

THE DETERMINATION OF GOLD LOSSES IN THE
FIRE ASSAY METHOD

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List of Symbols

Pb Weight	=	Weight lead foil used for cupellation.
Au Added	=	Weight gold used for analysis.
Ag Added	=	Weight silver powder added to the gold.
Sum	=	Weight of gold-silver bead obtained after cupellation
Surcharge	=	Weight parted bead less weight added gold
Ag Retained	=	Weight silver found in the parted bead
Au Found	=	Weight gold found in the parted bead
Au Loss	=	Weight gold added less weight gold found
s	=	Standard deviation
Ag:Au	=	Ratio of silver added to gold added
c/50sec.	=	Counts per 50.0 second counting interval
n	=	Number of trials

ABSTRACT

Gold losses in the various stages of the fire assay method were investigated as a function of experimental conditions and procedures. Losses were determined indirectly, by determining the extent of recovery of gold added to standard samples, and directly, by a radiochemical procedure. Procedures and conditions found to be optimum for milligram samples, were applied to several microgram sized samples as well as ores.

Determination of Gold Loss In The Fire Assay Method

A. Origins of the Fire Assay

The earliest known analytical procedure which is still in use today, is known as the fire assay⁽¹⁾. According to the same source, the development of fire assaying arose as a result of the need for controlling the purity of silver and gold, and preventing counterfeiting of these precious metals. Fire assaying is a method of quantitative determination in which a metal or metals are separated from impurities by fusion processes. It is particularly well suited for determination of the noble metals, which are readily reduced to the elemental state on heating. In a reducing atmosphere it can also be used for determination of some of the base metals.

One of the earliest references to the fire assay was found in the Tel al Amarna tablets dated around 1380 B.C., in which the Babylonian king complained that a bar of "gold" received from a merchant when tested by fire, proved to be largely dross⁽²⁾. A cupellation process for gold is mentioned by Siculus as being in use in the second century B.C. Several references to fire assaying can be found in both Old and New Testament. One such reference is the statement of the prophet Ezekiel, "Son of man, the house of Israel is to me become dross; they are even the dross of silver, As they gather silver and brass, and iron, and tin, into the midst of the furnace, to blow the fire upon it, to melt it ... As silver is melted in the midst of the furnace, so shall you be melted in the midst thereof."⁽³⁾ Pliny, the Roman historian, records the use of lead for the purification of gold and silver by Roman metallurgists⁽¹⁾. Geber, the great Arabian alchemist, also describes the determination of these metals by cupellation.

In England the assay of coinage utilizing cupellation was first recorded in the time of Henry II (1154-1189 A.D.), while the first extant official record of its use in France, dates to 1314 A.D.⁽²⁾. The "parting assay" in which gold is separated from silver by the action of nitric acid, was known by Geber (777 A.D.), though the first official document relating its use dates to 1343 by the French mint. In this connection it is interesting to note that the original name for nitric acid was "separating water"⁽¹⁾. Albertus Magnus (1193-1280 A.D.) gives an account of the preparation of nitric acid and its ability to separate silver from gold⁽¹⁾.

The first explicit records of assaying were published anonymously by a German early in the sixteenth century A.D.⁽²⁾. In 1666 Pepys gave an account of the parting process which he observed in the English mint and which according to Rose bears a strong resemblance to methods of the present day⁽²⁾.

With such an ancient history one might well ask on what basis current interest in the fire assay as an analytical method is justified. With the advent of sensitive instrumental techniques, exuberant claims are often made that the new methods make the old obsolete. Thus one source states that atomic absorption spectrophotometry is rapidly replacing fire assay methods⁽⁴⁾. This view is not supported by many experienced assayers of gold. In a general discussion of the problems associated with the various stages of the fire assay H. Britten makes the following comment: "In common with gold assaying elsewhere the classical methods of fire assay have continued to withstand all competition from the new methods of chemical analysis which have been adopted as standard practise in other fields"⁽⁵⁾. In a recent authoritative treatise the statement is made that, "Fire assaying is

the best method for determination of gold in most materials⁽⁶⁾". The latter statement leans perhaps too far to the other extreme and definitely requires qualification. There is no doubt, for instance, that neutron activation analysis of very poor gold-bearing geological materials is the preferred method of analysis.

In spite of its antiquity the interest in, and in some cases preference for, the fire assay method is based on solid reasons. Foremost amongst them is the question of analysis time. A complete fire assay can be accomplished within three hours after receiving the sample. In contrast wet methods requiring complete dissolution of an ore typically require from two to three days. Multiple analyses are readily conducted by carrying through a dozen or more samples simultaneously. Another problem which, if not overcome, is at least minimized by the fire assay method, is the problem of obtaining a representative sample. In highly sensitive methods such as neutron activation maximum sample sizes are limited to approximately 0.5 grams. Since gold ores are invariably heterogeneous the small size of sample increases the probability of sampling errors. This is then reflected in poor precision⁽²⁴⁾. For the fire assay, samples sizes from 15 to 60 grams are readily handled and yield a higher degree of apparent homogeneity. Finally the fire assay can be used for samples containing from 1.0 microgram to 1.0 gram of gold. At the upper levels and when dealing with relatively pure gold (eg. gold bullion) the fire assay method is undoubtedly more accurate and precise than any instrumental technique. In a paper presented at a symposium on the analysis of high purity gold, the claim was made that "no methods of any kind are available for determining the concentration of the major element with anything remotely approaching the precision obtainable for the analysis of gold

by the fire assay technique,"⁽⁷⁾.

In view of the foregoing and inspite of the rejection of the fire assay by analytical researchers reported in a recent book⁽⁸⁾ one cannot help but agree with the view expressed there that "by its rejection the researcher has eliminated from his experience one of the most fertile and useful areas of investigation and that the fire assay will retain its usefulness to those who have mastered its simple techniques"⁽⁸⁾.

B. The Fire Assay Method

The fire assay method or process can be divided conveniently and naturally into four stages. These are: fusion, cupellation, parting, and analysis. The problem of sampling ores, while very important, is a problem not unique to the fire assay and must be faced regardless of the method of assay chosen. Suffice it to say, that the method of sampling must be reported along with the results obtained.

I. Fusion

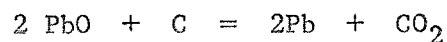
The object of this phase of the fire assay is to concentrate the precious metals of an ore in a lead button or phase which forms as a result of interactions between flux components. Under proper conditions for the fusion the remaining flux materials form a fusible slag. The molten, two phase, mass is poured into a metal mold where it is allowed to cool. After cooling, the lead button can be separated from the slag by gentle tapping with a hammer.

Commonly used flux materials include litharge (PbO), silica (SiO_2), soda (Na_2CO_3), borax glass ($\text{Na}_2\text{B}_4\text{O}_7$), and flour, the proportions of each varying, depending on the composition of the ore to be analysed and the preference of the assayer. Regarding an optimum slag composition Beamish⁽⁹⁾ states, "Whether or not there is an optimum slag composition for each ore is not known". In any case "... no two assayers working on the same ore will agree exactly on the flux proportions to use, so it is safe to say that, for any given ore, there is a comparatively wide range within which the four common flux constituents may be varied and still, in the hands of an able assayer, yield practically identical results."⁽¹⁰⁾

Regarding universal fluxing mixtures Smith⁽²⁾ states that "... fluxing materials suitable for fluxing all classes of ore are frequently

recommended, but although these mixtures may be suitable in many cases for certain classes of ore, they sooner or later lead to failure if used for all ores."

The chemistry of fusion processes is nowhere near being established. While reasonable guesses can be made concerning some of the reactions, a complete explanation for even a single ore awaits a more extensive study of these multicomponent systems. The commonly held view would be somewhat as follows (2,10,11,18,27). The finely divided ore and flux materials after intimate mixing are heated. In the absence of a plentiful supply of air the reducing agent (flour) causes reduction of some of the litharge throughout the mixture.

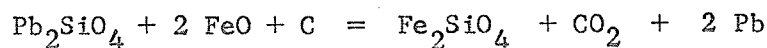
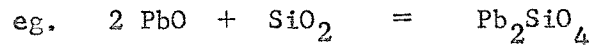


The accumulation of lead results in the formation of fine droplets, which in close contact with the ore, extract the gold from it forming a gold-lead alloy. As the temperature in the pot or crucible increases the lead droplets settle to the bottom carrying the gold, and other precious metals with them. It is generally believed to be important that the temperature must not be too high during the initial stages of fusion for then the lead falls too quickly without having fully extracted the gold. For this reason the fusion is often begun at a lower temperature and then gradually increased towards the end. At the higher temperature the very dense gold which has not been extracted may simply settle out and collect at the bottom with the lead. In all likelihood the overall process is a combination of the two.

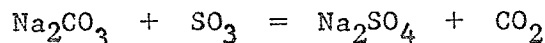
Some assayers prefer to make use of a cover. This is a layer of some material, not containing the ore, spread over the top of the charge. The intent of the cover is to prevent loss of ore by dusting or ebullition⁽¹⁰⁾. The cover material eventually enters the slag after

the fusion is well underway.

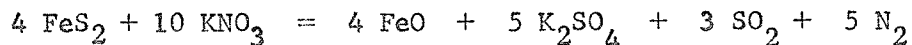
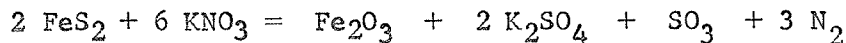
In addition to the reaction above, elemental lead may be formed as the litharge reacts with other components of the ore. Thus with silicate ores, in which gold is often found, litharge may react to form a lead silicate of low melting point which can further react with other base metals present, say as sulfides.



A basic flux such as soda, in addition to controlling the degree of acidity of the slag, aids in the process of desulfurization of an ore high in sulfur. This is desirable since sulfur from base metals has an extremely high reducing power and results in excessively large lead buttons.



In those ores where the sulfur content is objectionably high it is sometimes necessary to add an oxidizing agent such as KNO_3 . This method is the characteristic feature of the nitre assay.



The evolution of gases (CO_2 and N_2) helps to stir the fusion mixture and enhances the extraction process on which the method depends. Too violent an evolution of these gases can lead to mechanical losses of precious metal.

Regarding the optimum lead button size ". . . no data has been

recorded"⁽¹¹⁾. It is traditional to produce lead buttons between 25 and 35 grams. The size of lead button should bear some relation to the amount of charge⁽¹¹⁾.

While textbooks of fire assaying outline methods of calculating flux composition, a good deal of empiricism prevails. In the main this is due to the complex nature of ores whose composition is at best only partially known, the failure of oxidizing and reducing agents to achieve their theoretical oxidizing and reducing power, and our own meagre understanding of the basic chemical reactions involved.

II. Cupellation

The objective of cupellation is to separate the lead from the gold and silver which were combined in the lead phase formed during fusion. Silver is often present in gold ores and if lacking, is always added as it exerts a protective effect on gold losses. Cupellation consists of an oxidizing fusion in a porous vessel called a cupel.

When the lead-precious metal alloy is heated in the presence of air to a temperature slightly above the melting point of the alloy the lead is selectively oxidized to PbO. The greater portion (98.5%) of the litharge is absorbed by the cupel while the remainder is lost as vapor (10). Common cupel materials include bone-ash, cement, and magnesia. Bone-ash cupels absorb an equal weight of litharge. Magnesia cupels absorb about 3/4 their weight of litharge. This factor determines the maximum button size which can be handled by a given size of cupel. Thirty and forty gram cupels are common.

In the cupellation process, which is conducted in a muffle furnace at temperatures of 1700⁰F or higher, the lead alloy melts, initially forming a dark scum over the surface. If the cupels are pre-heated for at least 10 minutes this scum disappears and the molten

button becomes bright. This is referred to as "opening", and normally takes less than 5 minutes with the draft closed. The draft is then opened and the lead begins to oxidize rapidly thereby raising the temperature of the molten button so that it glows. The surface then becomes slightly convex and the molten litharge passes down over the surface and is absorbed by the cupel. The button is then said to drive. Towards the end of the cupellation the proportion of silver and gold increases requiring a higher temperature to maintain the liquid state and drive off the last of the lead. To achieve this the draft is closed and the cupellation "finished" for a concluding five minutes.

The basis of the separation of the lead from the precious metals is the fact that the PbO wets the cupel while the silver and gold do not. Thus the silver and gold remain as a small bead or prill on the surface of the cupel while the lead oxide is largely absorbed.

In a properly conducted cupellation the molten silver-gold bead must be removed slowly from the furnace since silver rich alloys have the capacity to absorb large quantities of oxygen which is released explosively on cooling quickly. Such beads are said to "sprout" or "spit" and cannot be relied upon to give accurate results. On cooling a bead, from which all but a trace of lead has been removed, a characteristic bright flash or "blick" is observed, as the latent heat of fusion is released. Failure to exhibit the "blick" is one indication that the cupellation has been arrested too soon. In some cases crystals of litharge form on the edge of the cupel and grow in towards the centre covering the "driving" bead. Such samples are described as "frozen" and must be rejected. The cause of freezing is the failure to maintain temperature. Since increasing the temperature of cupellation is commonly said to increase gold losses, the recommended temperature of

cupellation is one just high enough to prevent freezing. In any case losses during cupellation are widely held to be the main source of gold losses in the complete fire assay⁽¹²⁾.

III. Parting

Parting involves the separation of the silver from the silver-gold prill obtained from cupellation. Any base metals which may have been carried along to this point are also leached out of the bead by an acid treatment. While sulfuric acid is sometimes used the common acid is nitric. The exact procedure used probably varies more from one laboratory to another, than for any other phase of the total process. Variations in procedure depend on the kind of prill received (silver to gold ratio) and the preference of the assayer.

Early assayers held the view that complete removal of silver was impossible unless the initial silver to gold ratio was at least 3:1. In prills containing more than one-quarter gold, silver was added until the required ratio was attained. The process was referred to as inquartation. Rose⁽¹³⁾ held that the minimum ratio should increase with decreasing amounts of gold beginning with 2.5:1.0 for 200 mg. of gold and increasing to 10:1 for 0.2 mg. of gold. While a high silver to gold ratio increases the rate at which silver is dissolved it also tends to cause the bead to break up and make handling more difficult⁽¹⁴⁾. Beads containing less than a 2:1 silver to gold ratio would not part adequately even in strong acid. Decreasing the silver to gold ratio, also increases the digestion time required to attain a certain degree of silver removal.

Regarding acid strength, differences of opinion prevail here too. According to Bugbee⁽¹⁰⁾ the required acid strength depends on the silver to gold ratio. The higher this ratio the weaker the acid concentration

should be in order to maintain a coherent bead. He found that 1:7 nitric (acid:water) is safe for beads containing from 3:1 to 1000:1 silver to gold ratios. The stronger the acid the more rapid and complete the parting process is. On the other hand Smith⁽²⁾ quotes T.K. Rose as maintaining that 4:3 nitric (acid:water) is suitable for all silver to gold ratios and that no particular advantage obtains from use of more dilute acids. Keller⁽²⁾ is reported as recommending 1:9 nitric (acid:water) for all ratios and that all buttons remain coherent up to a silver to gold ratio of 500:1.

Time of contact between acid and button is another variable on which agreement is lacking. According to Shepherd and Dietrich⁽¹⁴⁾ "parting is practically complete when evolution of gas ceases for samples containing up to 20 mg. gold and when high silver to gold ratios are maintained." By contrast Bugbee⁽¹⁰⁾ recommends one parting with 1:7 nitric acid until action ceases and a second for 10 minutes with 1:1 nitric. Smith⁽²⁾ maintains a single 10 minute boiling is enough for 10 mg. gold beads, while for large beads a second parting in 2:1 nitric for 5-10 minutes is required.

With regard to temperature of the acid all sources consulted seem to agree that best results are obtained as to speed, completeness of parting, and coherence of gold if the parting acid is heated before use and kept just below boiling for parting. Actual boiling is not generally recommended in order to prevent mechanical losses of gold and reduce stress on the beads.

Many assayers also flatten the bead prior to parting to a thickness of 0.01 inch to aid more complete removal of silver. In fact a significant proportion of silver always resists dissolution⁽¹²⁾. The amount retained depends on the silver to gold ratio, the thickness to