensure adequate solution of impurities.

Hydrofluoric acid, which is sometimes used in chemical analysis to decompose silicates, has no place in the preliminary treatment of gold and silver ores, because its solvent action on gold is too pronounced.

Sulfuric acid has no action on gold but is not a rapid or reliable solvent for all the associated base-metal compounds that may be present. The most important applications of sulfuric acid in the present connection are in the assay of copper bullions, in the treatment of products containing metallic zinc, in the treatment of oxidized ores, and for the removal of selenium and tellurium. Sulfides are not readily attacked by sulfuric acid, hence, if the sample is composed largely of sulfides, nitric acid should be used.

Nitric acid attacks practically all the common minerals of the elements in the interfering group, except silicates and certain oxides. It is the best general solvent in combination assays for gold and silver and is particularly valuable for the decomposition of sulfides. Gold is slightly soluble in concentrated nitric acid, but its solubility in pure dilute acid of 1.26 sp. gr. or less is so slight that it may be disregarded in the assay of all materials except gold bullion. It is essential that the nitric acid be free from hydrochloric acid and chlorine to avoid the formation of aqua regia, in which gold is soluble. Complete data are lacking on the solubility of gold in nitric acid in the presence of various metal salts such as might be formed in the decomposition of

heterogeneous ore samples. That appreciable solubility may occur under certain conditions is indicated by the fact that the nitric acid methods for the assay of copper bullion are known to give low results on gold, which has been attributed by various authorities to the possible presence of sulfuric or hydrochloric acid or the chlorides or nitrates of base metals, particularly those of iron or copper.[1]

General Procedure for Combination Assays.—The following procedure will serve as a guide to the assay of materials, other than copper bullions, that require preliminary removal of impurities by acid treatment prior to a fusion process. Following this section specific procedures are given for copper bullion. The nitric acid treatment is suitable for the removal of copper, nickel, and other impurities from sulfide ores and products, and the sulfuric acid treatment is preferred for the decomposition of materials containing selenium or tellurium, for the oxidized ores of copper and nickel, and for products containing metallic zinc.

1*a*. *Nitric Acid Treatment.*—For sulfide ores and products the initial attack is expedited by using small increments of concentrated nitric acid and heating cautiously until the sulfides are decomposed. A maximum of approximately 60 to 75 ml. of acid is required for ¼-A.T. samples, and 90 to 100 ml. for ½-A.T. samples. Avoid prolonged heating and heat just sufficiently to decompose the sulfides and drive off the brown fumes of nitrous oxide, usually evaporating to about half of the original volume. Dilute nitric acid (1:1 to 1:3) is preferred for materials containing metals in metallic form or if considerable proportions of oxides are present, and may be used for sulfides to reduce the violence of the reaction that occurs when concentrated acid is used.

1*b*. *Sulfuric Acid Treatment.*—When sulfuric acid is used it is usually advisable to start the treatment with 1:1 rather than with concentrated acid, using up to a maximum of 200 ml. of the 1:1 acid for a 1-A.T. sample. Heat until visible dissolving action ceases, usually 1 to 2 hr., then evaporate to strong fumes of SO_3.

2. *Precipitation of Silver.*[2]—Cool the solution obtained from 1*a* or 1*b* and dilute with at least four times its volume of water.

[1] FULTON, C. H. and SHARWOOD, W. J., "A Manual of Fire Assaying," 3d ed., p. 160, McGraw-Hill Book Company, Inc., New York, 1929.

[2] See note *a*, p. 189.

Stir to break up cakes of precipitated salts. Heat to boiling to dissolve precipitated salts, adding additional water if necessary.

Precipitate the silver by adding a calculated small excess of sodium chloride solution, such that the resulting solution will approximate 0.01*N* chloride.[1] A preliminary assay of a small quantity of ore may be necessary to estimate the approximate silver content to permit the proper adjustment of the quantity of sodium chloride to be added. After adding the sodium chloride, heat to boiling and stir vigorously to agglomerate the precipitate, let stand for 1 hr., stir again if the solution is cloudy, then let settle thoroughly, preferably overnight. If much silver is present, keep in a dark place to avoid photodecomposition of the silver chloride.

Filter on double medium-textured filter papers or a single close-textured paper. Be careful to scrub the sides of the beaker thoroughly and to transfer all residues to the paper. If adherent crusts have formed, dissolve them in a small quantity of a hot solution of sodium hydroxide, acidulate with the same acid used in step 1, and wash into the filter. Wash three or four times with cold water or with 0.01 *N* NaCl and discard the filtrate.

3*a*. *Scorification Fusion.*—If the acid treatment resulted in little or no siliceous residue the precipitate from step 2 can be treated by scorification, otherwise use the crucible method described in step 3*b*.

Sprinkle a few grams of granulated lead on the inside of the filter paper containing the gold and precipitated silver. Remove the paper, fold it carefully, and place it in a 2½-in. scorifier containing 15 to 20 g. of silver-free granulated lead. Dry on a hot plate or in front of the muffle and then place in a dull-red muffle to incinerate the paper and decompose silver chloride. Remove from the muffle, add 15 to 20 g. of granulated lead and ½ g. each of borax glass and silica, and scorify in a hot muffle for 5 to 10 min. Pour, cupel, weigh and part as usual.

3*b*. *Crucible Fusion.*—If a large siliceous residue was left in step 1, or if considerable amounts of selenium or tellurium are known to be present, the residue and precipitate from step 2 should be treated by a crucible fusion instead of by scorification.

Sprinkle a few grams of litharge on the inside of the filter paper containing the gold and precipitated silver, transfer to a 20-g.

[1] See note *b*, p. 189.

crucible in which has been placed 1 or 2 A.T. of litharge, heat the crucible at a dull-red heat to incinerate the paper. Remove from the furnace, cover to prevent loss or contamination, and allow to cool. Calculate the required fluxes in the usual manner, provide for the reduction of a 20- to 25-g. button, and proceed with fusion, cupellation, weighing and parting in the usual manner.

Notes: *a.* Some assayers prefer to filter the gold and insoluble residue prior to the precipitation of silver in the belief that some gold may be dissolved in the presence of chloride. If excessive boiling is avoided after adding sodium chloride there is little danger of dissolving gold in the dilute acid at that stage.

b. The solubility of silver chloride is least in 0.01 *N* chloride solutions[1] at normal temperature and progressively increases with increased temperature, or chloride strength, or in the presence of excessive amounts of mineral acids, alkaline or alkaline-earth chlorides or nitrates, alkaline cyanides, or ammonium hydroxide.

If a solution containing 5.45 g. of NaCl per liter (0.0933 *N*) is prepared, 1 ml. will be equivalent to 10 mg. of silver. To obtain a 0.01 *N* chloride solution after adding sufficient chloride for the silver, add 12 ml. additional NaCl solution per 100 ml. of solution.

Lead acetate is used by some assayers in conjunction with sodium chloride for silver precipitation. If the sample was dissolved in nitric acid, a few milliliters of sulfuric acid are added with the lead salt, in order to form lead sulfate to aid in settling the silver chloride precipitate. This procedure is unnecessary unless the silver content is very low and is of doubtful value in any case.

Acid-treatment Methods for Copper Bullion.—Numerous acid-treatment methods have been described for the preliminary removal of copper from copper bullion. Nitric acid methods were developed by Greenwood[2] and Van Liew[3] while sulfuric acid methods were developed by Hunt,[4] Flinn,[5] and Keller.[6] Since

[1] FORBES, G. S., The Solubility of Silver Chloride in Chloride Solutions, *Jour. Am. Chem. Soc.*, vol. 33, p. 1937, 1911.

[2] BUGBEE, E. E., "Textbook of Fire Assaying," 2d ed., p. 224, John Wiley & Sons, Inc., New York, 1933.

[3] VAN LIEW, W. R., Losses in the Determination of Gold and Silver in Copper Bullion, *Eng. Min. Jour.*, vol. 69, p. 469, 1900.

[4] HUNT, F. F., Determination of Gold in Copper Bullion, *Eng. Min. Jour.*, vol. 87, p. 465, 1909.

[5] FLINN, F. B., Assay of Gold in Copper Bullion, *Eng. Min. Jour.*, vol. 87, p. 569, 1909.

[6] KELLER, E., Recent American Progress in the Assay of Copper Bullion, *Trans. A.I.M.E.*, vol. 46, p. 772, 1913.

any method of dissolving copper also allows silver to dissolve, provision must be made for the precipitation of silver from the solution used to extract the copper.

Nitric Acid Method.—The nitric acid method gives low results for gold, probably owing to the slight solubility of gold during the prolonged treatment. The results for silver are also low but can be corrected by check assay. The method is now used by some assayers for the assay of refined copper in which the amount of gold is so small as to be relatively unimportant. The nitric acid procedure is considerably shorter than the sulfuric acid method.

A typical procedure[1] for the assay of refined copper by the nitric acid method is given in the following steps.[2]

1. Weigh out 2 A.T. of the refined copper sample and place in a 1,500-ml. beaker. Assays are usually made in duplicate, and a check assay is prepared of c.p. copper and silver in approximately the same amounts as in the refined copper assay portions, in order to correct the silver result.

2. Add 200 ml. of water and 220 ml. of concentrated nitric acid. Cover and place on a steam plate and heat until action ceases.

3. Remove cover and evaporate on a hot plate to low volume in order to remove nearly all the nitric acid. Remove from hot plate and immediately add 4 or 5 drops of concentrated hydrochloric acid and a few milliliters of a kaolin suspension to aid the collection and settling of the precipitated silver chloride. Dilute to 1 l., stir, and allow to settle overnight.

4. Filter on double medium-textured filter papers. Wash two or three times with cold water. Excessive washing or the use of hot water will cause increased silver loss.

5. Carefully fold the paper into a roll and place in a 2½-in. scorifier. Cover with 30 g. of silver-free granulated lead.

6. Dry on a hot plate or in front of the muffle and then incinerate in a dull-red muffle until most or all of the paper is burned. Remove from the muffle.

[1] Adapted from a procedure given in a personal communication by M. A. Jackson, chief chemist of the Great Falls refinery of the Anaconda Copper Mining Co., Great Falls, Mont.

[2] The end of each numbered paragraph marks a convenient stopping place.

7. Add 30 g. of additional granulated lead and ½ g. each of borax glass and silica and then scorify in a hot muffle. Pour and separate the button from the slag.

8. Cupel the button and calculate the silver in ounces per ton, applying the correction as found in the check assay.

9. Wrap the beads from 20 or more samples in lead foil and cupel, part the bead, and calculate the gold in ounces per ton.

Notes: *a.* In step 3, a solution of sodium chloride may be used instead of hydrochloric acid. In either case, an excess of chlorine must be avoided. The amount suggested is sufficient for most refined copper samples. If in doubt, calculate the required amount stoichiometrically and add a slight excess.

b. In step 3, settling overnight or longer is necessary to secure complete precipitation of the silver.

c. A crucible fusion may be used in place of the scorification method described in steps 5 to 7.

d. In the solution as recommended, from 0.2 to 0.3 mg. of silver are dissolved. Hence the check should be of approximately that order of magnitude.

Mercury-sulfuric Acid Method.—Copper does not dissolve readily in sulfuric acid alone, and solution is incomplete if sulfide copper is present. However, if the copper is first amalgamated with mercury, complete solution is obtained without difficulty, and hence the assay methods for copper bullion based on sulfuric acid attack of the sample involve a preliminary amalgamation of the copper.

The method is widely used on blister and anode copper and with suitable modifications is successful for the metallic portion of refinery slags and for other products within the classification of copper bullions. A typical procedure follows:[1]

1. Weigh out 1 A.T. of the copper into an 800- or 1,000-ml. beaker.

2. Add 30 ml. of water, 10 ml. of a mercuric nitrate solution containing 25 g. of mercury per liter, and 10 ml. of concentrated sulfuric acid. Shake well, let stand until amalgamated, and then add 100 ml. of concentrated sulfuric acid.

[1] This procedure is a composite of information kindly supplied by the Anaconda Copper Mining Company, at Anaconda and Great Falls, Mont.; the International Smelting and Refining Company, Perth Amboy, N.J.; and the American Smelting and Refining Company, El Paso, Tex.

3. Cover and place on a medium hot plate, preferably overnight but in any case until all the copper is dissolved and SO_3 fumes are evolved. Near the finish the supernatant liquid becomes dark green and then changes to a light grayish blue at the finishing point.

4. Remove from the hot plate and cool. Some of the copper sulfate will crystallize as a sludge.

5. Add, with constant stirring, 100 ml. of cold water, then complete the dilution to 400 ml. with hot water with continued stirring. Bring to boiling and continue boiling if necessary to complete the solution of copper sulfate. Add a slight excess of hydrochloric acid or sodium chloride solution to precipitate silver and mercury and continue boiling for 5 to 10 min. until the silver chloride is coagulated, but avoid prolonged boiling. Remove from the hot plate, wash down the sides of the beaker, dilute to 500 to 900 ml. with cold water, and allow to settle overnight.

6. Filter on double medium-textured filter papers, such as Whatman No. 1, Munktell No. 100, or S. & S. No. 597. Wash two or three times with cold water but avoid excessive washing. Wipe out beaker with a small piece of filter or tissue paper and add to the original filter paper with a pinch of granulated lead.

7. Carefully fold the paper and place in a 2½-in. scorifier containing 15 to 20 g. of silver-free granulated lead.

8. Dry on a hot plate or in front of a muffle and then place in a dull-red muffle to incinerate the paper and decompose silver chloride. Remove from the muffle.

9. Add 15 to 20 g. of granulated lead and ½ g. each of borax glass and silica and scorify in a hot muffle for 5 to 10 min.

10. Cupel the button and detach the bead from the cupel.

11. Grind the slag and stained part of the cupel together, make a crucible fusion, cupel the bead, and weigh with the original bead.

12. Part both beads together and wash, dry, anneal, and weigh the gold.

Notes: *a.* The same procedure may be used for ¼-A.T., ½-A.T., or other sample weights by properly proportioning the critical reagents. The amount of mercuric nitrate suggested in step 2 is sufficient for 1 A.T. of pure copper. The mercuric nitrate solution may be prepared by dissolving 25 g. of mercury in 50 ml. of concentrated nitric acid and then diluting to 1 l.

b. The amount of chlorine required for the precipitation of silver and mercury should be calculated stoichiometrically, and a large excess avoided.

For example, a solution of sodium chloride containing 27.2 g. per liter will precipitate 50 mg. of silver or 45.6 mg. of mercury per milliliter. Some assayers use lead acetate with the salt, but this does not seem to be advantageous. After precipitation of the silver a long period of settling is necessary to ensure completion.

c. In step 5 the procedure of adding only part of the water as cold water, followed by dilution with hot water saves time, but all the dilution may be made with cold water if desired, provided the resultant solution is boiled long enough to dissolve all copper sulfate before precipitating the silver and mercury.

d. A crucible fusion may be used instead of the scorification procedure outlined in steps 7 to 9.

e. Step 11 is merely a simplified method of making a combined slag and cupel correction (see Chap. XIV for further details). If the silver and gold content of the copper bullion is relatively low, this step may be omitted.

CHAPTER XI

ASSAY OF SOLUTIONS FOR GOLD AND SILVER

The testing and control of processes that make use of aqueous solutions of gold and silver require frequent assays of these solutions. Cyanide solutions are widely used for the recovery of gold and silver from ores, and solution assays are regularly made at cyanide mills. Industrial electroplating establishments also use gold and silver cyanide solutions and occasionally require assays. The use of thiosulfate ("hyposulfite") solutions for the recovery of silver from ores has declined, but the hyposulfite process is still used for treating a few unusual materials.[1] The determination of silver in hyposulfite solutions is also encountered in connection with the recovery of silver from the hyposulfite solutions used to fix motion-picture film. The chlorination process for the recovery of gold from ores is no longer used, but gold chloride solutions are used in electrolytic gold refining (Wohlwill process).

The general methods used in assaying solutions for gold and silver are:

1. Evaporation to dryness with subsequent recovery of gold and silver from the residue by crucible assay, by scorification, or by direct cupellation with lead.

2. Precipitation of gold and silver sufficiently pure to weigh directly or in an impure form from which the gold and silver are recovered by crucible assay, by scorification, by cupellation with lead, or by colorimetric methods.

Evaporation, with crucible or scorification assay of the residue, is suitable for the assay of any solution, but more rapid and convenient methods have been developed to suit individual solutions.

Solution Assay Portions.—Assay portions of solutions are measured by volume with a pipette or graduated cylinder. In electroplating work the assay portion is measured in milliliters,

[1] POCHON, M., Radium from the Canadian Arctic, *Eng. Min. Jour.*, vol. 138, No. 9, p. 40, 1937; BABB, P. A., Refractory Patio Tailing Responds to Leaching, *Eng. Min. Jour.*, vol. 126, No. 21, p. 832, 1928.

and the assay result is expressed in grams per liter. In cyanide mills the assay portion is measured volumetrically in assay tons, assuming that 1 ml. of solution weighs 1 g. Pipettes, calibrated in assay tons, are available for measuring out assay-ton volumes of solution.

The assay portion of a homogeneous solution need be only large enough to produce a bead that can be weighed with the desired accuracy. Electroplating solutions are rich, and a 10-ml. assay portion of solution is ordinarily used. In cyanide mills the solutions vary in grade from the pregnant solution—about $3 per ton—to the barren solution that contains very little gold or silver. Assay portions of at least 30 assay tons are used for barren-solution assays, at either gold or silver cyanide mills. For pregnant-solution assays, assay portions of about 5 assay tons are used at gold mills, but at silver mills the pregnant solution contains a larger amount of metal, and a 1-assay-ton portion is sufficient.

Assay of Cyanide Solutions

The principal methods used for the assay of cyanide solutions are:

1. Litharge evaporation.
2. Lead-tray evaporation.
3. Zinc-lead precipitation.
4. Cuprous chloride precipitation.
5. Lead-acid precipitation.
6. Electrolytic precipitation.
7. Sulfuric acid precipitation.
8. Colorimetric test for gold.
9. Colorimetric test for silver.

Litharge Evaporation.—In the litharge-evaporation method an assay portion of solution is evaporated to dryness in a porcelain dish containing about 60 g. of litharge. The temperature should be held below 100°C., to avoid loss by spattering or by baking the residue. After evaporation the litharge containing the residue is removed with a spatula and placed in an assay crucible. Residue clinging to the dish may be wiped out with filter paper that has been moistened with dilute acid. The filter paper is then placed in the crucible with the litharge. Assay silica, soda, and reducing agent are mixed with the material in the crucible,

and the charge is fused to collect the gold and silver in a lead button, from which the gold and silver are recovered and weighed by the usual methods.

The litharge-evaporation method can be used for any solution, but it requires an unusually long time, for which reason it is seldom used.

Lead-tray Evaporation.—Lead trays for the lead-tray evaporation method are formed from square 4-in. sheets of lead foil, which are conveniently cut from a 4-in. roll of assay lead foil. A wooden block 2½ by 2½ in. is placed in the center of a sheet of lead foil, and tray sides of about ¾ in. are bent up around the wooden form. Trays of this size will just hold 2 assay tons of solution; assay portions of only 1 assay ton are generally used, however, in order that the evaporation may be completed in a short time.

Evaporation is carried out by placing the lead tray on a hot plate and adding the assay portion of solution. If the plate is hot at the start a 1-assay-ton portion of solution can be evaporated in 35 min. As soon as the solution has evaporated, the trays are removed from the hot plate and allowed to cool for easy handling. Each tray is then folded into a compact bundle, care being taken in enclosing the evaporated residue in the bundle that none be lost.

The bundle of lead foil containing the residue is frequently cupeled directly as a lead button from an ore fusion. Spitting, that is, the ejection of small droplets of lead into the air, is likely to take place soon after cupellation starts. This is caused by the action of the salts in the residue. Loss due to spitting is not so serious as one might expect; nevertheless, it should be avoided when high accuracy is desired. Spitting can be avoided by a brief preliminary scorification.

For scorification, add 30 g. of granulated lead and a few grams of borax glass to the lead-foil bundle, which has been put in a scorifying dish. Scorify for a few minutes or until a quiet fusion is formed and then pour and cupel the button as usual.

The lead-tray evaporation method is convenient and requires but little of the operator's time. It is widely used for rich solutions where an assay portion of 1 assay ton is sufficient. Other methods are preferable for low-grade solutions that require large assay portions.

Zinc-lead Precipitation.—In the zinc-lead precipitation (Chiddey) method, the gold and silver are precipitated in a lead sponge that can be cupeled.

Place the assay portion of solution in a beaker, add 20 ml. of a 10 per cent lead acetate solution and from ½ to 1 g. of zinc dust. Stir and heat nearly to boiling. Slowly add 30 ml. of dilute HCl (1:1) and continue heating for about ½ hr. or until the cessation of bubbling indicates that the zinc has dissolved. Decant the solution with care, that particles of lead may not be allowed to become detached and lost. Wash the lead sponge several times with water. Then press it into a ball with the fingers. Wrap the collected lead in lead foil, leaving a vent for the escape of steam, and cupel as usual.

If zinc is not entirely dissolved by the acid treatment, it burns vigorously on cupellation, causing loss and forming a scoria in the cupel, which may occlude globules of the precious metals.

The zinc-lead precipitation method is suitable for large or small assay portions, and it is one of the most popular methods for low-grade solutions. It gives good results with ordinary solutions, but impure solutions, particularly those containing copper, will not produce a coherent lead sponge. If the lead sponge is not coherent, filtration is required to recover all the precipitate. This makes the method inconvenient, as the filter paper should then be burned by scorification before cupellation. Fair results can be obtained by tearing off the clean top part of the filter paper, wrapping the precipitate with the rest of the filter paper in lead foil, and cupeling directly.

Cuprous Chloride Precipitation.—Addition of an excess of cuprous chloride to a cyanide solution containing gold and silver causes the precipitation of gold and silver cyanide, together with cuprous cyanide. The precipitate is finely divided, and, to facilitate collection by filtration, a copious cuprous ferrocyanide precipitate is produced by the addition of a small amount of potassium ferrocyanide. An excess of potassium ferrocyanide, over that which reacts with the remaining cuprous chloride, has a solvent action on gold and must be carefully avoided. King and Wolfe[1] have improved the method by substituting paper

[1] KING, J. T., and WOLFE, S. E., An Improved Cuprous Chloride Method of Assay for Gold in Cyanide Solutions, *Canadian Min. Jour.*, vol. 59, p. 6, January, 1938.

pulp for the ferrocyanide precipitate. The procedure given below is substantially that recommended by King and Wolfe.

A stock cuprous chloride solution is prepared by placing copper sulfate and strong hydrochloric acid ($1CuSO_4:3HCl$) in a flask with a considerable amount of copper wire. A reflux condenser is attached to the flask, and the mixture is boiled gently until the solution becomes clear. Then the condenser is detached, a layer of liquid petrolatum is introduced to prevent oxidation from the air, and a siphon is connected for dispensing.

Paper pulp for use in the process is prepared by moistening shredded filter paper with concentrated hydrochloric acid. After the paper has digested for 5 or 10 min., dilute with water and shake to form a suspension. The paper pulp is used to coat an ordinary filter paper in a filter funnel. This is done by filtering well-diluted paper pulp through the ordinary paper filter.

King and Wolfe recommend a stock flux of litharge 40 parts, sodium carbonate 36 parts, silica 8 parts, borax glass 4 parts, and flour 1 part for fusion of the cuprous cyanide precipitate. Only a small amount of reducing agent is required, because of the reducing effect of the filter paper that is introduced with the precipitate.

The assay is started by placing the assay portion in a beaker and adding 10 ml. of the completely reduced cuprous chloride solution. This is sufficient for an assay portion up to 20 assay tons. For every additional 10 assay tons in the assay portion, the amount of cuprous chloride should be increased by 2 ml. The solutions are mixed by stirring, and then a few minutes is allowed for the precipitation to take place. The precipitate is collected by filtration through a close-textured paper that has been coated with paper pulp. All precipitate must be policed out of the beaker and washed into the filter. After the solution has drained through the filter, the paper and precipitate are lifted out of the funnel and placed, apex down, in a 20-g. crucible containing about 10 g. of stock flux. It is then covered with 80 g. of stock flux. The charge is fused, and the resulting lead button cupeled as usual.

Cuprous chloride precipitation is sometimes also brought about by the addition of copper sulfate with sodium sulfide, which reduces the cupric copper to the cuprous form.

The cuprous chloride precipitation method is used mainly for gold solutions, where it gives equally good results on large or

small assay portions. Copper already in solution does not cause trouble. If much sulfocyanide is present, low results are obtained. Consequently, either the zinc-lead or lead-acid precipitation method is preferred for solutions from the treatment of sulfide ores.

Lead-acid Precipitation.—The lead-acid precipitation method was devised to avoid the difficulty encountered in the zinc-lead precipitation method when copper is present in the solution.

The assay portion is placed in a beaker and heated nearly to boiling. Then 8 to 10 g. of granulated lead are sprinkled over the bottom of the beaker. The solution is acidified with HCl, and an excess of about 10 ml. HCl added. (*Caution!* Poisonous HCN gas is formed upon acidifying a cyanide solution. The operation should be carried out under a well-ventilated hood.) A cover glass is placed on the beaker, and the solution boiled for from 10 to 15 min. The longer period should be used for large assay portions. The solution is decanted with care, to avoid loss of solid particles, or it may be poured rapidly through a coarse-textured filter paper. The remaining lead is washed twice by decantation and then dried on the hot plate. After drying, the lead cake is brushed onto a sheet of lead foil in which it is wrapped for cupellation.

If the solution has been decanted through a filter paper, the paper is examined for particles of lead. When particles of lead can be seen, the parts of the filter paper containing them are torn out and included in the lead-foil bundle before cupellation.

The lead-acid precipitation method is more convenient than the zinc-lead precipitation method, particularly when the solutions contain copper. It has given satisfactory results on solutions from laboratory cyanide tests of many kinds of ores;[1] it has not, however, as yet been tried with mill solutions.

Electrolytic Precipitation.—The electrolytic precipitation method of separating gold and silver from cyanide solutions is rarely used for assaying. It has given good results at the Kleinfontein Group Central Administration Assay Offices in South Africa. The method is described by Crichton.[2]

[1] Unpublished work of O. C. Shepard and A. K. Schellinger.

[2] CRICHTON, C., The Assay of Gold-bearing Cyanide Solutions by Electrolysis, *Jour. Chem. Met. Min. Soc. South Africa*, vol. 12, p. 90, 1911.

Ten-assay-ton portions of solution are placed in beakers that are held in a frame. Anodes of 5/16-in. arc-light carbons are clamped to a copper bar so that they can be lifted above the beakers or lowered to a position that places one carbon vertically in the center of each beaker. Cathodes consist of 2½ by 9-in. sheets of lead foil. One edge of each sheet is coarsely serrated, and at one end a strip ¼ in. wide is cut and bent up to connect with the negative source of potential. The lead-foil sheets are then formed into a cylinder around a bottle or wooden form 2½ in. in diameter. The ends of each lead-foil sheet are folded together to maintain the cylindrical shape after the form is removed.

One lead-foil cylinder is placed in each beaker, and the ¼-in. connecting strip is fastened to a copper bar carrying the negative potential. The anodes are lowered into the beakers, and electrolysis is allowed to proceed under a potential of 6 volts for a period of 4 hr. With very dilute solutions some additional cyanide should be added to lower the solution resistance, until a current of about 0.1 amp. is produced.

An adherent deposit of metallic gold is obtained on the lead cathode. At the end of the 4-hr. period the carbon anodes are raised. The lead cathodes are then taken out immediately and dried on a hot plate. After drying, the lead is folded into a compact bundle and cupelled.

Electrolytic precipitation is slower than other precipitation methods; it has an advantage, however, in that while precipitation is in progress the assayer is free to carry on other duties.

Sulfuric Acid Precipitation.—Sulfuric acid precipitation is sometimes used for the determination of gold in electroplating solutions, particularly where assay-furnace equipment is not available. The procedure is described by Kushner.[1]

An assay portion containing from 5 to 200 mg. of gold (10 ml. of a plating solution is usually sufficient) is placed in a 500-ml. Erlenmeyer flask with 50 ml. of water. A few drops of a dilute potassium iodide solution are added, after which the silver nitrate solution is run in from a burette until all the free cyanide is combined with silver, and yellow silver iodide starts to precipitate.

[1] KUSHNER, J. B., A Rapid Method for Gold in Cyanide Plating Solutions, *Ind. Eng. Chem., Anal. Ed.*, vol. 30, No. 11, p. 641, Nov. 15, 1938.

The flask is then placed in a well-ventilated hood, and H_2SO_4 is cautiously added until vigorous action ceases. Then 50 ml. additional H_2SO_4 is added, and the solution is boiled until the precipitate of gold turns light brown and the solution becomes clear.

The precipitate is allowed to settle, and the acid is decanted. An additional 50 ml. of concentrated H_2SO_4 is again boiled with the gold and decanted as completely as possible. After cooling, the remaining acid is carefully diluted with 200 ml. H_2O, and the gold is recovered by filtration through an asbestos mat in a tared Gooch crucible. The gold is washed, dried, and weighed in the Gooch crucible.

Colorimetric Methods.—Colorimetric methods are widely used for testing barren solution from cyanide-mill precipitation. Tests that can be quickly carried out and that indicate the presence of even a small amount of gold or silver are desired.

Colorimetric Test for Silver.—A portion of barren solution is placed in a test tube or beaker, and a few milliliters of a 10 per cent solution of sodium or potassium sulfide is added. In the absence of silver, only a white precipitate of zinc sulfide forms. When silver is present, dark silver sulfide precipitates. The amount of darkening of the solution indicates roughly the amount of silver present.

At cyanide mills treating silver ores, the barren solution is tested every few hours by this method, as a check on the precipitation operation. Precipitation is normally so perfect that no silver can be detected by the test.

Colorimetric Test for Gold.—One liter of barren solution is placed in a bottle or large beaker and treated with 2 drops of a saturated solution of lead acetate and ½ g. of sodium sulfite. About 2 g. of zinc dust are stirred into the solution. The zinc dust should be kept suspended in the solution by swirling or stirring for 2 min. The precipitate is then allowed to settle, and most of the solution is removed by decantation. The precipitate is washed into a small beaker, and the wash solution is decanted. The precipitated gold is dissolved by heating with 10 ml. aqua regia ($3HCl:1HNO_3$) and evaporated nearly to dryness. The residue is taken up in 2 ml. HCl and transferred to a small test tube. After cooling, a few drops of saturated stannous chloride solution are added.

The presence of gold is indicated by a purplish ring at the contact of the solutions or by a purplish tinge throughout, if the solutions are mixed. As little as 0.001 oz. of gold per ton of solution can be seen plainly. Some operators become so proficient in the colorimetric test that they can estimate with considerable accuracy the amount of gold in solution.

Assay of Thiosulfate Solutions

Thiosulfate leaching solutions are used only for the extraction of silver, but in treating ores a small amount of gold may also be dissolved. When both gold and silver are to be determined, the assay is best carried out by one of the evaporation methods as described for cyanide solutions.

Silver can be determined more rapidly in thiosulfate solutions by sodium sulfide precipitation than by evaporation, particularly when a large assay portion of solution is used for the assay. Sodium sulfide precipitation is not suitable for determining gold, as an excess of sodium sulfide holds some gold in solution.

In the sodium sulfide precipitation method the assay portion of solution is treated with a solution of sodium sulfide until no more precipitate forms. The silver sulfide precipitate is separated by filtration through a close-textured filter paper. After the solution has drained from the filter the paper containing the precipitate is removed from the filter funnel and placed in a scorifying dish on top of 40 g. of granulated lead and a few grams of borax glass. A little granulated lead is sprinkled on top of the paper, and the scorifier is placed at the front of a hot assay muffle where the filter paper will slowly burn. After the filter paper has burned, a short period of scorification is carried out as usual, and the resulting lead button is cupeled to recover the silver.

Assay of Gold Chloride Solutions

Gold chloride solutions can be assayed by the lead-acid method as described for cyanide solutions, by a modified evaporation method, or by precipitation.

If the gold chloride solution is nearly neutral, either of the evaporation methods described for cyanide solutions may be used. Acid solutions should be evaporated with assay silica containing charcoal, which will precipitate the gold from the

chloride compound. The dry residue is mixed with litharge and soda and then treated as an ordinary crucible assay.

Gold is easily precipitated from chloride solutions, and many different methods of precipitation could be used. The following scheme has been used for assaying solutions from the chlorination process:

The solution to be assayed is acidified with a few drops of HCl. An excess of a ferrous sulfate solution is added and the mixture is stirred, warmed, and allowed to stand for 1 hr. A few additional drops of ferrous sulfate solution may be added to test for complete precipitation. The gold precipitate is collected on a paper filter, which is subsequently thoroughly washed with water. After filtration, the paper is dried and burned over a sheet of lead foil in which the ash containing the gold is wrapped for cupellation. Ordinarily, the cupeled bead is free from silver and may be weighed directly for gold.

CHAPTER XII

THE FIRE ASSAY FOR THE PLATINUM METALS

The platinum group of metals consists of platinum (Pt), palladium (Pd), iridium (Ir), rhodium (Rh), osmium (Os), and ruthenium (Ru). Platinum is the most important metal of the group and occurs in greatest quantity. The other metals of the group are found associated with platinum and are produced as valuable by-products of platinum production.

Many copper and gold ores contain traces of platinum metals, and small amounts are usually recovered in refining copper and lead bullion. The main production of platinum metals comes from (1) the Sudbury nickel-copper deposit of Ontario, Canada; (2) the placer deposits of Colombia, the Ural Mountains, and Alaska; and (3) the igneous deposits of the Lydenberg, Potgietersrust, and Rustenburg districts of South Africa.

In placer deposits the platinum metals occur as water-worn grains and flakes of native metallic alloys, which frequently are associated with placer gold. The most abundant of the platinum grains contain from 60 to 90 per cent platinum alloyed with a small amount of the other platinum metals and also with gold, copper, and iron. A small amount of the grains found in placer deposits consists mainly of an alloy of osmium and iridium, called "osmiridium" or "iridosmine." Ruthenium, the least abundant of the platinum metals, comes mainly from osmiridium, which frequently contains about 5 per cent of ruthenium.

In primary deposits, platinum metals are found as native metals and as various compounds such as sperrylite ($PtAs_2$), cooperite [$Pt(AsS)_2$], and stibiopalladinite, containing mostly antimony and palladium. Usually in primary deposits, as in placer deposits, platinum is the predominant metal of the platinum group. In the primary sulfide ores of South Africa, however, palladium is sometimes found in greater abundance than is platinum. The platinum metals other than platinum and palladium are present only in relatively small amounts.

Determinations of the platinum metals are required of (1) ores and concentrates from primary deposits, (2) concentrates and bullion from placer deposits, (3) platiniferous products from the refining of copper and lead bullions, and (4) purified metals and alloys of the platinum metals. Fire assay methods are used to collect the platinum metals from ores, concentrates, and other low-grade materials into a rich bead, which is used for the separation and determination of the individual metals by wet chemical methods. Platinum and palladium are usually present in so much greater proportion than the other platinum metals that 20 mg. or more of platinum metals must be used to obtain weighable amounts of the rarer platinum metals. The separation and individual determination of the metals are long and expensive operations, which can be avoided on most routine mine samples by determining only the total of platinum metals and gold.

The proportion between the valuable metals can be determined by occasional complete assays of the collected beads. Separate determinations should be made on beads from different parts of a deposit, because the ratio between the platinum metals may not be uniformly constant. In the Rustenburg district, for example, the ratio of palladium to platinum is lower in the oxidized ore than in the sulfide ore.[1]

Fusions for the Platinum Metals.—The platinum metals present are collected in the lead button of an ordinary fire assay crucible fusion or scorification. When the assay is made particularly for the platinum metals, the fusion is customarily finished at a higher temperature than generally used for gold or silver work. A finishing temperature of 1200°C. is used for crucible fusions by Seath and Beamish,[2] who found no advantage in a higher temperature or in heating the charge for an unusually long time.

Crucible charges for platinum-bearing materials should be proportioned according to the material to be fluxed and according to the oxidizing or reducing effect of the ore, in exactly the same manner as for a gold or silver ore. Adam[3] found that when

[1] TYLER, PAUL M., and SANTMEYERS, R. M., Platinum, *U.S. Bur. Mines I.C.*, 6389, p. 56, 1931.

[2] SEATH, J., and BEAMISH, F. E., Assay for Platinum Metals in Ore Concentrates, *Ind. Eng. Chem., Anal. Ed.*, vol. 12, No. 3, p. 169, 1940.

[3] ADAM, H. R., Determination of the Platinum Metals in Ore and Concentrates, *Jour. Chem., Met., Min. Soc. South Africa*, vol. 29, p. 106, 1928.

good fusions are obtained, no serious slag loss occurs, but that, when poor fusions are obtained or when very rich samples are assayed, platinum metals can be recovered from the slag. A considerable slag loss of platinum metals was encountered by Seath and Beamish[1] in crucible fusions of a roasted platinum concentrate that contained copper, iron, and nickel oxides. They attributed the high slag loss to the presence of nickel oxide (18.6 per cent), and used a retreatment of the slag with extra litharge and flour to collect the lost platinum metals.

The lead buttons from fusions of a material containing considerable copper or nickel are likely to contain sufficient impurities to interfere with cupellation. In order to avoid this difficulty the lead buttons should be purified by melting and swirling with a small amount of litharge or with an excess litharge slag. After swirling, the charge should be allowed to stand molten for a short time, to allow settlement and collection of osmiridium, which does not alloy with lead.

Osmium, iridium, and ruthenium do not alloy with lead, but are "wetted" by it in an assay fusion, and because of their high density they sink into the lead and become mechanically held in the button. Davis[2] recommends cooling a fusion in the crucible, instead of pouring it into a mold, when platinum metals are to be determined. After the lead and slag have solidified the crucible can be broken, and the solid button separated from the slag and crucible with less danger of loss of the loosely held metals. There is no particular danger of loss of platinum, palladium, or rhodium during fusions, as these platinum metals alloy with lead and are collected the same as gold and silver.

Cupellation of Buttons Containing Platinum Metals.—Cupellation of a lead button containing more than fifteen times as much gold and silver as platinum metals proceeds normally. Platinum, palladium, and rhodium alloy with the gold and silver and are satisfactorily recovered in the final bead. Platinum causes a roughening of the surface of silver beads, which gives them a characteristic frosted appearance.

Iridium does not alloy with gold or silver; when present during cupellation it forms a black deposit that clings to the bottom of the bead.

[1] *Op. cit.*

[2] DAVIS, C. W., The Detection and Estimation of Platinum in Ores, *U.S. Bur. Mines, Tech. Paper* 270, 1921.

Osmium and ruthenium form volatile oxides when heated in air. Consequently they suffer a large loss during cupellation. Remaining ruthenium dioxide forms a blue-black coating on the bead. When an accurate determination of osmium and ruthenium is required, the lead button should be treated by wet chemical methods without cupellation.

Cupellation of lead containing platinum metals without a large proportion of gold or silver will not proceed to completion at ordinary cupellation temperatures. The high melting points of platinum-rich alloys cause the alloy to solidify when the lead has been reduced to form 40 to 60 per cent of the bead. Unabsorbed litharge, characteristic of the usual frozen cupel, is not exhibited with a finishing temperature of about 900°C, but a bead that solidifies with considerable lead, owing to its high platinum metal content, will not "brighten" and can usually be recognized by its dull and flattened appearance.

Many platinum-bearing placer concentrates contain sufficient gold for successful cupellation, but some placer concentrates and most platinum ores are deficient in gold and contain a negligible amount of silver. Cupellation of platinum-bearing lead buttons is carried out by:

1 Adding from ten to fifteen times as much silver as platinum metals and finishing at 900°C.

2. Adding about twenty times as much gold as platinum metals and finishing at 900°C.

3. Cupeling without the addition of gold or silver, and then giving the platinum-frozen bead a post treatment at 1300°C. for 1 hr.

When either the gold-addition or the post-treatment cupellation method is used on silver-free materials the weight of platinum metals plus gold can be obtained by weighing the bead directly (deducting the weight of gold added in the gold-addition method). Direct weighing is not feasible for beads from the silver-addition cupellation method, because of the considerable loss of silver during cupellation. The silver-addition method of cupellation is usually preferred when the platinum metals are to be separated and accurately determined. A modified sulfuric acid parting method can be used to make a preliminary separation of silver, in order to obtain quickly an approximate value for the platinum metals plus gold.

The post-treatment method of cupellation has been described by Adam.[1] It developed from a method used by O'Neill, at Potgietersrust, of adding neither gold nor silver to aid cupellation but of finishing cupellation at the highest temperature obtainable in his coal-fired muffle. The weight of beads from this treatment was used as a rough value for gold and the platinum metals. Correction factors were developed for the metals in the bead from periodic analyses of the collected beads. This plan worked reasonably well, and proved particularly attractive for assaying materials containing a large proportion of palladium. The Government Areas Laboratory in South Africa improved the method by cupeling at about the temperature previously used for silver-addition cupellation and then transferring the beads to small depressions in a bone-ash cupel for post treatment in an electric furnace at 1300°C. for 1 hr.

Adam[2] gives 6.69 dwt. per ton for the average of 110 assays by silver-addition cupellation and modified parting, while the post-treatment cupellation results on the same ores averaged 6.55 dwt. per ton. Analysis of the post-treatment beads gave 91.2 per cent precious metals. Seath and Beamish[3] found that, by introducing oxygen into the post-treatment furnace, lead was eliminated more rapidly and the time of treatment could be reduced to ½ hr. with a consequent reduction in the loss of platinum metals.

By the post-treatment method, lead can be almost completely eliminated from beads high in platinum. Elimination of lead is less complete when the bead contains a considerable proportion of other platinum-group metals. Seath and Beamish report that the presence of a considerable proportion of rhodium or iridium causes the bead to lose coherence, which increases the loss of metals in the process. It seems likely that osmium and ruthenium are completely converted to their volatile oxides and lost in the post-treatment process.

Parting Beads Containing Platinum Metals.—The nitric acid parting treatment, given doré silver beads for the assay of gold and silver, will dissolve palladium and part of the platinum that may be present. To avoid reporting these metals as silver, the spent acid from parting ordinary gold and silver assays should be

[1] ADAM, *op. cit.*, p. 108.
[2] *Ibid.*
[3] SEATH and BEAMISH, *loc. cit.*

watched for indications of platinum and palladium. A small amount of palladium produces a distinct yellow color in the acid, and the color becomes darker with increase in the amount of palladium. Platinum dissolves only when the bead contains at least ten times as much silver as platinum, and the amount that dissolves increases with increased proportion of silver. A considerable amount of platinum gives the solution a dark-brown color like a colloidal solution of carbon.

Rhodium, iridium, osmiridium, and part of any platinum present in a doré bead remain with the gold and give it a "not completely parted" appearance. The monetary error in reporting gold for rhodium and iridium is not so great as that in reporting silver for platinum; nevertheless the presence of platinum metals in ores should be detected and reported, so that the ore-treatment process may be adapted to their recovery.

Assay beads from platiniferous materials contain the gold, platinum metals, and silver from the ore, together with a small amount of lead, which is usually left from cupellation, and any gold or silver added to aid cupellation. The quantitative separation of these metals is a long and tedious process, requiring reagents not available in the ordinary assay office. Various methods of parting in acids have been devised for treating assay beads containing metals of the platinum group, in an effort to determine the most important metals by a simple process and with reagents ordinarily on hand.

Prior to 1920, practically all the platinum-metal production came from placer deposits in which gold and platinum were of predominant value. The determination of these metals was considered important, and the other platinum-group metals were neglected except by specialists at refineries and platinum works. A parting method for the determination of gold and platinum was developed and was commonly used by commercial assayers.

In the parting method for gold and platinum the material to be assayed was put through an assay fusion to which silver, for silver-addition cupellation, had been added. After cupellation the silver-platinum-gold bead was flattened and parted in boiling or nearly boiling sulfuric acid for a period of about 30 min. This treatment dissolved silver and most of the palladium present in the bead. The residue was weighed and recorded as gold plus

platinum. It was then inquarted with silver equal to ten times its weight and parted in nitric acid to dissolve platinum. Usually the inquarting and parting had to be repeated at least three times to remove all the platinum. The nitric acid residue was weighed and recorded as gold. Platinum was reported equal to the difference in weight between the sulfuric acid residue and the nitric acid residue.

The parting method for the separate determination of gold and platinum gives only approximate results. It furthermore has the serious fault of overlooking palladium. Complicated elaborations of the method have been devised, both to improve its accuracy and to allow for the presence of other platinum group metals, but other methods are better adapted for the determination of the separate platinum metals. For the rapid approximate determination of the value of an ore, methods are available that lump together gold and the platinum metals including palladium and require less time than the parting method for the separation of platinum and gold.

In the absence of silver the sum of the platinum metals and gold is given by the weight of the bead from either the gold-addition or the post-treatment method of cupellation. When the material to be assayed contains silver, or when silver is added to aid cupellation, modified sulfuric acid parting should be used in order to dissolve silver without palladium.[1]

Modified sulfuric acid parting consists of parting the bead (which should contain from 10 to 15 times as much silver as insoluble metals) in hot, but not boiling, slightly diluted sulfuric acid. The innovation of the modified process consists of removing the flask or parting cup from the source of heat as soon as the silver is dissolved, as indicated by the termination of bubbling. After the acid has cooled somewhat by standing for 10 or 15 min. it is carefully decanted from the residue by pouring down a glass rod into a pyrex beaker. The beaker should be clean and should be placed on white paper so that loss of particles of residue can be readily detected.

After decanting the strong acid the parting vessel should be allowed to cool before adding distilled water for washing. The first small amount of wash water is better if cold and must be

[1] GRAHAM, K. L., Platinum Assays, *South African Min. Eng. Jour.*, vol. 38, p. 57, Mar. 19, 1927.

very carefully added, as violent spattering is caused by adding water to hot concentrated sulfuric acid. As soon as the acid that has remained in the cup has been diluted with several volumes of water the danger of spattering is past and hot wash water can be used. The parting vessel is then filled about half full of wash water and heated nearly to boiling. Care must be taken to decant the hot wash water into a beaker separate from that containing the strong parting acid. Usually the residue contains some lead sulfate, which can be removed by treatment with a hot, strong solution of ammonium acetate followed by three washes with hot water. The washed residue is dried in air at 50 to 60°C. and weighed for platinum metals and gold.

A small amount of palladium is dissolved by the modified parting treatment, but this loss is usually overbalanced by the retention of silver in the residue. The amount of palladium lost, and the amount of silver retained, depend upon the size of the bead and the proportion of metals in the bead, as well as upon the temperature and time of acid treatment. It is advisable to obtain correction factors by means of check assays, made with known amounts of the platinum metals in approximately the proportion they occur in the ore, or by means of occasional analysis of the residue and parting acids.

The Determination of Gold, Silver, and Metals of the Platinum Group

Many methods of analysis have been proposed for the separation and determination of gold, silver, and the individual platinum metals. The treatment given here represents an attempt to combine selected parts of the various processes into a systematic general scheme. It can be simplified when the determination of only a few of the metals is required or when negligible amounts of some of the metals are present.

The determination of platinum, palladium, rhodium, iridium, and gold is commonly required for platiniferous materials. Either silver-addition or post-treatment cupellation beads are used for this purpose. When silver is present it must be separated, but on account of the loss of silver in high-temperature cupellation its determination is best made on the lead button from a separate fusion. Osmium and ruthenium should also

be determined without cupellation, and their determinations may be made on the lead button used for the silver determination.

Determinations of osmium and ruthenium are seldom required, since these metals are of relatively little economic importance. In ordinary analytical methods they separate in the acid-insoluble residue that is usually attacked by a fusion with alkaline oxidizing fluxes. Sodium osmate (Na_2OsO_4) and sodium ruthenate (Na_2RuO_4) are formed and can be dissolved in water. When considerable iridium and rhodium are present, the fusion may have to be repeated to extract the osmium and ruthenium completely. From solution, osmium and ruthenium are nearly always separated from other metals and from each other by distillation of their volatile tetroxides. Gilchrist has investigated the conditions of distillation, absorption, and determination of osmium[1] and ruthenium.[2] His methods of analysis for these metals are substantially followed in the procedure given below.

Procedure to Determine Silver, Osmium, and Ruthenium.—For the determination of silver, osmium, and ruthenium in ores and concentrates, collect the precious metals in a lead button by a crucible fusion. If the material to be assayed is low in these metals, use 2-A.T. samples or combine by scorification the buttons from several 1-A.T. fusions. Roll the final lead button into a thin strip with the bullion rolls, so that its rate of solution will be rapid. Then proceed with the analytical method outlined in Fig. 14 and described below.

Place the lead strip in a 250-ml. beaker and boil with dilute HNO_3 to dissolve lead, silver, palladium, and platinum. Filter through a small asbestos pad in a Gooch crucible and wash with hot H_2O. The filtrate is used for silver and the residue for osmium and ruthenium.

Silver.—Add a small amount of NaCl to the HNO_3 solution, to precipitate AgCl and some $PbCl_2$. Cool, filter, and wash with a hot NaCl solution to remove lead. Wash once with H_2O and then sprinkle granulated lead in the filter paper. Place the paper in a scorifying dish, cover with about 40 g. of granulated lead

[1] GILCHRIST, R., A Method for the Separation and Gravimetric Determination of Osmium, *Bur. Standards Jour. Research*, vol. 6, p. 421, 1931.

[2] GILCHRIST, R., A Method for the Separation of Ruthenium from Platinum, Palladium, Rhodium, and Iridium, *Bur. Standards Jour. Research*, vol. 12, p. 283, 1934.

and add about 1 g. of borax glass. Scorify a few minutes, pour, and cupel the button at a temperature suitable for silver.

Osmium.—Osmium and ruthenium are left in the insoluble residue from the HNO_3 treatment of the lead button. The

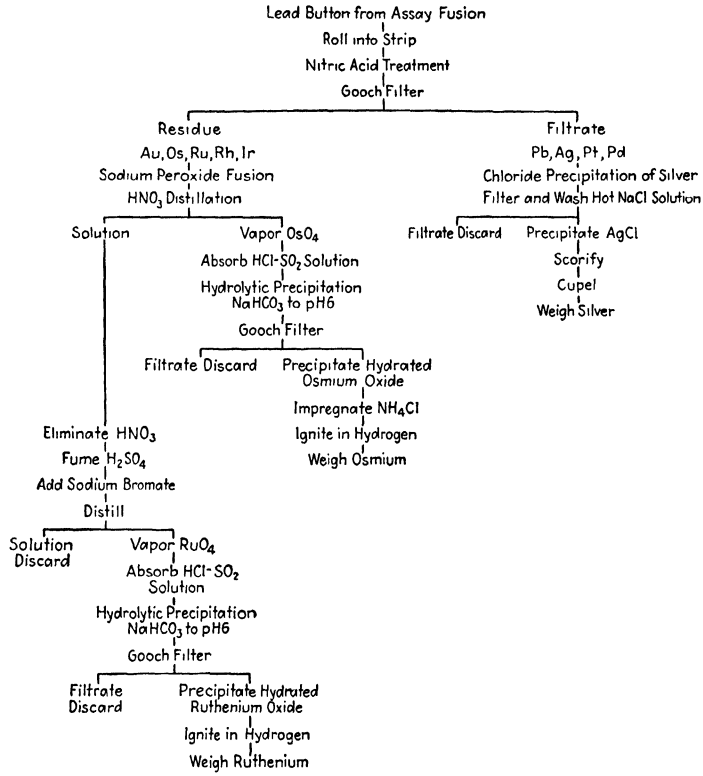


FIG. 14.—Outline of the method for the determination of silver, osmium, and ruthenium.

asbestos pad containing the residue is picked out from the Gooch and mixed with sodium hydroxide and sodium peroxide ($3NaOH:1Na_2O_2$) in an iron, nickel, or silver crucible. The material is then fused at red heat, cooled, and leached with 100 ml. H_2O in a pyrex beaker. Osmium is nearly all dissolved by this treatment while rhodium, iridium, and some ruthenium may remain

insoluble. Filter out the residue for retreatment and add the solution to a distilling flask attached by glass tubes and ground-glass joints to a series of three absorption flasks. The last flask should be attached to suction, so that a current of air can be bubbled through the distilling flask and the vapor bubbled through the liquid in the absorption flasks. Rubber connections and stop-cock lubrication are avoided, since organic compounds cause osmium dioxide to deposit from the tetroxide vapor. Add dilute hydrochloric acid solution ($1HCl:1H_2O$) saturated with SO_2 to the absorption flasks, start a slow current of air through the train and add 100 ml. H_2O and 30 ml. HNO_3 to the distilling flask. Boil gently for 1 hr. During this time the osmium is carried over into the absorption flasks. Save the liquid in the distilling flask for the determination of ruthenium and combine the liquid from the absorption flasks.

Evaporate the liquid from the absorption flasks on the steam plate four times with HCl, that the sulfite compounds of osmium may be decomposed. Then add 150 ml. H_2O, heat to boiling, add a few drops of bromophenol blue indicator and add slowly a solution of $NaHCO_3$ until a faint blue color (pH 6.5) is reached. Boil for 5 min., filter through a weighed Gooch crucible and wash with a hot 1 per cent NH_4Cl solution. Impregnate the residue with a saturated NH_4Cl solution, ignite in hydrogen for 10 min., cool, displace hydrogen with CO_2, and weigh as metallic osmium.

Ruthenium.—The HNO_3 solution left in the distilling flask, after the separation of osmium, is evaporated several times on a steam bath with HCl to eliminate HNO_3. Add 20 ml. dilute sulfuric acid ($1H_2SO_4:1H_2O$) and fume. Cool, carefully wash the solution into the distilling flask, and add 100 ml. H_2O. Place dilute HCl saturated with SO_2 in the absorption flasks and start a slow current of air through the system by suction. Add 100 ml. of a 10 per cent solution of $NaBrO_3$ to the distilling flask, and boil gently for 2 hr. Then combine the liquid from the absorption flasks and evaporate to a moist residue on a steam bath. Digest with a small amount of HCl, dilute with 50 ml. H_2O, and boil until the residue is dissolved. Dilute and neutralize the solution with $NaHCO_3$ to cause the hydrolytic precipitation of ruthenium in a manner similar to that used for osmium. Filter through a weighed Gooch crucible and wash with a hot 1 per cent $(NH_4)_2SO_4$ solution. Ignite, reduce in

hydrogen, wash out soluble salts with hot H_2O, dry, and weigh metallic ruthenium.

Procedure to Determine Platinum, Palladium, Rhodium, Iridium, and Gold.—The determination of platinum, palladium, rhodium, iridium, and gold in ores and concentrates is made by collecting the precious metals in a lead button that is cupeled by either the silver-addition or the post-treatment method. The bead of precious metals is then analyzed by wet chemical methods. In Fig. 15 a method of analysis suitable for silver-addition cupellation beads is outlined. This scheme closely follows that recommended by Beamish and Scott[1] for silver beads. When post-treatment cupellation has been used, sulfuric acid parting may be omitted and the treatment started with aqua regia.

Separation of Silver and Recovery of Palladium from Sulfuric Acid Parting Solution.—Do not clean or flatten the cupeled bead but part it directly in 30 to 40 ml. of hot, slightly diluted H_2SO_4. Keep the temperature below boiling and remove the parting vessel from the heat as soon as bubbling ceases. Let cool for 15 min. and then pour the acid into a beaker containing 150 ml. cold H_2O. Filter through a tight paper and wash with hot H_2O. Set aside the filtrate for the recovery of the small amount of palladium that dissolves with the silver and wash the residue with an ammonium acetate solution and hot H_2O to remove lead. Discard the washings.

Precipitate palladium from the filtrate by neutralizing the solution carefully to a pH of 6 with sodium bicarbonate in the presence of sodium bromate.[2] Boil to coagulate the brown palladium dioxide precipitate, and filter. Wash with hot distilled H_2O with pH of 6. Discard the filtrate and wash the palladium dioxide through the filter with hot dilute hydrochloric acid ($1HCl:1H_2O$). Dilute the palladium solution that has passed the filter so that it contains only about 3 per cent by volume of HCl. Cool and add a 1 per cent solution of dimethylglyoxime in 95 per cent ethyl alcohol (1 ml. of dimethylglyoxime solution is required for every 10 mg. of palladium). Let stand

[1] BEAMISH, F. E., and SCOTT, M., Analysis of Platinum Metals—Silver Assay Bead, *Ind. Eng. Chem., Anal. Ed.*, vol. 9, No. 10, p. 460, 1937.

[2] GILCHRIST, R., Methods for the Separation of Platinum, Palladium, Rhodium, and Iridium from One Another and for Their Gravimetric Determination, *Bur. Standards Jour. Research*, vol. 12, p. 296, 1934.

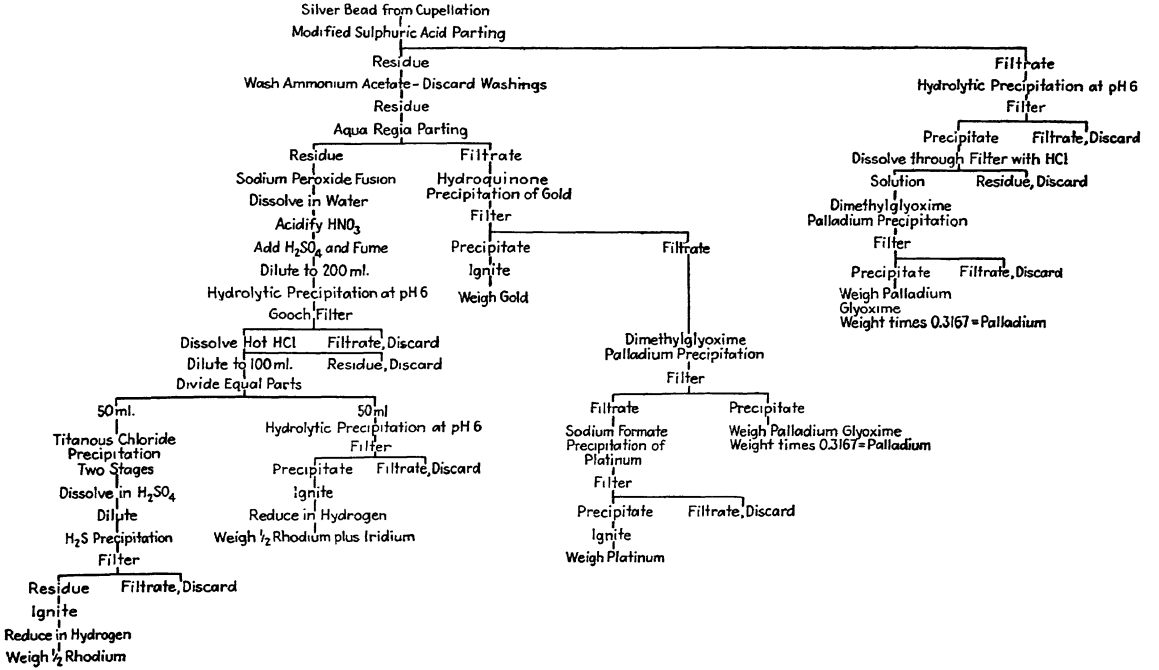


FIG. 15.—Outline of the method for the determination of platinum, palladium, rhodium, iridium, and gold.

for 1 hr. and filter on a weighed Gooch crucible. Wash with cold, followed by hot, H_2O. Dry at 110°C. and weigh. The weight of palladium glyoxime multiplied by 0.3167 gives the weight of palladium. The palladium recovered here is only a small part of that present in the bead. The remainder of the palladium is dissolved by aqua regia parting and is precipitated by dimethylglyoxime after the separation of gold.

Aqua Regia Parting.—Place the residue from H_2SO_4 parting or the cupeled bead, if post-treatment cupellation was used, in a beaker and digest for 2 hr. on a steam bath with 30 ml. of aqua regia. Filter and wash with hot H_2O. The residue contains rhodium and iridium and is reserved for their determination.

Evaporate the aqua regia solution containing platinum, palladium, and gold nearly to dryness three times with HCl on a steam bath, to eliminate HNO_3. Then digest with 25 ml. of hot H_2O and filter to remove silver chloride. Wash and discard the residue. The filtrate is treated to recover gold, palladium, and platinum.

Hydroquinone Precipitation of Gold.—The solution from aqua regia parting and the subsequent silver chloride separation amount to about 50 ml. Add 5 ml. concentrated HCl and a solution of hydroquinone. The weight of hydroquinone used should be about equal to the amount of gold to be precipitated. Boil 5 min., filter, and wash the precipitate. Set the filtrate aside for the precipitation of palladium. Ignite the gold precipitate and weigh metallic gold.

Dimethylglyoxime Precipitation of Palladium.—Dilute the filtrate from the gold precipitation to 350 ml. Add 5 ml. HCl and a 1 per cent alcoholic solution of dimethylglyoxime (1 ml. for every 10 mg. of palladium). Let stand for 1 hr., filter on a weighed Gooch crucible, and wash the precipitate with cold and then hot H_2O. Reserve the filtrate for the sodium formate precipitation of platinum. Dry the precipitate of palladium glyoxime at 110°C. and weigh. Multiply the weight of palladium glyoxime by 0.3167 to obtain the weight of palladium. If H_2SO_4 parting was used, combine the weight of palladium recovered here with that from the H_2SO_4 parting solution.

Sodium Formate Precipitation of Platinum.—Evaporate the filtrate from palladium precipitation to a sirup on the steam bath. Dilute to 100 ml. Add 3 g. of sodium acetate and 1 ml. of formic

acid. Heat nearly to boiling for 3 hr. Filter and wash free from chlorides. The filtrate may be given an additional sodium formate treatment, to be sure that precipitation is complete. Place the filter paper with the platinum precipitate in a porcelain crucible. Ignite and weigh metallic platinum.

Treatment of the Aqua Regia Residue.—The residue from aqua regia parting contains rhodium and iridium. Place it in a silver crucible with about 1.5 g. of sodium peroxide and fuse just below the melting point of silver for 5 or 10 min. Cool, and leach the melt in a beaker with 100 ml. H_2O. Wash out the crucible with a small amount of dilute HNO_3. Evaporate to about 10 ml. on a steam bath, add 10 ml. of $1{:}1H_2SO_4$ and heat to fumes. Cover the beaker and swirl over a burner until the condensing sulfuric acid cleans the sides of the beaker. Cool, add 100 ml. of H_2O, and boil. (There should be no insoluble material remaining at this point.) Neutralize the solution with $NaHCO_3$ to exactly pH 6, add 10 ml. of a 10 per cent solution of sodium bromate, and boil for the hydrolytic precipitation of rhodium and iridium. Filter through an asbestos mat in a Gooch crucible and wash with hot H_2O of pH 6. Discard the filtrate. Dissolve the precipitated dioxides of rhodium and iridium by digesting on a steam bath with dilute HCl ($1HCl{:}1H_2O$). Dilute and filter to remove asbestos and silver chloride. The filtrate is treated by the methods described by Gilchrist[1] for the determination of rhodium and iridium. A blank determination should be made, starting with the sodium peroxide fusion, to correct for metals such as copper, which are picked up from the silver crucible.

Determination of Rhodium and Iridium.—Dilute the HCl solution containing rhodium and iridium to exactly 100 ml. and pipette out 50 ml. for the determination of the sum of rhodium and iridium from one-half the sample. Reserve the remaining 50 ml. of solution for the determination of rhodium by titanous chloride precipitation.

Precipitate rhodium and iridium on the first 50-ml. portion of solution by the hydrolytic process with $NaHCO_3$ and sodium bromate at pH 6, as before. Filter, ignite the residue, reduce in hydrogen and weigh one-half of the total iridium and rhodium.

[1] GILCHRIST, R., A Method for the Separation of Rhodium from Iridium, *Bur. Standards Jour. Research*, vol. 9, p. 547, 1932.

Determination of Rhodium.—Add 10 ml. H_2SO_4 and a few milliliters of HNO_3 to the 50-ml. portion of solution reserved for the rhodium determination. Heat to fumes, cool, add 20 ml. H_2O, and again fume. Cool, dilute to 200 ml., and boil. Carefully add drop by drop a 20 per cent solution of titanous chloride until the solution assumes a slight purple tinge. Boil, filter, and wash with a cold 2 per cent H_2SO_4 solution. Place paper and precipitate in a 500-ml. Erlenmeyer flask, add 10 ml. H_2SO_4, and heat to fumes. Destroy organic matter with fuming HNO_3. Cool, dilute, and repeat the precipitation and solution. Add 20 ml. H_2O, 10 ml. HCl, and boil for 15 min. Dilute to 500 ml. and precipitate rhodium with H_2S passed through the boiling solution. Filter and wash with a 2 per cent H_2SO_4 solution. Ignite, reduce in hydrogen, and weigh metallic rhodium from one-half the sample.

Iridium is found by subtracting the rhodium result from the sum of the rhodium and iridium previously determined.

CHAPTER XIII

FIRE ASSAY METHODS FOR BASE METALS

Although in modern practice, fire assaying is almost exclusively confined to the assay of precious metals, approximate assays of certain base metals can be obtained by fusion methods, and a brief résumé of the procedures that have been used in the past will serve to indicate the potentialities and limitations of such methods.

In order that a fire assay method of a base metal be feasible the metal must be at least below iron in the electromotive force series and be present in some form that can be reduced to metal at reasonable temperatures, usually not exceeding 1100°C. in a fusion with iron or carbon as a reducing agent. Furthermore the metal must be the only one present that is reducible under the required conditions.

The metals that are amenable to the fire assay are, in the order of increasing difficulty and decreasing reliability of assay, lead, bismuth, tin, antimony, and copper.

Lead Assay.—The fire assay for lead was at one time used as the basis of settlement between buyers and sellers of ores. Even today a vestige of the former prestige of the fire assay remains in most smelter contracts, in which a flat deduction from the volumetric assay is made on the assumption that an equivalent amount of lead is lost in the smelting process.

The principal sources of error in the fire assay for lead are low results due to the volatility of lead oxide and lead sulfide and to the slagging of lead, and high results from the reduction of antimony, copper and certain other metals with the lead.

On rich ores relatively free from other base metals the fire assay is capable of giving results within 0.5 per cent of the true lead percentage and duplicate assays should check within 0.2 per cent lead, but when interfering elements are present the error may be 2 per cent or more. On account of excessive slag losses the fire method is unsuited to the assay of materials containing

less than 1 or 2 per cent of lead, unless it is possible to concentrate the lead-bearing minerals by panning a large sample.

The most common type of slag used for the lead assay is a subsilicate of soda (or potash), silica, and borax glass. A cyanide fusion is also feasible, as in the fire assay for bismuth, antimony, or tin, which see for details. The subsilicate slag for the lead assay is similar to the slags used in the crucible assay for gold and silver except that litharge is absent. The strongly alkaline slag has a solvent action on sulfides. The assay procedure is analogous to the soda-iron method described on page 146 in that metallic iron is used as a reducing agent. Iron is necessary not only to decompose sulfides according to the following reactions:

$$\left.\begin{aligned} 4Na_2CO_3 + 7PbS &= 4Pb + 3(Na_2S,PbS) + Na_2SO_4 + 4CO_2 \\ (Na_2S,PbS) + Fe &= (Na_2S,FeS) + Pb \end{aligned}\right\} (1)$$

$$PbS + Fe = FeS + Pb \qquad (2)$$

but also to secure a sufficiently strong reducing action to prevent the formation of lead silicate, or to reduce lead from silicates already present, as in the following reaction

$$2PbO.SiO_2 + 2Fe = 2FeO.SiO_2 + 2Pb \qquad (3)$$

The iron is provided as nails or spikes or by the use of an iron crucible. In addition to iron, flour or other carbonaceous agent is added to intensify the reducing action, particularly during the early stages of the fusion. Because argols were generally used as a source of carbon the method was generally known as the soda-argol method.

If much arsenic is present, part of it is volatilized as arsenic trioxide, and some enters the slag, probably as sodium arsenate, but in the presence of iron considerable speiss[1] may form, which will be found as a brittle layer on top of the lead button after pouring and cooling the fusion. Very little arsenic is reduced to the button, and if the speiss is removed carefully, the reliability of the lead assay is not affected.

Antimony is easily reduced, and most of it will be present in the lead button, unless the amount present is in excess of about half of the lead, when a speiss will form.

Any bismuth present will be reduced and practically all of it will be found in the lead button.

[1] See pp. 110*ff*.

Copper in sulfide form dissolves in the alkaline slag, but, if there is a deficiency of slag, matte will form. If copper is present in oxidized form, metallic copper is reduced and contaminates the button. Hence, sulfur should be added if necessary, in sufficient amount to form sulfide with all copper present.

Zinc is partly reduced and volatilized and partly remains in the slag. Zinc sulfide is not fusible at the temperatures reached in the lead assay nor is it so soluble in the slag as are the sulfides of copper and iron; hence if much zinc is present as sulfide or with other sulfides, the slags may be pasty, and considerable shotting of lead may result, causing inaccurate assays.

Procedure.—1. For rich ores and concentrates, use a 5- or 10-g. sample and a 15- or 20-g. crucible; for medium- and low-grade ores, use 20 g. of ore and a 30-g. crucible.

2. Add 2½ to 3 times as much sodium carbonate as ore, or a mixture of sodium and potassium carbonate, which has a slightly better carrying capacity for sulfides than either alkali alone. Use an equal weight of potassium and sodium carbonate if much zinc, iron sulfide, or basic gangue is present.

3. Add sufficient borax glass to form the equivalent of a subsilicate, but provide a minimum of one-fourth as much borax glass as ore, even on siliceous ores. For rich ores largely composed of lead sulfide, oxides, or carbonates, about half as much borax glass as ore will be required. For zincky ores it may be necessary to increase the acidity of the slag to a monosilicate, and part of the acidity should then be provided by silica. See examples of slag calculations in Chap. VII.

4. Add 4 to 6 g. of flour or other carbonaceous reducing agent. If copper is present in the absence of sulfides, add sufficient sulfur to form Cu_2S with the copper present.

5. Mix the charge and insert three tenpenny or two twenty-penny nails or other suitable form of iron into the crucible. An iron crucible is very suitable for high-grade ores instead of nails but is rapidly corroded with impure ores.

6. Place crucible in furnace at a dull-red heat (550 to 600°C). A reducing atmosphere is desirable; hence a muffle furnace gives better results than a pot furnace. A piece of coke or coal in the front of the muffle aids the maintenance of reducing conditions. Gradually raise the temperature over a period of 20 to 30 min. to a bright-yellow heat (1050 to 1150°C.), and hold at

that temperature for 20 to 30 min. A rapid fusion in a hot furnace is undesirable. The slower heating schedule favors the reduction of lead to metal before appreciable amounts are lost by volatilization and the prolonged heating at fusion temperature favors complete reduction of lead from the slag. The entire heating cycle should range from 45 to 60 min.

7. Test for completeness of fusion by removing a nail for inspection. If drops of lead adhere to the nail and are not removed by stirring the nail in the slag and then tapping it against the edge of the crucible, either the slag composition is incorrect or fusion is incomplete.

When completely fused, remove the crucible from the furnace with the crucible tongs held in one hand and, by means of short tongs in the other hand, remove the nails as quickly as possible one by one, washing them in the slag and tapping them on the sides of the crucible to remove adhering lead.

Pour into a conical mold, cool, detach slag, and speiss if any, and weigh the button.

Calculate as percentage of lead, to the nearest 0.1 per cent.

Notes: *a.* Slags should be glassy. If they are dull, insufficient acid flux was added.

b. Brittle buttons are an indication of the presence of antimony. Hard buttons indicate the presence of antimony or copper. If impurities are suspected, the buttons may be cupeled and the cupels examined for characteristic indications of copper, antimony, or bismuth (see Chap. IV).

c. If much silver and gold are present the amount should be deducted from the lead assay.

d. A corrected lead assay may be made by reassay of the slag. If the original slag was glassy, make the new slag more basic by the addition of 5 to 10 g. of sodium carbonate; if originally basic, add more borax glass. Use the same nails as in the original fusion. Heat to 700 to 800°C., drop in a lump of approximately 5 g. of potassium cyanide, heat to approximately 1100°C., pour (*do not inhale fumes*), recover the button and add to the lead from the original fusion.

Tin Assay.—The fire assay of tin can be applied successfully only to cassiterite (SnO_2) concentrates as free as possible from other substances, particularly silica and silicates, because tin acts as either an acid or a base, forming silicates with silica and stannates with iron and other bases. Ores and gravels containing cassiterite must first be concentrated by panning as far as possible without loss of tin. Then the concentrates are roasted to

remove sulfur and are treated with aqua regia to remove most of the impurities except quartz, some silicates, and tungsten minerals. If much quartz and silicates are left, a treatment with hydrofluoric acid in a platinum dish may be necessary. The final concentrate will then consist almost exclusively of cassiterite plus not more than a small percentage of silicates and a part of any tungsten minerals originally present. The fire assay itself is therefore largely a means of estimating the tin content of the concentrate and of verifying that the concentrated mineral is cassiterite rather than wolframite.

The best flux for cassiterite is potassium cyanide, which combines the functions of a flux and a reducing agent according to the following reaction:

$$2KCN + SnO_2 = Sn + 2KCNO$$

The KCN should be free from carbonates, sulfates, and sulfides, as these cause serious loss of tin in the slag. Cyanide is a powerful poison, and every precaution must be taken to avoid inhaling its dust or fumes.

Alkaline fluxes, such as sodium or potassium carbonate, with carbon reduction are not so satisfactory, mainly on account of the formation of stannates, especially in the presence of iron.

Procedure.—1. The amount of concentrates used should be close to 10 g. Use a 20-g. crucible and tamp in a layer of 2 to 3 g. of KCN. Mix the concentrate with three or four times its weight of KCN, place the mixture in the crucible and cover with 5 g. additional KCN.

2. Fire at 750 to 800°C. for 15 to 20 min. in a well-vented furnace. A longer fusion may be required if the concentrates are impure.

3. Remove from the furnace and cool under a hood.

4. Recover the button by breaking the crucible. The tin button should be soft and white if free from foreign metals.

Copper Assay.—The fire assay of copper possesses considerable merit for the determination of copper in materials rich in coarse metallic copper. Such materials are difficult to sample accurately, and larger samples are required than can be assayed by wet methods. The fire assay for copper was formerly used in the Lake Superior district for mine rock, mill concentrates, gravel and

tailings, and slags from reverberatories and remelting cupolas,[1] but according to data supplied by Professor N. H. Manderfield[2] the method is now used in that district only for coarse mill concentrates. Professor Manderfield presents the following typical crucible charge used by the amygdaloidal mills:

Weight of sample	1000 g.
Flux batch:	
Cream of tartar*	160 g.
Na_2CO_3	100 g.
Borax glass	80 g.
Total	340 g.

* The use of cream of tartar follows customary practice. Any other sulfur-free reducing agent would be suitable.

Sampling.—The concentrate is sampled with a shovel as it is being loaded into a car or with pipe sampler after the car is loaded. A sample weighing approximately 100 lb. is obtained in this manner, and in turn it is cut to about 5,000 g. with a Jones riffle.

Preparation of Samples.—Moisture is run on the total sample. Two 1,000-g. samples are riffled out, and each is mixed thoroughly with 340 g. of flux, when assaying finisher-jig concentrates containing 70 to 85 per cent copper, or with 255 g. for products containing 80 to 90 per cent copper. The samples are placed in Denver size L fire-clay crucibles and covered with a small amount of borax glass.

Fusion.—The crucibles are placed in the furnace and capped with clay covers and allowed to fuse for approximately 1 hr., finishing at 1100°C. or higher. After fusion the crucibles are removed and allowed to cool and set. The crucibles are then broken and the buttons are freed from slag, cleaned with a hammer, and weighed.

The percentage of copper in the original sample is computed from the weight of the copper buttons obtained.

Antimony and Bismuth Assay.—Approximate assays for antimony and bismuth in the absence of each other and of lead, copper, and tin can be made by a fusion of 5 or 10 g. of ore with four

[1] FULTON, C. H., and SHARWOOD, W. J., "A Manual of Fire Assaying," 3d ed., p. 251, McGraw-Hill Book Company, Inc., 1929.

[2] Personal communication, Apr. 11, 1940.

or five times its weight of potassium cyanide plus a cover of potassium cyanide, following the procedure given for the assay of cassiterite concentrates. The buttons will be brittle and care must be taken to avoid loss in separating them from slag. Better results are obtained with bismuth than with antimony, as antimony has a stronger tendency to enter the slag.

CHAPTER XIV

THE ACCURACY OF THE FIRE ASSAY FOR GOLD AND SILVER

The precision with which an assay result represents the average grade of the material from which the assay sample was taken depends upon the error introduced in each of the steps of the assay operation. There are errors peculiar to each of the usual steps in the assay process: (1) sampling, (2) fusion, (3) cupellation, (4) parting, and (5) weighing. In addition, serious error may be introduced at almost any stage of the process by salting.

Salting.—Salting consists of accidental or fraudulent introduction of extraneous gold or silver into the assay. Fraudulent salting occasionally occurs during sampling and assaying for valuation purposes. It is carried out by introducing metallic grains, metal filings, amalgam, cyanide precipitate, rich ore, concentrate, or solutions such as gold chloride, silver nitrate, or gold and silver cyanide into the sample or into the assay fluxes. The assayer's principal responsibility starts when he receives the samples, but he should subject important valuation samples to an examination for the purpose of detecting the presence of gold or silver in unnatural particles, and to a leaching test for detecting water-soluble gold or silver that may have been added before the samples reached the assay office.

In a sample salted with gold metal particles to about the grade of an average ore the salting particles are too few to be seen directly in the sample, and a concentrate should be panned out for examination. It is advisable to use a hand lens or a microscope for studying the concentrate, and any unusual characteristic of the valuable particles should be looked upon with suspicion.

A leaching test for soluble gold or silver is made by agitating a portion of the sample with H_2O for about ½ hr. Then filter or decant to separate the solution. Evaporate the solution to about 25 ml. in a beaker, and complete the evaporation in a small rectangular tray, made by bending up the edges of a sheet of

lead foil. After the solution has evaporated, roll the lead tray into a compact bundle and cupel. The presence of even a small amount of water-soluble gold or silver almost conclusively proves salting. A considerable part of the soluble gold or silver added to salt the sample may not redissolve in water, particularly if the sample has been heated to dry it for the ordinary assay.

In the assay office, valuation samples should be kept in a locked compartment, except when they are in process, and unauthorized persons should not be admitted to the sampling, fluxing, and furnace rooms. The secret introduction of a few samples of barren material in a series of valuation samples is a useful aid in detecting either accidental or fraudulent salting.

Common causes of accidental salting are:

1. Contamination of low-grade samples with rich material, owing to the careless handling of rich and low-grade samples during their preparation for assay.

2. Use of reagents such as mercury, litharge, and lead foil containing undetermined amounts of gold and silver.

3. Reuse of a crucible after an unsatisfactory previous fusion.

Contamination during sample preparation can be avoided by careful cleaning between samples. Grinding a small amount of barren rock between samples is desirable in order to clean the rubbing surfaces of the pulverizer, which may have become impregnated with gold from rich samples.

The best reagents obtainable for assaying contain some gold and silver. As a rule, the amount is so small that it may be neglected, but this point should always be determined by "blank" assays of the reagents. Each new lot of reagents should be tested by a blank assay, made with assay silica that is treated as a quartz ore. When running a blank for gold a small amount of silver should be added before cupellation, as a minute gold bead cannot be located and recovered from the cupel. Several assay-ton charges may be required to obtain a weighable amount of gold. Many assayers use commercial litharge and correct for its gold and silver content, rather than pay nearly twice as much for the "silver-free" variety of litharge. Silver-free litharge is not entirely barren and should be tested by a blank assay.

A fusion producing a lumpy slag, a shotted slag, or an insufficient lead button, leaves precious metals in the crucible to con-

taminate subsequent fusions. Such crucibles could be cleaned by a blank fusion in which a lead button is reduced, but it is generally cheaper to discard them. It is good practice either to discard crucibles that have been used on rich samples or to set them aside for use only with materials known to be rich. At a Western custom smelter, all assay crucibles are discarded after a single use, that the possibility of using salted crucibles may be avoided.

Sampling.—Two kinds of errors are encountered in sampling: (1) the normal error, due to chance variation in the number of rich or low-grade pieces that enter the sample; and (2) the error due to bias in the sampling method.

The error due to chance variation in sampling is discussed in Chap. II. In general the reliability of a sample is improved by increasing the weight of the sample, by increasing the number of units it contains, or by crushing and mixing the material before sampling to decrease the dispersion per unit of weight. Greatest reliability of sample is required at custom smelters where the sample is the basis of settlement between buyer and seller. Care is generally taken to secure samples that are accurate to within 1 per cent of the assay.

When single assays are used only as a general guide to operations, such as mining and milling, and when calculations from the assays are based upon the average of a large number of single assays, considerable chance variation may be allowed in each sample. The reliability of the average of a number of samples increases as the square root of the number of samples included in the average.

For example, the practical limit of error in daily mill-head samples at a gold mill could be as much as 0.05 oz. of gold per ton, yet the monthly metal-balance calculation would not have an error of more than 0.01 oz. of gold per ton due to chance variation in sampling.

Bias in the sampling method produces samples that consistently give either high or low results. It can be avoided by making sure that the difference in behavior of particles that vary in density or size does not affect their selection or rejection from the sample.

Fusions.—Two sources of error are encountered in assay fusion processes: (1) error due to disregarding the gold and silver content of the fluxes (salting), and (2) error due to lack of complete

recovery of the precious metals in the lead button. There is always some loss of precious metal, even in a normal fusion, but the loss should be less than 0.5 per cent of the precious metals. The metal lost is practically all in either the slag or crucible, and it can be recovered by remelting the slag with litharge and a reducer in the original crucible, which will produce a second lead button as in the corrected assay. Some assayers regularly "wash" the slag with lead by adding litharge with some additional reducing agent shortly before removing the crucible from the furnace. The purity of the lead button can be improved at the same time by adding more litharge than will be reduced. The extra litharge sinks through the slag and forms an excess litharge layer just above the lead button.

Flour or charcoal is generally used with loose litharge for washing the slag. In developing the oxidation-collection method of assay it was found that litharge with iron filings was much more effective than litharge with either flour or charcoal, in collecting the precious metals from a molten slag. It was also found that the best results were obtained by briquetting the litharge and iron filings. Similarly the addition of a collector briquette of litharge and iron filings should give the best slag washing.

Materials are sometimes encountered that are claimed to contain precious metals in a colloidal or volatile form that are not recovered by standard assay methods. Experiments have shown that gold added as the volatile chloride or as a colloid is invariably recovered in ordinary assay fusions even from mysterious ores that are reputed to cause volatilization or other loss. Claims of recovering more gold than revealed by the fire assay are usually based upon experiments in which mercury that is salted with gold has been used.

Cupellation.—The cupellation process is subject to (1) loss of precious metals by volatilization, (2) absorption or loss of precious metals that enter the body of the cupel, and (3) retention of base metals, causing a gain in weight of the silver bead.

Loss of precious metals by volatilization during cupellation is inappreciable with normal conditions.

Loss of precious metals by cupel absorption accounts for the greatest normal loss in the fire assaying process. Roughly the loss amounts to from 0.1 to 0.5 per cent of gold beads, and from

1 to 3 per cent of silver beads. Cupel absorption increases with (1) the temperature of cupellation, (2) amount of lead in the button, (3) presence of impurities in the button, and (4) size of the bead. The type of cupel, and the ratio of gold to silver in the bead, also affect cupel absorption.

Temperature.—The loss of precious metals increases rapidly with increase in temperature of the cupeling alloy; consequently the temperature should be maintained at the lowest point at which the process will proceed. This is slightly above the melting point of litharge—888°C. The muffle temperature must reach this point for cupellation to start. After the button opens, the heat furnished by the rapidly oxidizing lead raises the temperature of the alloy despite the lowered muffle temperature. Measurement of the temperature of the cupeling alloy is difficult, and as a result cupellation temperatures are generally given as muffle temperatures. At any muffle temperature the temperature of the cupeling alloy varies with the amount of lead oxidizing and the rate at which heat is removed from the alloy.

For example, the temperature of the cupeling alloy in a dense magnesia cupel does not rise so far above muffle temperature as it does in a bone-ash cupel, because the magnesia cupel is a better conductor of heat. This is the principal reason for good magnesia cupels giving lower losses than bone-ash cupels.

Amount of Lead.—The loss of silver increases slightly with increase in the amount of lead to be cupeled, when other conditions are held as nearly constant as possible.

For example, if cupeling 20 mg. of silver with 10 g. of lead produces a loss of 2 per cent, cupeling with 15, 20, and 30 g. of lead will produce losses of about 2.8, 4.5, and 5 per cent, respectively. Gold and large amounts of silver do not show so marked an increase in loss with increase in amount of lead.

Impurities.—Practically all impurities in the lead button increase the loss of precious metals during cupellation. The effects of harmful impurities in the lead button are to (1) lower the surface tension of the alloy, allowing increased cupel absorption; (2) cause the bead to freeze unless an unduly high cupellation temperature is used; and (3) form high-melting-point oxides that occlude small globules of precious metals in a solid scoria. Serious loss can be expected if sufficient impurities are present to require an unusually high cupellation temperature, or

if solid scoriae are left in the bowl of the cupel. Such assays should be repeated with fusion conditions adjusted to reduce the amount of impurities in the lead button.

Size of Bead.—The loss of precious metals during cupellation increases with the amount present, but the percentage loss decreases slightly with the size of the bead. Sharwood[1] proposed the rule that, other conditions being equal, the loss on cupellation

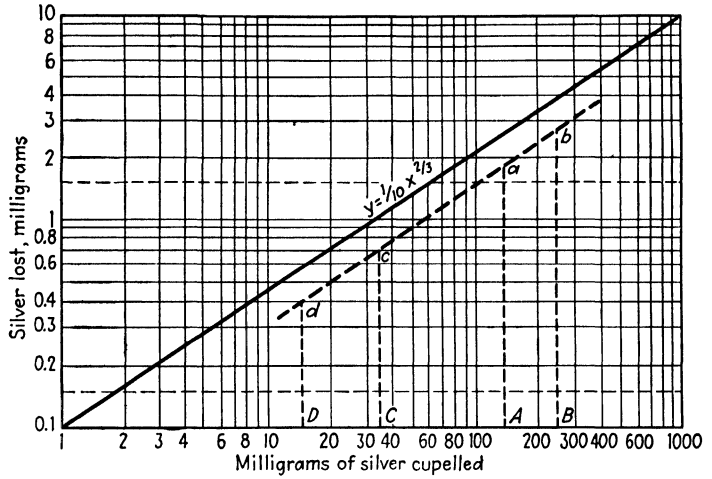


FIG. 16.—Curve representing silver losses in cupellation, plotted on logarithmic cross-section paper. (*After Fulton and Sharwood, Manual of Fire Assaying.*

is proportional to the surface of the finished bead. The loss would thus be proportional to the two-thirds power of the bead weight. This relation between milligrams of bead weight and milligrams of weight lost is a straight line on logarithmic cross-section paper, parallel to a line representing $y = x^{\frac{2}{3}}$. By the aid of a logarithmic chart, such as Fig. 16, the cupellation loss of beads of different sizes can be estimated from loss obtained by cupeling a proof with a known amount of gold and silver.

For example, point *a* in Fig. 16 represents the loss of 1.8 mg. of silver. Then, from the diagram, silver beads *b*, weighing 250 mg.; *c*, weighing 35 mg.; and *d*, weighing 15 mg.; cupeled under the same conditions, should be expected to have lost

[1] SHARWOOD, W. J., A Rule Governing Cupellation Losses, *Trans. A.I.M.E.*, vol. 52, p. 179, 1915.

2.85 mg., 0.72 mg., and 0.40 mg., respectively, and may be corrected accordingly.

Ratio of Silver to Gold.—Gold loss during cupellation can be estimated on the logarithmic chart, provided the ratio of silver to gold during cupellation is the same in the proof as in the assays to be corrected. The ratio of silver to gold is important, as the loss of gold during cupellation decreases with increase in the proportion of silver to gold. Rose[1] found a loss of 1.2 per cent of the gold in cupeling 1 mg. of gold with 4 mg. of silver and 25 g. of lead at 900°C. A similar cupellation of 1 mg. of gold with 6 mg. of silver gave a gold loss of 1.05 per cent, and an increase of silver to 10 mg. reduced the loss still further to 0.80 per cent of the gold.

Retention of Base Metals.—The retention of base metals in the silver bead increases its weight, but ordinarily the error is inappreciable. In any event the gold weight is not affected, because the base metals are separated by nitric acid parting.

A minute amount of lead is generally retained in the bead, particularly when the finishing cupellation temperature is low. The amount of retained lead is too small to warrant correction, but it tends to cause large beads to break up during parting.

Copper aids in the elimination of lead from the bead and, for this reason, some copper is added in the gold-bullion assay if it is not already present. When the lead button in a silver assay contains insufficient copper to interfere with the cupellation process, the weight of copper retained in the bead may be neglected.

When bismuth is present in an ore being assayed, it concentrates in the lead button, and an appreciable amount is retained in the bead, which gives a plus error for silver. The amount retained varies with the silver and bismuth content of the ore. A correction to the silver assay of bismuth-bearing ores is commonly made at smelters, by deducting the bismuth content of the silver beads (determined by wet analysis of the silver beads). Bugbee[2] gives a typical example, showing a correction amounting to 2 per cent of the silver for a concentrate containing 0.3 per cent bismuth and giving an uncorrected silver assay of 78 oz. per ton.

[1] ROSE, T. K., Cupellation and Parting, *Eng. Min. Jour.*, vol. 79, p. 708, 1905.

[2] BUGBEE, E. E., "A Textbook of Fire Assaying," 2d ed., p. 211, John Wiley & Sons, Inc., New York, 1933.

Parting.—The error in parting ordinary gold assays should be negligible. A small amount of gold may dissolve in the parting acid,[1] but under ordinary conditions a larger amount of silver stubbornly remains with the gold, resulting in a net gain in weight of about 0.1 per cent.

Mechanical loss of particles of gold in the parting acid or wash water can be seen by the operator. Such loss, however, can be avoided by careful manipulation.

Weighing.—Errors may be introduced in the weighing operation by (1) mistakenly recording a different weight than the balance indicates, (2) using a faulty balance or weights, or (3) the natural error of the balance due to lack of perfect sensitivity.

Mistakes in reading and recording the weight indication of the balance can be avoided. The operator should check the balance reading for each bead, by recording the weight and then reading the weight again before proceeding with the next bead.

The assayer should make certain that his assay balance and weights are in good order. The rider can be checked against the 1-mg. weight, and the total of several small weights checked with a larger weight. It is desirable to reserve a precision set of assay weights in the office for occasional comparison with the weights in use.

The assay balance may cause error in weighing if the knife-edges are damaged, or if the arms are of unequal length. Damaged knife-edges are readily detected by the sluggish and erratic behavior of the balance. Unequal length of arms is a more serious fault, as it produces results that are consistently either high or low. This difficulty is seldom encountered but should be checked frequently by weighing a large bead in both the left-hand and right-hand pans. If the two weights obtained are not equal, the length of the balance arms is probably at fault.

Every assay balance has a definite natural error equal to the smallest unbalanced load that noticeably affects equilibrium. Assay balances can be purchased with a rated sensitivity of 0.002 mg. Gold beads are commonly weighed to the nearest 0.005 mg. The error in any one weighing can be held within 0.003 mg., but this represents an appreciable percentage of small gold beads.

[1] FULTON, C. H., and SHARWOOD, W. J., "A Manual of Fire Assaying," 3d ed., p. 208, McGraw-Hill Book Company, Inc., New York, 1929.

For example, a weighing error of 0.003 mg. represents an error of 5 per cent in a 1-assay-ton assay of a low-grade ore containing 0.06 oz. of gold per ton. The error can be reduced by taking a larger sample.

Composite Samples.—The composite method of checking is frequently employed as a safeguard against abnormal errors in a sequence of single assays. As a check on assaying alone a simple arithmetical average can be used, in which case an equal weight is taken from each individual sample in the series, and the composite sample is then thoroughly mixed and assayed. The assay of the composite is compared with the arithmetical mean of the individual assays.

Weighted composite samples, prepared by taking for the composite a weight in proportion to the tonnage applying to each sample, are used to check the cumulative value of concentrate or ore over a period of time. Table XIX shows an example of a weighted composite sample used to check daily mine samples for a 6-day week.

TABLE XIX.—EXAMPLE OF WEIGHTED COMPOSITE ASSAY

Day	Tons mined	Weight taken in composite, grams	Daily gold assay, ounces per ton	Total gold (tons × assay), ounces
1	375.2	37.5	0.32	120.0
2	401.8	40.2	0.28	112 5
3	386.6	38.7	0.41	158 5
4	260.4	26.0	0.29	75.5
5	348.1	34.8	0.50	174.0
6	416.3	41.6	0.37	154.0
Total	2,188.4	....	....	794.5

Computed mean is 794.5/2,188.4 = 0.363 oz. per ton. Assay of composite is 0.35 oz. per ton.

The assay error between the composite (0.35 oz. per ton) and the weighted mean of the daily assays (0.363 oz. per ton) in Table XIX is only 0.013 oz. per ton. This is within the limits of error of routine gold assay practice.

Metal Balances.—Metal balances are the best means of checking the accuracy of weighing, sampling, and assaying operations. They should be made for all metallurgical testing as well as for mill and smelter operations. The balance most commonly used

is that between the calculated recovery of precious metals (calculated by subtracting the precious metals in the tailing from that in the feed) and the actual recovery of the precious metals (determined from weights and assays of concentrate and bullion, or from mint and smelter returns). Table XX shows a typical yearly metal balance at a small gold mill producing bullion from amalgamation, which is sold to the mint, and concentrate from flotation, which is sold to a smelter. In Table XX there is a discrepancy of 125 oz. between the calculated and actual recovery of gold for the year. This error is less than half of 1 per cent of the total gold involved and represents particularly good work. Careful weighing of ore and concentrate, and corrected assays, are required to obtain so close a check.

TABLE XX.—TYPICAL YEARLY GOLD-MILL METAL BALANCE

Material	Dry weight	Gold assay	Calculated gold content (weight × assay), ounces
Feed	49,253 tons	0.675 oz/ton	33,246
Tailings	48,047* tons	0.035 oz/ton	1,681
Calculated gold recovered			31,565
Flotation concentrate	1,206 tons	5.07 oz/ton	6,112
Amalgamation bullion	31,155 oz.	821 fine	25,578
Actual gold recovered			31,690

Actual gold recovered, 31,690 oz.; calculated gold recovered, 31,565 oz. = 125 oz. discrepancy.

* Feed and concentrate are usually weighed, and the weight of the tailings is obtained by difference.

In addition to the metal balance shown in Table XX a further check of the gold recovered is made with the mint and smelter returns. Usually another check is made by calculating the mine production of metal separately, for comparison with the precious metal in the mill feed.

Monthly and annual metal balances are made at mills and smelters. Metal balances for shorter terms are troublesome and unreliable, because of the variable amount and grade of ore in transit, storage, and process.

Control Assays and Splitting Limits.—Four samples are generally taken by mills and smelters purchasing ore, as shown in

Fig. 5. One sample is furnished the seller for assay, and one sample is assayed by the purchaser. These are known as "control assays." If the control assays check within previously specified limits, called "splitting limits," the difference is ordinarily split and settlement is made on the average. Some purchasers, however, pay only on their own assay, except when an umpire is called for.

A difference between control assays of 0.02 oz. per ton is usually split on gold assays of less than 2 oz. of gold per ton. The splitting limit is increased to 1 per cent of the assay for richer ores. Silver assays, on ores containing less than 50 oz. of silver per ton, are allowed splitting limits of from 0.2 to 0.5 oz. per ton. The splitting limit for higher grade ores is increased to approximately 1 per cent of the silver assay.

If the discrepancy between the control assays is greater than the splitting limit, the third sample is sent to a disinterested commercial assay office for an "umpire assay." Umpire assays are usually made in quadruplicate and the results averaged.

When the umpire assay falls between the two controls, settlement is, as a rule, made on the umpire assay, and the cost of the umpire is shared by buyer and seller. If the umpire assay falls outside the controls, the nearest control is used for settlement and the one whose assay is farthest from the umpire pays its cost.

Control and umpire assays of ores and concentrates are made without correction for normal fusion and cupellation losses; consequently they are likely to be from 0.1 to 1.0 per cent low for gold and from 1 to 4 per cent low for silver.

Corrected-assay Methods

An assay that has been corrected for errors is known as a "corrected assay." Corrected assays are used to obtain accurate metal balances and to evaluate rich products such as bullion and cyanide precipitate. Smelters seldom accept corrected assays as a basis of payment for ores and concentrates.

Corrected-assay methods may be classified as direct or indirect, according to whether the correction is determined directly on the assay in question, or a separate "check" assay, or some other indirect means is used to estimate the correction.

Indirect Corrected Assays.—The indirect method is generally made by correcting an assay for the error found in treating a

weighed amount of pure gold and silver in a synthetic "check" assay of approximately the same composition as the regular assay and run under the same conditions. Check-assay corrections give highest accuracy and should be used whenever the approximate composition of the material to be assayed is known or can be easily determined. It is the standard method for assaying gold bullion and is also used in the fire assay method for assaying silver bullion.

In the assay of mill feed and products the composition of each material and the conditions of assay frequently remain fairly constant. Rough corrections, based upon the usual errors encountered in assaying these products, are of great advantage in obtaining accurate metal balances.

For example, at a mill treating a silver ore by the cyanide process the calculated silver recovery—obtained by subtracting the silver in the tailing from the silver in the mill feed—was generally found to be about 2 per cent below the silver actually recovered as bullion. An investigation revealed that uncorrected assays had been used in the calculations and that the usual greater loss of silver in the feed assay compared with that in the tailing assay accounted for most of the discrepancy. It was found by experiment that the average feed assay of about 25 oz. per ton suffered a normal loss of 2.3 per cent or 0.57 oz. per ton, while the average tailing assay of about 3 oz. per ton suffered a loss of 4.5 per cent or 0.14 oz. per ton. The difference in loss, 0.43 oz. per ton, amounted to 1.7 per cent of the average feed assay. Subsequently the feed assays were arbitrarily increased by 1.7 per cent, and yearly metal balances were obtained that checked within 0.5 per cent. This method of correction could be refined by varying the correction according to the size of the bead, with the aid of a chart such as Fig. 16.

Direct Corrected Assays.—When a direct corrected assay is to be made, the customary assay is carried out, and the slag, crucible, and cupel are saved. In order to recover the lost precious metals for the correction the slag and cupel are then assayed, using the original crucible, in a manner similar to an ore assay. The corrected result is likely to be slightly high, particularly with large beads, because the plus errors (due to retention of base metals in the silver bead and of silver in the parted gold) are neglected. Neglected losses by volatilization and losses in the

second slags and cupels aid in reducing the plus error, but the neglected losses seldom exactly balance the weight of retained impurities. The appreciable plus error, which may be introduced by correcting for the major losses and neglecting gain in weight —due to retention—can be seen from the check-assay correction, or surcharge, for gold bullion.

A minus surcharge is generally obtained in assaying impure gold bullion that is less than 700 fine. With bullions between 700 and 800 fine, the plus errors about balance the total losses, and the surcharge is nearly zero. In assaying gold bullion that is more than 800 fine the plus errors are usually greater than the total losses, and a plus surcharge is obtained that must be subtracted in order to correct the assay. Seriously high assays of high-grade gold bullion would be obtained if retention were neglected, and if the cupellation loss were determined and added to the assay.

The assay of ores and concentrates differs in several respects from the assay of gold bullion, and the result of a properly conducted direct corrected assay of most ores and concentrates is considerably nearer the true assay than the result of an ordinary uncorrected assay.

The direct corrected assay is the usual method of reducing the error of a normal fire assay of materials whose approximate composition cannot readily be duplicated in a check assay.

Assay of Slags.—Many authorities postulate that it is necessary to alter the composition of the original slag and, in particular, to reduce all the litharge from the slag, replacing it with soda in order to obtain good recovery of its gold and silver content. Extensive experiments have shown that there is no advantage in altering the slag composition, and that replacement of the litharge with soda is in many instances detrimental to good recovery, on account of the failure of the new slags to retain some of the impurities in the original slag. Furthermore the addition of sodium carbonate makes the charge bulky and increases the danger of loss by boiling.

An assay of a slag that was of good composition in the first assay can be made as follows: Grind the slag to 35-mesh or finer. Mix the ground slag with 30 g. of litharge and sufficient reducing agent to reduce a 25-g. button. Fuse in the original crucible and proceed as with any other crucible assay.

Assay of Cupels.—Cupels may be composed of bone ash, portland cement, mixtures of cement and bone ash in varying proportions, or magnesia. Typical compositions are given below:

Type of Cupel	Typical Composition
Bone ash	$Ca_3(PO_4)_2$, 80–90 per cent
Cement	CaO, 60 per cent; SiO_2, 25 per cent
Magnesia	MgO, 80 per cent

The cupels ordinarily are of bone ash, bone ash-cement (1:1), or magnesia; straight portland-cement cupels are rarely used.

It is desirable to keep to a minimum the amount of cupel material which must be handled in the assay fusion. This can be accomplished by limiting the size of the original lead button to about 25 g. and by discarding all but the litharge-saturated portion of the cupel. A 25-g. button produces 27 g. of PbO; but approximately 5 g. volatilizes during cupellation, leaving 22 g. of PbO absorbed in the cupel. Bone-ash cupels absorb approximately their own weight of litharge, bone-ash–cement cupels (1:1) absorb slightly more than their weight, and magnesia cupels absorb about 75 per cent of their weight. Thus a 25-g. button will saturate roughly 22 g. of a bone-ash cupel, 22 g. of a bone-ash–cement cupel, or 30 g. of a magnesia cupel.

Magnesia and portland cement from cupels are fluxed in the same manner as similar constituents in an ore (Table XI, page 125). Bone ash disperses in a slag as inert particles and does not affect the silicate degree. The addition of fluorspar equal to one-half the amount of bone ash is recommended by some authorities. Fluorspar acts as a slag diluent, increasing the slag fluidity, but it can just as well be omitted.

Cupel materials, with the exception of cement, are not readily attacked by fluxes. Consequently, cupels should be ground to at least 65-mesh before mixing in the assay charge. Litharge contained in the cupels tends to smear on the rubbing surfaces of the grinding machine and should be cleaned off with the silica that is to be used in the cupel fusion.

The crucible-charge compositions as given in Table XXI are satisfactory for the assay of from 40 to 60 g. of litharge-saturated cupel. Usually the slag and cupel corrections need not be separated, and the slag and cupel may be ground and assayed together, with consequent saving in time and materials.

TABLE XXI.—CRUCIBLE CHARGES FOR CUPELS

	Bone ash, grams	Bone-ash–cement, grams	Magnesia, grams
Cupel material (approximate).	Bone ash 25 PbO 25	Bone ash 12 Cement 12 PbO 25	Magnesia 30 PbO 25
PbO	30	30	30
Na_2CO_3	30	30	30
Borax glass	15	15	20
Silica	10	10	30
Reducing agent	(Sufficient for a 25-g. button)		

Examples of Direct Corrected Assays.—Corrected assays of a zinc box precipitate from the cyanide process (containing approximately 60 per cent zinc), and of a pyrargyrite-galena-pyrite-quartz ore, are given in Table XXII.

TABLE XXII.—EXAMPLES OF DIRECT CORRECTED ASSAYS

	Zinc box precipitate, milligrams per 0.1 A.T.			Pyrargyrite ore, milligrams per 0.25 A.T.		
	Assay 1	Assay 2	Assay 3	Assay 1	Assay 2	Assay 3
Ore fusion:						
Doré	400.20	399.72	399.16	512.42	510.65	511.41
Au	13.30	13.27	13.31			
Ag	386.90	386.45	385.85			
Slag refusion:						
Doré	1.24	1.19	0.96	0.92	2.01	1.16
Au	0.06	0.08	0.06			
Ag	1.18	1.09	0.90			
Cupel fusion:	(Calmix, magnesia cupels)			(Bone-ash–cement cupels)		
Doré	4.77	4.54	4.72	10.26	10.22	10.57
Au	0.02	0.02	0.02			
Ag	4.75	4.52	4.70			
Total:						
Au	13.38	13.37	13.39			
Ag	392.83	392.06	391.45	523.60	522.88	523.14
Corrected assay (ounces per ton)						
Au	133.8	133.7	133.9			
Ag	3,928.3	3,920.6	3,914.5	2,094.4	2,091.5	2,092.6

CHAPTER XV

THE PREPARATION OF GOLD AND SILVER BULLION FROM AMALGAM AND CYANIDE PRECIPITATE

At many gold and silver mines, particularly those having a small production, the assayer is responsible for the preparation of bullion from rich mill products such as amalgam, free-gold concentrates, and cyanide precipitates. All these products contain more or less silver, but gold is the dominant precious metal except at silver mines using the cyanide process, when the cyanide precipitate will consist largely of silver.

This chapter takes up only the bullion-production phase of milling. For other metallurgical information, standard metallurgical texts should be consulted.[1]

Amalgam Retorting.[2]—The amalgam obtained from milling operations is seldom sufficiently free from extraneous substances to permit retorting without cleaning. At large plants, various mechanical devices are used to separate the amalgam from clean-up products, but in small operations the final cleaning of the amalgam is done by hand—either by panning or by a small hydraulic classifier such as that illustrated in Fig. 17, which is in use at a California mine.

At many small gold mines the mercury is distilled from amalgam, and the retort metal is sold without melting and casting into bars. The metal is acceptable by the mint in this form, and the

[1] ROSE, T. K., and NEWMAN, W. A. C., "The Metallurgy of Gold," 7th ed., J. B. Lippincott Company, Philadelphia, 1937.

HAMILTON, E. M., "Manual of Cyanidation," McGraw-Hill Book Company, Inc., New York, 1920.

DORR, J. V. N., "Cyanidation and Concentration of Gold and Silver Ores," McGraw-Hill Book Company, Inc., New York, 1936.

[2] In the preparation of this section, valuable assistance was given by E. M. Smith, assistant mill superintendent and metallurgist, Argonaut Gold Mining Company, Jackson, Calif., and D. L. Wooster, superintendent, Western Quartz Mining Company, Murphys, Calif.

producer is saved the expense of melting and, in the United States, the cost of a gold melter's license.

Amalgam retorts, furnaces, and condensers of various sizes and designs can be purchased from equipment dealers or can be made locally. Retorts are usually made of cast iron, and if only

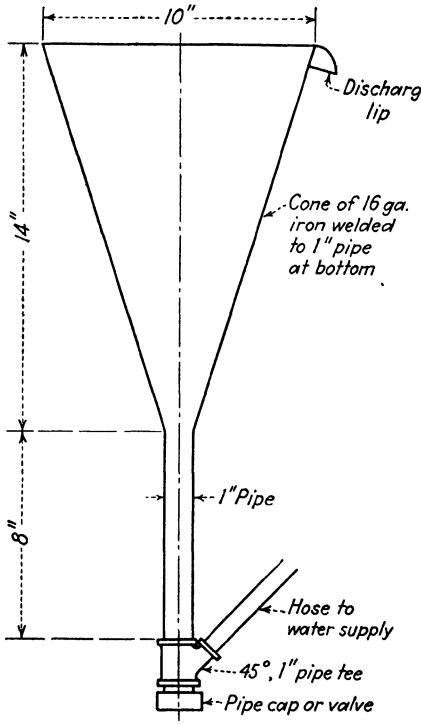


FIG. 17.—Simple hydraulic cone classifier for cleaning mercury and amalgam.

the retort is purchased the condenser and furnace can be made at moderate cost with the tools and supplies ordinarily available at an operating mine. The condenser can be made from standard pipe and fittings, using an inner pipe whose diameter fits the retort outlet and an outer pipe about 30 in. long and four or five times the diameter of the delivery pipe, fitted with a small inlet and outlet tube for circulating water. The inlet should enter the lower end of the water jacket. The condenser delivers into

a pail partly filled with water, and the delivery pipe should always be about 2 in. above the surface of the water. Before use the water circulation through the condenser should be tested, and the delivery tube checked to see that it is free from obstructions. Care should be taken to avoid inhalation of mercury vapor.

A simple and economical method of heating small retorts is to suspend the retort and condenser assembly on an iron rod or pipe over a carbide can or an oil drum with the top removed. Holes are cut near the bottom of the can for the admission of air, and a wood fire is used. Any other suitable fuel may be used, in appropriate furnaces.

To prevent adhesion of the metal to the retort the inside should be coated with lime, fire clay, or iron oxide wash or lined with several thicknesses of paper, prior to charging with amalgam.

The entire lot of amalgam should be weighed just before retorting, and the recovered gold sponge and mercury should also be weighed. Any abnormal losses indicate leakage of the retort and condenser system.

After charging the amalgam the cover of the retort must be carefully luted on with stiff mud or other suitable seal and preferably should be clamped with an asbestos joint. A stiff wire should be available for clearing obstructions in the delivery pipe, particularly if the amalgam contains base metals such as antimony or zinc.

The entire retort should be heated gradually to redness. A temperature of about 800°C., slightly below normal cupellation heat, is sufficient, provided the entire retort is so heated. The mercury[1] distills over and condenses and is delivered in a series of drops. After the steady drip of mercury ceases to come over, the heating is continued for ½ hr. to 1 hr. longer at full temperature, after which the firing is stopped, and the retort is allowed to cool well below the boiling point of mercury (357°C.) before the condenser is disconnected and the retort is opened. The condenser is swabbed out with a rag tied to a rod to collect all the mercury.

The normal amount of mercury remaining in the bullion is from 3 to 5 per cent of the weight of the retorted metal. The weight of the retorted metal plus the recovered mercury is usually from 1 to 2 per cent less than the original weight of the amalgam.

[1] Mercury is colloquially known as "quick," from quicksilver.

The loss is caused by free moisture in the amalgam, vapor-pressure loss of mercury, slight leakage of mercury, and slight absorption of mercury in the condenser. Higher losses should be investigated.

The total time for retorting varies from 2 hr. for small lots of a few pounds of amalgam up to 7 or 8 hr. for large lots.

Bullion Melting.—Bullion, whether from amalgam retorts, gravity concentration, or other sources, may be put into more acceptable form for marketing by melting and partial refining followed by casting into bars. One reason for the practice of bullion melting at the mine is that the danger of theft of gold is less when readily identifiable bars of gold are produced than when loose gold or retort sponge is shipped. Furthermore, bullion melting removes some of the impurities, increasing the market value of the product and decreasing express charges, and also provides a product that is amenable to accurate sampling and assaying.

Bullion melting is usually conducted in graphite crucibles, which are actually a mixture of graphite and fire clay. If oxidizing fluxes are to be used, a fire-clay lining or a fire-clay crucible fitted into the graphite crucible is preferable. Graphite crucibles should be thoroughly dried and annealed at a low temperature before using for the first time, otherwise they may spall badly due to the sudden expulsion of water vapor.

In melting retort sponge, or clean free-gold concentrates, the only flux needed is borax. The amount of flux to use can be ascertained by small-scale trials in an assay crucible and is usually from 5 to 15 per cent of the weight of the bullion. If much silica is present, sodium carbonate should be added. Some operators charge and melt the flux before charging the bullion, others mix and charge the flux and bullion together. The temperature required for melting is in excess of 1100°C., and the operation should be completed in about 45 min. after charging into a hot furnace. If a longer time is required, either the temperature was too low or incorrect fluxes were used.

A clean borax slag is very fluid and tends to follow the bullion into the molds on pouring. This does no harm, as the slag can be hammered free after solidification, but some operators prefer to pour off part of the slag into a separate mold, then thicken the remaining slag with silica or bone ash so that it can be held back,

or skimmed off separately. The second slag is remelted with the next charge, and if silica was used to thicken it instead of bone ash, it is more easily fluxed, using sodium carbonate in proper proportions. Before discarding slags they should be crushed and panned to remove prills and shots of gold. It is good practice to return the crushed slag, after panning, to the mill feed, unless it interferes with cyanidation or flotation, in which case the slags should be accumulated for shipment to a smelter or for separate treatment by gravity concentration or in an amalgamating barrel.

Bullion molds should be coated with chalk or iron oxide or swabbed with oily waste before use, to prevent the bullion from adhering to the mold.

The melting of impure materials, as, for example, free-gold concentrates containing arsenic, antimony, or other base metals, requires special oxidizing fluxes. The general principles are discussed in connection with the melting of cyanide precipitates.

Melting of Cyanide Precipitates.—Appropriate melting practices for cyanide precipitates and impure free-gold concentrates depend upon the nature and amount of impurities present. The precipitates from efficient modern plants are often quite clean and may require only 2 to 5 per cent of borax flux, by weight of precipitate. If the cyanide solution prior to precipitation is fouled with base metals, or is imperfectly clarified, the precipitates will be dirty, and a considerable quantity of fluxes, together with an oxidizing agent, is required. Small-scale tests in an assay crucible may be necessary to ascertain the best flux combination for melting. Preliminary sulfuric acid treatment is sometimes needed to remove excessive zinc, as from zinc-box precipitates or zinc shorts. (*Caution!* If the precipitates contain arsenic, take care to vent fumes, which may contain arsine, a powerful poison.) With ordinary precipitates, the material may be roasted in the drying pan to effect sufficient oxidation of zinc to facilitate direct melting without acid treatment.

The flux for precipitates should make an acid slag in sufficient volume to hold the oxidized base-metal impurities. A combination of borax glass, sodium carbonate, and silica sand is generally used. The grade of the bullion can be raised in the melting operation by adding an oxidizing agent. Potassium nitrate or manganese dioxide is used for this purpose. Manganese

dioxide is generally avoided with silver precipitates because of the belief that it increases the silver loss in the slag. Typical flux proportions are given in Table XXIII.

TABLE XXIII.—TYPICAL FLUXES FOR CYANIDE PRECIPITATES

Constituent	Pounds of flux per 100 lb. of precipitate		
	Yellow Aster* (gold)	Mountain Copper† (gold)	Typical silver (over 800 fine)
Borax glass	23–35	...	5–10
Borax	.....	40	
Silica	35	32	3–5
Sodium carbonate	15	24	3–5
Fluorspar	1		
Niter	10–20		
Manganese dioxide	3	9	
Total	87–109	105	11–20

* FROLLI, A. W., Open-pit Mining and Milling Methods and Costs at the Yellow Aster Mine, *U.S. Bur. Mines I.C.* 7096, p. 41, 1940.

† YOUNG, G. J., Cyaniding Low-grade Gold Ore, *Eng. Min. Jour.*, vol. 131, No. 12, p. 563, 1931.

Gold is melted in crucible furnaces. Graphite crucibles are used except when a considerable amount of an oxidizing agent is present in the charge. When oxidizing agents are added, a fire-clay-lined crucible should be used. Various other types of furnaces, designed to handle large amounts of material with greater ease and fuel economy, are used for silver.

The precipitate and fluxes are mixed together, and the mixture is commonly placed in paper bags and charged to the hot crucible with a pair of tongs. After melting, the bullion is cast and the slag treated as described under bullion melting.

CHAPTER XVI

ASSAY EQUIPMENT AND SUPPLIES

Factors affecting the selection and operation of assay equipment and supplies are dealt with in this chapter. Detailed descriptions and illustrations of manufactured equipment are omitted, because up-to-date information can be obtained from catalogues issued by assay supply houses.

The first step in planning the installation of an assay office is to request catalogues and price lists from the distributors of assay equipment and supplies serving the territory in which the assay office is to be established. A representative list of the leading assay supply houses of the world, as of 1940, is given in Appendix *C*. To aid in ordering equipment and supplies for the establishment of an assay office, the minimum items of equipment for a small assay office and their approximate costs are listed in Appendix *A*. In Appendix *B* the minimum quantity lots and costs of assay supplies and reagents for 1,000 assays are listed.

Assay Furnaces and Accessories

Assay furnaces are of two general types: (1) crucible or pot furnaces for melting only, in which the crucible is in contact with the fuel or the flame; and (2) muffle furnaces, needed primarily for cupellation but also used for melting, in which the contents are heated in an enclosed muffle out of contact with the flame. One of the popular types of furnaces for small assay offices combines a melting chamber for crucibles and a small muffle for cupellation and scorification. Another modification is the use of plate muffles, which have some of the advantages of a full muffle at some saving in maintenance cost and a slightly greater capacity.

Large muffle furnaces are preferred by most assayers for both fusion and cupellation where the volume of work is sufficient to justify their use. To conserve floor space and to secure fuel economy, two muffles may be built into a single furnace, either side by side or superimposed, or three muffles may be arranged

with two below and one above. These designs have been used frequently with furnaces that are fired with coal or wood, but separately heated muffles are preferred with gas- or oil-fired furnaces, to secure greater operating flexibility and more accurate temperature control.

Fuel and Furnaces.—Assay furnaces may be designed to utilize any desired fuel, or may be heated by electricity. Furnaces heated by any of the solid fuels—wood, coal, charcoal, or coke—are usually built in place, whereas furnaces fired with oil, gasoline, or gas are usually purchased ready-made, complete with burners and other accessories, but may be made locally or converted from a furnace formerly fired with solid fuel. Electrically heated furnaces may be obtained on special order from various manufacturers, or may be made locally and the resistor units and electrical control purchased separately.

The relative cost of different fuels is often compared on the basis of the cost per million B.t.u. For example, if a certain grade of bituminous coal contains 11,000 B.t.u. per pound and costs $12 per short ton delivered at the assay office, the cost per million B.t.u. is $0.55. A light Diesel or stove oil at 8 cts. per gallon having a specific gravity of 0.85 and containing 19,500 B.t.u. per pound costs $0.58 per million B.t.u. Electricity at 1 ct. per kw.-hr. (1 kw.-hr. = 3413 B.t.u.) costs $2.93 per million B.t.u. Since the efficiency of the various heating media varies widely, a cost comparison based on theoretical heating value is misleading.

Solid fuels are the least efficient, because much heat is lost in the waste gases, ash, unburned fuel, and in starting and stopping the furnace. From the operating standpoint, furnaces fired with solid fuel require more attention and respond more slowly to temperature adjustment than other types. Hence, such furnaces are advantageous only where the unit cost of fuel per million B.t.u. is much less than that of other available fuels, and especially where they are to be used for a large volume of work and are kept under continuous fire for relatively long periods of time.

Bituminous coal or wood produces a long flame and is preferred to other types of solid fuel for muffle furnaces. Anthracite coal, coke, or charcoal produces a short flame, requiring that the muffle be surrounded with burning fuel.

A typical design of a two-muffle soft-coal-fired furnace is shown in Fig. 18. The coal consumption is approximately 45 lb. per hour. Each muffle holds fifteen 20-g. crucibles, allowing room for a heater brick or a row of empty crucibles in the front. The temperature of the upper muffle will be considerably less than that of the lower muffle, which disadvantage is eliminated in designs providing for placing the muffles side by side. For wood

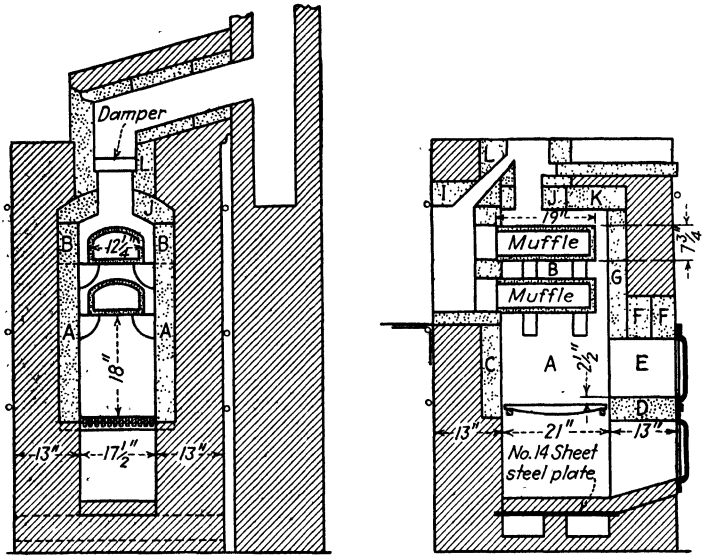


FIG. 18.—Two-muffle coal-fired assay furnace. (*After Fulton and Sharwood, Manual of Fire Assaying.*)

firing the grate should be 8 to 10 in. below the bottom of the fire door to provide a firebox sufficiently deep for good combustion and uniform heating.

Pulverized coal has been used in a few installations and is nearly as satisfactory as a gaseous fuel, except for the accumulation of ash in the furnace and the comparative complexity of the pulverizing and blowing equipment.

Liquid or gaseous fuels have a much higher combustion efficiency than solid fuels and are much more satisfactory for assay service because of ease and cleanliness of operation, quick adjustment of temperature, and saving of fuel when not in actual use.

Gasoline is used only for small furnaces, which are usually of the combination type. Light Diesel or other fuel oil in the range of 24 to 35°A.P.I. (American Petroleum Institute)[1] gravity is widely used throughout the Western United States and is generally preferred to heavy fuel oil of 12 to 14°A.P.I. which requires preheating to secure atomization and tends to clog burner orifices. Natural gas, where available, is an excellent

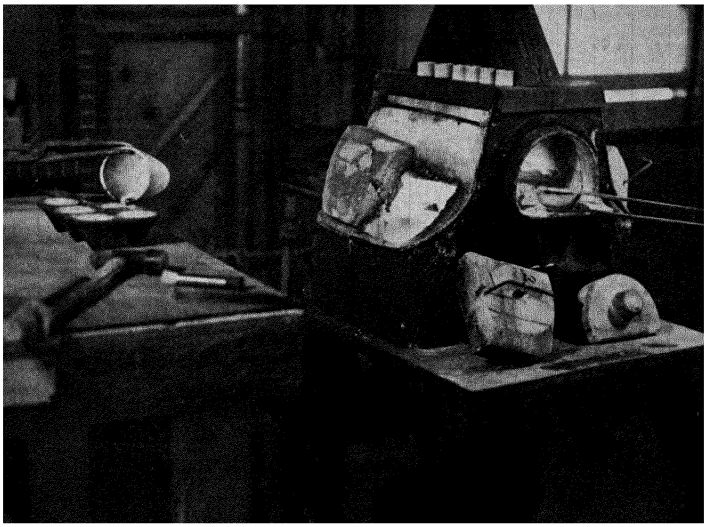


FIG. 19.—Braun gas-fired combination furnace. (*Photograph by W. Vernon Smith, Sacramento Junior College.*)

fuel. Manufactured city gas, butane, and compressed gas in cylinders are used in some localities, but the cost is high relative to other fuels.

A popular type of gas- or gasoline-fired combination furnace widely used in small assay offices is illustrated in Fig. 19. This furnace is made in two sizes. The smaller furnace (Braun Type 42) holds six 20-g. crucibles and the larger one holds ten 20-g. crucibles, and the muffle sizes are 4¾ by 8 by 3 in. and 6 by 10 by 4 in., respectively. The average gasoline consumption is ½ to ¾ gal. per hour, and the consumption of natural gas (1150 B.t.u. per cubic foot) is about 50 cu. ft. per hour. The same

[1] Specific gravity = 141.5/(131.5 + °A.P.I.).

furnace is available for firing with kerosene or light fuel oil, or with natural, city, or cylinder gas.

Several successful types of oil-fired muffle furnaces have been placed on the market, one of which is illustrated in Fig. 20. This

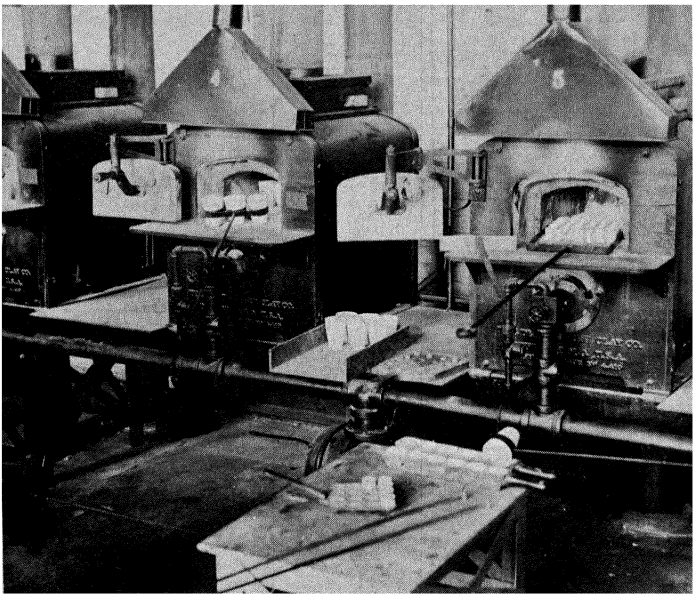


FIG. 20.—Denver oil-fired muffle furnaces. (*Photograph by Eric Nordman, Stanford University.*)

furnace uses light Diesel or fuel oil, atomized with air. Two sizes are available, the smaller of which has a 12- by 20- by 7¾-in. (size LF) muffle, and the larger a 14- by 20- by 6½-in. (size LG) muffle. The effective capacities are fifteen and twenty 20-g. crucibles, respectively. Oil consumption under full fire is approximately 2.5 gal. per hour, or 1.5 gal. per hour at operating temperature.

Electric assay furnaces are ideal from the standpoint of convenience, cleanliness, absence of noise, accuracy of temperature control, and uniformity of heating throughout the heating chamber. They also give up to 40 per cent longer life to crucibles. Although the first cost of the installation is more than three times

that of other furnaces, the maintenance costs are reasonably low. In regions where electric power can be obtained for 1ct. per kilowatt-hour or less, the actual cost of heat compares favorably with that of fuel-fired furnaces because the thermal efficiency of the electric furnace is from five to six times as great as that of a

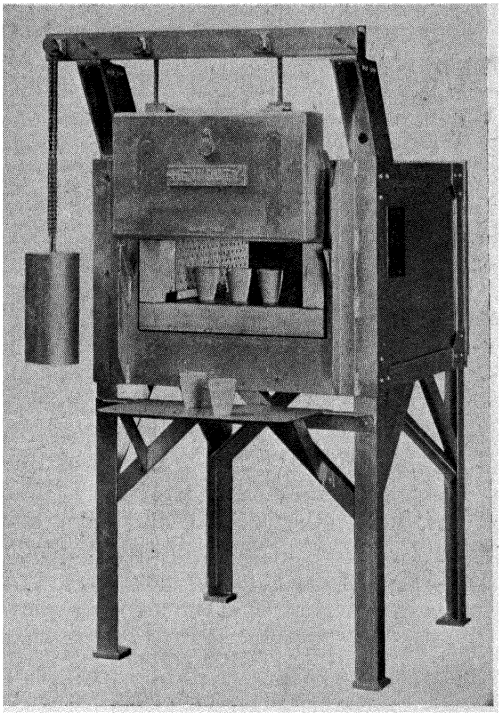


FIG. 21.—Hevi-Duty electric assay furnace. *(Photograph by D. G. McAllister, Pacific Scientific Co., San Francisco.)*

fuel-fired furnace owing to the absence of products of combustion and the compactness of design, which permits good insulation and close proximity of the working chamber to the source of heat. In 4 or 5 years' operation at full capacity for 8 hr. per day, the saving in crucible consumption may offset the higher first cost of the furnace. The effective capacity of an electric furnace of given hearth dimensions is greater than that of fuel-fired furnaces, especially for cupellation, because of more uniform heating from

front to rear of the working chamber. Furthermore, fusions and cupellations can be made by unskilled operators, as no judgment is required to control temperatures within the desired limits. Assaying accuracy is improved by the maintenance of nearly ideal temperature cycles for cupellation and the ability to reproduce the same cycle from day to day. The chief disadvantage of electric assay furnaces, aside from their first cost, is the greater amount of time required to bring them to operating temperature. For example, a 12-kw. furnace with net hearth dimensions of 15½ by 20¾ in. requires from 1½ to 2 hr. to reach a temperature of 1050°C., whereas an oil-fired furnace with a muffle 14- by 20-in. hearth area will reach the same temperature in ¾ to 1 hr. This time loss is unimportant, as the assayer is usually occupied with the preparation of charges and other matters while the furnace is heating, and in most localities the furnace could be started at an earlier hour by a watchman, janitor, or other employee. A typical electric furnace is illustrated in Fig. 21.

The Hevi-Duty Electric Co. of Milwaukee, Wis., has recently installed electric assay furnaces at a number of plants. The Hevi-Duty furnace is heated with a rod type of metallic heating element and is equipped with an autotransformer, thermocouple, and potentiometer-type automatic temperature controller. A similar furnace has also been designed by the Denver Fire Clay Company of Denver, Colo. The Carborundum Company of Niagara Falls, New York, manufactures carborundum heating elements, known as Globar elements, but does not manufacture complete furnaces. A number of mining companies have used Globar elements in furnaces that have been constructed locally.

Table XXIV gives data on the size, cost, capacity, heating rate, and average fuel or electric consumption of various types of assay furnaces. In some cases the effective crucible capacity given in the table is less than manufacturers' ratings, because the manufacturers seldom allow for the fact that the front 3 or 4 in. of a muffle furnace is too cool to be used for melting crucible assay charges. Most assayers use a brick or a row of empty crucibles in front of the muffle to act as a warmer for the charged crucibles. In calculating cupel capacity, ample allowance must be made for portions of the furnace that are unusable on account of too high or too low temperatures. If plate muffles are used in

TABLE XXIV.—DATA ON TYPICAL ASSAY FURNACES

Type of furnace	Cost f.o.b. shipping point	Muffle No.	Muffle size (outside), inches			Effective 20-gram crucible capacity*	Approx. heating time to 1050°C., hr.	Typical aver. fuel cons. per 8 hours
			Width	Length	Height			
Braun combination type 42:†		S-627-10	4¾	8	3	6	½	
Gasoline	$ 83.00							4 gal.
Natural gas	130 00							400 cu. ft.
Braun combination type 40:†		S-627-2	6	10	4	10	½	
Gasoline	100.50							5 gal.
Oil	200 00							5 gal.
Natural or city gas	145 00							500 cu. ft.
D.F.C. oil fired‡	355 00	LF	12	20	7¾	15	¾	12 gal.
D.F.C. oil fired‡	370 00	LG	14	20	6½	20	1	12 gal.
Hevi-Duty electric HDT-16217 with automatic temperature control	1,200 00		16	21¾	7	24	2	80 kw.-hr.
D.F.C. model 3929A electric furnace, with electric door lift, exhaust fan, and automatic temperature control	1,288.00		16¼	25	7¾	30	2	120 kw.-hr.
Same with hand-operated door, natural draft, and manual temperature control	920.00		16¼	25	7¾	30	2	120 kw.-hr.
Coal fired, locally built	150 00 (est.)	LG	14	20	6½	20	2	240 lb.

* Allowing one blank row at front of muffle furnace.

† Braun furnaces also available for cylinder gas.

‡ Denver Fire Clay Company furnaces are also available in two- or three-muffle design, muffles placed side by side and separately fired.

a well-designed gas-fired furnace, almost the entire hearth area can be used for cupellation, but in most fuel-fired furnaces, if the highest silver accuracy is desired, it is unwise to attempt to cupel more than three or four rows of cupels in depth, otherwise the rear rows will be too hot even though the front row is cupeled at the minimum possible temperature. If gold only is being assayed, a wider temperature range is permissible in cupellation, and some furnaces may be almost completely filled with cupels, except for the front two or three rows, and a clearance of 2 or 3 in. from the rear wall of the muffle. Electric furnaces have a lower temperature gradient from front to rear, with correspondingly greater cupellation capacity.

Muffles.—Manufacturers of assay clay goods produce a number of stock sizes of fire-clay muffles. The short life of fire-clay muffles, especially when used for fusions as well as for cupellation, has led to the extensive adoption of muffles made of silicon carbide, known under the trade name of Carbofrax or Crystolon. These muffles have an indefinitely long life if properly supported in the furnace, as durable patches can be made with silicon carbide cement. Silicon carbide has a higher heat conductivity and a lower specific heat than fire clay, and hence muffles of this material heat more rapidly than fire-clay muffles and are more responsive to heat control. The cost of silicon carbide muffles is from three to four times that of fire-clay muffles.

An increasing number of large assay offices have adopted plate muffles, which consist of a hearth with a low flange around the two sides and rear. The advantages of this muffle over the completely enclosed type are greater capacity per unit of hearth area and less maintenance cost. The greater capacity is obtained through the possibility of setting crucibles close to the outer edges of the plate, so that the upper part of the crucible, which is wider than the base, actually projects beyond the edges of the muffle plate. Furthermore, large crucibles can be loaded without the necessity for using exceptionally high muffles, provided that the door and the heating chamber are sufficiently high. Plate muffle furnaces are fired with gas or oil and are also used in electrically heated furnaces. One operator using a gas-fired plate muffle furnace reports that the heat distribution is so uniform that the entire furnace, with the exception of about 3 in. at the front, is used for cupellation.

Furnace Refractories.—Fire-clay refractories are generally used for furnace linings and muffle supports in fuel-fired furnaces. The furnace should be designed so that all destructible parts can be readily replaced. Muffle replacements are the most common when fire-clay muffles are used. Muffle supports and flame baffles also deteriorate rapidly. If silicon carbide muffles are used it is recommended that muffle supports and flame baffles also be made of the same material, which will well repay their extra cost in increased life and freedom from the annoyance and expense of frequent furnace repairs. If prefabricated supports are not available, they can be formed from Carbofrax or equivalent cement in plaster molds cast from models of the required shapes, allowing from 5 to 8 per cent linear drying and firing shrinkage. After drying, the shapes may be fired by placing them in the assay furnace and gradually increasing the temperature up to the maximum operating temperature over a period of 6 or 8 hr., then holding at maximum temperature for 1 hr. or more.

In a few installations the annoyance of muffle rest failures has been eliminated by the use of water-cooled pipe supports.

Furnace parts not subjected to bearing loads, corrosive slags, lead or litharge fumes, or to the direct impingement of a gas or oil flame require but little repair. The resistance of fire-clay refractories to corrosive slags or flame action can be increased by coating them with a wash of Carbofrax or other high-temperature cement.

The side covers of small combination furnaces are subjected to severe spalling conditions, on account of the necessity of removing them when crucibles are loaded into and removed from the furnace. By removing only the front covers on each side of the furnace, the life of a set of four covers can be nearly doubled, and old, badly damaged covers may be used in the rear positions, as is shown in Fig. 19.

Elements of Assay-furnace Design.—The special service requirements of assay furnaces govern their design. The important factors to be considered are rapid heating, rapid and accurate temperature control, manipulative convenience, and easy replaceability of destructible parts. Fuel economy is of subordinate importance as the cost of crucibles and other supplies, the operating labor cost, and the importance of accuracy and efficiency far outweigh extreme costs of fuel or electrical heating.

The typical daily cycle of an assay furnace is rapid heating from a cold start to a temperature of 1000° to 1100°C., followed by a period of several hours' operation at that temperature until all fusions are completed and then several hours' operation for cupellation. Each cupellation cycle should start at approximately 900°C. muffle temperature, drop to 810 to 840°C. during the greater part of the cupellation process, and then rise to 850 to 870°C. at the finish. The initial heating period should not be unduly prolonged, and 1½ to 2 hr. is the maximum time allowable in most cases, unless someone is delegated to start the furnace before the assayer starts his day's work. During the fusion period of the day the furnace is being charged with a load of cold crucibles and their contents at intervals of 25 to 30 min., requiring a rapid heat input to heat the crucible contents to melting temperature.[1] The drop in temperature after the start of cupellation should be effected in 4 or 5 min. or less, and the increase at the finish should be done in the shortest time possible.

To obtain the desired flexibility of temperature control the furnace must not only be provided with a great excess of fuel-burning (or electrical heating) capacity, but the thermal characteristics of the furnace walls must be properly designed. The optimum furnace-wall design is obtained with a relatively thin interior lining of firebrick or other high-temperature refractory having a relatively low thermal conductivity, surrounded by one or more layers of insulating material. If too much firebrick is used, the heat capacity of the furnace walls becomes excessive, rendering the furnace sluggish in responding to changes of firing and requiring a prolonged period of firing to reach equilibrium at a given temperature. At the other extreme, if the refractory lining is too thin, or has too high a heat conductivity, and no insulation is used, heat losses are excessive, the furnace does not heat uniformly, and temperature control is too erratic. An appropriate degree of insulation conserves heat and prevents sudden fluctuations of temperature. Just enough refractory protection should be used on the interior so that the temperature of the refractory in contact with the insulation does not exceed the safe working limit of the insulating material.

[1] Twenty-four average fusions in 20-g. crucibles require about 10,000 B.t.u. to raise their temperature from the cold to 1050°C.

Most of the manufactured oil- or gas-fired assay furnaces have firebrick linings 3 or 4 in. thick, surrounded by a ½- to 1-in. layer of insulating material such as diatomite or mineral wool, the whole enclosed in a sheet-steel shell. Electric furnaces are usually lined with molded aluminum oxide or silicon carbide, backed with several inches of insulating material. The insulation is usually applied in layers, using several grades, each of which is best suited for the particular temperature range to which it is to be subjected.

Furnace Tools.—Manufacturers' catalogues should be consulted for illustrations and prices of the common furnace tools required for the handling of crucibles, scorifiers, and cupels. Any of these tools can be made by a local blacksmith if desired, often at considerable saving in cost. The minimum complement of furnace tools and accessories required for a small assay office is listed in Appendix *A*, and photographs showing typical assemblies are shown in Figs. 19 and 20.

For handling a large volume of work a number of specially designed devices have been developed, some of which have already been described in the chapters on cupellation and the crucible assay. For keeping a furnace load of crucibles in order for charging with fluxes and loading into the furnace, a wooden tray having the same area as the firing chamber of the furnace is convenient. Such a tray is illustrated in Fig. 12, and its use is described on page 154. A multiple charging fork such as that illustrated in Fig. 20 is very efficient for charging an entire row of crucibles into a muffle furnace, and a single fork of similar design is often used for withdrawing and pouring crucibles. For placing a number of cupels in the furnace at a single operation, a simple tray with pusher is commonly used. Multiple button-charging devices have been developed at a few custom-smelter assay offices where an exceptionally large volume of assaying is involved.

Two common types of button molds are shown in Figs. 19 and 20. A different type of mold is illustrated in Fig. 13, and the practice of pouring directly on a flat plate is described on page 160.

For pounding buttons, a heavy steel plate, a small blacksmith's anvil, or a short section of rail may be used.

Equipment for Sample Preparation.—Manufacturers' catalogues present a wide range of crushing and grinding equipment for the preparation of assay samples. For small-scale work a hand-power jaw crusher and bucking board and muller are sufficient, but power-driven equipment is necessary for efficient operation if more than 15 or 20 samples per day are to be prepared. For coarse crushing, jaw crushers are generally used, but various types of cone crushers are also available. For fine grinding, disk pulverizers are popular, but cone and ring grinders are used in some localities. For quantity production, especially with large samples, crushing rolls are very desirable for intermediate crushing. A bucking board should always be provided for grinding small lots.

In planning the layout of a sampling room, care should be taken to provide ample workbench area, so that samples can be mixed with a mixing cloth with full freedom of action. It is desirable that the top of the mixing bench be covered with sheet metal, for convenience of cleaning. The sampling room should be isolated or partitioned off from other parts of the assay office to avoid salting from dust. A suction fan over the crushing units is desirable, and a compressed-air nozzle for cleaning the crusher, benches, pans, scoops, etc., is a *sine qua non* in a busy assay office.

A drying rack should be provided in a room other than the crushing room. with sufficient capacity for the daily array of samples.

Sample pans, scoops, brushes, riffles, and other incidental equipment are selected in accordance with anticipated needs.

A suggested list of equipment for sample preparation is included in Appendix *A*.

Assay Supplies and Reagents

Assay crucibles, scorifiers, cupels, and parting cups are described elsewhere in the text. Manufacturers' catalogues should be consulted for details of size, shape, and prices. A list of the essential supplies for 1,000 assays is given in Appendix *B*.

Assay Reagents.—The nature and function of all necessary assay reagents are discussed throughout the text in connection with their specific applications. The minimum number of reagents and suitable quantities of each for 1,000 assays are given in Appendix *B*.

The principal assay reagents, especially sodium carbonate, litharge, borax, borax glass, granulated lead, and sheet lead, are available in special grades for assaying, the chief requirement of which is that they be free from, or contain a uniformly distributed small amount of, silver and gold. Two grades of litharge are obtainable, commercial and silver-free. The commercial grade costs about half as much as the silver-free grade and is generally acceptable if care is taken to thoroughly mix each new lot and obtain an accurate assay of its silver and gold content to be applied as a correction to all assays. Corrections of the order of 0.1 to 0.2 mg. of silver and not over 0.0025 mg. of gold per assay ton are normal, but occasional lots of litharge may contain greater amounts of precious metals. Assay granulated lead is usually nearly free from precious metals, but lead foil frequently contains some silver, and the silver content may vary in different parts of the same roll. Assay reagents other than lead or litharge are generally quite free from precious metals, but it is advisable as a routine precaution against accidental or intentional salting to assay new lots of all reagents.

Besides the specific reagents mentioned in Appendix *B*, certain additional reagents and substitutes are favored by some assayers. Red lead, the peroxide of lead, approximately Pb_3O_4, is sometimes used instead of litharge but is usually more costly per unit of lead and has no advantages compared with litharge.

Sodium bicarbonate was formerly favored by assayers for some applications instead of the normal carbonate but contains only 63 per cent as much Na_2O and gives off nearly twice as much gas per unit weight. Potassium carbonate, replacing part or all of the sodium carbonate, gives a more powerful fluxing action on some ores, but its use is seldom warranted on account of greater cost.

The choice between borax and borax glass is partly a matter of cost per unit of $Na_2O.2B_2O_3$ and partly a question of avoiding the undesirable effect of the evolution of water vapor from borax in assay fusions. Borax is much cheaper and may be used as a cover, but the glass should be used if it is to be mixed with the charge.

Lime (CaO) or limestone ($CaCO_3$) is useful in fluxing ores high in alumina, as noted in Table XI. Smelter-flux limestone or commercial lime are suitable for assay purposes, after grinding.

Fluorspar (CaF_2) is favored by many assayers to improve the fluidity of some slags, for example, when bone-ash cupels are fluxed, but is of doubtful value, as it merely introduces an inert diluent in the slag, and sufficient fluidity can always be obtained by proper flux balance without fluorspar.

The selection of reducing agents has been discussed in Chap. VII, and various reducing agents are listed in Table XIII. Flour is commonly the cheapest and most generally available carbonaceous reducing agent. It is desirable to have a small stock of powdered sulfur and iron filings on hand for experimental purposes, as on some ores, one or the other of these reducers may prove more effective than carbonaceous reducing agents.

Summary of Equipment and Supplies Cost.—From Appendix *A*, it will be noted that the minimum cost of assay equipment for a small assay office to handle 30 to 40 assays per day with hand-power crushing and grinding is approximately $600 f.o.b. shipping point. With motor-driven crushing and grinding equipment, the minimum cost is $860. These figures do not include shipping costs, sales tax, if any, or the cost of housing and installation of equipment. The minimum floor space required without uncomfortable crowding is about 225 sq. ft., which should preferably be partitioned into a sampling room, a furnace room, and a balance room. A separate storeroom is also desirable.

Supplies for a minimum of 1,000 assays cost approximately $150 f.o.b. shipping point. The quantities recommended in Appendix *B* are selected on the assumption that there will be about an equal number of siliceous ore and pyritic concentrates to be assayed and should be adjusted in accordance with the anticipated character of the samples. After the first 1,000 or more assays have been made, the assayer can readily calculate the actual average consumption of supplies, and order accordingly in the future.

APPENDIXES

APPENDIX A

MINIMUM EQUIPMENT FOR A SMALL ASSAY OFFICE

Fire assay for gold and silver only.

Capacity 30 to 40 assays per day, with one assayer and helper, including sample preparation and cupel making.

Benches, tables, and machinery installation not estimated.

* Articles marked with an asterisk can often be made better and more cheaply locally.

	Approximate Cost, F.o.b. Shipping Point
A-1: *Sample grinding by hand power.*	
1. Hand-power jaw crusher, 6- by 3-in. jaw	$ 75.00
2. Bucking board and muller, 18 by 20 in	12.50
3. Paint brush, 3 in	1.25
Total, hand-grinding equipment	$ 88.75
A-2: *Sample grinding by electric power.*	
1. Jaw crusher, 6- by 3-in. jaw, tight and loose pulley	$125.00
2. Disk pulverizer, tight and loose pulley	135.00
3. 2-hp. motor, 1,750 r.p.m., with starter and base	65.00
4. Line shaft, pulleys, bearings, coupling, safety collars, grease cups, and belts	19.50
5. Bucking board and muller, 18 by 20 in	12 50
6. Scoop for feeding pulverizer*	1.25
7. Paint brush, 3-in	1.25
Total, power-grinding equipment	$359.50
B. Sampling equipment.	
1. Jones riffle, 8 by 8 in., with four sample pans, scoop, and cleaning brush (optional)	$ 14.65
2. Tyler standard sieve, 8-in., 100-mesh	5.25
3. Tyler sieve-bottom pan, 8-in	2.40
4. Tyler sieve cover, 8-in. (optional)	1.25
5. 1 doz. (minimum) sample pans, approximately 1 qt. capacity and 6 in. in diameter and 1½ in. deep. Pie tins are suitable for samples to be dried; bread tins are useful for temporary storage of samples	1.50
6. 4-in. spatula, stainless-steel blade	0.40
7. 6-in. gold pan (for general use)	0.40
Total, sampling equipment	$ 25.85
C. Fluxing and furnace-room equipment.	
1. Flux box (locally made)	$ 5.00
2. Measuring scoops, see page 156	
3. Pulp balance, 150-g. capacity, 2 mg. sensitivity, open type (or 60-g. balance, 1 mg. sensitivity at slightly lower cost)	24.00

	Approximate Cost, F.o.b. Shipping Point
4. Set of weights, assay ton, 0.05 to 4 A.T.	$ 8.00
5. Set of weights, metric, 10 mg. to 50 g.	2.50
6. 1 pt. aluminum cocktail shaker, with sieve removed or sealed. (Optional, for quick mixing of charges, see page 157)	0.50
7. Braun combination assay furnace, type 42, 4¾- by 8- by 3-in. muffle, gasoline-fired. (See Table XXIV for alternative choices.)	83.00
8. Carbofrax muffle for furnace	4.50
9. Table-model cupel machine, 1¼- and 1½-in. dies (suitable table to be designed, also provide drying rack for cupels. Omit if cupels to be purchased)	45.00
10. Crucible tongs*	1.25
11. Scorifier tongs for 2½- or 3-in. scorifiers*	1.25
12. Cupel tongs*	1.00
13. 6-hole pouring mold	0.75
14. Button forceps, 6-in	0.10
15. Button brush, stiff, double-end	0.75
16. Cupel tray, for 16 cupels	0.85
17. Ball-peen hammer, 16-oz	0.65
18. Blacksmith's anvil, 70-lb., or a short length of railroad rail, or use top of pouring table, if covered with heavy steel plate*	12.50
Total, fluxing and furnace-room equipment	$191.60
D. Bead handling and parting equipment.	
1. Curved pliers, 5-in	$ 0.70
2. Bead anvil, 2¼ by 1¼ by ½ in., hardened tool steel*	0.30
3. Bead hammer, or square-headed tack hammer	0.50
4. Two parting-cup trays, for 12 cupels each*	2.00
5. Nichrome crucible tongs, 9-in., for handling parting cups	3.25
6. Electric or other hot plate or stove, 8-in. round or larger.	11.75
7. Still, heated by gasoline, gas, or electricity, or on a stove, minimum capacity 1 qt. per hour (omit if distilled water to be purchased)	30.00
8. Gasoline blow torch with vertical burner, stand and nichrome triangles or nichrome wire gauze (the assay muffle is more convenient for annealing sets of gold partings, but a good burner is essential for other purposes, and is useful for annealing when the furnace is not in operation)	10.00
Total, bead-handling and parting equipment	$ 58.50
E. Bead-weighing equipment (should be in separate room).	
1. Keller assay balance, type 3B, or equivalent (provide substantial bench on piers separate from building)	$200.00
2. Set fractional weights, 1 mg. to 1 g., with 2 1-mg. riders. "A" grade, having a 0.005-mg. tolerance is preferred, but "B" grade with a 0.01-mg. tolerance can be substituted at about two-thirds of the cost	22.50
3. Curved forceps, brass with ivory tips, 4 in. long	1.00
Total, bead-weighing equipment	$223.50
Total equipment cost, using hand crushing and grinding	$588.20
Total equipment cost, using power crushing and grinding	$858.95

APPENDIX B

LIST OF ASSAY SUPPLIES AND REAGENTS

Nearest minimum quantity lots for 1,000 assays, with equipment listed in Appendix *A*. Includes replacement parts that should be carried in stock for emergency repairs.

	Approximate Cost, F.o.b. Shipping Point
A. Glassware and porcelainware.	
50 porcelain crucibles (parting cups), size 00	$ 7.00
6 porcelain crucibles, size 1, for bullion parting	1.20
2 150-ml. beakers, pyrex	0.38
2 400-ml. beakers, pyrex	0.52
2 1,000-ml. beakers, pyrex	1.00
4 2½-l. bottles. Need not purchase, as temporary bottles can be used until empty acid bottles are available. Acid carboys of 5 or 12 gal. capacity are necessary for parting acid and water storage for quantity production	
1 wash bottle, consisting of a 1,000-ml. pyrex flash with wicker- or asbestos-covered neck and 2-hole No. 6 rubber stopper. Make blowtube and delivery tube and nozzle with glass and rubber tubing. For quantity work, an overhead hot distilled water system is indispensable, for which order more glass and rubber tubing than listed	1.60
1 graduated cylinder, 1,000-ml	2.00
2 glass funnels, 3 in. diameter, 6-in. stems	0.44
½ lb. glass tubing, 6 mm. and 8 mm. outside diameter, assorted	0.50
½ lb. glass rod, 4 to 6 mm. diameter	0.20
Total glassware and porcelainware	$ 14.84
B. Clay goods.	
384 (4 cartons) clay crucibles, 20-g., or 384 (3 cartons) 15-g. crucibles if most assays are on ½-A.T. samples of simple ores, for which deduct 80 cts. per 100	$ 27.85
84 (1 carton) clay crucibles, 30-g	7.75
126 (1 carton) clay crucibles, 10-g. Omit if preliminary assays not needed. Increase if found possible to flux ½-A.T. charges in this size crucible	6.68
25 scorifiers, 2½-in. Increase and include 3-in. size if many scorifications are planned	0.80
1 set furnace-renewal parts as follows:	
Covers	$1.50
Burner-hole boss	0.30
Muffle plug	0.50
Dome	8.00
End bricks with muffle rests	4.50
Deflecting brick	0.50
Total	15.30
(Bottom and side bricks seldom need to be replaced)	

	Approximate Cost, F.o.b. Shipping Point
10 lb. Hytempite or other refractory cement	$ 1.00
5 lb. Carbofrax cement	0.60
Total clay goods	$ 59.98
C. Reagents and consumable materials.	
150 lb. litharge, commercial for assaying. Increase to 200 lb. if high-copper ores are to be assayed	$ 13.25
100 lb. sodium carbonate (soda ash), 58 per cent, light	2.00
50 lb. borax glass for assaying (Considerable cost saving if borax is substituted for borax glass when possible)	8.00
25 lb. silica, powdered. Increase quantity if most ores to be assayed are basic	0.50
25 lb. potassium nitrate, powdered, U.S.P. Decrease if most samples are nonreducing	2.50
5 lb. flour	0.30
5 lb. granulated lead, c.p., assay grade	1.50
5 lb. lead foil, c.p., assay grade	1.35
1 oz. silver foil, c.p. Increase if many bullion assays required	1.50
5 g. proof gold foil. This is sufficient for initial stock for gold-bullion assays. Additional gold may be recovered and purified from assays, for which add hydrochloric acid and oxalic acid to this list	10.00
4 oz. sheet copper, about 22-gage ($\frac{1}{32}$ in.) or thinner. Commercial sheet metal satisfactory if tested for precious metals. Omit if no bullion assays required	0.25
3 7-lb. bottles nitric acid, c.p.	4.50
1 lb. calcium chloride, technical, granulated, for desiccation. Not necessary in dry climate	0.25
1 pkg. (1,000) Hermann inquarts	2.50
50 lb. bone ash, Denver XX or equivalent. Omit if cupels purchased and allow $20.00 for 1,000 cupels	5.00
50 lb. cement. Omit if cupels purchased	0.60
Total, reagents and consumable materials	$ 54 00
D. Miscellaneous supplies.	
1 pr. asbestos mittens	$ 3.00
1 pkg. 11-cm. filter papers, No. 1 Whatman or others	0.30
1,000 sample envelopes, Kraft paper, with metal fastener 4 by 7 in., or substitute 1-oz. grocery bags at $0.50 per M	7.50
2 yd. 20 to 24-oz. rubberized mixing cloth	3.00
1 ft. rubber tubing, $\frac{3}{16}$ in. inside diameter. For wash bottle connections. Increase if gravity-feed wash-water system is used for parting	0.10
2 (extra) 1- mg. riders, loop in plane of legs, tolerance 0.005 mg	1.60
2 (extra) 1- mg. weights, tolerance 0.005 mg	2.00
1 (extra) 2- mg. weight, tolerance 0.005 mg	1.00
Total miscellaneous supplies	$ 18.50
Total cost of supplies for approximately 1,000 assays	$147.32

APPENDIX C

ASSAY SUPPLY HOUSES

United States		
California	Los Angeles	The Braun Corporation
		The Calkins Co.
	San Francisco	Braun-Knecht-Heimann Co.
Colorado	Denver	The Denver Fire Clay Company
		Mine & Smelter Supply Company
Idaho	Wallace	Coeur d'Alene Hardware & Foundry Co.
Illinois	Chicago	E. H. Sargent & Company
Missouri	St. Louis	Henry Heil & Company
Montana	Butte	Montana Hardware Co.
New York	New York City	The Denver Fire Clay Company
		Eimer and Amend
		J. & H. Berge
Oregon	Portland	Scientific Supplies Co.
Texas	El Paso	The Denver Fire Clay Company
		Mine & Smelter Supply Company
Utah	Salt Lake City	The Denver Fire Clay Company
		Mine & Smelter Supply Company
Washington	Seattle	Braun-Knecht-Heimann Co.
		Steward and Holmes Drug Co.
	Spokane	C. M. Fassett & Company
Canada		
Alberta	Swastika	George Taylor Hardware, Ltd.
British Columbia	Vancouver	Marshall-Wells, B. C., Ltd.
		Cave and Company
Manitoba	Winnipeg	Marshall-Wells Company, Ltd.
Ontario	Cobalt	George Taylor Hardware, Ltd.
	New Liskeard	George Taylor Hardware, Ltd.
	Toronto	Canadian Laboratory Supplies, Ltd.
		Fisher Scientific Co.
Quebec	Montreal	Canadian Laboratory Supplies, Ltd.
		Fisher Scientific Co.

Philippine Islands	Manila	Marsman Trading Corporation Fisher Scientific Co. Philippine American Drug Co.
	Baguio, Mt. Prob.	Marsman Trading Corporation
Central and South America		
Argentina	Buenos Aires	Eduardo Alvarez de Toledo
Brazil	Rio de Janeiro	Adolpho Botelho
Chile	Santiago	W. R. Judson
Colombia	Bogota	Almacen Padco
Mexico	Mexico D. F.	Hoffmann-Pinther & Bosworth, S. A.
	Monterrey	Sanford Supply Company
Peru	Lima	A. y F. Wiese, S. A.
Others		
Australia	Sydney	H. B. Selby & Co. Pty., Ltd.
Belgium	Brussels	Henkart, Van Velsen and Laoureux
China	Shanghai	Harvey, Main & Co., Ltd. Anderson, Meyer and Co., Ltd. Schmidt & Co., Ltd. (in all principal cities)
Dutch East Intlies	Batavia	N. V. Otto Pfeiffer
East Africa	Nairobi, Kenya Colony	Gailey & Roberts, Ltd.
England	London	Baird and Tatlock Gallenkamp and Co.
France	Paris	Poulence Frères Maison Wiesnegg
Japan	Tokyo	Suzuki Sohati Company

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Slag Factors, Equivalent Weights per Unit of Silica

Dominant element	Compound	Original form	Combining form	Wt. orig. form per unit wt. SiO_2			
				Silicate degree			
				Sub	Mono	Sesqui	Bi
Acid Fluxes							
Boron	Borax glass	$Na_2O.2B_2O_3$	$Na_2O.2B_2O_3$*	1.2	1.3	1.5	1.7
Boron	Borax	$Na_2O.2B_2O_3.10H_2O$	$Na_2O.2B_2O_3$*	2.2	2.4	2.8	3.1
Basic Fluxes							
Lead	Litharge	PbO	PbO	14.9	7.4	4.9	3.7
Sodium	Sodium carbonate	Na_2CO_3	Na_2O	7.1	3.5	2.4	1.8
Potassium	Potassium carbonate	K_2CO_3	K_2O	9.2	4.6	3.1	2.3
Basic Ore Constituents							
Antimony	Antimony trioxide	Sb_2O_3	Sb_2O_3	6.5	3.2	2.2	1.6
	Stibnite	Sb_2S_3	Sb_2O_3	7.5	3.8	2.5	1.9
Calcium	Calcium oxide (lime)	CaO	CaO	3.7	1.9	1.2	0.9
	Calcite or limestone	$CaCO_3$	CaO	6.7	3.3	2.2	1.7
Copper	Cuprous oxide	Cu_2O	Cu_2O	9.5	4.8	3.2	2.4
	Cupric oxide	CuO	Cu_2O	10.6	5.3	3.5	2.7
	Chalcocite	Cu_2S	Cu_2O	10.6	5.3	3.5	2.7
	Chalcopyrite	$CuFeS_2$	$Cu_2O.2FeO$	6.1	3.1	2.0	1.5
Iron	Ferrous oxide	FeO	FeO	4.8	2.4	1.6	1.2
	Hematite	Fe_2O_3	FeO	5.3	2.7	1.8	1.3
	Magnetite	Fe_3O_4	FeO	4.9	2.5	1.6	1.2
	Pyrite (marcasite)	FeS_2	FeO	8.0	4:0	2.7	2.0
Lead	Lead oxide (litharge)	PbO	PbO	14.9	7.4	4.9	3.7
	Galena	PbS	PbO	15.9	8.0	5.3	4.0
Magnesium	Magnesium oxide (magnesia)	MgO	MgO	2.7	1.3	0.9	0.7
	Magnesite	$MgCO_3$	MgO	5.6	2.8	1.9	1.4
Manganese	Manganous oxide	MnO	MnO	4.7	2.4	1.6	1.2
	Pyrolusite	MnO_2	MnO	5.8	2.9	1.9	1.4
Zinc	Zinc oxide	ZnO	ZnO	5.4	2.7	1 8	1.3
	Sphalerite	ZnS	ZnO	6.5	3.2	2.2	1.6

Note: The fluxing of aluminum and arsenic is explained in Table XI.

* The slag factors for borax and borax glass compensate the silicate degree for the base Na_2O in the borax or borax glass.

REDUCING POWER OF CERTAIN SULFIDE MINERALS

Mineral	Formula	S, per cent	Normal slag-forming oxides	R.P., grams per gram of mineral		
				Computed R.P.	Actual R.P.	
				S to SO_2	Preliminary assays*	Niter charges†
Galena	PbS	13.4	PbO	3.46	2.9	2.9
Chalcocite	Cu_2S	20.2	Cu_2O	5.20	4.5	4.7
Arsenopyrite	FeAsS	19.7	FeO, As_2O_5	8.25	8.1	7.4
Stibnite	Sb_2S_3	28.6	Sb_2O_3	7.35	5.9	5.8
Chalcopyrite	$CuFeS_2$	34.9	Cu_2O, FeO	8.44	8.2	8.2
Sphalerite	ZnS	32.9	ZnO	8.51	8.2	8.1
Pyrite	FeS_2	53.4	FeO	12.07	11.6	11.0

* The charge in all cases was 3 g. sulfide, 45 g. PbO, 15 g. Na_2CO_3, 5 g. SiO_2.

† The values in this column were determined with monosilicate slags under normal assaying conditions with niter and excess litharge. U.S.P. niter was used which had an O.P. of 4.0.