THE DETERMINATION OF GOLD LOSSES IN THE

FIRE ASSAY METHOD


Siegfried Gerhard Wall


A thesis submitted in conformity with the

requirements for the degree of Doctor of Philosophy at

the University of Manitoba

August 1972

## TABLE OF CONTENTS

# LIST OF TABLES

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 seperated 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.

Inspite 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 ($Na_2B_4O_7$), 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.

$$2 \; PbO \; + \; C \; = \; 2Pb \; + \; CO_2$$
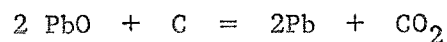
The accumulation of lead results in the formation of fine
droplets, which in close contact with the ore, extract the gold from it
forming a gold-lead alloy. As the temperature in the pot or crucible
increases the lead droplets settle to the bottom carrying the gold, and
other precious metals with them. 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.

eg.    $2 PbO + SiO_2 = Pb_2SiO_4$

$$Pb_2SiO_4 + 2 FeO + C = Fe_2SiO_4 + CO_2 + 2 Pb$$
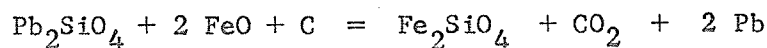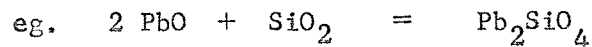
A basic flux such as soda, in addition to controlling the degree of acidity of the slag, aids in the process of desulfurization of an ore high in sulfur. This is desirable since sulfur from base metals has an extremely high reducing power and results in excessively large lead buttons.

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

$$Na_2CO_3 + SO_3 = Na_2SO_4 + CO_2$$
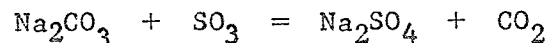
In those ores where the sulfur content is objectionably high it is sometimes necessary to add an oxidizing agent such as $KNO_3$. This method is the characteristic feature of the nitre assay.

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

$$4 FeS_2 + 10 KNO_3 = 4 FeO + 5 K_2SO_4 + 3 SO_2 + 5 N_2$$
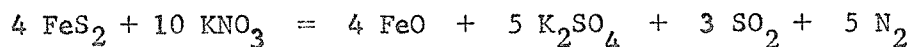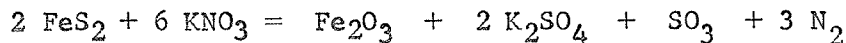
The evolution of gases ($CO_2$ and $N_2$) helps to stir the fusion mixture and enhances the extraction process on which the method depends. Too violent an evolution of these gases can lead to mechanical losses of precious metal.

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 $1700^0$F 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

which it has been rolled, the strength and number of acid treatments. It is also claimed that annealing of the flattened prill is vital if the concentration of silver retained is to be low and reproducible[15].

After decanting the parting acid, the gold residue is washed several times with hot water to get rid of any silver nitrate which undoubtedly remains in the pores of the gold. At this point the bead is soft and spongy and is easily broken if not handled with reasonable care. With incoherent beads this requirement is increased. The bead is then gently dried and annealed. The unannealed bead is black in color. The annealed bead attains the usual gold color associated with the metal and is ready for the final step of the process.

IV. Analysis

In the classical fire assay the analysis step involves the weighing of the annealed bead on a microbalance. It is assumed in the classical process that the final bead is pure gold or that the error due to incomplete parting is of no consequence. In fact there are compensating errors in the process which only rarely can be expected to offset each other. In more accurate work this problem is overcome by assaying standard samples along with the unknowns and applying an appropriate correction. The difference between the weight of parted bead and gold added to the standard sample is referred to as the surcharge.

In more recent times a modified or semi-classical variety of fire assay has evolved. In these the fusion and cupellation phases of the classical process are used with modifications introduced at the parting and analysis stage. In some cases parting is eliminated entirely, with the gold content of the prill being determined in the presence of the silver by such varied techniques as atomic absorption[28], spectrography[29],

neutron activation[26], and x-ray fluorescence[30]. Such a synthesis utilizing the advantages of the older classical techniques and those of the newer methods seems to be exemplary of the "fertile and useful areas of investigation" referred to above.

C. Gold Losses

The losses of gold during fire assaying can conceivably, arise in a variety of ways including the following:

1. Fusion losses due to:

    a. dusting and/or spattering,

    b. ad - and/or absorption of gold on the crucible,

    c. solubility of gold in the slag,

    d. volatilization of gold.

2. Cupellation losses due to:

    a. absorption of gold by the cupel,

    b. volatilization of gold.

3. Parting losses due to:

    a. solubility of gold in the parting acid,

    b. decanting of small particles of gold with the parting acid.

In point of fact not all the conceivable sources of loss have been demonstrated to be significant. According to Dewey[16] "...it is common to blame irregular assay results upon volatilization (of gold) but that there is no real evidence for a loss sufficient to appreciably affect the result in a properly conducted assay". In a more recent source[12] the loss of gold by volatilization is considered possible though the lack of direct evidence is conceded.

A similar situation arises with respect to solubility losses of gold in the parting acid. Again Dewey[17] points out that if there is any statement that is firmly established in the general chemical literature it is, that gold is not soluble in any single acid. In the literature of assaying, however, may be found various statements to the effect that, in parting gold from silver in assaying, gold may go into

solution in the nitric acid used. To resolve the discrepancy Dewey proceeds to demonstrate that in boiling concentrated acid (120°C) as much as 0.6 grams of gold will dissolve per liter. However, and this is the key point, the parting of gold from silver never occurs under such drastic conditions as were here used to demonstrate the solubility of gold. Thus it is possible to demonstrate a potential source of gold loss by employing conditions which no assayer would in fact employ. In the particular case cited Dewey goes on to agree with the practical conclusion of a previous study[17] "....that the solubility of gold in the parting acid in ordinary ore assaying is negligible...". In spite of this it is not uncommon to find references which give solubility of gold in the parting acid as a possible source of gold loss.

In a recent (1962) critical review of methods for the analysis of high purity gold bullion Finkelstein[12] lists a variety of studies relating to gold losses in the assay process. According to these sources, losses increase with the temperature of cupellation[18], with the quantity of lead added[2], and with the concentration of base metals added[2]. Silver is cited as having a protective effect on gold losses, while varying the nature of the cupel also affects the extent of loss[19]. All of these earlier studies are deficient, however, in that they omit essential details and in that in no investigation have all the significant variables been controlled[2]. In cupellation temperature studies for example, invariably the temperature reported is that of the muffle air, while the significant parameter is the temperature of the bead itself. While not readily obtainable, especially before the advent of the optical pyrometer, bead temperatures can vary considerably from the muffle air temperature since the oxidation of lead occurs exothermally. Thus the bead temperature depends on

the supply of oxygen as well as general air temperature. It is
commonly held that the increase in gold losses on cupellation depends
on lowering the viscosity of the gold. If so, this variable should
depend on bead, and not air temperature.

While much of the earlier work is suspect for the reasons given
above, several interesting studies of gold losses have been attempted
since then. In particular, a systematic study of gold losses was
undertaken to determine "the magnitude of systematic errors in the
standard fire assay for gold, under conditions prevailing in
representative assay laboratories on the Witwatersrand"[20]. They
report that under optimum conditions routine mine assays give values
about 2% low due to 0.5% gold loss to crucibles, slags, and button
dressing, 0.7% gold loss to the cupel, and 1.2% dilution by iron during
pulverizing. In this study radioactive gold was used to determine
these losses. Bead weights ranged from 0.5 to 8 mg. Unfortunately,
the extent of gold recovery in the fusion studies averaged only 96.69%
for 72 determinations. On the basis of a statistical study of their
results, the authors felt compelled to conclude that the radioactive
gold did not behave as the carrier gold from the ore. "The real
losses to slags and crucibles must therefore be considered to be
unknown".[20]

With regard to cupellation losses in the same study a different
problem arises. While the total recovery of radioactive gold
averaged 99.77% for 90 determinations one cannot     help but wonder
why the active gold should now begin to behave like carrier gold if
it did not do so in the fusion study. In both cases radioactive gold
was a gelatin stabilized colloidal gold suspension. Even if the radio
and carrier gold behaved similarly, an even more difficult problem remains.

In attempting to determine cupellation losses it is customary to accurately weigh out portions of high purity gold on a lead foil of approximately 25 g. To this is added sufficient silver to make parting feasible. The lead foil is then folded carefully to encase the silver and gold, and cupelled as the normal lead button one would have obtained from a fusion process. In this way one hopes to eliminate losses from the first stage of the overall fire assay and thereby obtain a measure of the cupellation and parting losses. The question now arises whether gold losses in such a simulated cupellation are the same as for the cupellation of a lead button in what must be close to a homogeneous lead button. In an attempt to overcome this problem Coxon et al[20] prepared an alloy button of the lead and gold. The method of **preparation** was not described. Most studies have not been concerned to even make this distinction and have generally assumed that cupellation losses measured from unalloyed buttons are valid estimates of the cupellation losses in the overall fire assay process.

A second study of interest was undertaken by Sinclair[21] in which it was pointed out that for samples requiring little pulverizing the 1.2% pulverizing error could be eliminated. Losses to slags , based on 132 residue fusions were 2.20%. Losses to cupels determined from 44 residue fusions were 0.52%. The silver retained by the parted bead was found to be 1.91%.

Since a sensitivity of $5.0 \times 10^{-12}$ g. has been reported using a neutron activation method[8] one would expect such a method to be particularly well suited for the determination of small gold losses in the fire assay process. Sensitivity notwithstanding, Kim et al[22] using a neutron activation method examined flux constituents, slags, pot walls, lead buttons, and cupels and found gold losses for the fire

assay to be negligible. While some gold was detected on the cupel amounts were reported as negligible. As Beamish and Van Loon[8] point out in their recent book, these results are difficult to explain. The problem is somewhat heightened since the neutron activation of the lead buttons produced by the fire assay, and the ore itself, indicates a gold content of 0.89 oz/ton and 0.90 oz/ton respectively. The single value of 0.84 oz/ton from a complete fire assay procedure indicates an appreciable error either in the fire assay or in the activation results.

Loss of gold in the fire assay was also studied by Shima[23]. The major loss of gold was reported as occuring during cupellation. From **autoradiographs** it was shown that the bulk of the cupel loss was at the point of contact between the prill and cupel. This was also found by Coxon et al[15]. The losses to the pot wall were found to be concentrated in the area "immediately above the fused lead-slag interface (ie. near the bottom of the pot) and extended over those regions wetted by the charge. No details were given regarding sampling, method of mixing tracer and sample, or even temperatures of fusion and cupellation. Again gold recovery was not quantitative and may indicate inadequate technique as suggested by Beamish and Van Loon[8].

At the microgram level very little has been done to establish the extent of gold recovery and gold losses. Chow[24] reported 97% recovery of gold for microgram size samples. Losses were not explicitly studied in this case. A spectrophotometric method was used for the determination of gold content in the silver bead.

A limited study[26] involving 0.1 and 0.5 mg. quantities of gold should be mentioned. A preliminary fusion of the flux materials removed any gold and silver into a lead button which was discarded.

The slag was reground, mixed with sufficient reducer and the gold and assayed to produce a carefully regulated size of lead button. This button was then irradiated before the addition of silver to reduce background due to $^{110}$Ag. After irradiation the silver was added in the form of lead wire containing 2.1% silver and cupelled together with the lead button. Gold recoveries ranged from 97.0 to 99.0%. Cupel losses ranged from 1.5% to 0.5%, and slag losses from 1.5 to 0.3%. Fusion temperature was maintained at 900 - 1000°C for 1 hour intervals. Cupellation temperatures were not reported. The total recovery of gold was exactly 100.0% in each of the seven samples examined. Perhaps as a result, crucibles were not even counted.

At the nanogram level a very extensive study of a variety of noble metals has been reported by Beyermann[25]. While the bulk of the study dealt with the other noble metals, some interesting results were reported for gold as well. Parting losses of 0.4% and 0.8% were reported using 50% v/v sulfuric acid on gold-silver beads containing 1.0% and 0.005% gold. Recoveries of gold from feldspar, galena and roasted ore were 100%, 92%, and 94% respectively. Also of interest is the reported coprecipitation of 10% and 2% of the gold in a solution containing 2 micrograms and 2 mg. of gold **respectively, from which 5 mg. silver was precipitated.**

In view of the contradictory statements found in the literature, it was considered desirable to attempt to shed some light on the matter by studying gold losses under a variety of conditions using synthetic gold ores. In the process it was hoped that the optimum conditions and procedures could be determined as well as obtaining a direct measure of the gold losses in the various stages of the complete

fire assay process. In such a manner a comparison of the losses determined directly, could be made to the losses **determined by difference** from the extent of recovery. The methods developed were then to be tested on an actual ore or ores.

D. Experimental, Results and Discussion

I. Equipment and Reagents

1. Apparatus

    Lindberg Hevi-Duty 20 KW electric furnace.

    Perkin Elmer 306 Atomic Absorption Spectrophotometer

    Unicam SP 90 Atomic Absorption Spectrophotometer

    Unicam SP 500 Ultra-Violet-Visible Spectrophotometer

    Baird Atomic Sodium Iodide Scintillation Counter

    Epic Inc. Optix Universal Optical Pyrometer

    Sartorius Type 1802 Microbalance

    Ohaus Harvard trip balance

    Magnesia Cupels produced by Leonard Light Industries
    (Benoni, South Africa)

    Crucibles produced by A.P. Green Refractories
    (Western Ontario, Canada)

2. Reagents

    Gold, unfluxed powder (Johnson Matthey & Mallory)

    Silver, precipitated powder (Johnson Matthey & Mallory)

    Lead, 0.004" foil (Matheson Coleman & Bell)

    Silica, about 240 mesh floated powder (Fisher)

    Calcium oxide, Baker analyzed reagent (Canlab)

    Sodium carbonate, Baker analyzed reagent (Canlab)

    Litharge, Baker Analyzed reagent (Canlab)

    Litharge, Anachemia reagent grade (Robson)

All acids used were Baker analyzed reagent except hydrobromic acid which was the colorless fraction obtained by distillation of the reagent grade acid.

3. Standard Solutions

    Gold: Approximately 2 grams of the metal were dissolved in aqua

regia. Nitrous oxides were removed by repeated evaporations with hydrochloric in the presence of some sodium chloride. The solution was diluted to 1 l. by addition of 0.1N HCl and standardized using the hydroquinone method according to Beamish, Seath and Russell[31]. Dilute gold solutions were obtained by dilution with 0.1N HCl. For atomic absorption standards the matrix was matched with the sample.

Silver: A stock solution containing 1000 p.p.m. of silver was prepared by accurately weighing out 1.0 gram of the silver powder, dissolving in sufficient $HNO_3$ to make a 1 l. volume approximately 0.1N in $HNO_3$. Dilute silver solutions were obtained by dilution with 0.1N $HNO_3$. For atomic absorption standards the matrix was matched with the sample.

Lead: A stock solution containing 100.3 p.p.m. of lead was prepared by accurately weighing 100.3 mg. of lead foil. The lead was dissolved in 20 ml. 5M $HNO_3$ by heating on a steam bath for several hours. Dilution to 1 l. was made using 0.1M $HNO_3$ yielding a stock solution 0.2M in $HNO_3$ and 100.3 p.p.m. lead. Dilute lead solutions were made from the stock. For atomic absorption standards the matrix was matched with the sample.

II. General Considerations

1. Rejection of discordant results

Discordant results were rejected for a variety of reasons. Whenever an experimental source of error was noticed samples were rejected. Frozen or sprouted beads are examples. In addition careless pouring of the fused charge sometimes resulted in some of the lead phase being physically trapped in the slag. Whenever beads of lead phase were observed in the slag, the samples were rejected. More rarely the cupelled molten beads rolled off the cupel in the process of handling

with the cupel tongs. Such beads were simply lost. Finally, in those cases where no experimental reason for rejection of a discordant result was known, a statistical basis for rejection was applied. In all such cases rejection was always made at the 95% confidence level.

## 2. Weighing procedure

In order to determine the weight of the initial gold taken for analysis and the final weight of parted bead, weighings were made on a microbalance to the nearest microgram. To obtain reproducible results a standard procedure for making weighings had to be adopted. To illustrate, consider the weighing of a typical parted bead. To begin a series of weighings the door was opened and the pan cleaned with a camel's hair brush. The door was then closed; 25 seconds were counted off; the pans were released, and the zero adjusted at the end of a second 25 second interval. The pans were then arrested; the door opened; the bead placed on the pan and the same procedure repeated as for zeroing except that at the end of the second counting interval the weight was read off. To check the procedure a 60 mg. gold bead was weighed ten times in succession. The average weight was 60.313 mg. with an average deviation of 1.4 microgram and a range of 6 micrograms. While the balance had been calibrated and corrections were always applied, the weight of gold taken was controlled so that the same weights could be used for the initial and final weighings of the gold. In this way it was hoped to reduce variations in the gold loss due to calibration drift from day to day.

## III. Cupellation and Parting Losses

### Introduction

In an attempt to eliminate gold losses normally incurred in the fusion stage of the fire assay a series of experiments were conducted

utilizing an abbreviated fire assay which has been described above as a 'simulated cupellation'. That is, gold and silver powder were accurately weighed out onto a lead foil, carefully folded to encase the two in the lead, and then cupelled. The folded lead formed a cube of approximately 3/4" dimensions for 25 g. lead. Only as a consequence of subsequent studies was the validity of this procedure called into question. In any case, the results indicate how that conclusion was reached. Furthermore, in gold bullion analysis the fusion step is in fact by-passed so that cupellation losses of what is here referred to as a simulated cupellation would be comparable to cupellation losses in bullion analysis.

All cupellations were conducted in the same manner. The magnesia cupels were preheated in the furnace at the temperature used for cupellation. Unless noted otherwise the temperature of cupellation was 1800°F (982°C). The lead buttons prepared as indicated above were added to the cupels as quickly as possible to prevent an excessive temperature drop. After an initial heating interval of five minutes with the draft and door closed the lead was molten and both draft and door were opened. The door opening was controlled by placing a 1/4" steel plate under the door. The draft was always opened to the same extent by pulling a lever to a constant marker. The resulting flow of air caused the muffle air temperature to drop approximately 30-50°F. Under these conditions the driving of the lead occurred at a rate of approximately 1 gram per minute. Thus a 20 gram button would require a 20 minute driving period. The temperature of the driving button taken after 5 minutes into the driving stage corresponded very closely to the initial temperature of cupellation. The temperature of the

driving bead was obtained with an optical pyrometer previously compared
with a dual junction thermocouple. The hot junction was placed well
into the furnace near the cupel at which the optical pyrometer had
been focused, while the cold end was immersed in an ice bath. Temperature
readings by the two methods differed by less than $10^{o}F$. After the
driving stage was completed, the door (air supply) was closed and the
cupellation finished by heating for a final 5 minutes. Closing the
door caused the muffle air temperature to increase and ensured
essentially complete removal of the lead from the silver-gold beads.
A determination of the lead content of a series of such beads indicated
an average lead residue of 1.4 micrograms. Since the majority of
beads weighed were of the order of 20 mg. this error was taken to be
of no consequence and was not corrected for.

After the cupellation was complete, the door was opened and the
cupels withdrawn slowly in two stages so as to prevent sprouting.
After an initial cooling period of about 1 minute, the cupels were
moved to the furnace door where the buttons were allowed to solidify.
In the vast majority of beads observed the characteristic "blick" of
a lead free bead was seen. The beads were then allowed to cool for
one hour, removed from the cupels and weighed. In the earlier
experiments, the beads were cleaned of cupel material by scraping with
a platinum spatula prior to weighing.

A blank determination for gold content of the silver powder and
25 grams of lead foil indicated no detectable gold in 4 replicate
samples. The modified bromaurate spectrophotometric method of Chow and
Beamish[32] was used. In view of the conditions used this meant an
upper limit of 10 micrograms of gold could be set. In view of a similar
blank determination[24] utilizing longer cells and reported to be **1microgram,**

the blank again was ignored for the more than 20 mg. samples of gold.
Errors thus introduced would be at most 0.05% and probably more like
.005%. Since determination of the gold loss involved measurement of
the silver content at the 1-2% accuracy level this procedure would
appear to be justified.

1. Effect of Lead Weight on Cupellation Losses of Gold

In order to study the effect of lead weight on the cupellation loss twelve pieces of lead foil (.004") were cut for each weight to be considered. The first series of lead buttons of 6, 12, 18 and 24 grams was cupelled on 30 gram magnesia cupels. The second series of 24, 32 and 40 grams was cupelled on 40 gram cupels. In each case approximately 20-30 mgs. of gold was taken with about three to four times as much silver. With such a silver to gold ratio a one hour parting treatment at steam bath temperatures with 10 ml. of 1:2 nitric acid (acid:water) was required to obtain an adequate removal of silver. The parted bead was washed three times with hot water, annealed over a bunsen burner, and weighed. In almost all cases the parted bead weighed more than the gold added in the first place. In addition, this difference, or surcharge, varied considerably from sample to sample. In view of the foregoing and the claim reported by Coxon[20] that significant amounts of silver are retained by the parted beads it was deemed necessary to analyse each parted bead for silver content.

To do this, the parted bead was dissolved in 3 ml. aqua regia with gentle heating. The beads reacted immediately and dissolved completely within the one hour digestion period normally allowed. Sufficient concentrated hydrochloric acid was added to completely complex all of the silver, followed by dilution to an appropriate volume so that the silver concentration would be between 2-10 p.p.m. In this region the atomic absorption calibration curve was linear. Standards were made up with the stock silver solution (above), and the matrix was matched with the samples. The weight of silver found was then deducted from the weight of the parted bead to yield the weight of gold found or recovered. The difference between gold added and found, represented

the gold loss. The results of both series of experiments (30 and 40 g. cupels) are found in Table I. From them it can be seen that the gold recovery varied from 99.37-99.39% for 30 gram cupels (first four pages of the table) and varied from 99.37-99.44% for 40 gram cupels (last three pages of the table). This represents a range of about 7 parts in 10,000 for all trials.

To test whether there were any significant differences between the trials a test of significance was applied. A comparison of the results for 30 g. cupels indicated no significant difference at the 99% confidence level. Similarly for the experiments using 40 g. cupels no significant difference was observed. A grouping of all experiments using 30 g. cupels led to an average value which was compared to a grouping of the results with 40 g. cupels. Again at the 99% confidence level there was no significant difference. As a result all values of the gold loss could be grouped together giving an overall average gold loss of 0.61% with a standard deviation of 0.08%. Expressed as a gold recovery, this would be a 99.39% gold recovery.

From the foregoing it would appear that losses of gold in the simulated cupellation do not vary significantly as a function of lead weight used over the range of 6-40 grams, at the confidence level indicated.

It should be pointed out that for one trial, using 12 grams of lead, the loss of gold was found to be anomolously high at 1.18% with a correspondingly high standard deviation of 0.65%. No experimental reason was known. This trial varied significantly from all the other trials at the 99% confidence level, and therefore was rejected and repeated. The repeat is reported in Table I. A summary of all the results for this study is found in Table II.

TABLE I

Effect of Lead Weight On Cupellation

Losses of Gold

| Pb Weight (g.) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 6.02 | 19.401 | 65.0 | 83.9 | 19.430 | 0.029 | 0.185 | 19.245 | 0.156 | 0.80 |
| 6.02 | 19.770 | 59.2 | 78.7 | 19.884 | 0.114 | 0.218 | 19.666 | 0.104 | 0.53 |
| 6.02 | 25.550 | 71.3 | 96.4 | 25.702 | 0.152 | 0.290 | 25.412 | 0.138 | 0.61 |
| 6.03 | 22.610 | 63.9 | 85.8 | 22.745 | 0.135 | 0.268 | 22.477 | 0.133 | 0.59 |
| 6.02 | 20.765 | 64.6 | 84.8 | 20.868 | 0.103 | 0.231 | 20.638 | 0.127 | 0.61 |
| 6.01 | 24.333 | 75.3 | 99.2 | 24.483 | 0.150 | 0.264 | 24.219 | 0.114 | 0.47 |
| 6.02 | 18.051 | 57.4 | 74.7 | 18.094 | 0.043 | 0.155 | 17.939 | 0.112 | 0.62 |
| 6.03 | 19.270 | 57.4 | 76.1 | 19.364 | 0.094 | 0.205 | 19.159 | 0.111 | 0.58 |
| 6.02 | 23.429 | 60.4 | 83.5 | 23.486 | 0.057 | 0.193 | 23.293 | 0.136 | 0.58 |
| 6.01 | 24.296 | 76.1 | 99.4 | 24.255 | -0.041 | 0.161 | 24.094 | 0.202 | 0.83 |
| 6.03 | 21.681 | 65.2 | 85.6 | 21.678 | -0.003 | 0.130 | 21.548 | 0.133 | 0.61 |
| 6.03 | 25.629 | 83.1 | 107.6 | 25.682 | 0.053 | 0.185 | 25.497 | 0.132 | 0.52 |

Average Gold Recovery 99.39%

Average % Loss 0.61%

s = 0.10

| Pb Weight (g.) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 11.97 | 20.062 | 59.5 | 78.5 | 21.293 | 0.231 | 0.351 | 20.942 | *-0.860 | ---- |
| 11.99 | 25.446 | 82.9 | 106.7 | 25.645 | 0.199 | 0.392 | 25.253 | 0.193 | 0.76 |
| 11.97 | 21.745 | 65.4 | 85.8 | 21.953 | 0.208 | 0.341 | 21.612 | 0.133 | 0.61 |
| 12.00 | 30.247 | 106.1 | 134.5 | 30.474 | 0.227 | 0.450 | 30.024 | 0.223 | 0.74 |
| 11.99 | 30.810 | 86.2 | 115.2 | 31.223 | 0.413 | 0.543 | 30.680 | 0.130 | 0.42 |
| 11.98 | 27.815 | 96.3 | 122.4 | 27.962 | 0.047 | 0.321 | 27.641 | 0.174 | 0.63 |
| 11.99 | 23.984 | 90.5 | 112.4 | 24.093 | 0.109 | 0.276 | 23.817 | 0.167 | 0.70 |
| 11.98 | 26.199 | 72.5 | 97.1 | 26.576 | 0.377 | 0.540 | 26.036 | 0.163 | 0.62 |
| 11.99 | 19.718 | 56.7 | 75.1 | 19.817 | 0.099 | 0.234 | 19.583 | 0.135 | 0.68 |
| 11.99 | 19.412 | 54.2 | 72.6 | 19.501 | 0.089 | 0.251 | 19.250 | 0.162 | 0.84 |
| 11.98 | 22.040 | 74.4 | 94.9 | 22.145 | 0.105 | 0.204 | 21.941 | 0.099 | 0.45 |
| 11.98 | 18.922 | 52.5 | 70.4 | 19.110 | 0.188 | 0.278 | 18.832 | 0.090 | 0.48 |

Average Gold Recovery = 99.37%    Average % Loss = 0.63

s = 0.13

* rejected on statistical grounds

| Pb Weight (g.) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 18.01 | 25.966 | 97.3 | 121.9 | 26.078 | 0.112 | 0.252 | 25.827 | 0.139 | 0.54 |
| 18.00 | 29.817 | 82.3 | 111.0 | 30.012 | 0.195 | 0.385 | 29.627 | 0.190 | 0.64 |
| 18.02 | 19.051 | 70.9 | 89.2 | 19.137 | 0.086 | 0.202 | 18.935 | 0.116 | 0.61 |
| 18.00 | 23.607 | 67.1 | 90.0 | 23.778 | 0.171 | 0.305 | 23.473 | 0.134 | 0.57 |
| 18.01 | 18.888 | 59.2 | 77.5 | 18.909 | 0.021 | 0.155 | 18.754 | 0.134 | 0.71 |
| 18.00 | 23.166 | 65.5 | 87.5 | 23.247 | 0.081 | 0.220 | 23.027 | 0.139 | 0.60 |
| 18.02 | 23.445 | 78.2 | 100.8 | 23.544 | 0.099 | 0.248 | 23.296 | 0.149 | 0.63 |
| 18.01 | 24.106 | 66.0 | 90.0 | 24.287 | 0.181 | 0.310 | 23.970 | 0.136 | 0.56 |
| 18.02 | 18.063 | 54.5 | 72.3 | 18.042 | -0.021 | 0.118 | 17.924 | 0.139 | 0.77 |
| 18.01 | 20.772 | 61.6 | 81.8 | 20.789 | 0.017 | 0.147 | 20.642 | 0.130 | 0.65 |
| 18.00 | 31.644 | 92.3 | 122.5 | 31.755 | 0.111 | 0.278 | 31.477 | 0.167 | 0.53 |
| 17.98 | 24.785 | 67.7 | 92.0 | 24.864 | 0.079 | 0.251 | 24.613 | 0.172 | 0.69 |

Average Gold Recovery = 99.37%

Average % Loss = 0.63

s = 0.07

| Pb Weight (g.) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 23.99 | 35.773 | 112.8 | 137.0 | 35.960 | 0.187 | 0.389 | 35.571 | 0.202 | 0.56 |
| 24.02 | 20.572 | 67.1 | 86.9 | 20.647 | 0.075 | 0.219 | 20.428 | 0.144 | 0.70 |
| 24.02 | 20.804 | 76.8 | 96.6 | 20.875 | 0.071 | 0.202 | 20.673 | 0.131 | 0.63 |
| 23.86 | 25.435 | 77.6 | 102.1 | 25.551 | 0.116 | 0.276 | 25.275 | 0.160 | 0.63 |
| 24.02 | 24.705 | 74.0 | 97.9 | 24.810 | 0.105 | 0.247 | 24.563 | 0.142 | 0.58 |
| 24.02 | 25.302 | 59.8 | 84.2 | 25.409 | 0.107 | 0.284 | 25.125 | 0.177 | 0.70 |
| 24.02 | 25.142 | 71.4 | 95.7 | 25.243 | 0.101 | 0.244 | 24.999 | 0.143 | 0.57 |
| 24.02 | 21.460 | 67.5 | 88.3 | 21.562 | 0.102 | 0.222 | 21.340 | 0.120 | 0.56 |
| 23.97 | 20.906 | 57.6 | 78.0 | 20.929 | 0.023 | 0.153 | 20.776 | 0.130 | 0.62 |
| 23.99 | 20.768 | 64.5 | 84.4 | 20.775 | 0.007 | 0.137 | 20.638 | 0.130 | 0.62 |
| 24.01 | 18.360 | 59.1 | 77.5 | 18.363 | 0.003 | 0.131 | 19.232 | 0.128 | 0.66 |
| 24.03 | 21.334 | 62.5 | 83.3 | 21.376 | 0.042 | 0.162 | 21.214 | 0.120 | 0.56 |

Average Gold Recovery = 99.38%          Average % Loss = 0.62

s = 0.05

| Pb Weight (g.) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 24.00 | 27.602 | 83.2 | 110.7 | 27.748 | 0.146 | 0.437 | 27.311 | 0.291 | 1.05 |
| 24.03 | 22.283 | 61.7 | 84.2 | 22.579 | 0.295 | 0.412 | 22.167 | 0.116 | 0.52 |
| 23.99 | 26.647 | 76.6 | 102.7 | 26.912 | 0.265 | 0.421 | 26.491 | 0.156 | 0.59 |
| 24.03 | 21.044 | 73.3 | 93.6 | 21.152 | 0.108 | 0.241 | 20.911 | 0.133 | 0.63 |
| 23.98 | 22.544 | 70.1 | 92.4 | 22.698 | 0.154 | 0.278 | 22.420 | 0.124 | 0.55 |
| 24.00 | 22.909 | 61.1 | 83.6 | 23.260 | 0.351 | 0.448 | 22.812 | 0.097 | 0.42 |
| 23.99 | 22.061 | 74.2 | 95.2 | 22.185 | 0.124 | 0.262 | 21.923 | 0.138 | 0.69 |
| 23.99 | 22.384 | 80.8 | 102.5 | 22.503 | 0.119 | 0.247 | 22.256 | 0.128 | 0.57 |
| 24.00 | 25.104 | 101.4 | 125.4 | 25.152 | 0.048 | 0.205 | 24.947 | 0.157 | 0.63 |
| 23.99 | 22.036 | 82.6 | 105.3 | 22.090 | 0.064 | 0.185 | 21.905 | 0.131 | 0.55 |
| 23.98 | 19.945 | 59.7 | 79.2 | 20.013 | 0.068 | 0.210 | 19.803 | 0.142 | 0.71 |
| 23.98 | 24.851 | 69.4 | 103.2 | 25.008 | 0.157 | 0.318 | 24.690 | 0.161 | 0.65 |

Average % Loss = 0.59

s = 0.08

Average Gold Recovery = 99.41%

| Pb Weight (g.) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 32.09 | 29.326 | 141.2 | 169.1 | 29.416 | 0.090 | 0.261 | 29.155 | 0.171 | 0.58 |
| 32.05 | 20.039 | 61.1 | 81.2 | 20.125 | 0.086 | 0.197 | 19.928 | 0.111 | 0.55 |
| 31.96 | 22.563 | 72.0 | 94.5 | 22.656 | 0.093 | 0.224 | 22.432 | 0.131 | 0.58 |
| 32.03 | 26.077 | 71.2 | 96.9 | 26.192 | 0.115 | 0.274 | 25.918 | 0.159 | 0.61 |
| 31.98 | 20.826 | 69.6 | 90.1 | 20.853 | 0.027 | 0.171 | 20.682 | 0.144 | 0.69 |
| 32.02 | 21.719 | 70.2 | 91.6 | 21.880 | 0.161 | 0.206 | 21.674 | 0.045 | 0.21* |
| 32.02 | 32.903 | 88.0 | 120.5 | 33.066 | 0.163 | 0.346 | 32.720 | 0.183 | 0.56 |
| 32.00 | 17.484 | 51.4 | 69.6 | 17.524 | 0.040 | 0.165 | 17.359 | 0.125 | 0.72 |
| 32.02 | 22.009 | 83.0 | 104.8 | 22.038 | 0.029 | 0.136 | 21.902 | 0.107 | 0.49 |
| 32.02 | 18.410 | 66.4 | 84.7 | 18.374 | -0.036 | 0.090 | 18.280 | 0.130 | 0.71 |
| 31.99 | 18.429 | 54.5 | 73.7 | 18.424 | -0.005 | 0.132 | 18.292 | 0.137 | 0.74 |
| 31.88 | 21.220 | 65.9 | 87.2 | 21.285 | 0.065 | 0.212 | 21.073 | 0.147 | 0.69 |

Average Gold Recovery = 99.37%        Average % Loss = 0.63

s = 0.08

* rejected on statistical grounds

| Pb Weight (g.) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 39.97 | 21.711 | 69.8 | 91.6 | 21.805 | 0.094 | 0.096 | 21.709 | 0.002 | 0.01* |
| 39.99 | 19.437 | 58.8 | 78.6 | 19.517 | 0.080 | 0.168 | 19.349 | 0.088 | 0.45 |
| 39.98 | 29.870 | 102.0 | 131.4 | 29.983 | 0.113 | 0.308 | 29.675 | 0.195 | 0.65 |
| 40.01 | 27.300 | 96.6 | 123.6 | 27.403 | 0.103 | 0.238 | 27.165 | 0.135 | 0.49 |
| 40.01 | 23.917 | 61.8 | 85.8 | 24.116 | 0.199 | 0.346 | 23.770 | 0.147 | 0.61 |
| 39.96 | 22.022 | 68.9 | 91.1 | 22.137 | 0.115 | 0.248 | 21.889 | 0.133 | 0.60 |
| 39.99 | 24.164 | 69.6 | 93.9 | 24.332 | 0.168 | 0.288 | 24.044 | 0.120 | 0.50 |
| 40.00 | 23.030 | 67.0 | 90.4 | 23.172 | 0.142 | 0.269 | 22.903 | 0.127 | 0.55 |
| 39.95 | 24.559 | 76.6 | 101.1 | 24.612 | 0.053 | 0.199 | 24.413 | 0.146 | 0.59 |
| 40.00 | 18.735 | 73.1 | 92.2 | 18.728 | -0.007 | 0.111 | 18.617 | 0.118 | 0.63 |
| 39.98 | 25.102 | 91.4 | 116.2 | 25.151 | 0.049 | 0.228 | 24.923 | 0.179 | 0.71 |
| 40.00 | 27.661 | 76.2 | 103.7 | 27.818 | 0.157 | 0.362 | 27.456 | 0.105 | 0.38 |

Average Gold Recovery = 99.44%

Average % Loss = 0.56

s = 0.10

* rejected on statistical grounds

## TABLE II

### Summary of Effect of Lead Weight On

### Cupellation Losses of Gold

| Weight Lead | Au Loss % | S | | |
|---|---|---|---|---|
| 6.0 grams | 0.61 | 0.10 | | |
| 12.0 | 0.63 | 0.13 | 30 g. cupels | |
| 18.0 | 0.63 | 0.07 | Average Au Loss % = 0.62 | |
| 24.0 | 0.62 | 0.05 | | s = 0.08 |
| 24.0 | 0.59 | 0.08 | 40 g. cupels | |
| 32.0 | 0.63 | 0.08 | Average Au Loss % = 0.59 | |
| 40.0 | 0.56 | 0.10 | | s = 0.09 |

Overall Average Au Loss % = 0.61

s = 0.08

2. Effect of Silver to Gold Ratio on Cupellation Losses of Gold

The objective of this study was to see how gold losses would vary during cupellation as a result of varying the silver to gold ratio. In theory this can be accomplished by increasing the amount of silver, or by decreasing the amount of gold or both. In practise decreasing the amount of gold is limited by the weighing error whereas increasing the amount of silver is limited by the capacity of the parting acid to dissolve it. For convenience the study was begun with a series of samples containing about 20 mg. gold and ten times as much silver. A second trial containing about 5 mg. gold and ten times as much silver was compared to the first to see whether the quantity of gold had any significant effect. Two more trials followed in which the silver to gold ratio was increased to 20:1.0 and 30:1. keeping the gold weight approximately constant at 5 mg. To enhance the tendency of the parted beads to remain coherent, thereby reducing mechanical losses, a more dilute parting acid was used. In all cases 6 ml. 1:6 nitric (acid: water) was used with a 1 hour digestion period of the beads at steam bath temperatures. The residue was washed three times with hot water, annealed, and weighed on the microbalance. The silver content of the parted bead was determined in the standard way outlined in the previous study.

In order to reduce the silver retained, the beads obtained from the cupellation process were flattened on a hydraulic press prior to parting. While a later study indicated that this effect is achieved to some extent, the effect of using a more dilute parting acid more than offsets the effect of a reduction in thickness. Thus the silver retained in this study averaged 1.46% as compared to an average of 1.07% in the previous study. A later study showed that the temperature

of the parting acid had an important bearing on this factor.

The detailed results of this study are to be found in Table III with a summary in Table IV. A comparison of the first two trials of constant silver to gold ratio (10:1) and varying gold weight indicates no significant difference due to gold weight at the 99% confidence level. A comparison of the remaining three trials at constant gold weight (5 mg.) and varying silver to gold ratio indicates a minimum gold loss for a maximum silver to gold ratio but no consistent pattern emerges with no significant differences at the usual confidence level of 99%.

Thus it seems safe to conclude that there is no significant effect on gold losses during cupellation and parting as a result of varying the silver to gold ratio from 10-30:1.0.

While no experiments were conducted at silver to gold ratios less than 10:1 the overall average gold loss of 0.61% for this complete study is identical with the gold losses for the previous study where the silver to gold ratio was in the range of about 3.5:1.0. This inspite of a much stronger (1:2) parting acid in the latter case.

Since silver to gold ratios lower than 2.5:1.0 are not recommended in the literature, there seemed no point in extending this study beyond the above. The average gold recovery ranged from 99.32-99.43%, a difference of only 1 part per thousand.

3. Effect of Parting Procedure On Gold Losses

In this study all the samples were cupelled with 4" x 6" x .004" lead foil. Since lead weight had been demonstrated to have no effect on gold losses, variations in lead weight were of no consequence. Thus the weight chosen was an arbitrary choice somewhere within the range

**TABLE III**

Effect of Silver to Gold Ratio on Cupellation

Losses of Gold

| Ag:Au | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 11.0:1.0 | 18.901 | 207.8 | 223.2 | 19.167 | 0.266 | 0.355 | 18.812 | 0.089 | 0.47 |
| 10.0:1.0 | 21.065 | 210.2 | 227.4 | 21.299 | 0.234 | 0.373 | 20.926 | 0.139 | 0.66 |
| 9.9:1.0 | 20.700 | 205.4 | 222.6 | 20.996 | 0.296 | 0.362 | 20.634 | 0.066 | 0.32 |
| 10.0:1.0 | 19.620 | 196.8 | 212.8 | 19.837 | 0.217 | 0.332 | 19.505 | 0.115 | 0.59 |
| 10.1:1.0 | 18.833 | 190.2 | 205.8 | 19.135 | 0.302 | 0.315 | 18.820 | 0.013 | 0.07* |
| 10.1:1.0 | 20.444 | 206.0 | 222.9 | 20.708 | 0.279 | 0.368 | 20.340 | 0.104 | 0.51 |
| 10.1:1.0 | 19.407 | 196.5 | 212.6 | 19.612 | 0.205 | 0.318 | 19.294 | 0.113 | 0.58 |
| 10.0:1.0 | 19.626 | 196.8 | 213.0 | 19.837 | 0.211 | 0.389 | 19.448 | 0.178 | 0.91 |
| 10.0:1.0 | 21.344 | 213.8 | 232.0 | 21.593 | 0.249 | 0.366 | 21.227 | 0.117 | 0.55 |
| 9.9:1.0 | 20.356 | 200.5 | 218.4 | 20.631 | 0.275 | 0.417 | 20.214 | 0.142 | 0.70 |
| 9.9:1.0 | 22.105 | 217.9 | 236.7 | 22.412 | 0.307 | 0.449 | 21.963 | 0.042 | 0.19* |
| 10.0:1.0 | 19.385 | 195.0 | 211.8 | 19.618 | 0.233 | 0.321 | 19.297 | 0.088 | 0.45 |

Average Au Loss % = 0.57

s = 0.16

* rejected on statistical grounds

| Ag:Au | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 10.0:1.0 | 5.221 | 52.3 | 56.6 | 5.278 | 0.057 | 0.072 | 5.206 | 0.015 | 0.29* |
| 10.1:1.0 | 4.825 | 48.7 | 53.0 | 4.853 | 0.028 | 0.057 | 4.796 | 0.029 | 0.60 |
| 10.2:1.0 | 4.820 | 49.1 | 53.1 | 4.846 | 0.026 | 0.059 | 4.787 | 0.033 | 0.68 |
| 10.0:1.0 | 5.587 | 55.9 | 60.4 | 5.618 | 0.031 | 0.069 | 5.549 | 0.038 | 0.68 |
| 10.0:1.0 | 4.828 | 48.1 | 50.9 | 4.849 | 0.021 | 0.058 | 4.791 | 0.037 | 0.77 |
| 10.0:1.0 | 5.710 | 57.0 | 61.4 | 5.747 | 0.037 | 0.069 | 5.678 | 0.032 | 0.56 |
| 10.3:1.0 | 5.184 | 53.1 | 57.1 | 5.226 | 0.042 | 0.069 | 5.157 | 0.027 | 0.52 |
| 10.1:1.0 | 5.031 | 50.9 | 55.1 | 5.066 | 0.035 | 0.065 | 5.001 | 0.031 | 0.62 |
| 9.9:1.0 | 4.824 | 47.8 | 51.8 | 4.852 | 0.028 | 0.055 | 4.797 | 0.027 | 0.58 |
| 10.2:1.0 | 4.935 | 50.2 | 54.2 | 4.969 | 0.034 | 0.066 | 4.903 | 0.032 | 0.65 |
| 10.0:1.0 | 5.517 | 55.5 | 60.1 | 5.563 | 0.046 | 0.077 | 5.486 | 0.031 | 0.56 |
| 10.0:1.0 | 5.125 | 51.2 | 55.3 | 5.166 | 0.041 | 0.068 | 5.098 | 0.027 | 0.55 |

Average Au Loss % = 0.62

s = 0.07

* rejected on statistical grounds

| Ag:Au | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 20.0:1.0 | 5.854 | 117.7 | 121.5 | 5.886 | 0.032 | 0.112 | 5.854 | 0.080 | 1.37* |
| 20.0:1.0 | 4.825 | 96.2 | 99.4 | 4.861 | 0.036 | 0.071 | 4.790 | 0.035 | 0.73 |
| 18.3:1.0 | 4.987 | 91.4 | 95.0 | 5.029 | 0.042 | 0.074 | 4.955 | 0.032 | 0.64 |
| 20.0:1.0 | 5.243 | 104.6 | 107.9 | 5.290 | 0.047 | 0.087 | 5.203 | 0.040 | 0.76 |
| 20.0:1.0 | 5.147 | 103.1 | 106.4 | 5.172 | 0.025 | 0.076 | 5.096 | 0.049 | 0.95 |
| 20.1:1.0 | 4.918 | 99.1 | 102.6 | 4.960 | 0.042 | 0.072 | 4.888 | 0.030 | 0.61 |
| 19.9:1.0 | 4.926 | 98.1 | 101.4 | 4.979 | 0.053 | 0.075 | 4.904 | 0.022 | 0.45 |
| 20.0:1.0 | 4.875 | 97.4 | 101.3 | 4.926 | 0.051 | 0.078 | 4.848 | 0.027 | 0.55 |
| 20.0:1.0 | 5.139 | 102.1 | 105.6 | 5.188 | 0.049 | 0.085 | 5.103 | 0.036 | 0.70 |
| 20.0:1.0 | 4.943 | 98.6 | 102.2 | 4.990 | 0.047 | 0.077 | 4.913 | 0.030 | 0.61 |
| 20.1:1.0 | 5.048 | 101.3 | 104.9 | 5.088 | 0.040 | 0.077 | 5.011 | 0.037 | 0.73 |
| 19.9:1.0 | 4.850 | 96.7 | 100.4 | 4.900 | 0.050 | 0.088 | 4.812 | 0.038 | 0.78 |

Average Au Loss % = 0.68

s = 0.13

* rejected on statistical grounds

| Ag:Au | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 30.2:1.0 | 4.964 | 149.9 | 152.1 | 4.995 | 0.031 | 0.057 | 4.938 | 0.026 | 0.53 |
| 28.0:1.0 | 5.525 | 154.1 | 156.5 | 5.548 | 0.023 | 0.064 | 5.484 | 0.041 | 0.74 |
| 30.0:1.0 | 5.051 | 151.8 | 154.1 | 5.073 | 0.022 | 0.054 | 5.019 | 0.032 | 0.63 |
| 32.5:1.0 | 6.395 | 202.2 | 204.7 | 6.435 | 0.040 | 0.077 | 6.358 | 0.037 | 0.58 |
| 30.2:1.0 | 5.055 | 152.7 | 154.9 | 5.087 | 0.032 | 0.055 | 5.032 | 0.023 | 0.46 |
| 30.0:1.0 | 5.862 | 176.5 | 179.6 | 5.887 | 0.025 | 0.069 | 5.818 | 0.044 | 0.76 |
| 30.0:1.0 | 4.851 | 145.5 | 147.8 | 4.882 | 0.020 | 0.054 | 4.828 | 0.023 | 0.48 |
| 30.1:1.0 | 5.279 | 159.0 | 161.6 | 5.309 | 0.030 | 0.061 | 5.248 | 0.031 | 0.59 |
| 30.0:1.0 | 4.833 | 145.1 | 147.3 | 4.856 | 0.023 | 0.058 | 4.798 | 0.035 | 0.73 |
| 30.0:1.0 | 6.206 | 186.9 | 190.6 | 6.259 | 0.053 | 0.078 | 6.181 | 0.025 | 0.40 |
| 29.9:1.0 | 6.816 | 204.3 | 208.0 | 6.857 | 0.041 | 0.084 | 6.773 | 0.043 | 0.63 |
| 29.9:1.0 | 5.330 | 159.3 | 162.1 | 5.360 | 0.030 | 0.061 | 5.299 | 0.031 | 0.58 |

Average Au Loss % = 0.59

s = 0.11

## TABLE IV

### Summary of Silver to Gold Ratio Effect

### On Cupellation Losses of Gold

| Au Added (mg.) | Ag:Au | s | Thickness (inch) | s (inch $\times 10^{-3}$) | Surcharge (mg.) | s | Ag Retained (%) | s | Au Loss % | s |
|---|---|---|---|---|---|---|---|---|---|---|
| 20.148 | 10.1:1.0 | 0.3 | 0.0347 | 1.3 | 0.256 | 0.036 | 1.80 | 0.14 | 0.57 | 0.16 |
| 5.134 | 10.1:1.0 | 0.1 | 0.0230 | 3.5 | 0.036 | 0.010 | 1.27 | 0.08 | 0.62 | 0.07 |
| 5.063 | 19.9:1.0 | 0.5 | 0.0290 | 1.3 | 0.043 | 0.008 | 1.59 | 0.14 | 0.68 | 0.13 |
| 5.514 | 30.1:1.0 | 1.0 | 0.0274 | 0.4 | 0.031 | 0.010 | 1.16 | 0.05 | 0.59 | 0.11 |

of lead weight normally taken for cupellation (i.e. 20 g.). The
weight of gold taken was approximately 20-30 mg. and between 6 and 7
times as much silver. In the first five procedures, the time of contact
between the preheated acid and the gold-silver prill was 35 minutes.
In order to determine the effect of a second parting, trial VI involved
a second parting with a more concentrated acid. An earlier attempt
to reduce the silver content with a second parting had proved to be of
no effect. This was in agreement with the finding of Chow[24]. However
in both earlier trials the beads had been annealed prior to the second
parting. In procedure VI the beads were annealed only after the
second parting treatment. The time of digestion chosen, was based on
the time required for action (evolution of nitrogen oxides) to cease
in the most dilute acid. The time of contact for procedure VI was
15 minutes for each strength of acid. The parting acids were carefully
decanted and the beads washed three times with hot water. After
washing the beads were carefully annealed over a bunsen flame while
still in the 30 ml. beakers used for parting. The beads were then
weighed and analyzed for silver content as usual.

The other variable which was systematically varied was the
thickness of the gold-silver bead. Beads were either not flattened
at all (Procedures III and VI) or flattened to either 50 or 25
thousandth of an inch. For flattening the beads were placed in the
hole of a metal washer of the appropriate thickness, between two
stainless steel plates on a hydraulic press. The ease with which the
desired thickness could be achieved depended a great deal on the total
size of bead.

Table V gives a detailed tabulation of the results and Table
VI is a summary of the same. From these, the following generalizations

**TABLE V**

Effect of Parting Procedure On

Gold Losses

Parting Procedure I

Acid Strength:  1:6 (conc. HNO$_3$:H$_2$O)

Flattened to a Thickness of 0.0504 inch,  s = 0.0009 inch

| Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|
| 23.285 | 152.5 | 173.9 | 23.776 | 0.491 | 0.715 | 23.061 | 0.224 | 0.96 |
| 20.856 | 116.5 | 135.4 | 21.683 | 0.827 | 0.943 | 20.740 | 0.116 | 0.56 |
| 20.152 | 121.5 | 140.2 | 20.733 | 0.581 | 0.704 | 20.029 | 0.123 | 0.61 |
| 23.850 | 133.5 | 155.7 | 24.764 | 0.914 | 1.040 | 23.724 | 0.126 | 0.53 |
| 21.819 | 130.8 | 151.1 | 22.460 | 0.641 | 0.758 | 21.702 | 0.117 | 0.54 |
| 19.644 | 116.9 | 135.0 | 20.220 | 0.576 | 0.699 | 19.521 | 0.123 | 0.63 |
| 20.803 | 129.5 | 148.9 | 21.371 | 0.568 | 0.680 | 20.691 | 0.112 | 0.54 |
| 20.028 | 126.3 | 145.1 | 20.563 | 0.535 | 0.656 | 19.907 | 0.121 | 0.60 |
| 25.062 | 154.7 | 178.3 | 25.648 | 0.586 | 0.766 | 24.882 | 0.180 | 0.72 |
| 21.654 | 131.9 | 152.3 | 22.319 | 0.665 | 0.810 | 21.509 | 0.145 | 0.67 |
| 23.919 | 175.7 | 197.6 | 24.415 | 0.496 | 0.699 | 23.716 | 0.203 | 0.85 |
| 24.122 | 177.4 | 199.6 | 24.319 | 0.197* | 0.685 | 23.634 | 0.488 | 2.02* |

Average Au Loss %  =  0.65

s  =  0.14

* rejected since the bead broke on annealing with loss of

some gold

Parting Procedure II

Acid Strength: 1:6 (conc. HNO₃:H₂O)

Flattened to a Thickness of 0.0249 inch    s = 0.0006 inch

| Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|
| 19.479 | 132.7 | 149.8 | 20.090 | 0.611 | 0.718 | 19.372 | 0.107 | 0.55 |
| 20.948 | 134.8 | 153.4 | 21.754 | 0.806 | 0.949 | 20.805 | 0.143 | 0.68 |
| 19.497 | 123.1 | 140.6 | 20.350 | 0.853 | 0.980 | 19.370 | 0.127 | 0.65 |
| 19.751 | 123.4 | 141.2 | 20.315 | 0.564 | 0.685 | 19.630 | 0.121 | 0.61 |
| 20.275 | 140.6 | 158.9 | 20.716 | 0.441 | 0.554 | 20.162 | 0.113 | 0.56 |
| 20.330 | 140.0 | 158.3 | 20.775 | 0.445 | 0.565 | 20.210 | 0.120 | 0.59 |
| 23.011 | 145.5 | 166.0 | 23.600 | 0.589 | 0.705 | 22.895 | 0.116 | 0.50 |
| 20.493 | 139.8 | 157.8 | 20.997 | 0.504 | 0.639 | 20.358 | 0.135 | 0.66 |
| 23.201 | 154.2 | 175.3 | 23.703 | 0.502 | 0.616 | 23.087 | 0.114 | 0.49 |
| 20.628 | 139.6 | 158.5 | 21.039 | 0.411 | 0.513 | 20.526 | 0.102 | 0.49 |
| 19.041 | 124.2 | 141.8 | 19.404 | 0.363 | 0.486 | 18.918 | 0.123 | 0.65 |
| 19.290 | 126.8 | 144.1 | 19.643 | 0.353 | 0.492 | 19.151 | 0.139 | 0.72 |

Average Au Loss % = 0.60

s = 0.08

Parting Procedure III

Acid Strength: 1:4 (conc. $HNO_3$:$H_2O$)

Thickness: not flattened

| Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|
| 19.853 | 138.5 | 155.5 | 20.207 | 0.354 | 0.462 | 19.745 | 0.108 | 0.54 |
| 22.514 | 146.6 | 166.1 | 22.853 | 0.339 | 0.472 | 22.381 | 0.160 | 0.71 |
| 21.828 | 144.5 | 163.8 | 22.197 | 0.369 | 0.477 | 21.720 | 0.108 | 0.49 |
| 22.493 | 156.3 | 175.5 | 22.859 | 0.366 | 0.546 | 22.313 | 0.180 | 0.80 |
| 23.366 | 150.5 | 171.1 | 23.741 | 0.375 | 0.581 | 23.160 | 0.206 | 0.88 |
| 21.114 | 141.6 | 160.2 | 21.486 | 0.372 | 0.586 | 21.000 | 0.114 | 0.54 |
| 21.416 | 143.7 | 162.8 | 21.757 | 0.341 | 0.451 | 21.306 | 0.110 | 0.52 |
| 20.454 | 139.3 | 157.3 | 20.772 | 0.318 | 0.421 | 20.351 | 0.103 | 0.50 |
| 19.277 | 123.4 | 140.8 | 19.521 | 0.244 | 0.378 | 19.143 | 0.134 | 0.70 |
| 23.342 | 162.3 | 183.2 | 23.728 | 0.386 | 0.501 | 23.227 | 0.115 | 0.49 |
| 22.087 | 149.8 | 169.6 | 22.493 | 0.406 | 0.525 | 21.968 | 0.119 | 0.54 |
| 21.754 | 137.8 | 157.4 | 22.100 | 0.346 | 0.462 | 21.638 | 0.116 | 0.54 |

Average Au Loss % = 0.60

s = 0.13

Parting Procedure IV

Acid Strength:  1:4  (conc. $HNO_3:H_2O$)

Flattened to a Thickness of 0.0259 inch.    s = 0.0008 inch.

| Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | P rted Bead (mg.) | Surcharge (mg.) | g Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|
| 22.140 | 136.9 | 157.0 | 22.419 | 0.279 | 0.389 | 22.030 | 0.110 | 0.50 |
| 19.153 | 118.2 | 135.3 | 19.358 | 0.205 | 0.328 | 19.030 | 0.123 | 0.64 |
| 20.180 | 124.5 | 143.3 | 20.430 | 0.250 | 0.369 | 20.061 | 0.119 | 0.59 |
| 20.062 | 129.1 | 147.4 | 20.311 | 0.249 | 0.134* | 20.177 | -0.115 | £ |
| 26.192 | 169.0 | 191.8 | 26.558 | 0.366 | 0.122* | 26.436 | -0.244 | £ |
| 23.475 | 161.0 | 182.9 | 23.822 | 0.347 | 0.448 | 23.374 | 0.101 | 0.43 |
| 21.019 | 127.9 | 147.2 | 21.279 | 0.255 | 0.369 | 20.905 | 0.114 | 0.54 |
| 22.755 | 138.7 | 160.2 | 23.068 | 0.313 | 0.418 | 22.650 | 0.105 | 0.46 |
| 23.024 | 148.5 | 170.1 | 23.340 | 0.316 | 0.430 | 22.910 | 0.114 | 0.50 |
| 22.709 | 141.7 | 162.9 | 23.019 | 0.310 | 0.418 | 22.601 | 0.108 | 0.48 |
| 25.913 | 162.0 | 186.0 | 26.312 | 0.399 | 0.502 | 25.810 | 0.103 | 0.40 |
| 19.755 | 123.6 | 142.5 | 20.025 | 0.270 | 0.362 | 19.663 | 0.092 | 0.47 |

Average Au Loss % = 0.50    s = 0.07

* the Ag analysis for these beads is unexpectedly low, perhaps a temporary blockage of the aspirator of the atomic absorption spectrophotometer.

£ rejected since suspect Ag analysis led to an increase in Au weight.

Parting Procedure V

Acid Strength:  1:3  (conc. $HNO_3$ : $H_2O$)

Flattened to a thickness of .0271 inch.    s = 0.0014 inch.

| Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|
| 27.508 | 171.7 | 197.5 | 27.805 | 0.297 | 0.468 | 27.337 | 0.171 | 0.62 |
| 25.857 | 150.3 | 174.4 | 26.079 | 0.222 | 0.460 | 25.619 | 0.238 | 0.92 |
| 21.836 | 129.4 | 150.1 | 22.021 | 0.185 | 0.362 | 21.659 | 0.177 | 0.81 |
| 19.034 | 115.6 | 133.3 | 19.169 | 0.135 | 0.407 | 18.762 | 0.272 | 1.43 |
| 19.612 | 120.7 | 138.9 | 19.735 | 0.123 | 0.342 | 19.393 | 0.219 | 1.12 |
| 20.986 | 128.1 | 148.0 | 21.169 | 0.183 | 0.364 | 20.805 | 0.181 | 0.86 |
| 21.728 | 144.3 | 164.7 | 21.924 | 0.196 | 0.430 | 21.494 | 0.234 | 1.08 |
| 26.660 | 173.3 | 197.6 | 26.888 | 0.228 | 0.392 | 26.496 | 0.164 | 0.62 |
| 21.877 | 147.6 | 167.6 | 22.061 | 0.184 | 0.390 | 21.671 | 0.206 | 0.94 |
| 23.333 | 144.6 | 166.3 | 23.550 | 0.217 | 0.485 | 23.065 | 0.268 | 1.15 |
| 19.863 | 140.7 | 159.5 | 20.049 | 0.186 | 0.340 | 19.709 | 0.154 | 0.78 |
| 22.799 | 124.3 | 145.9 | 23.047 | 0.248 | 0.444 | 22.603 | 0.196 | 0.86 |

Average Au Loss %  = 0.93

s  = 0.23

Parting Procedure VI

    Acid Strength:   1:4  (conc. $HNO_3$:$H_2O$)  for first treatment

                     1:1  (conc. $HNO_3$:$H_2O$) for second treatment

    Thickness: not flattened

| Au Added (mg.) | Ag Added (mg.) | Sum* (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|
| 19.720 | 129.3 | | 19.765 | 0.045 | 0.232 | 19.533 | 0.187 | 0.95 |
| 20.820 | 148.4 | | 20.852 | 0.032 | 0.239 | 20.613 | 0.207 | 0.99 |
| 23.149 | 186.8 | | 23.221 | 0.072 | 0.250 | 22.971 | 0.178 | 0.77 |
| 20.642 | 145.2 | | 20.694 | 0.052 | 0.204 | 20.490 | 0.152 | 0.73 |
| 20.880 | 141.7 | | 20.933 | 0.053 | 0.200 | 20.733 | 0.147 | 0.70 |
| 19.503 | 124.3 | | 19.553 | 0.050 | 0.197 | 19.356 | 0.147 | 0.75 |
| 21.753 | 139.0 | | 21.831 | 0.078 | 0.218 | 21.613 | 0.140 | 0.64 |
| 21.785 | 141.7 | | 21.861 | 0.076 | 0.216 | 21.645 | 0.140 | 0.64 |
| 23.447 | 148.0 | | 23.514 | 0.067 | 0.214 | 23.300 | 0.147 | 0.63 |
| 18.799 | 116.2 | | 18.846 | 0.047 | 0.199 | 18.647 | 0.152 | 0.81 |
| 20.113 | 138.8 | | 20.174 | 0.061 | 0.199 | 19.975 | 0.138 | 0.68 |
| 23.886 | 158.8 | | 23.984 | 0.098 | 0.244 | 23.740 | 0.146 | 0.61 |

Average Au Loss %  = 0.74

s  = 0.12

* this parameter was not measured due to an oversight.

## TABLE VI

Summary of Parting Procedures

| Procedure | Acid Strength | Thickness (inch) | s | Surcharge (mg.) | s | Ag Retained (%) | s | Au Loss (%) | s |
|---|---|---|---|---|---|---|---|---|---|
| I | 1:6 | 0.0504 | 0.0009 | 0.625 | 0.133 | 3.47 | 0.53 | 0.65 | 0.14 |
| II | 1:6 | 0.0249 | 0.0006 | 0.537 | 0.160 | 3.22 | 0.83 | 0.60 | 0.08 |
| III | 1:4 | unflattened | -- | 0.351 | 0.041 | 2.22 | 0.16 | 0.60 | 0.13 |
| IV | 1:4 | 0.0259 | 0.0008 | 0.297 | 0.056 | 1.82 | 0.07 | 0.50 | 0.07 |
| V | 1:3 | 0.0271 | 0.0014 | 0.200 | 0.047 | 1.81 | 0.19 | 0.93 | 0.23 |
| VI | 1:4 & 1:1 | unflattened | -- | 0.061 | 0.018 | 1.03 | 0.08 | 0.74 | 0.12 |

-seem to be indicated:

a). decreasing the thickness of the bead decreases the surcharge and
the percentage of silver retained. (Compare Procedure I vs II
and III vs IV)

b). increasing the acid strength decreases the surcharge and the
percentage of silver retained. (Compare Procedures II vs IV
and IV vs V)

c). decreasing the thickness reduces gold losses. (Compare Procedure
I vs II and III vs IV)

d). increasing acid strength (to a point) reduces gold losses.
(Compare Procedures II vs IV and I vs IV)

e). increasing acid strength decreases the deviation in the silver
retained. (Compare Procedures I vs II and III vs VI)

f). a second parting is effective in reducing the silver retained.
(Compare Procedures II vs VI)

The reasons for the first two conclusions seem straight forward.
Since acid attack occurs at the surface, the removal of silver is
enhanced when the surface area of the bead is increased. Flattening
the bead increases surface area. The reduction in the silver retained
by **use of a stronger acid b) is probably due to the constant time of digestion**
and the failure to reach equilibrium. For a given length of time the
more concentrated would be more likely to leach out a greater proportion
of silver. The increase in precision of the percentage of silver
retained **by use of more concentrated acids must be due to a similar effect.**
(e) For a given length of time of digestion, the equilibrium state
is more likely to be reached with the stronger acid. Since bead weights
differ, the larger beads, containing more silver, will be more effectively

-leached in the stronger acid. As a result deviations in the percent silver retained due to incomplete leaching will occur more frequently in the dilute acid.

The reason for the reduced gold losses due to a decrease in thickness of bead (c), and increase of acid strength (d), is not as readily apparent. A consideration of the gold-silver phase diagram [37] near the melting points of the two metals indicates a simple diagram, with no eutectics or compounds. Since the melting point of gold is approximately 100°C higher than that of silver, the first crystals forming on solidification of the bead would be gold rich while the converse would apply near the end of solidification. As a result the exterior would be high in silver. On pressing the bead to reduce bead thickness, considerable frictional forces must be overcome, thus momentarily generating heat. As the temperature increases diffusion of silver and gold would be encouraged. Such a bead when exposed to acid treatment would have a more regular surface than a bead in which a silver rich surface prevailed. The more irregular the surface the more likely would be the loss of small even invisible gold particles. Essentially all reported parting losses are of such a nature. While the mechanism of diffusion put forward here may sound far fetched a similar theory has been advanced to justify the annealing of the gold-silver beads prior to parting [20].

It would appear that increasing the acid strength reduces gold losses only if the acid is not too strong. With a silver to gold ratio of about 6.5:1.0 that point was reached around 1:4 nitric (acid: water). While no reasons can be advanced for the generalization d) regarding acid strength, an application of the t test for significant differences indicates the comparisons upon which it is based, represent

significant differences at the 99% confidence level.

The final conclusion that a double acid parting treatment reduces the silver content is clearly indicated by the reduced surcharge and percentage silver retained. The failure of previous double digestions must have been due to a closing of the pores of the bead on annealing and thereby preventing the acid from coming in contact with significant amounts of silver. The increased gold loss in this case seems to indicate too strong an acid for the second parting.

An attempt was made at this point to determine some of the gold losses directly. Several(4), parting solutions from Procedure V were collected together with the wash water. The solution was taken to near dryness. The residue was treated with 6 ml. aqua regia, which resulted in the precipitation of considerable silver (approximately 600 mg.). In attempting to dissolve this, 78 ml. of concentrated hydrochloric acid was added which generated large quantities of nitrogen oxides as the excess nitrate in solution interacted with the added acid. This solution was then taken to near dryness once again, and finally treated with 6 ml. aqua regia and 10 ml. hydrochloric acid. The residue which remained was filtered off. The filtrate after dilution to volume in a 100 ml. volumetric was examined by atomic absorption for gold content. No gold was found. Under the conditions used the minimum amount detectable would have been 12 micrograms. In view of the ability of AgCl to co-precipitate gold referred to above, the negative test may have been due to this effect. Alternatively, it may be that the sensitivity of the procedure was too low. If so, losses to the parting acid and wash solutions would be less than 3 micrograms per sample. In any case a radiochemical procedure was planned, to examine

this loss at a later point in the research.

Two attempts were made to determine the gold content of the cupel material. In the first test the cupels from Procedure V were drilled to a depth of 3/16" using a 7/32" bit for samples 1-6 and a 9/32" bit for samples 8-12. Sample 7 was lost. Each sample was treated with 6 ml. aqua regia and 10 ml. HCl. This treatment brought all samples into solution on heating. The solutions were evaporated to dryness and then treated with 3 ml. aqua regia and 5 ml. conc. hydrochloric acid. In this volume the samples failed to dissolve. The samples were diluted to 50 ml. in a volumetric flask and aspirated with the precipitate at the bottom of the flask. The samples were individually aspirated and gold content determined by atomic absorption. The average signal was just barely detectable and indicated the presence of 5-6 micrograms of gold. Again the presence of the precipitate may have had a significant effect on the result.

The second test for gold in the cupels was somewhat modified. Cupels 1-6 from Procedure IV were drilled over the entire upper surface in such a way that the total cupel material taken was about ½ that of the previous test. These scrapings or drillings dissolved cleanly in 6 ml. aqua regia and 10 ml. HCl after heating for several hours. Each sample was then diluted to 50 ml. in a volumetric flask and aspirated as the previous case. The average gold content was 25 micrograms with a standard deviation of 4 micrograms. Since the total gold lost in this particular trial was of the order of 100 micrograms, considerable gold remained to be accounted for. Further consideration of this matter was postponed until a more satisfactory assay could be made of the cupel material.

4. Volatilization

The object of this portion of the study was to determine whether gold volatilizes to a significant extent under cupellation conditions. In a preliminary experiment, the results of which are reported in Table VII, twelve beads of approximately equal size (80 mg.) were made up by weighing out four samples of pur gold, four of pure silver and four of a 1:3 mixture of gold and silver respectively. These were encased in 5" x 6" x .004" lead foil and cupelled in t he usual way. Since the lead foil was known to contain an average of 58 $\pm$ 4 micrograms of silver per gram, the significant changes occur after a cupelled bead was obtained. In 25 g. of lead foil the silver content could add as much as 1.5 mg. to the bead weight provided no losses occurred. This could explain, at least partially, why the gold bead obtained after cupellation was on the average 1.0 mg. heavier than the gold added.

On heating the cupelled beads some interesting changes occurred. The first heating interval was for 30 minutes and approximately the time required for cupellation. The gold beads systematically increased in weight by an average of 0.126 mg. s = 0.024 mg. The silver beads decreased in weight by an average of 0.162 mg. s = 0.080 mg. while the gold-silver (1:3) beads decreased in weight by 0.042 mg. s = 0.018 mg. All heatings were made on the same cupel used for the cupellation of a particular bead. A second heating of the same beads for a one hour interval indicated an approximately proportional decrease in weight for the pure silver and the mixed beads. The gold beads, however, now began to decrease slightly (0.016 mg. s = 0.024 mg.) in weight. In view of the high relative uncertainty here and the fact that one of these gold beads actually increased in weight, and in view of the fact

TABLE VII

Effect of Heating Gold, Silver, and Gold-Silver

Beads

Volatility Study I

| Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Weight After 1st heating (mg.) | Weight After 2nd heating (mg.) | Change In Weight After 1st heating (mg.) | Change In Weight After 2nd heating (mg.) |
|---|---|---|---|---|---|---|
| 80.578 | -- | 81.607 | 81.740 | 81.701 | +0.133 | -0.039 |
| 79.334 | -- | 80.318 | 80.411 | 80.428 | +0.093 | +0.017 |
| 80.996 | -- | 82.017 | 82.143 | 82.139 | +0.126 | -0.004 |
| 89.858 | -- | 90.842 | 90.993 | 90.957 | +0.151 | -0.036 |
| Average | | 83.696 | 83.822 | 83.806 | +0.126 | -0.016 |
| s | | | | | 0.024 | 0.024 |
| -- | 82.660 | 81.834 | 81.776 | 81.377 | -0.058 | -0.399 |
| -- | 89.098 | 87.974 | 87.833 | 87.394 | -0.141 | -0.439 |
| -- | 80.288 | 79.416 | 79.177 | 78.721 | -0.239 | -0.456 |
| -- | 80.394 | 79.541 | 79.330 | 78.841 | -0.211 | -0.489 |
| Average | | 82.191 | 82.029 | 81.583 | -0.162 | -0.446 |
| s | | | | | 0.080 | 0.037 |
| 20.765 | 60.207 | 80.766 | 80.698 | 80.684 | -0.068 | -0.014 |
| 19.445 | 59.907 | 79.050 | 79.020 | 78.892 | -0.030 | -0.128 |
| 21.768 | 60.716 | 81.984 | 81.945 | 81.854 | -0.039 | -0.091 |
| 22.921 | 62.743 | 85.335 | 85.304 | 85.000 | -0.031 | -0.304* |
| Average | | 81.784 | 81.742 | 81.608 | -0.042 | -0.078 |
| s | | | | | 0.018 | 0.058 |

* rejected since bead formed a rootlet into the cupel on this heating

that one of the mixed beads had to be rejected for an experimental reason it was decided to make a more thorough examination of the effect of heating on bead weight.

The following tentative conclusions were made. If the relative rates of vaporization of the two metals are the same in the mixed bead as in the pure substances, then approximately 3% of the weight loss in the mixed bead is due to gold (i.e. 3 micrograms/hr). Since the silver to gold ratio is 3:1 the loss of gold could be reasonably expected to be less. In addition the actual cupellation process would involve only 30 minutes instead of one hour so that gold losses from volatilization would be less than 1 microgram per bead.

In the second test of volatility, 12 samples of gold only were prepared and cupelled in the normal way. Again the weight of the beads increased by approximately 1.0 mg. Two heating periods of the cupelled beads followed. Both periods were of 30 minutes duration. After the first such heating the weight of the gold beads increased by an average of 0.142 mg. s = 0.085. The second heating produced a slight decrease in weight of 0.011 mg. on the average. The results of this experiment are recorded in Table VIII. These results are quite in agreement with the limited results of the previous experiment.

In the third test of volatility 12 samples of silver only were prepared and cupelled in the normal manner. The results of one heating period of 30 minutes duration of a cupelled bead indicated an average loss of weight of 0.168 mg. in this experiment as compared to 0.162 mg. in the preliminary study. There seemed to be no point in continuing this study. The beads of the preliminary study had behaved in[a]representative manner as was confirmed by the last two studies. The loss in weight of the silver beads on cupellation is consistent with

TABLE VIII

Effect of Heating Gold Beads

Volatility Study II

| Au Added (mg.) | Weight Bead Obtained (mg.) | Weight Bead After 1st heating (mg.) | Weight Bead After 2nd heating (mg.) | Change in Weight After 1st heating (mg.) | Change in Weight After 2nd heating (mg.) |
|---|---|---|---|---|---|
| 79.395 | 80.329 | 80.523 | 80.524 | +0.194 | +0.001 |
| 81.975 | 82.929 | 82.956 | 82.969 | +0.027 | +0.013 |
| 76.971 | 77.809 | 77.954 | 77.980 | +0.145 | +0.026 |
| 85.228 | 86.092 | 86.172 | 86.159 | +0.080 | -0.013 |
| 81.469 | 82.513 | 82.670 | 82.612 | +0.157 | -0.058 |
| 99.485 | 100.367 | 100.722 | 100.511 | +0.355 | -0.211* |
| 79.689 | 80.701 | 80.867 | 80.827 | +0.166 | -0.040 |
| 79.128 | 80.176 | -- | -- | -- | -- |
| 84.656 | 85.667 | 85.753 | 85.763 | +0.086 | +0.010 |
| 86.746 | 87.701 | 87.806 | 87.813 | +0.105 | +0.007 |
| 78.315 | 79.296 | 79.400 | 79.394 | +0.104 | -0.006 |
| 59.213 | 60.313 | 60.452 | 60.406 | +0.139 | -0.046 |
| Average 81.022 | 81.991 | 82.133 | 82.122 | +0.142 | -0.011 |
| s | | | | 0.085 | |

\* rejected on statistical grounds

TABLE IX

Effect of Heating Silver Beads

Volatility Study III

| Ag Added (mg.) | Weight Bead Obtained (mg.) | Weight Bead After 1st heating (mg.) | Change in Weight After 1st heating (mg.) |
|---|---|---|---|
| 198.756* | 195.318 | 195.000 | -0.318* |
| 80.204 | 79.126 | 78.995 | -0.131 |
| 59.028 | 58.497 | 58.279 | -0.218 |
| 106.331 | 104.672 | 104.580 | -0.092 |
| 80.235# | 79.091# | 79.225# | +0.134# |
| 80.074 | 79.077 | 78.983 | -0.094 |
| 77.630 | 76.892 | 76.771 | -0.121 |
| 77.046 | 76.392 | 76.317 | -0.075 |
| 80.819 | 79.990 | 79.830 | -0.160 |
| 81.212 | 80.450 | 80.366 | -0.084 |
| 79.922 | 79.309 | 79.004 | -0.305 |
| 83.131 | 82.948 | 82.548 | -0.400 |
| Average | | | |
| 80.539 | 79.735 | 79.567 | -0.168 |

# rejected on statistical grounds

* this bead excluded due to much larger size

reports in the literature[33]. Allowing for the silver blank of
1.35 mg. and the real loss of 0.89 mg. the total silver loss amounts
to 2.24 mg. or 2.78% of the original weight of silver.

In order to better understand the cause of the increase in weight
of the gold beads 6 samples of high purity gold wire were cut and
weighed. Each sample was placed on a clean unused cupel and heated
under the same conditions as for cupellation. The results are summarized
in Table X along with a similar series for silver wire. The weight of
gold wire before and after heating remained constant within the
experimental weighing error. The weight of silver wire decreased on
the average by 0.138 mg. On the basis of these results it would appear
that the used cupel has some effect on the gold beads. One possibility
would be the diffusion of some elemental lead back into the gold bead.
While this reversal of lead movement seemed highly unlikely, a lead
analysis of the gold beads was suggested.

Each bead was dissolved in 6 ml. aqua regia and 10 ml. concentrated
hydrochloric and diluted to 100 ml. Lead standards were prepared with
a matched matrix. The average lead content was 0.140 mg. s = 0.048.
The increase in weight of gold beads on first heating averaged to 0.142
mg. s = 0.085.

It would appear that the increase in weight on heating a pure gold
bead is due to diffusion of lead from the cupel, back into the bead.
Eventually, a state of equilibrium is attained and the bead begins to
lose small (0.01%) amounts of its weight on subsequent heatings. A
search of the literature indicated that the increase in weight under
discussion here had been observed before[34]. These authors left gold
beads in the furnace for varying lengths of time to see whether gold

TABLE X

Effect of Heating Gold and Silver Wires

Volatility Study IV

| Weight Au Wire Taken (mg.) | Weight After Heating Once (mg.) | Change in Weight After Heating (mg.) |
|---|---|---|
| 57.762 | 57.764 | +0.002 |
| 70.111 | 70.107 | -0.004 |
| 93.453 | 93.449 | -0.004 |
| 104.269 | 104.268 | -0.001 |
| 105.629 | 105.628 | -0.001 |
| 93.377 | 93.374 | -0.003 |
| Average 87.434 | 87.432 | - .002 |

| Weight Ag Wire Taken (mg.) | Weight After Heating Once (mg.) | Change in Weight After Hearing (mg.) |
|---|---|---|
| 82.372 | 82.341 | -0.031 |
| 109.101 | 108.887 | -0.214 |
| 87.260 | 87.043 | -0.217 |
| 92.399 | 92.333 | -0.066 |
| 86.547 | 86.386 | -0.161 |
| 112.390 | 112.253 | -0.137 |
| Average 95.012 | 94.874 | -0.138 |

losses would increase  They found that "no constant losses were observed ..... but curiously enough there seemed to be a slight tendency to increase in weight.  To what this could be attributed is not clear."[34].  It is possible that the increase in weight of gold beads is due to another unknown reason and that the lead had simply not been removed from the bead in the first instance.  In that case the close agreement between the weight increase on heating and the weight of lead retained would be fortuitous.  While this might not be difficult to prove, the matter was not considered important enough to the aim of this research and therefore this study was terminated at this point.

On the basis of the volatility studies it seems safe to say that gold losses via volatilization are not significant under the conditions studied.

5.  Effect of Cleaning Beads

Up until this point in the work, the beads obtained from the cupellation process were cleaned of all cupel material by scraping with a platinum spatula.  Since, however, all sources seemed to agree that the largest loss of gold in the cupellation process occurred at the point of contact between bead and cupel it seemed highly likely that this cupel material adhering to the bead would be relatively rich in gold.  It was therefore considerable desirable to treat six samples in the usual manner and leave six samples untouched.  It was previously established that the cupel material readily dissolved in the parting acids used, (15 minutes 1:4 nitric followed by 15 minutes 1:1 nitric) under the conditions of parting.  Table XI is a summary of these two trials.

From Table XI it is evident that the gold loss is increased by

TABLE XI

Effect of Cleaning Unparted Beads

On Gold Losses

## TABLE XI

Effect of Cleaning[1] Unparted Beads on Gold Losses

| Au Added (mg.) | Ag Added (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % (mg.) |
|---|---|---|---|---|---|---|---|
| **Scraped Beads** | | | | | | | |
| 19.720 | 129.3 | 19.765 | 0.045 | 0.232 | 19.533 | 0.187 | 0.95 |
| 20.820 | 148.4 | 20.852 | 0.032 | 0.239 | 20.613 | 0.207 | 0.99 |
| 23.149 | 186.8 | 23.221 | 0.072 | 0.250 | 22.971 | 0.178 | 0.77 |
| 20.642 | 145.2 | 20.694 | 0.052 | 0.204 | 20.490 | 0.152 | 0.73 |
| 20.880 | 141.7 | 20.933 | 0.053 | 0.200 | 20.733 | 0.147 | 0.70 |
| 19.503 | 124.3 | 19.553 | 0.050 | 0.197 | 19.356 | 0.147 | 0.75 |
| | | | | Average Au Loss | = | 0.170 mg. | 0.82 % |
| | | | | s | = | 0.025 mg. | 0.12 % |
| **Unscraped Beads** | | | | | | | |
| 21.753 | 139.0 | 21.831 | 0.078 | 0.218 | 21.613 | 0.140 | 0.64 |
| 21.785 | 141.7 | 21.861 | 0.076 | 0.216 | 21.645 | 0.140 | 0.64 |
| 23.447 | 148.0 | 23.514 | 0.067 | 0.214 | 23.300 | 0.147 | 0.63 |
| 18.799 | 116.2 | 18.846 | 0.047 | 0.199 | 18.647 | 0.152 | 0.81 |
| 20.113 | 138.8 | 20.174 | 0.061 | 0.199 | 19.975 | 0.138 | 0.68 |
| 23.886 | 158.8 | 23.984 | 0.098 | 0.244 | 23.740 | 0.146 | 0.61 |
| | | | | Average Au Loss | = | 0.144 mg. | 0.67 % |
| | | | | s | = | 0.005 mg. | 0.07 % |

1 Beads were cleaned by scraping

with a spatula.

26 micrograms on the average when the bead is scraped. Thus the practise of cleaning beads of cupel material was stopped from this point on in this research.

IV. Losses of Gold in The Complete Fire Assay

1. Effect of Mixing Procedure of Ore and Flux

Since fairly large containers (crucibles) are required for the fusion process samples were prepared in groups of six. Initially flux components were individually weighed out from a scoop type harvard trip balance to the nearest 1/10 gram. and transferred directly to a cellophane sheet. Here they were thorougly mixed by tumbling back and forth for approximately 30 minutes. This procedure was found to be cumbersome, slow and required the wearing of a dust mask. Dust from the flux components is injurious to health. In order to speed up this process and reduce the health hazard the flux components were mixed in large utility sized polyethylene bags known as "baggies" (produced in Canada by Colgate Palmolive). In these the flux components could be vigorously tumbled and mixing was adequate after 15 minutes.

Two experiments were performed, the results of which are recorded in Table XII. In the one test the flux components were weighed and transferred directly to the fusion crucible. The accurately weighed amounts of gold were added to a slight hollow in the centre of the flux mixture and sufficient silver was added so that the silver to gold ratio would be between 6:1 and 7:1. The flux, silver and gold were mixed as thoroughly as possible with a spatula. No visible amounts of flux, silver or gold adhered to the spatula.

The other six samples, for the second test, were prepared by transferring the flux materials from the balance to what is known as a "sandwich size baggie" (polyethylene bag weighing approximately 1.0

TABLE XII

Effect of Polyethylene Bags On  Gold Losses

For Complete Fire Assay

I. No baggies[1]

| Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|
| 19.548 | 132.3 | 145.3 | 19.376 | 0.116 | 19.260 | 0.288 | 1.47 | 19.4 |
| 22.127 | 141.9 | 158.0 | 21.898 | 0.141 | 21.757 | 0.370 | 1.68 | 18.2 |
| 20.680 | 137.1 | 152.4 | 20.603 | 0.120 | 20.483 | 0.197 | 0.95 | 18.6 |
| 21.015 | 136.0 | 152.3 | 20.595 | 0.129 | 20.466 | 0.549 | 2.61 | 19.2 |
| 18.231 | 126.6 | 140.2 | 18.082 | 0.113 | 17.969 | 0.262 | 1.44 | 18.5 |
| 19.521 | 122.3 | 137.4 | 19.456 | 0.113 | 19.343 | 0.178 | 0.91 | 19.4 |

Average Au Loss % = 1.51

s = 0.62

II. Baggies

| Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|
| 15.367 | 102.4 | 113.7 | 15.261 | 0.101 | 15.160 | 0.207 | 1.34 | 31.5 |
| 27.754 | 176.0* | -- | -- | -- | -- | -- | -- | -- |
| 20.941 | 127.6 | 144.2 | 20.889 | 0.131 | 20.758 | 0.183 | 0.88 | 29.9 |
| 26.564 | 146.3 | 167.4 | 26.582 | 0.258 | 26.324 | 0.240 | 0.90 | 31.2 |
| 23.168 | 147.1 | 165.5 | 23.152 | 0.157 | 22.995 | 0.173 | 0.75 | 31.8 |
| 31.859 | 211.6 | 235.7 | 31.665 | 0.236 | 31.429 | 0.430 | 1.35 | 31.3 |

Average Au Loss % = 1.04

s = 0.28

* lost due to cracking of pot in furnace

1 baggies were approximately 1.0 g. polyethylene bags

gram). The gold and silver, in the same proportions as before, were transferred directly from the balance into this baggie. The baggies were tied off, and thoroughly and vigorously mixed for 5 minutes each. The flux materials, gold, silver and baggie were then placed in the crucibles for fusion.

In this particular comparison, the assay samples were placed into the furnace at an initial temperature of 1950°F and heated as quickly as possible to 2100°F. The samples were allowed to remain in the oven for 2½ hours, after which the crucibles were removed from the furnace and their contents poured into a conical iron mold. After a one hour interval for cooling, the slag was separated from the lead button by gentle tapping with a metal bar.

The lead buttons were weighed to the nearest 1/10 gram and cupelled at 1800°F as usual. After cupellation and cooling the beads were weighed on a milligram balance and parted as indicated in Procedure VI. The beads were no longer scraped to remove cupel material. The beads were washed three times with hot water, annealed and weighed accurately to obtain the weight of the parted bead. The silver content was determined as described for the cupellation studies and the gold recovered was deduced in the usual way.

In the first test, with no baggies, the average gold loss was 1.51% s = 0.62 while with baggies for mixing, the average gold loss was 1.04% s = 0.28. Thus both gold loss and deviations in the process are reduced when baggies are used for mixing. In subsequent experiments this practise was adopted.

2. Effect of Fusion Temperature on Gold Losses

The basic procedure for preparation of samples and their fusion was the same as described above, with the polyethylene bags used for

mixing. The cupellation of all the lead buttons obtained was achieved at a temperature of 1800°F as in the cupellation studies. The parting of the gold-silver beads was with two 15 minute treatments with 10 ml. of 1:4 and 1:1 nitric (acid:water) respectively. The acid was pre-heated in 35 ml. beakers on a steam bath. The beads were then washed three times with hot water, annealed and weighed. The silver content of the parted beads was determined by the usual methods outlined above.

As indicated in the introduction, assayers often adopt the practise of using a low initial temperature for the fusion process and then increase the temperature towards the end. Two trials with initial temperatures of 1850°F and 1950°F were completed at a final temperature of 2100°F (first page of Table XIII). The first trial, with the lower initial temperature, resulted in a lower gold loss of 0.81% s = 0.10 as compared to 0.97% s=0.21 for the other. The trial at the higher temperature is actually a repeat of a similar trial reported in Table XII in which the gold loss was 1.04% s = 0.28. Thus the lower initial temperature appears to enhance gold recovery and improve precision.

Since the initial temperature of the charge is always lower than the final temperature in any case, it was thought that perhaps this change in furnace temperature during the process was an unnecessary refinement of the procedure. With this in mind a series of trials were made at which furnace settings remained constant after the initial temperature had been set. The remainder of Table XIII includes the results of these investigations. Table XIV is a summary of the constant temperature trials.

The number of replicate samples varied somewhat throughout this

**TABLE XIII**

Effect of Fusion Temperature

on Gold Losses

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 1850-2100[1] | 17.211 | 113.9 | 127.7 | 17.167 | 0.090 | 17.077 | 0.134 | 0.78 | 18.3 |
| 1850-2100[1] | 23.597 | 147.8 | 166.6 | 23.516 | 0.140 | 23.376 | 0.221 | 0.98 | 17.4 |
| 1850-2100[1] | 21.844 | 133.4 | 150.8 | 21.786 | 0.119 | 21.667 | 0.177 | 0.81 | 16.0 |
| 1850-2100[1] | 26.516 | 178.7 | 199.3* | 26.377 | 0.152 | 26.225 | 0.291 | 1.10 | 17.7 |
| 1850-2100[1] | 24.487 | 160.3 | 179.3 | 24.440 | 0.140 | 24.300 | 0.187 | 0.76 | 16.2 |
| 1850-2100[1] | 22.312 | 124.5 | 142.5 | 22.302 | 0.151 | 22.151 | 0.161 | 0.72 | 16.7 |

Average Au Recovery = 99.19%  Average Au Loss % = 0.81  s = 0.10

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 1950-2100[1] | 19.674 | 135.1 | 150.8 | 19.547 | 0.107 | 19.440 | 0.234 | 1.19 | 17.7 |
| 1950-2100[1] | 21.230 | 148.4 | 160.0* | 20.613 | 0.097 | 20.517 | 0.713 | 3.36 | 15.4 |
| 1950-2100[1] | 26.347 | 181.8 | 202.9 | 26.267 | 0.127 | 26.140 | 0.207 | 0.79 | 16.5 |
| 1950-2100[1] | 22.045 | 154.5 | 171.3 | 21.986 | 0.117 | 21.869 | 0.176 | 0.80 | 18.4 |
| 1950-2100[1] | 25.475 | 160.2 | 181.5 | 25.396 | 0.146 | 25.250 | 0.225 | 0.88 | 18.6 |
| 1950-2100[1] | 16.130 | 105.5 | 118.8 | 16.008 | 0.072 | 15.936 | 0.194 | 1.20 | 18.2 |

Average Au Recovery = 99.03%  Average Au Loss % = 0.97  s = 0.21

[1] the lower temperature indicates the initial temperature and the higher temperature indicates the final temperature attained within an hour,

* these beads formed rootlets on cupellation and were rejected.

—70—

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 1900 | 25.992 | 164.2 | 184.4 | 25.958 | 0.242 | 25.716 | 0.276 | 1.06 | 15.1 |
| 1900 | 25.750 | 163.8 | 184.7 | 25.771 | 0.242 | 25.529 | 0.221 | 0.86 | 16.6 |
| 1900 | 30.455 | 188.9 | 214.3 | 30.530 | 0.276 | 30.254 | 0.201 | 0.66 | 16.7 |
| 1900 | 23.746 | 146.9 | 166.1 | 23.795 | 0.226 | 23.569 | 0.177 | 0.75 | 16.8 |
| 1900 | 27.582 | 176.9 | 199.6 | 27.655 | 0.280 | 27.275 | 0.307 | 1.07 | 16.1 |
| 1900 | 26.385 | 167.1 | 189.0 | 26.297 | 0.258 | 26.039 | 0.346 | 1.31 | 14.8 |
| | | | Average Au Recovery = 99.05% | | | Average Au Loss% = 0.95 | | s = 0.24 | |
| 2000 | 19.658 | 129.9 | 145.3 | 19.647 | 0.175 | 19.472 | 0.186 | 0.95 | 17.7 |
| 2000 | 20.334 | 135.7 | 152.6 | 20.337 | 0.176 | 20.161 | 0.173 | 0.85 | 16.9 |
| 2000 | 22.895 | 145.4 | 164.0 | 22.962 | 0.216 | 22.746 | 0.149 | 0.65 | 17.2 |
| 2000 | 24.558 | 147.8 | 167.6 | 24.581 | 0.263 | 24.318 | 0.240 | 0.98 | 16.1 |
| 2000 | 28.974 | 183.5 | 208.0 | 29.265 | 0.475 | 28.790 | 0.180 | 0.62 | 16.9 |
| 2000 | 25.601 | 174.3 | 195.8 | 25.682 | 0.280 | 25.402 | 0.199 | 0.78 | 16.4 |
| | | | Average Au Recovery = 99.19% | | | Average Au Loss % = 0.81 | | s = 0.15 | |

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 2100 | 22.295 | 126.5 | 144.8 | 22.355 | 0.200 | 22.155 | 0.140 | 0.63 | 17.7 |
| 2100 | 19.434 | 134.5 | 150.7 | 19.412 | 0.118 | 19.294 | 0.140 | 0.72 | 19.0 |
| 2100 | 19.199 | 128.0 | 143.8 | 19.196 | 0.157 | 19.039 | 0.160 | 0.83 | 17.6 |
| 2100 | 22.701 | 148.7 | 168.0 | 22.720 | 0.116 | 22.604 | 0.097 | 0.43 | 17.6 |
| 2100 | 21.804 | 137.9 | 156.3 | 21.814 | 0.137 | 21.677 | 0.127 | 0.58 | 18.4 |
| 2100 | 21.088 | 141.3 | 158.5 | 21.091 | 0.126 | 20.965 | 0.123 | 0.58 | 17.6 |

Average Au Loss % = 0.63

s = 0.14

Average Au Recovery = 99.37%

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 2200 | 32.244 | 192.8 | 218.3 | 32.293 | 0.232 | 32.061 | 0.183 | 0.57 | 16.8 |
| 2200 | 23.763 | 154.9 | 170.6* | 23.401 | 0.131 | 23.270 | 0.493 | 2.08* | 18.4 |
| 2200 | 23.398 | 138.8 | 157.7 | 23.362 | 0.126 | 23.236 | 0.162 | 0.69 | 17.2 |
| 2200 | 21.165 | 149.1 | 165.4 | -- | -- | -- | -- | -- | 18.0 |
| 2200 | 25.794 | 163.0 | 182.7 | 25.792 | 0.131 | 25.661 | 0.133 | 0.52 | 17.2 |
| 2200 | 24.868 | 148.8 | 168.7 | 25.762 | 0.143 | 24.619 | 0.247 | 0.99 | 17.9 |
| 2200 | 20.264 | 136.7 | 151.9 | 20.196 | 0.098 | 20.098 | 0.166 | 0.82 | 17.7 |
| 2200 | 33.356 | 214.6 | 240.4 | 33.332 | 0.174 | 33.158 | 0.198 | 0.59 | 17.5 |
| 2200 | 21.153 | 135.9 | 151.5 | 21.086 | 0.106 | 20.980 | 0.173 | 0.82 | 18.2 |
| 2200 | 28.741 | 172.3 | 194.2 | 28.648 | 0.145 | 28.503 | 0.238 | 0.83 | 18.1 |
| 2200 | 19.552 | 120.0 | 135.4 | 19.540 | 0.107 | 19.433 | 0.119 | 0.61 | 16.0 |
| 2200 | 29.774 | 193.2 | 216.9 | 29.754 | 0.147 | 29.607 | 0.167 | 0.56 | 17.3 |

Average Au Loss % = 0.70

s = 0.16

* rejected since bead formed rootlets

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 2300 | 23.378 | 149.8 | 165.8 | 23.387 | 0.232 | 23.155 | 0.223 | 0.95 | 16.8 |
| 2300 | 35.041 | 198.4 | 224.6 | 35.196 | 0.500 | 34.696 | 0.345 | 0.99 | 16.0 |
| 2300 | 26.238 | 165.7 | 183.6 | 26.394 | 0.336 | 26.058 | 0.180 | 0.69 | 15.2 |
| 2300 | 24.586 | 157.6 | 174.6 | 24.741 | 0.312 | 24.429 | 0.157 | 0.64 | 15.8 |
| 2300 | 28.252 | 173.4 | 194.5 | 28.462 | 0.392 | 28.070 | 0.182 | 0.64 | 17.1 |
| 2300 | 25.270 | 145.2 | 165.0 | 25.390 | 0.306 | 25.084 | 0.186 | 0.74 | 16.7 |

Average Au Recovery = 99.22%

Average Au Loss % = 0.78

s = 0.16

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 2400 | 18.168 | 117.2 | 128.2 | 18.166 | 0.111 | 18.055 | 0.113 | 0.62 | 15.4 |
| 2400 | 20.052 | 138.1 | 145.9 | 19.592 | 0.114 | 19.478 | 0.574 | 2.86* | 15.9 |
| 2400 | 22.294 | 150.2 | 163.5 | 22.272 | 0.139 | 22.133 | 0.161 | 0.72 | 14.8 |
| 2400 | 27.156 | 165.7 | 182.1 | 27.165 | 0.186 | 26.979 | 0.177 | 0.65 | 13.9 |
| 2400 | 23.376 | 144.7 | 159.5 | 23.362 | 0.147 | 23.215 | 0.161 | 0.69 | 15.7 |
| 2400 | 25.679 | 148.2 | 166.5 | 25.716 | 0.201 | 25.515 | 0.164 | 0.64 | 16.1 |
| 2400 | 28.991 | 175.5 | 197.2 | 29.425 | 0.672 | 28.753 | 0.238 | 0.81 | 18.1 |
| 2400 | 21.036 | 133.9 | 142.4 | 20.286 | 0.330 | 19.956 | 1.080 | 5.14* | 15.4 |
| 2400 | 24.507 | 152.8 | 170.9 | 24.782 | 0.485 | 24.297 | 0.210 | 0.86 | 16.3 |
| 2400 | 25.184 | 151.1 | 167.0 | 25.345 | 0.572 | 24.773 | 0.411 | 1.63* | 16.2 |
| 2400 | 21.333 | 133.8 | 149.4 | 21.559 | 0.470 | 21.089 | 0.244 | 1.14 | 16.7 |
| 2400 | 34.474 | 213.3 | 238.3 | 34.969 | 0.734 | 34.235 | 0.239 | 0.69 | 15.6 |

Average Au Loss % = 0.88

s = 0.19

* rejected since visible portions of the lead button were dispersed through the slag.

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 2500 | 32.389 | 178.7 | -- | -- | -- | -- | -- | -- | |
| 2500 | 23.854 | 153.4 | 165.4 | 23.722 | 0.178 | 23.544 | 0.310 | 1.30 | |
| 2500 | 22.465 | 139.6 | 150.0 | 22.470 | 0.192 | 22.278 | 0.187 | 0.83 | |
| 2500 | 23.122 | 150.1 | -- | -- | -- | -- | -- | -- | |
| 2500 | 24.432 | 164.1 | 180.9 | 24.428 | 0.192 | 24.236 | 0.196 | 0.80 | |
| 2500 | 26.597 | 177.7 | 198.5 | 26.660 | 0.214 | 26.446 | 0.151 | 0.57 | |

Average Au Loss % = 0.88     s = 0.31

Samples 1 & 4 at 2500 were lost due to seepage of the charge through the crucible.

Charge used for temperature study:

15.0 g. $SiO_2$; 85.0 g. PbO; 21.1 g. $Na_2CO_3$; 4.5 g. CaO; 0.9 g. flour. 0.9 - 1.2 g. polyethylene bag

## TABLE XIV

Summary of Effect of Fusion Temperature on Gold Losses

| Temperature (°F) | Au Loss % | s | n | Ag:Au | Weight Lead Button (grams) |
|---|---|---|---|---|---|
| 1900 | 0.95 | 0.24 | 6 | 6.3:1.0 | 16.0 |
| 2000 | 0.81 | 0.15 | 6 | 6.5:1.0 | 16.9 |
| 2100 | 0.63 | 0.14 | 6 | 6.5:1.0 | 18.0 |
| 2200 | 0.70 | 0.16 | 10 | 6.4:1.0 | 17.5 |
| 2300 | 0.78 | 0.16 | 6 | 6.1:1.0 | 16.3 |
| 2400 | 0.88 | 0.19 | 9 | 6.3:1.0 | 16.0 |
| 2500 | 0.88 | 0.31 | 4 | 6.4:1.0 | 16.4 |

study. In general a repeat trial was performed whenever the number of

rejected samples was more than one or when the results were contrary

to expectations. For the trial at 2500°F this practise was not followed

since it became evident that the process was visibly breaking down.

At this high temperature the slag actually permeated through the crucible

wall without any apparent breakage of the crucible itself. Two samples

were entirely lost in this way. This temperature was thus taken to

be above the practical upper limit for the process. The excessively

high deviation in this trial supports this conclusion.

A consideration of the remaining results would seem to indicate

that the practise of lowering the initial temperature and then raising

it towards the end, does not yield the best results with regards to

minimal gold losses. While the number of temperature combinations

studied was limited to two, these are commonly used temperatures for

gold assaying.

With regards to the constant temperature studies, an optimum

temperature is indicated at 2100°F. At temperatures above this, gold

losses increase to a maximum of 0.88% and at temperatures lower than

this gold losses increase to a maximum of 0.95%. The reason for the

breakdown at the higher temperatures has already been suggested, but

the explanation for the lower temperature results is not as obvious.

No doubt as temperature decreases the increased viscosity of the flux

components militates against the settling of the gold particles which

have not been collected by the lead. Perhaps also of significance, is

the fact that 1900°F is the only temperature below the melting point

of gold (1945°F). At this lower temperature the significant decrease

in precision is consistent with the view that fusions should not be

conducted below 2000°F.

While application of a statistical test indicates a significant difference between the 2100°F trial and only one other (1900°F), and that only at the 95% confidence level, a fairly consistent trend towards a minimum gold loss at 2100°F does appear to be indicated. Whether increased losses with increasing temperature can be attributed to increased losses to the pot wall as the gold viscosity decreases, or to increased volatility of the gold can not be deduced from this research. The overall average gold loss was 0.76% s = 0.18.

It should also be noted that the weight of lead button passes through a maximum at the temperature where gold losses are minimized. This would suggest that the effect of lead button weight might explain the observed trend.

3. Effect of Lead Button Weight on Gold Losses

In this series of experiments the gold losses were determined in exactly the same fashion as in the temperature study just discussed above. The aim of these experiments was to determine the relationship between gold losses and the weight of lead button formed.

The charge used was, except for the weight of reducing agent, unchanged from the temperature study and is given at the bottom of Table XV. This table is a summation of the results obtained with Table XVI being an abbreviated summary of the same.

Using no added reducing agent, the average weight of lead button can be seen to be 7.3 grams s = 0.7. Addition of varying amounts of reducing agent (flour) increases the weight of lead button but in an irregular way. The first 0.5 grams flour increases button weight by about 4 grams while the next 0.4 grams increases button weight by almost 9 grams. The next two additions of 0.5 grams flour causes the button weight to increase by about 7 grams. The relatively small

**TABLE XV**

Effect of Lead Button Weight On Gold

Losses

| Weight Flour (grams) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| nil | 29.288 | 189.7 | 210.6 | 29.325 | 0.254 | 29.071 | 0.217 | 0.74 | 8.1 |
| nil | 21.129 | 134.5 | 148.7 | 21.102 | 0.145 | 20.957 | 0.172 | 0.82 | 7.4 |
| nil | 25.210 | 173.9 | 191.2 | 25.214 | 0.177 | 25.037 | 0.173 | 0.69 | 7.4 |
| nil | 26.244 | 184.1 | 202.3 | 26.217 | 0.179 | 26.038 | 0.206 | 0.79 | 7.7 |
| nil | 27.444 | 183.0 | 202.5 | 27.055 | 0.188 | 26.867 | 0.577 | 2.11* | 7.0 |
| nil | 22.408 | 141.0 | 156.5 | 22.350 | 0.155 | 22.195 | 0.217 | 0.95 | 6.0 |
| | | | | Average Gold Recovery = 99.20% | | Average Au Loss % | | = 0.80 | 7.3 |
| | | | | | | | s | = 0.10 | 0.7 |
| 0.5 | 28.558 | 172.6 | 194.5 | 28.571 | 0.239 | 28.332 | 0.226 | 0.79 | 11.0 |
| 0.5 | 36.503 | 218.7 | 246.5 | 36.519 | 0.325 | 36.194 | 0.309 | 0.85 | 10.5 |
| 0.5 | 17.227 | 118.5 | 131.5 | 17.198 | 0.116 | 17.082 | 0.145 | 0.84 | 11.2 |
| 0.5 | 22.118 | 137.2 | 153.9 | 22.176 | 0.206 | 21.970 | 0.148 | 0.67 | 10.7 |
| 0.5 | 30.837 | 210.4 | 233.9 | 30.844 | 0.275 | 30.569 | 0.268 | 0.87 | 10.9 |
| 0.5 | 30.067 | 194.0 | 218.9 | 30.112 | 0.261 | 29.851 | 0.216 | 0.72 | 12.3 |
| | | | | Average Gold Recovery = 99.21% | | Average Au Loss % | | = 0.79 | 11.1 |
| | | | | | | | s | = 0.08 | 0.6 |

* rejected on statistical grounds

| Weight Flour (grams) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 0.9 | 22.295 | 126.5 | 144.8 | 22.355 | 0.200 | 22.155 | 0.140 | 0.63 | 17.7 |
| 0.9 | 19.434 | 134.5 | 150.7 | 19.412 | 0.118 | 19.294 | 0.140 | 0.72 | 19.0 |
| 0.9 | 19.199 | 128.0 | 143.8 | 19.196 | 0.157 | 19.039 | 0.160 | 0.83 | 17.6 |
| 0.9 | 22.701 | 148.7 | 168.0 | 22.720 | 0.116 | 22.604 | 0.097 | 0.43 | 17.6 |
| 0.9 | 21.804 | 137.9 | 156.3 | 21.814 | 0.137 | 21.677 | 0.127 | 0.58 | 18.4 |
| 0.9 | 21.088 | 141.3 | 158.5 | 21.091 | 0.126 | 20.965 | 0.123 | 0.58 | 17.6 |

Average Au Loss % = 0.63  
s = 0.14

Average Gold Recovery = 99.37%

Average 18.0, 0.6

| Weight Flour (grams) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 1.5 | 22.443 | 147.4 | 166.5 | 22.480 | 0.231 | 22.258 | 0.185 | 0.83 | 21.1 |
| 1.5 | 24.650 | 167.3 | 186.8 | 24.656 | 0.258 | 24.398 | 0.252 | 1.02 | 21.2 |
| 1.5 | 26.597 | 166.0 | 188.8 | 26.568 | 0.244 | 26.324 | 0.273 | 1.02 | 20.0 |
| 1.5 | 28.641 | 177.6 | 203.3 | 28.759 | 0.312 | 28.447 | 0.194 | 0.68 | 21.6 |
| 1.5 | 19.164 | 133.6 | 149.3 | 19.220 | 0.178 | 19.042 | 0.122 | 0.64 | 19.0 |
| 1.5 | 20.660 | 134.0 | 154.2 | 20.706 | 0.180 | 20.526 | 0.134 | 0.65 | 20.7 |

Average Au Loss % = 0.81  
s = 0.18

Average Gold Recovery = 99.19%

Average 20.6, 1.0

| Weight Flour (grams) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 2.0 | 21.269 | 147.0 | 164.8 | 21.329 | 0.183 | 21.146 | 0.123 | 0.58 | 27.0 |
| 2.0 | 22.256 | 148.6 | 166.5 | 22.282 | 0.194 | 22.088 | 0.168 | 0.75 | 26.5 |
| 2.0 | 20.117 | 131.1 | 146.9 | 20.063 | 0.147 | 19.916 | 0.181 | 0.90 | 28.1 |
| 2.0 | 20.366 | 130.2 | 146.2 | 20.415 | 0.175 | 20.240 | 0.126 | 0.62 | 27.2 |
| 2.0 | 28.017 | 189.5 | 212.3 | 28.015 | 0.226 | 27.789 | 0.228 | 0.82 | 27.2 |
| 2.0 | 20.839 | 135.0 | 152.5 | 20.849 | 0.161 | 20.688 | 0.151 | 0.73 | 27.0 |
| | | | | Average Gold Recovery = 99.27% | | | Average Au Loss % = 0.73 | | 27.2 |
| | | | | | | | | s = 0.12 | 0.5 |
| 2.5 | 28.279 | 170.7 | 193.7 | 28.220 | 0.282 | 27.938 | 0.341 | 1.20* | 34.3 |
| 2.5 | 27.098 | 170.8 | 192.6 | 27.034 | 0.230 | 26.804 | 0.294 | 1.08 | 32.1 |
| 2.5 | 26.915 | 170.3 | 193.2 | 26.962 | 0.245 | 26.717 | 0.198 | 0.74 | 34.3 |
| 2.5 | 21.780 | 143.2 | 161.3 | 21.812 | 0.197 | 21.615 | 0.165 | 0.76 | 33.9 |
| 2.5 | 24.367 | 161.2 | 180.3 | 24.422 | 0.196 | 24.226 | 0.141 | 0.58 | 33.7 |
| 2.5 | 26.298 | 167.7 | 189.8 | 26.375 | 0.220 | 26.155 | 0.143 | 0.54 | 34.9 |
| | | | | Average Gold Recovery = 99.26% | | | Average Au Loss % = 0.74 | | 33.9 |
| | | | | | | | | s = 0.21 | 1.0 |

* rejected due to spitting of the cupelled bead

Charge used: flour-varied; 15.0 g. $SiO_2$; 85.0 g. PbO; 21.1 g. $Na_2CO_3$; 4.5 g. CaO

## TABLE XVI

Summary of Effect of Lead Button Weight on Gold

Losses

| Weight Flour (grams) | Au Loss (%) | s | Ag:Au | Weight Lead Button (grams) | s |
|---|---|---|---|---|---|
| nil | 0.80 | 0.10 | 6.6:1.0 | 7.3 | 0.7 |
| 0.5 | 0.79 | 0.08 | 6.4:1.0 | 11.1 | 0.6 |
| 0.9 | 0.63 | 0.14 | 6.5:1.0 | 18.0 | 0.6 |
| 1.5 | 0.81 | 0.18 | 6.6:1.0 | 20.6 | 1.0 |
| 2.0 | 0.73 | 0.12 | 6.6:1.0 | 27.2 | 0.5 |
| 2.5 | 0.74 | 0.21 | 6.4:1.0 | 33.9 | 1.0 |

increase in button weight of 2.6 grams on addition of 0.6 grams flour to 0.9 grams may have been due to an experimental reason. The draft of the furnace was accidentally left open from the previous cupellation. Since the door of the furnace was not exactly air-tight, an increased flow of air in the furnace may have maintained a less effective reducing atmosphere. The larger standard deviation in the weight of lead button in this experiment, as well as the final one of the series, may reflect inadequate mixing of the flux components.

A statistical analysis of the results indicated variations in gold loss as a function of lead button weight were not significant at the 99% confidence level. In the development of an optimum procedure the trial having a lead button weight of 18 grams was chosen merely because the gold loss was a minimum for this weight of lead.

The average gold loss for this study was thus found to be 0.73% $s = 0.14$. Since neither temperature or weight of lead button were observed to have a significant effect upon the gold losses at the 99% confidence level a statistical test of significant differences should confirm this. The overall average gold loss of 0.76% $s = 0.18$ for the temperature study when compared to the overall average loss for the study under consideration indicated no significant differences between the two trials. This would be the case even at the 95% confidence level.

4. Effect of Fusion Time on Gold Losses

The objective of this portion of the research was to determine the shortest time required for the smallest gold losses. Fusion and cupellation temperatures were 2100°F and 1800°F respectively, for all assays. Samples were prepared as previously described with a charge as indicated at the bottom of Table XVIII. Table XVII is a detailed record of the results of the time study and Table XVIII is a summary of the same.

Since assays were done in groups of six, and since some samples

**TABLE XVII**

Effect of Fusion Time on

Gold Losses

| Time (hrs) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 0.5 | 21.965 | 140.7 | 159.5 | 21.984 | 0.176 | 21.808 | 0.157 | 0.71 | 18.0 |
| 0.5 | 16.921 | 111.6 | 125.1 | 16.928 | 0.129 | 16.799 | 0.122 | 0.72 | 16.7 |
| 0.5 | 26.691 | 183.4 | 208.6 | 29.753 | 0.236 | 29.517 | 0.174 | 0.59 | 17.8 |
| 0.5 | 24.513 | 164.2 | 185.4 | 24.553 | 0.207 | 24.346 | 0.167 | 0.68 | 17.8 |
| 0.5 | 22.615 | 151.6 | 171.0 | 22.632 | 0.186 | 22.446 | 0.169 | 0.75 | 17.6 |
| 0.5 | 24.212 | 160.2 | 180.7 | 24.226 | 0.226 | 24.000 | 0.212 | 0.87 | 16.1 |
| 0.5 | 16.281 | 110.7 | 123.7 | 16.276 | 0.111 | 16.165 | 0.116 | 0.71 | 18.5 |
| 0.5 | 22.981 | 135.7 | 154.7 | 22.306 | 0.163 | 22.143 | 0.144 | 0.65 | 17.5 |
| 0.5 | 22.287 | 152.1 | 170.8 | 22.998 | 0.153 | 22.845 | 0.136 | 0.59 | 17.7 |
| 0.5 | 25.050 | 163.9 | 185.1 | 25.061 | 0.162 | 24.899 | 0.151 | 0.60 | 18.4 |
| 0.5 | 28.323 | 173.2 | 197.1 | 28.242 | 0.206 | 28.036 | 0.287 | 1.01 | 17.2 |
| 0.5 | 24.042 | 154.3 | 174.7 | 24.060 | 0.190 | 23.870 | 0.172 | 0.72 | 16.7 |

Average Au Loss % = 0.72

s = 0.12

Average Gold Recovery = 99.28%

| Time (hrs) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 1.0 | 27.262 | 170.0 | 192.8 | 27.296 | 0.193 | 27.103 | 0.159 | 0.58 | 16.2 |
| 1.0 | 22.432 | 151.2 | 170.0 | 22.460 | 0.159 | 22.301 | 0.131 | 0.58 | 16.7 |
| 1.0 | 30.635 | 185.6 | 210.9 | 30.674 | 0.212 | 30.462 | 0.173 | 0.57 | 18.0 |
| 1.0 | 26.547 | 165.2 | 187.6 | 26.609 | 0.220 | 26.389 | 0.158 | 0.60 | 17.0 |
| 1.0 | 23.809 | 149.9 | 169.9 | 23.830 | 0.170 | 23.660 | 0.149 | 0.63 | 17.6 |
| 1.0 | 21.576 | 144.8 | 162.6 | 21.586 | 0.160 | 21.426 | 0.150 | 0.69 | 17.6 |
| 1.0 | 19.735 | 128.0 | 144.5 | 19.714 | 0.085 | 19.629 | 0.106 | 0.54 | 17.2 |
| 1.0 | 27.718 | 180.5 | 202.5 | 27.685 | 0.147 | 27.538 | 0.180 | 0.65 | 18.1 |
| 1.0 | 25.242 | 154.1 | 175.1 | 25.224 | -- | -- | -- | -- | 18.4 |
| 1.0 | 24.716 | 164.0 | 183.8 | 24.680 | 0.101 | 24.579 | 0.137 | 0.56 | 18.3 |
| 1.0 | 29.354 | 190.2 | 214.4 | 29.325 | -- | -- | -- | -- | 19.2 |
| 1.0 | 27.663 | 178.3 | 198.8 | 27.628 | 0.162 | 27.466 | 0.197 | 0.71 | 18.4 |

Average Au Loss % = 0.61

s = 0.06

Average Gold Recovery = 99.39%

| Time (hrs) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 1.5 | 22.297 | 145.5 | 163.5 | 22.267 | 0.082 | 22.185 | 0.112 | 0.50 | 17.9 |
| 1.5 | 22.285 | 152.0 | 170.7 | 22.198 | 0.071 | 22.127 | 0.158 | 0.70* | 17.1 |
| 1.5 | 23.567 | 148.1 | 167.8 | 23.509 | 0.072 | 23.437 | 0.130 | 0.55 | 19.1 |
| 1.5 | 27.534 | 168.9 | 192.9 | 27.478 | 0.097 | 27.381 | 0.153 | 0.56 | 18.3 |
| 1.5 | 27.242 | 164.5 | 187.3 | 27.209 | 0.127 | 27.082 | 0.160 | 0.59 | 16.7 |
| 1.5 | 21.871 | 130.3 | 149.3 | 21.889 | 0.132 | 21.757 | 0.114 | 0.52 | 18.5 |
| 1.5 | 19.457 | 130.4 | -- | -- | -- | -- | -- | -- | -- |
| 1.5 | 30.641 | 185.0 | 209.8 | 30.655 | 0.188 | 30.467 | 0.174 | 0.57 | 17.0 |
| 1.5 | 23.937 | 158.8 | 178.8 | 23.937 | 0.134 | 23.803 | 0.134 | 0.56 | 19.3 |
| 1.5 | 24.113 | 158.2 | 178.1 | 24.116 | 0.144 | 23.472 | 0.141 | 0.59 | 21.2 |
| 1.5 | 25.634 | 160.0 | 181.8 | 25.686 | 0.197 | 25.489 | 0.145 | 0.57 | 18.9 |
| 1.5 | 20.263 | 127.8 | 145.8 | 20.250 | 0.125 | 20.125 | 0.138 | 0.58 | 20.3 |

Average Au Loss %  = 0.56

s   = 0.03

Average Gold Recovery = 99.44%

| Time (hrs) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 2.0 | 24.937 | 154.2 | 175.3 | 24.915 | 0.110 | 24.805 | 0.132 | 0.53 | 19.5 |
| 2.0 | 22.447 | 146.8 | 165.6 | 22.399 | 0.104 | 22.295 | 0.152 | 0.68 | 19.0 |
| 2.0 | 25.676 | 158.1 | 179.2 | 25.654 | 0.127 | 25.527 | 0.149 | 0.58 | 19.0 |
| 2.0 | 26.240 | 164.3 | 186.2 | 26.238 | 0.131 | 26.107 | 0.133 | 0.51 | 18.0 |
| 2.0 | 26.564 | 171.3 | 193.5 | 26.529 | 0.142 | 26.387 | 0.177 | 0.67 | 17.9 |
| 2.0 | 23.732 | 160.5 | 180.0 | 23.753 | 0.135 | 23.618 | 0.114 | 0.48 | 18.3 |

Average Au Loss % = 0.58

s = 0.08

Average Gold Recovery = 99.42%

| Time (hrs) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 2.5 | 21.684 | 141.5 | 160.7 | 21.634 | 0.094 | 21.540 | 0.144 | 0.66 | 18.1 |
| 2.5 | 23.200 | 149.0 | 168.8 | 23.200 | 0.161 | 23.039 | 0.161 | 0.69 | 15.2 |
| 2.5 | 23.254 | 156.7 | 176.2 | 23.258 | 0.135 | 23.123 | 0.131 | 0.62 | 17.0 |
| 2.5 | 21.524 | 142.9 | 163.7 | 21.486 | 0.102 | 21.384 | 0.140 | 0.65 | 18.1 |
| 2.5 | 26.836 | 176.9 | 201.9 | 26.837 | 0.157 | 26.680 | 0.156 | 0.58 | 18.6 |
| 2.5 | 21.575 | 151.5 | 172.7 | 21.533 | 0.106 | 21.427 | 0.148 | 0.69 | 19.1 |
| 2.5 | 22.295 | 126.5 | 144.8 | 22.355 | 0.200 | 22.155 | 0.140 | 0.63 | 17.7 |
| 2.5 | 19.434 | 134.5 | 150.7 | 19.412 | 0.118 | 19.294 | 0.140 | 0.72 | 19.0 |
| 2.5 | 19.199 | 128.0 | 143.8 | 19.196 | 9.157 | 19.039 | 0.160 | 0.83 | 17.6 |
| 2.5 | 22.701 | 148.7 | 168.0 | 22.720 | 0.116 | 22.604 | 0.097 | 0.43 | 17.6 |
| 2.5 | 21.804 | 137.9 | 156.3 | 21.814 | 0.137 | 21.677 | 0.127 | 0.58 | 18.4 |
| 2.5 | 21.088 | 141.3 | 158.5 | 21.091 | 0.126 | 20.965 | 0.123 | 0.58 | 17.6 |

Average Au Loss % = 0.64

s = 0.10

Average Gold Recovery = 99.36%

| Time (hrs) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|---|
| 3.5 | 31.480 | 189.7 | 214.7 | 31.515 | 0.249 | 31.266 | 0.214 | 0.68 | 16.8 |
| 3.5 | 18.829 | 119.2 | 133.7 | 18.858 | 0.147 | 18.711 | 0.118 | 0.63 | 16.3 |
| 3.5 | 20.866 | 137.3 | 151.9 | 20.755 | 0.158 | 20.597 | 0.269 | 1.28* | 17.5 |
| 3.5 | 18.591 | 122.3 | 137.3 | 18.613 | 0.146 | 18.467 | 0.124 | 0.67 | 19.3 |
| 3.5 | 17.026 | 117.8 | 131.2 | 17.033 | 0.117 | 16.916 | 0.110 | 0.65 | 16.1 |
| 3.5 | 22.131 | 130.6 | 148.1 | 22.130 | 0.194 | 21.936 | 0.195 | 0.88 | 15.6 |
| 3.5 | 20.561 | 130.5 | 145.4 | 20.449 | 0.137 | 20.292 | 0.269 | 1.30* | 16.7 |
| 3.5 | 22.270 | 140.3 | 157.6 | 22.255 | 0.162 | 22.093 | 0.177 | 0.79 | 14.0 |
| 3.5 | 21.567 | 133.9 | 151.4 | 21.582 | 0.159 | 21.423 | 0.144 | 0.67 | 15.6 |
| 3.5 | 20.798 | 144.5 | 162.0 | 20.792 | 0.154 | 20.638 | 0.160 | 0.77 | 17.8 |
| 3.5 | 26.747 | 163.7 | 186.5 | 26.796 | 0.205 | 26.591 | 0.156 | 0.58 | 16.0 |
| 3.5 | 24.342 | 158.8 | 178.5 | 24.392 | 0.201 | 24.191 | 0.151 | 0.62 | 17.2 |

Average Au Loss % = 0.69

s = 0.09

Average Gold Recovery = 99.31%

* rejected on statistical grounds

## TABLE XVIII

Summary of Effect of Fusion Time on Gold Losses

| Time (hrs) | Au Loss (%) | s | n | Ag:Au | Weight Lead Button (grams) |
|---|---|---|---|---|---|
| 0.5 | 0.72 | 0.09 | 5 | 6.5:1.0 | 17.3 |
| 0.5 | 0.71 | 0.15 | 5 | 6.4:1.0 | 17.7 |
| 1.0 | 0.61 | 0.05 | 6 | 6.4:1.0 | 17.2 |
| 1.0 | 0.62 | 0.08 | 4 | 6.4:1.0 | 18.3 |
| 1.5 | 0.54 | 0.04 | 5 | 6.3:1.0 | 17.9 |
| 1.5 | 0.57 | 0.01 | 5 | 6.4:1.0 | 19.3 |
| 2.0 | 0.58 | 0.08 | 6 | 6.4:1.0 | 18.6 |
| 2.5 | 0.65 | 0.04 | 6 | 6.6:1.0 | 17.7 |
| 2.5 | 0.63 | 0.14 | 6 | 6.5:1.0 | 18.0 |
| 3.5 | 0.70 | 0.10 | 5 | 6.3:1.0 | 16.9 |
| 3.5 | 0.69 | 0.09 | 5 | 6.4:1.0 | 15.7 |

Charge used: 15.0 g. $SiO_2$; 85.0 g. PbO; 21.1 g. $Na_2CO_3$; 4.5 g. CaO

1.0 g. flour

had to be rejected on occasion it was decided that each assay should
be repeated by a duplicate trial. In this way some idea would also be
obtained of the reproducibility of the complete fire assay process.
The results found in Table XVIII reflect this comparison and with the
exception of the 2 hour trial which was not repeated the difference
between any two repeat trials was never greater than 0.03%. Put in
another way, the reproducibility of gold recovery is of the order of
3 parts in 10,000.

A consideration of the results of Table XVII indicates a definite
trend in gold losses beginning with a maximum gold loss of 0.72% for
a ½ hour fusion and losses of 0.61, 0.56, 0.58, 0.64 and 0.69% for
1.0, 1.5, 2.0, 2.5 and 3.5 hours respectively. A statistical analysis
of the results indicates that the minimum gold loss which occurred for
a fusion time of 1.5 hours is significantly different from the 0.5
hour and 3.5 hour trials at the 99% confidence level and also differs
from the 2.5 hour trial at the 95% confidence level. The optimum time
of fusion would therefore seem to lie in the range of 1-2 hours with
little to chose between those limits.

It should of course be remembered that the gold of the samples
under consideration is not chemically bound, but merely a mixture. In
those cases where the ore involves a chemical combination the best
length of time for the fusion process may differ significantly. In
point of fact most gold in nature is in the elemental state and
conclusions reached here should be applicable provided the ore is finely
divided.

A consideration of Table XVIII also indicates that the weight of
lead button may vary by as much as 1.5 g. under apparently identical
conditions without any significant effect on the gold loss. This fact

is consistent with the conclusion of the related study considered above. (Effect of Weight Lead Button)

5. Effect of Cupellation Temperature on Gold Losses

It will be recalled that claims are frequently made that the temperature of cupellation is one of the most important variables affecting gold loss. The cupellation loss reported in the literature is often based on gold losses for a process which was earlier labelled as a "simulated cupellation". The losses determined here involve the cupellation of a lead button containing the silver and gold in what must be close to a homogeneous alloy of the metals involved. The behaviour of gold in such a button, may differ significantly from the pure gold and silver wrapped in lead foil of the same weight.

The fusion temperature was maintained constant at 2100°F with a charge identical to that used for the time study (bottom of Table XVIII). Sample preparation was in the usual way. The cupellation procedure involved an initial time of 5 minutes heating with the door and draft closed, a driving interval dependent on the size of the largest lead button, and a 5 minute finishing period. The parting procedure involved two acid treatments with 1:4 and 1:1 nitric (acid: water) followed by three washings with hot water. The annealed bead was weighed and then analyzed for silver by atomic absorption as usual.

The individual entries from this study are reported in Table XIX and summarized in Table XX. For the four temperatures studied the maximum difference between repeat trials occurred at the highest temperature of 2000°F and corresponded to 6 parts per 10,000 with the minimum difference of 3 parts in 10,000 occurring at the two lowest temperatures of 1800°F and 1700°F. The minimum gold loss occurred at 1800°F, the usual temperature of cupellation used throughout this

TABLE XIX

Effect of Cupellation Temperature

On Gold Losses

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 2000 | 20.789 | 138.6 | 153.4 | 20.802 | 0.013 | 0.171 | 20.631 | 0.158 | 0.76 |
| 2000 | 19.001 | 123.7 | 138.2 | 19.017 | 0.016 | 0.146 | 18.871 | 0.130 | 0.68 |
| 2000 | 20.369 | 131.2 | 146.1 | 20.298 | -0.071 | 0.154 | 20.144 | 0.225 | 1.10 |
| 2000 | 25.428 | 171.8 | 190.5 | 25.451 | 0.023 | 0.204 | 25.247 | 0.181 | 0.71 |
| 2000 | 23.928 | 163.3 | 180.0 | 23.902 | -0.026 | 0.211 | 23.691 | 0.237 | 1.00 |
| 2000 | 24.363 | 159.6 | 179.2 | 24.323 | -0.040 | 0.203 | 24.120 | 0.243 | 1.00 |
| | | | | | | | Average Au Loss % = 0.88 | | |
| | | | | | | | | s = 0.18 | |
| 2000 | 21.426 | 136.1 | 151.9 | 21.366 | -0.060 | 0.114 | 21.252 | 0.174 | 0.81 |
| 2000 | 24.836 | 152.1 | 170.2 | 24.676 | -0.160 | 0.118 | 24.558 | 0.278 | 1.12 |
| 2000 | 25.049 | 160.0 | 177.7 | 24.998 | -0.051 | 0.136 | 24.862 | 0.187 | 0.78 |
| 2000 | 23.027 | 145.1 | 162.9 | 22.959 | -0.068 | 0.103 | 22.856 | 0.171 | 0.74 |
| 2000 | 21.292 | 143.4 | 159.8 | 21.232 | -0.060 | 0.103 | 21.129 | 0.163 | 0.77 |
| 2000 | 28.558 | 191.3 | 212.5 | 28.496 | -0.062 | 0.133 | 28.363 | 0.195 | 0.68 |
| | | | | | | | Average Au Loss % = 0.82 | | |
| | | | | | | | | s = 0.16 | |

Average for both trials at 2000 °F.

Au Loss % = 0.85    s = 0.16    n = 12

Ag:Au = 6.5    s = 0.2    n = 12

Lead Weight = 15.0 grams    s = 1.3    n = 12

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 1900 | 26.539 | 164.3 | 185.8 | 26.554 | 0.015 | 0.165 | 26.389 | 0.150 | 0.59 |
| 1900 | 27.256 | 172.4 | 193.0 | 27.176 | -0.080 | 0.165 | 27.011 | 0.245 | 0.90 |
| 1900 | 21.306 | 137.9 | 154.0 | 21.276 | -0.030 | 0.132 | 21.144 | 0.162 | 0.76 |
| 1900 | 25.290 | 168.5 | 188.3 | 25.266 | -0.024 | 0.137 | 25.129 | 0.161 | 0.64 |
| 1900 | 22.805 | 151.2 | 169.7 | 22.805 | 0.000 | 0.133 | 22.672 | 0.133 | 0.58 |
| 1900 | 22.538 | 141.5 | 159.3 | 22.539 | 0.001 | 0.147 | 22.392 | 0.146 | 0.65 |

Average Au Loss % = 0.69

s = 0.12

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 1900 | 26.916 | 165.5 | 185.6 | 26.926 | 0.010 | 0.171 | 26.755 | 0.161 | 0.60 |
| 1900 | 23.162 | 152.8 | 169.4 | 23.132 | -0.030 | 0.145 | 22.987 | 0.175 | 0.76 |
| 1900 | 18.359 | 123.3 | 135.6 | 18.349 | 0.010 | 0.102 | 18.247 | 0.112 | 0.61 |
| 1900 | 22.647 | 141.5 | 159.4 | 22.651 | 0.004 | 0.137 | 22.514 | 0.133 | 0.59 |
| 1900 | 27.626 | 170.6 | 192.9 | 27.620 | -0.006 | 0.183 | 27.437 | 0.189 | 0.68 |
| 1900 | 25.410 | 161.8 | 180.6 | 25.426 | 0.016 | 0.179 | 25.247 | 0.163 | 0.64 |

Average Au Loss % = 0.65

s = 0.06

Average for both trials at 1900°F   Au loss % = 0.67   s = 0.10 n = 12

Ag:Au = 6.4   s = 0.2   n = 12

Lead Weight = 14.0 grams   s = 0.8   n = 12

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 1800 | 22.297 | 145.5 | 163.5 | 22.267 | -0.030 | 0.082 | 22.185 | 0.112 | 0.50 |
| 1800 | 22.285 | 152.0 | 170.7 | 22.198 | -0.087 | 0.071 | 22.127 | 0.158 | 0.70* |
| 1800 | 23.567 | 148.1 | 167.8 | 23.509 | -0.058 | 0.072 | 23.437 | 0.130 | 0.55 |
| 1800 | 27.534 | 168.9 | 192.9 | 27.478 | -0.056 | 0.097 | 27.381 | 0.153 | 0.56 |
| 1800 | 27.242 | 164.5 | 187.3 | 27.209 | -0.031 | 0.127 | 27.082 | 0.160 | 0.59 |
| 1800 | 21.871 | 130.3 | 149.3 | 21.889 | +0.018 | 0.132 | 21.757 | 0.114 | 0.52 |
| | | | | | | Average Au Loss % = | | | 0.54 |
| | | | | | | s = | | | 0.04 |
| 1800 | 19.457 | 130.4 | lost | lost | lost | lost | lost | lost | lost |
| 1800 | 30.641 | 185.0 | 209.8 | 30.655 | 0.014 | 0.188 | 30.467 | 0.174 | 0.57 |
| 1800 | 23.937 | 158.8 | 178.8 | 23.937 | 0.000 | 0.134 | 23.803 | 0.134 | 0.56 |
| 1800 | 24.113 | 158.2 | 178.1 | 24.116 | 0.003 | 0.144 | 23.972 | 0.141 | 0.59 |
| 1800 | 25.634 | 160.0 | 181.8 | 25.686 | 0.052 | 0.197 | 25.489 | 0.145 | 0.57 |
| 1800 | 20.263 | 127.8 | 145.8 | 20.250 | -0.013 | 0.125 | 20.125 | 0.138 | 0.58 |
| | | | | | | Average Au Loss % = | | | 0.57 |
| | | | | | | s = | | | 0.01 |

Average for both trials 1800°F Au Loss % = 0.56    s = 0.03    n = 10

Ag:Au = 6.3    s = 0.2    n = 10

Lead Weight = 18.7 grams    s = 1.4    n = 10

* rejected on statisical grounds

-96-

| Temperature (°F) | Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Surcharge (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % |
|---|---|---|---|---|---|---|---|---|---|
| 1700 | 26.802 | 161.8 | 185.3 | 26.815 | 0.013 | 0.171 | 26.644 | 0.158 | 0.59 |
| 1700 | 28.491 | 197.3 | 223.2 | 28.537 | 0.046 | 0.154 | 28.283 | 0.208 | 0.73 |
| 1700 | 21.198 | 142.4 | 160.5 | 21.181 | -0.017 | 0.124 | 21.057 | 0.141 | 0.67 |
| 1700 | 18.806 | 120.7 | frozen | frozen | frozen | frozen | frozen | frozen | frozen |
| 1700 | 26.109 | 156.6 | 182.0 | 26.101 | -0.008 | 0.137 | 25.964 | 0.145 | 0.56 |
| 1700 | 26.115 | 162.7 | frozen | frozen | frozen | frozen | frozen | frozen | frozen |
| | | | | | | | Average Au Loss % = | | 0.64 |
| | | | | | | | s = | | 0.08 |
| 1700 | 25.511 | 162.1 | 183.9 | 25.485 | -0.026 | 0.107 | 25.378 | 0.133 | 0.52 |
| 1700 | 23.190 | 152.5 | 172.1 | 23.187 | -0.003 | 0.142 | 23.045 | 0.145 | 0.63 |
| 1700 | 25.219 | 161.3 | 182.7 | 25.246 | 0.027 | 0.163 | 25.083 | 0.136 | 0.54 |
| 1700 | 20.950 | 140.3 | 158.4 | 20.924 | -0.026 | 0.104 | 20.820 | 0.130 | 0.62 |
| 1700 | 28.362 | 187.1 | 212.2 | 28.309 | -0.053 | 0.172 | 28.137 | 0.225 | 0.79 |
| 1700 | 22.686 | 141.7 | 162.8 | 22.704 | 0.018 | 0.145 | 22.559 | 0.127 | 0.56 |
| | | | | | | | Average Au Loss % = | | 0.61 |
| | | | | | | | s = | | 0.10 |

Average for both trials at 1700°F    Au loss % = 0.62    s = 0.09    n = 10

Ag:Au    = 6.4    s = 0.3    n = 10

Lead Weight    = 15.3 grams    s = 0.9    n = 10

**TABLE XX**

Summary of Effect of Cupellation Temperature

On Gold Losses

| Temperature ($^{o}$F) | Au Loss % | s | n | Ag:Au | Lead Weight (grams) |
|---|---|---|---|---|---|
| 2000 | 0.86 | 0.16 | 12 | 6.5 | 15.0 |
| 1900 | 0.67 | 0.10 | 12 | 6.4 | 14.0 |
| 1800 | 0.56 | 0.03 | 10 | 6.3 | 18.7 |
| 1700 | 0.62 | 0.09 | 10 | 6.4 | 15.3 |

research. A cupellation temperature of 1800°F produces a gold loss which is significantly different from all the other temperatures studied at the 95% confidence level and differs significantly from the higher temperatures at the 99% confidence level.

The above results verify in part the generalization that increasing temperature of cupellation increases gold losses. It is in contradiction to the generalization that the best temperature of cupellation is the lowest temperature which prevents freezing of the cupelling buttons.

## 6. Effect of A Cover

In order to test the effect of a cover, two trials, consisting of a dozen samples each, were run; one trial with, and other without a cover. The cover consisted of 25 grams of excess charge but not salted with gold and silver. The results are summarized in Table XXI. Since the results for the cupellation study had not been analyzed, the temperature of cupellation was 1700°F. Sample preparation and remaining aspects were the same as usual, with the charge the same as for the time study. The average gold loss without a cover was 0.62% s = 0.09 while with a cover it was 0.61% s = 0.08. The virtual coincidence of these results indicates that a cover is not worth the extra bother involved.

## 7. Miscellaneous Considerations

While not strictly related to gold losses in fire assaying a few points of interest to assaying are worthy of mention.

## a. Effect of Temperature on Percentage Silver Retained by Gold Beads

Since all partings were performed on the same steam bath the assumption was made that the temperature of the parting acid(s) was essentially constant or at least did not involve significant variations.

TABLE XXI

Effect of 25.0 g. Cover on Gold Losses of

Complete Fire Assay

I  no cover

| Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|
| 26.802 | 161.8 | 185.3 | 26.815 | 0.171 | 26.644 | 0.158 | 0.59 | 14.8 |
| 28.491 | 197.3 | 223.2 | 28.537 | 0.154 | 28.283 | 0.208 | 0.73 | 16.8 |
| 21.198 | 142.4 | 160.5 | 21.181 | 0.124 | 21.057 | 0.141 | 0.67 | 15.3 |
| 18.806 | 120.7 | -- | -- | -- | -- | -- | -- | 15.9 |
| 26.109 | 156.6 | 182.0 | 26.101 | 0.137 | 25.964 | 0.145 | 0.56 | 15.6 |
| 26.115 | 162.7 | -- | -- | -- | -- | -- | -- | 17.3 |
| 25.511 | 162.1 | 183.9 | 25.485 | 0.107 | 25.378 | 0.133 | 0.52 | 16.0 |
| 23.190 | 152.5 | 172.1 | 23.187 | 0.142 | 23.045 | 0.145 | 0.63 | 13.3 |
| 25.219 | 161.3 | 182.7 | 25.246 | 0.163 | 25.083 | 0.136 | 0.54 | 14.5 |
| 20.950 | 140.3 | 158.4 | 20.924 | 0.104 | 20.820 | 0.130 | 0.62 | 15.4 |
| 28.362 | 187.1 | 212.2 | 28.309 | 0.172 | 28.137 | 0.225 | 0.79 | 15.5 |
| 22.686 | 141.7 | 162.8 | 22.704 | 0.145 | 22.559 | 0.127 | 0.56 | 15.6 |

Average Au Loss % = 0.62

s = 0.09

Average Gold Recovery = 99.38%

II  25 g. cover

| Au Added (mg.) | Ag Added (mg.) | Sum (mg.) | Parted Bead (mg.) | Ag Retained (mg.) | Au Found (mg.) | Au Loss (mg.) | Au Loss % | Weight Lead Button (grams) |
|---|---|---|---|---|---|---|---|---|
| 19.452 | 127.9 | 144.6 | 19.390 | 0.137 | 19.253 | 0.199 | 1.02* | 17.0 |
| 19.756 | 136.5 | 153.5 | 19.788 | 0.140 | 19.648 | 0.108 | 0.55 | 18.6 |
| 24.121 | 150.4 | 172.0 | 24.155 | 0.173 | 23.982 | 0.138 | 0.58 | 17.0 |
| 25.155 | 153.4 | 177.4 | 25.193 | 0.188 | 25.005 | 0.150 | 0.60 | 19.3 |
| 24.107 | 159.2 | 187.5 | 24.072 | 0.140 | 24.932 | 0.175 | 0.73 | 17.5 |
| 21.906 | 147.0 | 166.3 | 21.953 | 0.164 | 21.789 | 0.117 | 0.53 | 19.5 |
| 23.077 | 148.2 | 168.0 | 23.113 | 0.183 | 22.930 | 0.147 | 0.64 | 17.4 |
| 19.838 | 130.1 | 146.5 | 19.837 | 0.146 | 19.691 | 0.147 | 0.74 | 17.3 |
| 20.699 | 135.4 | 153.3 | 20.728 | 0.139 | 20.589 | 0.110 | 0.53 | 19.0 |
| 23.164 | 150.8 | 170.2 | 23.178 | 0.179 | 22.999 | 0.165 | 0.71 | 20.0 |
| 20.696 | 127.3 | 145.6 | 20.753 | 0.169 | 20.584 | 0.112 | 0.54 | 18.0 |
| 22.262 | 144.6 | 164.0 | 22.297 | 0.164 | 22.133 | 0.129 | 0.58 | 18.2 |

Average Au Loss % = 0.61

s = 0.08

Average Gold Recovery = 99.39%

*  rejected on statistical grounds

As more and more experiments were performed this did not prove to be the case. Eventually an abrupt change in the percentage silver retained by the parted beads was traced to a reduced steam flow rate through the steam bath. On measuring the temperature for a series of partings, variations as large as 25°C were observed over a period of time. Table XXII represents a selection of three partings chosen from a larger group. The reason for the selection of these trials was a common silver to gold ratio of 6.6:1.0 approximately constant weight of gold, and a common parting procedure. For the majority of the other partings the temperature of the parting acid was not measured.

From the table it is evident that the percentage silver retained increases in a pronounced manner as temperature decreased. Thus reports in the literature that a specified percentage of silver is retained by the gold beads are meaningless without stating the parting procedure and the temperature of the parting acid. Unfortunately this effect was not recognized at the time when the study of parting procedures was made. The reduced steam flow rate which could be recognized audibly, occurred because of a sudden drop in pressure in a central steam heat system as outside temperatures dropped and placed a greater demand on the heating system. Since the parting procedure study was begun in July and finished in September of the same year variations in steam flow rate were not recognized and temperature variations were probably of no great effect. In any case the significant conclusions relate to the gold losses which were not affected by these temperature variations.

b. Surcharge

As indicated earlier the surcharge is the difference between the weight of the parted bead and the weight of gold added or taken. It is customary, especially in the assaying of high purity gold (gold

TABLE XXII

Effect of Temperature on Percentage Silver

Retained by Gold Beads

| Temperature $^\circ$C | Ag Retained* (%) | Ag:Au | Au Added (mg.) |
|---|---|---|---|
| 94.0 | 0.43 | 6.5:1.0 | 21.684 |
| 94.0 | 0.70 | 6.4:1.0 | 23.200 |
| 94.0 | 0.58 | 6.7:1.0 | 23.254 |
| 94.0 | 0.48 | 6.7:1.0 | 21.524 |
| 94.0 | 0.59 | 6.6:1.0 | 26.836 |
| 94.0 | 0.49 | 6.6:1.0 | 21.575 |
| Average | 0.54 | 6.6:1.0 | 21.346 |
| s | 0.10 | 0.1 | |
| 83.0 | 0.82 | 6.7:1.0 | 20.789 |
| 83.0 | 0.77 | 6.5:1.0 | 19.001 |
| 83.0 | 0.76 | 6.4:1.0 | 20.369 |
| 83.0 | 0.80 | 6.8:1.0 | 25.428 |
| 83.0 | 0.88 | 6.8:1.0 | 23.928 |
| 83.0 | 0.83 | 6.5:1.0 | 24.363 |
| Average | 0.81 | 6.6:1.0 | **22.313** |
| s | 0.04 | 0.2 | |
| 78.0 | 1.02 | 6.6:1.0 | 22.443 |
| 78.0 | 1.04 | 6.8:1.0 | 24.650 |
| 78.0 | 0.92 | 6.2:1.0 | 26.597 |
| 78.0 | 1.08 | 6.2:1.0 | 28.641 |
| 78.0 | 0.93 | 7.0:1.0 | 19.164 |
| 78.0 | 0.87 | 6.5:1.0 | 20.660 |
| Average | 0.98 | 6.6:1.0 | 23.692 |
| s | 0.08 | 0.3 | |

\* Parting Procedure - The bead was treated with 10 ml. portions of 1:4 and 1:1 $HNO_3$ for 15 minutes in each. The parting acid was poured off and the bead washed three times with 5 ml. portions of hot water.

bullion) to determine the surcharge experimentally for each assay by simultaneously assaying several standard samples with check gold. According to the literature the weight of parted bead is usually greater than the weight of gold taken. This implies that the gain in weight due to incomplete parting is greater than the gold losses[20,27]. An examination of even a few results (eg. Table I) indicates that under the conditions of parting used in this research the magnitude of the surcharge varys by as much as 0.400 mg. within a single parting. (second page of Table I) If this particular parting is taken as an example a random selection of any three samples would yield an average surcharge ranging from 0.112 mg. to 0.296 mg. If the average weight of gold taken is 24 mgs. then the two results one would obtain using the extreme values of the surcharge indicated above, would vary by about 0.8%. This is a considerably larger difference than can be tolerated in view of the reproducibility attainable in fire assaying. While this particular example was chosen deliberately because of the large variations, it does show up the limitations of simply applying the surcharge as a correction factor to obtain the gold content.

It is true that a closer control of conditions such as temperature, thickness, weight of gold, and silver to gold ratio reduces variations of the surcharge, it also greatly increases the time required for analysis. The determination of the silver content by atomic absorption when set up on a routine basis should in fact reduce the time involved. This was the practice throughout the present research.

V. Application and Extension of Optimum Assay Procedures to Microgram Sized Samples

Since many economic ores have gold contents in the range of an

ounce or less of gold per ton of ore it was thought desirable to test the assaying of samples in which the concentration of gold was less than 1 oz./ton of ore.

In assaying, the concept of the assay ton has arisen. For convenience an assay ton is defined as that weight which contains the same number of milligrams as there are troy ounces in the avoirdupois ton. Since there are 29,166 troy ounces in the avoirdupois ton an assay ton is 29.166 grams. Thus the number of milligrams of gold in an assay ton of ore is also the number of ounces of gold per ton of ore. In this research the ore was simulated by approximately ½ assay ton of silica. Many gold ores are in fact silicate ores.

1. Standard Gold Samples

The preparation of the samples was a slight modification of that used for milligram samples, with a difference in the procedure of salting the charge with silver and gold. Instead of weighing out the silver and gold, standard solutions of gold and silver were prepared. Appropriate dilutions of these solutions yielded working solutions from which varying volumes of gold were pipetted into a hollow in the previously mixed flux constituents. In each case 2.0 ml. of the 1000 p.p.m. silver solution was also added. The salted flux was placed in a oven at 65°C and allowed to dry overnight or at least one hour for every milliter of solution added. After drying the mixture was mixed for 5 minutes in the polyethylene bags.

The mixed samples were then placed back in their crucibles and fused at 2100°F and cupelled at 1800°F as usual. The bead obtained from cupellation was weighed and then analyzed directly for gold without parting, using a procedure similar to that of Van Loon[28]. To each bead was added 0.5 ml. of concentrated nitric acid in order

to leach out the silver. The beads were heated at intervals until all action stopped and then treated with sufficient concentrated hydrochloric acid to make the final solution 50% by volume acid. Again the solution was heated to dissolve all the gold. Failure to first leach the silver with nitric acid results in the formation of a silver chloride coating on the bead which hinders dissolution. After cooling and bringing the solution to volume in an appropriate volumetric, the gold content was determined by atomic absorption spectrophotometry using the Perkin Elmer 306 model.

Two blank determinations were made on the flux containing the usual amount of silver. In one case the litharge used was produced by Anachemia and in the other by Baker. The corresponding blanks were 0.98 micrograms s = 0.37 and 1.12 micrograms s = 0.30. Each blank was determined on 6 replicate samples.

The results of these experiments are recorded in Table XXIII. For samples sizes of 490, 245, 98 and 24.5 micrograms the average gold recoveries were 101% s = 0.7, 100% s = 0.6, 101% s = 1.5, 101% s = 1.8 respectively. Within experimental error these results indicate complete recovery. Losses of gold are apparently less than can be observed by atomic absorption with the number of samples examined. The results reported here compare favourably with those reported by Van Loon[28]. The latter study, involving a more difficult problem, in that the gold was determined in the presence of platinum and palladium reported recoveries ranging from 97% to 105% depending on the amount of other noble metals.

Scale expansion techniques were used in those cases where the absorbance was less than 0.2 and increased to this value. In this way the absorbance reading could be obtained to the nearest part in 200.

TABLE XXIII

Application of Optimum Assay Procedures

to Micogram sized Samples

| Au Added $\mu$-grams | Ag Added $\mu$-grams | Sum $\mu$-grams | Au Found $\mu$-grams | % Recovery |
|---|---|---|---|---|
| 490 | 2000 | 2555 | 511* | 104.3 |
| 490 | 2000 | 2501 | 498 | 101.6 |
| 490 | 2000 | 2539 | 494 | 100.8 |
| 490 | 2000 | 2541 | 503 | 102.7 |
| 490 | 2000 | 2525 | 491 | 100.2 |
| 490 | 2000 | 2538 | 491 | 100.2 |
| 490 | 2000 | 2559 | 493 | 100.6 |
| 490 | 2000 | 2517 | 494 | 100.8 |
| 490 | 2000 | 2578 | 496 | 101.2 |
| 490 | 2000 | 2522 | 494 | 100.8 |
| 490 | 2000 | 2520 | 491 | 100.2 |
| 490 | 2000 | 2539 | 494 | 100.8 |
| Average 490 | 2000 | 2536 | 494 | 101 |
| s | | 21 | 4 | 0.7 |
| 245 | 2000 | 2310 | 216 | 88.6* |
| 245 | 2000 | 2295 | 249 | 101.6 |
| 245 | 2000 | 2301 | 244 | 99.6 |
| 245 | 2000 | 2302 | 246 | 100.4 |
| 245 | 2000 | 2287 | 246 | 100.4 |
| 245 | 2000 | 2296 | 246 | 100.4 |
| 245 | 2000 | 2288 | 244 | 99.6 |
| 245 | 2000 | 2277 | 244 | 99.6 |
| 245 | 2000 | 2313 | 244 | 99.6 |
| 245 | 2000 | 2325 | 244 | 99.6 |
| 245 | 2000 | 2303 | 246 | 100.4 |
| 245 | 2000 | 2382 | 246 | 100.4 |
| Average 245 | 2000 | 2307 | 245 | 100 |
| s | | 2 | 2 | 0.6 |

* rejected since a particle of gold had failed to dissolve

| Au Added $\mu$-grams | Ag Added $\mu$-grams | Sum $\mu$-grams | Au Found $\mu$-grams | % Recovery |
|---|---|---|---|---|
| 98 | 2000 | 2105 | 97.4 | 99.4 |
| 98 | 2000 | 2095 | 97.4 | 99.4 |
| 98 | 2000 | 2115 | 100.4 | 102.4 |
| 98 | 2000 | 2113 | 98.9 | 100.9 |
| 98 | 2000 | 2108 | 100.9 | 103.0 |
| 98 | 2000 | 2133 | 99.9 | 101.9 |
| 98 | 2000 | 2145 | 101.4 | 103.5 |
| 98 | 2000 | 2127 | 98.9 | 100.9 |
| 98 | 2000 | 2174 | 99.8 | 101.8 |
| 98 | 2000 | 2099 | 97.9 | 99.9 |
| 98 | 2000 | 2127 | 96.9 | 98.9 |
| 98 | 2000 | 2086 | 98.9 | 100.9 |
| Average 98 | 2000 | 2119 | 99.1 | 101 |
| s | | 24 | 2 | 1.5 |
| 24.5 | 2000 | 2037 | 24.4 | 99.6 |
| 24.5 | 2000 | 2004 | 24.9 | 101.6 |
| 24.5 | 2000 | 2051 | 24.9 | 101.6 |
| 24.5 | 2000 | 2048 | 25.1 | 102.5 |
| 24.5 | 2000 | 2059 | 24.9 | 101.6 |
| 24.5 | 2000 | 2047 | 25.2 | 103.3 |
| 24.5 | 2000 | 2067 | 24.9 | 101.6 |
| 24.5 | 2000 | 2088 | 24.1 | 98.4 |
| 24.5 | 2000 | 2012 | 23.7 | 96.7 |
| 24.5 | 2000 | 2325* | 24.9 | 101.6 |
| 24.5 | 2000 | 2007 | 24.7 | 100.8 |
| 24.5 | 2000 | 2065 | 24.3 | 99.2 |
| Average 24.5 | 2000 | 2044 | 24.7 | 101 |
| s | | 27 | 0.5 | 1.8 |

\* rejected on statistical grounds

Charge used:  15.0 g. $SiO_2$, 85.0 g. PbO, 21.1 g. $Na_2CO_3$, 4.5 g. CaO, 1.0 g. flour, 1.0 g. polyethylene bag

Gold standards were aspirated after every other unknown. Drift was of no consequence over such short periods. The aspirator used was a corrosion resistant one since difficulties had been reported[36] in the aspiration of hydrochloric acid solutions of gold. They found that gold reduction occurred in a steel aspirator.

2. Gold Ores

In this study two gold ores were chosen having a previously determined gold content[24] of less than an ounce per ton. The sample preparation was exactly as outlined in the previous section with two modifications. Since the ore contained the gold the samples were only salted with silver and no silica was taken for the ore blank but rather 15 grams of the ore itself was taken.

Since the precision and accuracy obtained with any method depends on the sampling procedure the procedure used in this research is outlined here. The sample received consisted of a previously crushed and sieved ore. The entire ore passed through 100 mesh screen and 90-100% passed through 200 mesh screen for both samples. Approximately 1-2 pounds of the ore was placed on a large cellophane sheet and rolled or tumbled by lifting alternate corners of the sheet. The ore had been previously inverted and shaken for about 20 minutes in its container. After approximately 30 minutes tumbling the sample was spread out evenly on the cellophane and marked off into 1" squares. The sample was then obtained by taking a small portion on a spatula, from each of the squares. The spatula was extended down to the bottom each time. The sample was weighed after each row of squares had been sampled. In this way variations were kept to a minimum.

After weighing the sample accurately in a polyethylene bag the flux constituents were added in the usual way. In each case 2 ml. of

the standard silver solution (2 mg. silver) was added and the samples were dried for at least two hours. The chunks which tended to develop were broken up and the ore, flux, and added silver were mixed for 5 minutes.

Fusion, cupellation and analysis of the samples was then achieved as in the other microgram sized samples described above. The results of this study are found in Table XXIV. Each assay of six samples was repeated in duplicate in order to obtain some idea of the reproducibility of the method. The gold content of the two ores examined was found to be 0.313 oz./ton  s = 0.034 for ore #305 and 0.470 oz./ton  s = 0.012 for ore #294. The relative standard deviation for the two ores was 10.9% and 2.9% respectively as compared to 0.81% for a comparable concentration of a standard gold sample. From this it is evident that the precision of the method is a function not only of the sampling method, but also the nature of the ore. If the precision were affected by the sampling method only then the two ores should have approximately equal relative standard deviations. In fact they differ by almost 300%.

Since the particular ore samples used had been previously analyzed[24] a comparison of the results with those obtained here, was possible. The previous study involved a prior parting of the silver from the gold, collection of the gold on a filter, ashing the filter paper, dissolution of the residue and determination of the gold content by the bromaurate spectrophotometric method referred to earlier. By virtue of the larger number of manipulations alone, increased deviations and losses were to be expected. The results of duplicate trials consisting of six samples each was for ore #294; Trial #1 0.440 oz./ton s = 0.014; Trial #2 0.469 oz./ton s = 0.024 with a combined result of 0.455 oz./ton s = 0.026 and for Ore #305 Trial #1 0.290 oz./ton s = 0.029;  Trial #2

TABLE XXIV

Application of Optimum Assay Procedures

To Gold Ores

| Ore designation | #305 | #294 |
|---|---|---|
| Mine | ---- | Buffalo Amberlite |
| | Trial I | Trial I |
| Gold Concentration (oz./ton) | 0.297 | 0.457 |
| | 0.289 | 0.462 |
| | 0.622* | 0.457 |
| | 0.306 | 0.475 |
| | 0.376 | 0.474 |
| | 0.356 | 0.485 |
| Average | 0.325 | 0.468 |
| s | 0.038 | 0.011 |
| | Trial II | Trial II |
| Gold Concentration (oz./ton) | 0.285 | 0.473 |
| | 0.293 | 0.469 |
| | 0.280 | 0.463 |
| | 0.282 | 0.464 |
| | 0.352 | 0.467 |
| | 0.323 | 0.498 |
| Average | 0.302 | 0.472 |
| s | 0.029 | 0.013 |

Combined result:

| Average | 0.313 | 0.470 |
|---|---|---|
| s | 0.034 | 0.012 |

* rejected on statistical grounds

0.259 oz./ton s = 0.025 with a combined result of 0.274 oz./ton s = 0.031.
While the actual gold content of an ore is unknown, the application of
the procedures developed in this research seems to have increased the
gold recovery by 3.2% and 14.2% for Ores #294 and #405 respectively.
The precision of the analysis of Ore #305 is essentially the same for
the two procedures while the precision for Ore #294 is increased
considerably as evidenced by a standard deviation a little less than
one-half that of the earlier study. As evidenced by a larger standard
deviation, the analysis of Ore #305 was not very satisfactory. While
the recovery was considerably increased, the separation of the lead
button and the slag was not clean and this, no doubt, contributed to
the increase in deviations. The difference between duplicate trials
was found to be 6.5% vs 0.85% (this study) for Ore #294, and 12.0% vs
7.6% (this study) for Ore #305.

In summary it would seem safe to conclude that the method of
analysis developed for microgram sized samples has a satisfactory
application to the analysis of gold bearing ores in the concentration
range of an ounce per ton and less.

VI. Radiochemical Evaluation of Fire Assay for Gold

1. General Procedure

At this point it was decided that an attempt should be made to
obtain a direct measure of the gold losses with the help of a radioactive
tracer. The tracer used in this study was gold-195 which has a half-life
of 180 days. It was prepared by bombardment of platinum foil for 2
hours, by 25 m.e.v. protons in a cyclotron. The active gold was separated
by appropriate radiochemical procedures and left unused for more than
a year.

At the time of use the total sample had an activity of approximately

2 million counts per 50 second counting interval. The total sample was diluted to 50 ml. and 3 ml. aliquots were taken for each sample and counted in test tubes which fit exactly into the well of the Baird sodium iodide scintillation counter. The background was determined before and after each series of measurements over 15 counting intervals. The activity of all samples was determined by counting for 5 counting intervals, averaging, and correcting for background. Two aliquots of the stock solution were retained throughout as calibration standards.

The preparation of the flux constituents and the carrier gold of about 20 mg. was the same as usual. After thorough mixing the active gold was added to a hollow formed in the charge with a spatula. The samples were allowed to dry overnight at about $50^{o}C$. The test tubes in which the active gold had been counted were counted again and found to retain varying and significant amounts of activity. The activity added to the sample was determined by difference.

After drying the samples, they were mixed once more for about 5 minutes and any chunks which formed were crushed. The samples were placed in their appropriate crucibles, fused at $2100^{o}F$ and poured into the iron mold as usual. After cooling the slag and button were placed in a polyethylene bag and gently tapped to separate the slag and button dressing from the lead button. The lead button was weighed and cupelled as usual at $1800^{o}F$. The slags and associated button dressing were labelled and kept together for counting. The crucibles from the fusion were numbered and set aside for counting also.

When the cupelled beads had cooled each cupel was labelled and set aside for counting. The gold-silver beads were not weighed but were parted directly with a double acid treatment as outlined in Parting Procedure VI. The parting acids were set aside for counting. The

parted beads were then washed three times with hot water and the washings were collected for each sample and set aside for counting.

The parted beads were then annealed and then directly placed into the original test tubes used for counting. In the interim the test tubes were cleaned with aqua regia and checked for activity. No activity was retained. The beads were then dissolved in 3 ml. aqua regia in the usual way and set aside for counting.

## 2. Counting Procedure and Results

The decay of the active gold was allowed for by measuring the activity of the standards each day and in the case of the dissolved beads, immediately after their measurement. The total activity decreased by only 2% over the time used for the complete study. In addition to the decay correction the presence of 20-30 mg. carrier gold in the samples necessitated a correction for self-absorption. This amounted to about 3% of the total count as determined from duplicate evaluations.

### a). Parted Beads

After dissolution as outlined above the beads containing more than 99% of the gold were counted in the same volume (3 ml.) as the standards and in the same containers. After correction for decay and self-absorption these measurements should represent the gold recovered. The average gold recovery (Table XXV) of 99.5% s = 0.3% agrees very well with that obtained by direct weighing of the beads (see Table XIX 1800°F).

### b). Crucibles

Initially the crucibles were counted whole. The crucible was inverted over the counting well and counted for 5 intervals of 100 seconds each. The background based on the average of 15 counting intervals before and 15 intervals after the crucible counts was 1010

TABLE XXV

Tracer Study of Gold Losses in The

Complete Fire Assay

| Au Added (mg.) | Activity (c/50 sec.) | Activity in Parted Bead (%) | Activity in Crucible (c/50 sec.) | (%) | Activity in Cupel (c/50 sec.) | (%) | % Activity Recovered |
|---|---|---|---|---|---|---|---|
| 26.247 | 137,694 | 99.7 | 870 | 0.63 | 32 | 0.023 | 100.3 |
| 20.501 | 137,418 | 98.9 | 758 | 0.55 | 35 | 0.025 | 99.4 |
| 30.029 | 136,733 | 100.9* | 1060 | 0.77 | 41 | 0.030 | 101.7* |
| 28.054 | 137,494 | 99.6 | 986 | 0.71 | 53 | 0.038 | 100.3 |
| 23.744 | 136,157 | 100.0 | 1074 | 0.78 | 37 | 0.027 | 100.8 |
| 23.486 | 137,326 | 99.8 | 1054 | 0.76 | 52 | 0.038 | 100.6 |
| 19.929 | 136,098 | 99.9 | 858 | 0.63 | 35 | 0.026 | 100.6 |
| 23.176 | 137,922 | 99.3 | 990 | 0.71 | 43 | 0.031 | 100.1 |
| 25.083 | 136,937 | 99.8 | 972 | 0.71 | 38 | 0.028 | 100.5 |
| 24.429 | 134,552 | 99.6 | 966 | 0.72 | 50 | 0.037 | 100.3 |
| 19.286 | 136,767 | 99.2 | 842 | 0.61 | 39 | 0.028 | 99.9 |
| 23.404 | 137,652 | 99.1 | 1196 | 0.86 | 33 | 0.024 | 100.0 |
| | | Average % = 99.5 | Average % = 0.70 | | Average % = 0.030 | | 100.2 |
| | | s = 0.3 | s = 0.09 | | s = 0.005 | | 0.4 |

\* rejected on statistical grounds

Charge used: 15.0 g. $SiO_2$, 85.0 g. PbO, 21.1 g. $Na_2CO_3$, 4.5 g. CaO, 1.0 g. flour, 1.0 g. polyethylene bag

s = 18. In view of the large size of the crucibles the lid of the counter could not be lowered and hence the high background. The background was determined with a previously used crucible which had contained no active gold. The average count for all the crucibles used with active gold ranged from 987-1045. The overall average of all twelve crucibles was actually lower (1006), than the average background.

In view of the fact that some of the crucibles had an average count higher than background, it was thought that perhaps the effect of geometry might be significant. The part of the crucible which according to autoradiographs was the most likely to be active[23] was the most remote from the counting well. As a result one crucible was placed in a polyethylene bag and broken by hitting with a hard object. It was possible to do this in such a way that no pieces were larger than would fit under the lowered lid of the counter. Each piece was counted either alone or together, in the case of the smaller pieces with one other piece. The fines and very small pieces were counted together. In each case the side of the crucible which had been wet by the charge was placed face down above the counting well. The result was surprising. In each case the total activity was significant and averaged 0.70% s = 0.09, of the original bead activity. It is recognized, of course, that these results cannot be taken as exactly quantitative since a geometric effect applies. The face of the counting well on which the crucible pieces were counted, were several centimeters from the bottom of the well where the standards were counted.

c). Slag

The slag remained in one large piece except for a small quantity of button dressing. The whole slag pieces were counted along with the button dressing. That part of the slag which had been in contact with

the lead button was put face down on the counter well. The background determined before and after the slag count, was obtained with a similar piece of slag from a previous non-active trial, and averaged 128 per 50 second counting interval. The range of activity for the slags from the "active" run was 109-130 counts for the same time, with an average activity of 122 counts. Within experimental sensitivity the activity of the slag was considered to be insignificant. An activity of 7 counts per 50 second counting interval would represent 0.01% of the total count for the average sample. As can be seen from Table XXV the amount of activity added was not exactly constant from sample to sample.

d). Metal Mold

The mold into which the fused samples were poured were checked for activity also. In order to obtain a background the mold was placed over the counting well with the unused side facing down over the well. This was repeated three times with varying positions of the mold. The overall average was 552 counts per 50 second interval. The counting was repeated over the same interval with three different positions of the "active" side face down. The result was an average count of 540 counts. The standard deviation in both cases was 30 counts. It was concluded that no significant activity was lost to the mold. The lid of the counter was up throughout.

e). Parting Solutions

The parting solutions were counted in test tubes placed directly in the counting well. For the first parting acid (1:4 nitric) the range of activity found corrected for background was 4-10 counts with an overall average of 7 counts $s = 2$ per 50 second interval. For the average sample this represents a loss of 0.01% gold. The second parting

acid, counted in the same way, gave an average count of only 2 counts per 50 second interval. This represented a loss which could be ignored.

f). Washing Solutions

The combined wash solutions for each sample were counted in 30 ml. beakers placed directly over the counting well. Again the activity, corrected for background, was on the average only 1 count per 50 second interval. Losses to the wash solution were considered negligible.

g). Cupels

The cupels were counted whole. According to autoradiographs, cupel absorption was mainly a surface effect with the maximum penetration not more than about ¼". The cupels were hence inverted over the counting well and counted for 5 replicate intervals of 50 seconds. The range of activity in this period corrected for background was 32-53 with an overall average of 41 counts s = 7. This represented a gold loss of only 0.030% s = 0.005.

3. Summary of Tracer Study

A consideration of Table XXV, which includes all the activity measurements for those sources contributing more than 0.01% of the total activity, indicates that the overall average recovery of the active gold including losses was 100.2% s = 0.4. In view of the differing counting techniques this must be considered as being, at least partially, fortuitous.

The significant conclusions are that the major source of gold loss is undoubtedly not to cupel absorption but due to crucible losses. While these conclusions were not entirely surprising they certainly were contrary to findings based on what has here been described as "simulated cupellations". It would appear that the cupellation of gold and silver powder encased in lead foil cannot be compared to the

cupellation of the lead button customarily obtained at the end of a fusion. The approximately equality of the gold losses to crucibles in the complete assay, and the gold losses to cupels for the abbreviated process, would appear to be fortuitous and misleading.

Suspicions that the above conclusions might be true, began to grow when gold losses for the complete assay were reduced to the point where they were less than had been found for a segment of the overall process. In particular compare the average gold loss of 0.56% s = 0.03 recorded for optimum conditions in the cupellation temperature study, (Table XIX) to a loss of 0.61% s = 0.08 the average gold loss for the "simulated cupellation" recorded in Table I. This difference represents a significant difference at a confidence level somewhere between 95-99% and closer to the latter.

Losses to parting acids and wash solution were neglibible as expected, since the beads remained nicely coherent under the conditions of parting.

It is to be expected that losses to slag in particular and crucible wall to a lesser degree would vary, both with variations in flux mixtures and hence in the nature of an ore. In the bulk of the work reported on here the flux components were known almost exactly (impurities excepted) and hence the losses reported on here, should be viewed as characteristic of the conditions used and as an ideal situation which one would aspire to in the more real conditions of assaying ores.

E.   Summary

In a recent review of neutron activation and tracer methods for the determination of the noble metals, Beamish et al[35] point out the lack of even a single adequate study of gold losses in the fire assay method, "...despite the commercial significance of the method and the many decades of its application." They go on to say that a variety of phenomena may be involved and that consideration of many factors will be required.  This study has been an attempt to meet this need.

On the basis of the results of this study several generalizations would appear to be in order.  With regards to the abbreviated fire assay, (simulated cupellation) variations in the weight of lead foil, in the silver to gold ratio, and in the size of cupel, did not produce significant changes in the gold loss under the conditions studies. No evidence was found for significant losses as a result of volatilization. The cleaning of cupelled beads by removing the small quantity of adhering cupel material, increased gold losses and is to be discouraged. While reducing the thickness of the gold-silver beads prior to parting reduces gold losses the time involved is hardly worth the effort. Increasing acid strength also reduces gold losses in the parting process, provided coherent beads are obtained.  The conclusions regarding the cleaning of cupelled beads and parting procedures should be valid for beads obtained from the complete fire assay also.  Both processes (abbreviated and complete) produce a gold-silver bead free of essentially all lead.

For the complete fire assay the weight of lead button between the limits of 7-34 grams had no significant effect on gold losses. Excess charge used as a cover was also of no effect.  The use of polyethylene bags for mixing of the flux, silver and gold, on the other hand,

greatly reduced gold losses. The length of time used for the fusion process was important, with increased losses if either too short or too long a fusion time was used. The optimum time for this phase of the process was found to be 1½ hours. Fusion and cupellation temperature both were significant variables, in terms of their effect on gold losses. For fusion, a maximum temperature of 2500°F was indicated as the crucibles became porous to the slags at this temperature. A lower limit of 2000°F is desirable and an optimum temperature of 2100°F is recommended to minimize gold losses. The effect of varying cupellation temperature was not nearly as pronounced as expected from some statements found in the literature. According Hillebrand and Allen,[34] gold losses due to increasing temperature from front to back of a gas fired furnace ranged from 0.5% to 4.0% due to a temperature difference of about 100°C. In this study losses ranged from 0.56% to 0.86% for temperatures between 1700-2000°F.

The use of radioactive tracer permitted the determination of gold losses directly in the various stages of assaying. Losses of about 0.70% to the crucible wall, 0.03% to the cupel, and 0.01% to the parting acids were the major losses. Losses to the slag, the iron mold, and the wash solutions were not detectable.

An atomic absorption - fire assay method applied to standard microgram sized samples showed that losses were smaller than experimental error. Within the precision of the method recovery was complete. The same method applied to two different ores indicated a somewhat improved method of analysis over a previous effort. The precision varied with the nature of the ore and was dependent on the sampling procedure used.

Probably the most significant finding in the course of this study was the conclusion that the major loss of gold occurs during fusion as

gold is retained by the crucible wall. Taken together with the very low cupel losses it would appear that the cupellation of a lead button as obtained from fusion is not a comparable process to the cupellation of a mixture of gold and silver powders encased in lead foil.

While variations, in at least some of the conditions employed, resulted in significant variations in gold losses, the overall impression obtained was that the fire assay for gold is remarkably insensitive to changes in the conditions of assaying. Furthermore in those cases where gold losses did vary significantly reproducible assaying was possible even at conditions other than those which minimized losses. Perhaps this is one of the reasons why the fire assay for gold is considered to be, along with the gravimetric chloride, one of the most reliable analytical methods known. Even though gold losses of almost 1% may be involved the practise of determining these losses from standard samples under the same conditions of analysis as the unknowns makes accurate work possible.

Bibliography

1. Szabadvary, F., *History of Analytical Chemistry*  Pergamon Press
   New York, (1966)

2. Smith, E.A., *The Sampling and Assay of The Precious Metals*, 2nd
   Ed.  Griffin and Co. Ltd.  London (1947)

3. Ezekiel 22; 18-22  *King James Bible*

4. Slavin, W., *Atomic Absorption Spectrophotometry*  Interscience
   Publishers  New York,(1968)

5. Britten, H., Trans. Commonwealth Min. and Met. Congr.  3 1005, (1961)

6. Kolthoff, I.M., & Elving, P.J., *Treatise on Analytical Chemistry*
   Part II  Vol. 4  Interscience Publishers  New York,(1966)

7. Mowat, D., J.S. African Inst. Mining Met.  62 (12), 693, (1962)

8. Beamish, F.E., & Van Loon, J.C., *Recent Advances in The Analytical
   Chemistry of The Noble Metals*  Pergamon Press,  New York, (1972)

9. Beamish, F.E.,  Talanta  5  1, (1960)

10. Bugbee, E.E., *A Textbook of Fire Assaying*  2nd Ed.  Wiley,
    New York, (1933)

11. Beamish, F.E., *The Analytical Chemistry of The Noble Metals*
    Pergamon Press  New York, (1966)

12. Finkelstein, N.P., J.S. African Inst. Mining Met.  62 (12), 700, (1962)

13. Rose, T.,  J. Chem. Met. Mining Soc.  5 , 165  (1905)

14. Shepherd, O.C., & Dietrich, W.F., *Fire Assaying*  McGraw-Hill Book
    Co.  New York, (1940)

15. Coxon, C.H.S.,  J.S. African Assayers  4 (9), 5, (1961)

16. Dewey, F.P.,  Mining & Met.  No. 58, 31 (1920)

17. Hillebrand, W.F., & Allen, E.T.,  Bull. Am. Inst. Mining Eng.  705,
    (1909)

18. Beringer, C., & Beringer, J.J., <u>A Textbook of Assaying</u> 15 Ed. Charles Griffin London, (1921)

19. Dewey, F.P., Trans. Am. Inst. Mining Eng. 1941, (1917)

20. Coxon, C.H., Verwey, C.J., & Lock, C.J., J.S. African Inst. Mining Met. <u>62</u> (10), 546 (1942)

21. Sinclair, W.A., J.S. African Inst. Mining Met. <u>64</u> , 333 (1964)

22. Kim, J.I., Kim, C.K., Chang, W.P., Daehan Hwahak Hwoejee <u>7</u>, 165 (1963)

23. Shima, M. Radioisotopes <u>5</u> (2), 1, (1957)

24. Chow, A. Ph.D. Thesis U. of Toronto (1966)

25. Beyermann, K., Z Anal. Chem. <u>200</u> , 183, (1964)

26. Simon, F.O., & Millard, H.T., Anal. Chem. <u>40</u> , 1150 (1968)

27. Rose, T., <u>The Metallurgy of Gold</u> 4th Ed. Charles Griffin & Co. Ltd. (1902)

28. Van Loon, J., Z Anal. Chem. <u>246</u> , 122, (1969)

29. Chow, A., Lewis, C.L., Moddle, D.A., Beamish, F.E., Talanta <u>12</u>, 277, (1965)

30. Chow, A., Beamish, F.E., Talanta <u>13</u> , 539 (1966)

31. Beamish, F.E., Russell, J.J., Seath, J., Ind. Eng. Chem. Anal. Ed. <u>9</u> (4), 174, (1937)

32. Chow, A., Beamish, F.E., Talanta <u>10</u> , 883, (1963)

33. Faye, G.H., Inman, W.R., Anal. Chem. <u>31</u> , 1072, (1959)

34. Hillebrand, W.F., & Allen, E.T. U.S. Geological Survey Bull. 253, 7

35. Beamish, F.E., Chung, K.S., Chow, A. Talanta <u>14</u>, 1, (1967)

36. Kallmann, S., Hobart, E.W., Talanta <u>17</u> , 845, (1970)

37. Metals Reference Book

Acknowledgment

The author wishes to express his sincere thanks to Professor A. Chow for his encouragement, patient audience and helpful advice throughout the course of this research.

The author is also indebted to a patient and encouraging wife and family.