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On the fire assay of gold, silver, and lead

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Thesis
on the fire assay
Gold - Silver and Lead,
for the degree of
Engineer of Mines,
by
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Outfit for Assay Office

Two furnaces are necessary.

(a) A wind furnace.

(b) A Muffle furnace.

(a) The Wind furnace should be about 18" square in longitudinal cross section and about 18" deep to the gate bars. It should be built of fire brick and covered with an iron cover lined beneath with fire clay. The cover should be hinged at upper side and raised and lowered by means of a weight connected by a chain passing over a pulley above.

Near the bottom of the furnace should be placed gate bars to support the fuel and should be sufficiently far apart to assure the proper draught. The flue from the wind furnace may lead direct to the chimney from the muffle furnace.

(b) The muffle furnace should be built of brick and lined with fire brick. The gate bars should be properly arranged about 4" below the bottom of the muffle

The furnace should be fired from the rear to prevent the heat from the fire door annoying the operator. Beneath the fire grate should be an ash pit and this should be occasionally filled with water to cool the lining of the furnace and also form gases whose combustion helps heat the furnace.

The flame passes directly around the muffle on both sides to the chimney which should be about 30' high.

The door to the fire box may be easily handled by the aid of a counter weight supported from a pulley above.

Bituminous coal may be used as fuel.

The muffle is supported by projecting bricks in the rear and shelf in front. The most convenient size for muffle is:-

Length 17½"
Width 12½"
Height 6"

All inside measurement.

In front of the furnace and on a level with the bottom, the large muffle should be an iron plate, this gives a convenient place for boards of crucibles, &c in fixing the preparatory to charging besides gives a place by which the muffle door may be slid or taken or shut to any required degree.

The muffle door should be made of —

(a) Asbestos, sheet asbestos,

(b) Iron door.

The asbestos is cut sufficiently large to cover the front of the muffle.

The iron door should have a [nut on the back], so that while lying on the iron plate and leaning back on the iron [nob it may be slid back]ward and forward to adjust the asbestos plate to any required degree.

There should be Crucible, Crucible tongs and Cupel moulds and boards. The Cupel moulds should be covered on one side with sheet asbestos, so as not to be burnt by placing hot cupels on them.

There should also be moulds, Hammer and Anvil Cupel board rack, table, Chisels for cutting bullion, refined lead &c. also cupel mould in the furnace room.

A good cupel mould may be made as follows:-

The brass cupel mould is mounted on to an iron rod 2' long. This rod vertically through a hole in the top of the table, this hole is provided with an iron ferrule just fitting the mould.

Near the floor a horizontal rod is connected at one end to the vertical rod and is pivoted by a pin to the leg of the table which acts as a fulcrum. The other end is joined by a pedal and power is exerted there by the foot. The vertical rods drop down and the cavity thus formed in the mould filled with bone ash prepared for making cupels. Then the pedal is moved with the foot and the bone ash kept in place by the aid of a flat plate of iron fixed within the top of the table and fastened at one end

while the other end slides under a hood. This cover is then removed and the rod pressed a little higher as the crucible may be removed this device while simple is very expeditious for making crucibles

It is best to have the furnace room separated from the fuel and balance rooms by partitions.

The fuel room may contain bins for rock Coal, Coke and Charcoal with a passage between them to the back of the furnace where the firing door is.

The tools for this room are a shovel crow bar and hoe.

The balance room contains bins for crucibles reducing fluxes, also shelves for samples and tables for scales.

There balances are necessary, One a cheap Beam scale for the weighing of large amounts of flux previous to mixing this flux is charged by measure. The second balance is for use and should be sensitive to .01 gm.

The third balance should be very sensitive for weighing gold and silver buttons, it should be of the best make and should weigh to .00001 gm. This room should be well lighted and free from draught that might interfere with the weighing

Sampling

In sampling the ore is taken by shovel falls in proportionate alternations.

If lots are small say one or two car loads. It is to be crushed down to the size of walnuts this sample then to be quartered down if small lots to 1000 # if two or three car lots to 2000 # and if large is to 4000 # Then put through rolls and crushed to size of Cherries. Then quartered down to three wheelbarrow loads, then crushed until it will pass through 1/4 mesh screen, Then quartered down until 2/3 each is left if a small lot and 1/2 each if large lots.

Do if ore is rich, this remainder to be put through the grinder entirely and the ground sample to be quartered down until from 4 to 10 #

is left. This remainder to be ground still finer on the bucking plate until all is it will pass through a 80 mesh screen, then from this sample 1# is to be taken by quarting and rubbed down until all will pass through an 80 mesh screen.

Assay of Lead.

A charge of 10 gms (one measure) of flux is put in a No 1 clay crucible, then 10 gms of added and all intimately mixed, then a second measure of flux is poured on top and if it contains sulphur three or four 12d nails are stuck in charge.

The ore should be run hot for about 30 min, a fairly quick hot fusion for lead renders a higher and more accurate result than a slower and colder fusion.

For running slags when a very small amount of lead exists a larger charge of ore should be used generally about 20 gms, to this added a weighed silver button of about 0.05 m.g. to collect the lead, weigh the resulting button and deduct

The weight of the silver. The latter may be expelled at any convenient time and the silver saved.

Flux for lead

Potassium Carbonate	14	Parts by wt
Sodium Carbonate	10	" " "
Calcined Borax	10	" " "
Wheat Flour	4	" " "

Gold

The assay may be in the form of the Matte, Speiss, Bullion or Dore

If ore is matte form in crucible as a larger charge may be used and thus a greater quantity of gold is obtained to work upon. If Speiss or Matte moderately rich in copper run by Scorification Bullion if pure may be directly cupelled, if containing unweighed quantities of precious metals other than lead, Scorify the cupel If Dore dissolve a weighed quantity and weigh gold.

Crucible Assay for Gold.

Use 20 dm crucibles.

The ore may be in the form of

Sulphide, Chloride, Telluride, Bromide, Carbonate, Silicate, Arsenide & Selenide, also Slags and Dull & Hearth Accretions and Flue Dust.

Flux for Crucible Assay.

Equal weights of Sodium Carbonate and Litharge are intimately mixed and a measure of the mixture taken that will contain 30 grs of the Litharge. To this is added ½ Av. oz and an amount of finely ground vitrified borax.

If ore is Sulphide add Potassium Cyanide, I find this acts much more uniformly as an ore than nitre and dissipates the danger of the silver being carried off by the evolution of Sulphur gases, as the Sulphur goes into the slag, perhaps mostly as an alkaline Sulphocyanide.

Potassium Cyanide may take the place of nitre in all cases in ore assaying except in the fire assay, even then if charge is in reducing atmosphere a direct oxidizer must be employed.

To this charge add 4 or 5 - 20 d nails.

If ore is Silicate, Carbonate, Chloride & Bromide

add about ½ gm flour to reduce every litharge to form a lead button large enough to carry down all the silver.

Mix this charge intimately in crucible with a little and cover with another cap of borax. Salt is unnecessary when the assay is run in a muffle. It plays no important part Chemically increases the slags and dissolves the moulds, but when the crucibles are run in a wind furnace a salt cover is beneficial because it protects the charge from the reducing flames and to some degree [as small particles of carbon that fly into the crucible from acting on the charge.

If ore is very basic as pyrite, add silica.

This charge should be fused hot for from 30 to 45 min as quick [hot fusions make the best moulds, except in the case of ores containing much pyrite. Then an extremely hot fusion forms a thick [ferruginous matte which cannot be separated entirely from the lead by hammering. It is necessary in case this is found to scorify the button as it is impossible to obtain good

results by trying to cupel this mixture.

Crucible assays give good check for silver but the results should not be taken as conclusive, for they will not check as close & be as high in silver as scorification assays.

I have run mattes for gold and silver successfully by crucible casting as high as 18% Cu.

Scorification Assay.

Use 2½ in scorifier.

Crossing in Copper & Arsenic Ores, Mattes and Matte Bullion should be run by scorification.

Clean Bullion may be directly cupelled.

If ore contains much volatile constituents it should be started at a low heat so that all these volatile matters may be slowly expelled, and the heat gradually raised to the required temperature.

Too rapid expulsion of these volatile substances is always accompanied by loss of silver.

If ore contains volatile matter in small amounts it may be started hot and thus some time saved.

The time of running a scorification assay,

sometimes running as high as 50 mins

It is a good idea to bank up the front of the muffle with coke This increases the heat in the front and by regulating the muffle door the heat may be kept uniform throughout the muffle and thus all the work finished at once

Three Charges when scorified until the button rises and is round, hammered and cupelled

Charge for Scorification Assay

Ore 1 A.T.

Test Lead 42 grms

a little fused borax or Soda increases the fluidity of the slag.

In case ore is strong in Copper, Nickel, Arsenic & Antimony, or if ore is Blende or rich Telluride as much as 50 grms test lead is needed, but the appearance of resulting lead button will indicate any foreign metals present, and it is of rare occurance that such strong ores are met That 42 grms may be taken as general Charge for test lead and in those

few rare occurrences. The buttons may be reconified.

After the buttons are obtained from cupellation they are weighed to determine the amount of silver present. These assays should check to within 1/3 silver per ton between the lightest and heaviest buttons, generally four assays are run on each ore.

The Gold should check to .02 3 parts on

The assay ballance should weigh to .02 mg.

After the silver buttons are weighed they are dissolved in parting flask with first

Nitric Acid 1 part by measure

Water 3 " " 27 "

This liquid is decanted into the silver residue jar and the remainder subjected to

Nitric Acid 2 parts.

Water 1 "

Specific Gravity 1.26

This liquid is decanted into the silver residue jar and distilled water poured on the gold.

The parting flask is inverted over an annealing cup until gold settles in cup. Then the water is poured off and the gold dried and weighed.

The object in using dilute acid first is to obtain the gold in bright heavy particles, if strong acid is used at first, the gold will be in fine black specks and will be more difficult to handle.

In case the button from cupellation contains much gold and little silver, the silver will not all be dissolved by the acid, in this case it will be necessary to fuse some pure silver with the button by blow pipe or some simple means, when all the silver will be readily soluble.

In case the ore is known to contain much Gold and little silver, it is well to add to the charge a pure silver button and run this charge for gold alone.

Silver.

All silver assays should be made by concentration as higher and more accurate results may be obtained by this method than by crucible, except when ore is very poor in silver.

Obviously if assay is to be made on pure button the charges may be directly cupelled but if button

contains dross or marked amount of Copper or Cuttings it should be scorified, In the latter case it may be necessary to add some test lead.
The scorification is run as described under Gold.

Slags

Run by Crucible

Use 1" A.T. or, 12 gms lead flux, 40 gm PbO, also little borax, cupel button obtained & weigh silver.

Refined Lead

Use 2, A.T. Scorify to required size and cupel

Matte Stony in Copper.

These should be assayed by Scorification and checked by some simple Wet method.

Wet Method

Dissolve in wilt Nitric acid filter if insoluble residue, To filtrate add little Sulphuric acid and lead Acetate to form a copious precipitate collect precipitate & silver, then add Sodium Bromide to precipitate silver as Silver Bromide filter again and add precipitate to insol. residue and run by crucible or Scorification

This leaves the copper in the filtrate with the silver and gold are all in the precipitate and must reunited

Copper Scraps

Copper filings & scraps to be assayed for silver should be melted in a graphite crucible in a wind furnace, charcoal should be added to keep the copper reduced. If the scraps are very dirty and an assay is wanted of the scraps alone, the lump must be remelted and the dirt removed by fluxing, remelted and granulated by pouring in a thin stream while molten from a few feet above into a basin of cool water below. If the scraps are clean they may be granulated the first fusion

In case an assay is wanted of the entire mass, weigh before melting and after granulating and calculate the results from this data

Granulated copper gives a finer sample for silver than when cast in moulds.

Sample to be from the granulated copper by coning method

Bullion is usually obtained in small "lots" and "bricks". These should be melted quickly in graphite crucible with charcoal and moulded. From the moulded cake take four samples, one from each side by chipping through the cake with a cold chisel.

The sample should be chipped directly thro the cake as the top and bottom of the cake may vary widely in richness in gold and silver. If a sample of the bullion contains copper or zinc, the gold will readily alloy with it as will also some of the silver and as the alloy is lighter than lead it will settle to the top of the cake before the mass is solidified, and thus a sample from the top may give much higher results, especially in gold than one directly under it at the bottom of the cake. ~~5~~ Ans. is taken from each of these samples and directly combined if desired but if bullion contains mercury quantity of which matter it will be necessary to first decrease.

Metallic Zinc

Zinc powder, strong zinc ore or even metallic zinc may be assayed for gold and silver by crucible by adding sufficient litharge to oxidize the zinc.

$$ZnO + Pb = PbO + Zn$$

The resulting lead button will have to be scorified to reduce zinc.

Manganese Ores.

Strong manganese ores may be run by either crucible or scorification, but often the resulting button should be scorified before cupellation.

Iron Ores.

Occasionally strong iron ores not to be assayed for gold and silver. In this case add sufficient silica to form an acid flux.

Metallic Tin

It is difficult to assay metallic tin for Gold and Silver. The best method is to add sufficient litharge to oxidize the tin in crucible and scorify the resulting button.

19

Fine Silver

To determine the fineness of silver regulus and
The samples are obtained by running some of
the silver from the crucible into water to
granulate it. Samples are then taken from each
one of silver cast. From these samples six
or eight assays are taken which are rubbed down
on a smooth porcelain until they each weigh
exactly 200 Mg. The same number of samples
of pure silver are taken and each button is
rolled in lead foil made by running refined
lead through rolls until a piece 1" by
and about 3" long weighs 3 gms.

This lead should only give a trace of silver
when 2 A.T. is cupelled.

These buttons are all cupelled in a hot
muffle together. The lead foil removes the
copper, antimony, lead & other impurities.

These cupels must be gradually moved
toward the front of the muffle after the button
has "brightened" if cooled too quickly the buttons
will flash and sparting is generally accompanied

by loss of silver

Cracking may be due to two causes.

1. Silver at a high heat absorbs oxygen from the air, and if cooled too rapidly, the oxygen in its effort to escape may cause the button to crack.

2. If a silver button is cooled too rapidly the surface will solidify and contract on the molten interior. This force of contraction may be sufficient to cause the crust to crack and the button to crack.

After the cupellation is completed the buttons are removed and weighed. The loss of weight by oxidation of the pure silver is added to the weight of the silver being assayed. This weight multiplied by 2 gives the fineness of the silver.

Cupellation

There is a diversity of opinions among assayers as to the best method of cupellation. My experience for silver is that much higher and more accurate results may be obtained by cupelling the buttons as "cold" as possible and

Then quickly increase the heat to "wind up".
The heat may be kept down in the muffle by surrounding the cupels with empty crucibles & confines the heat also by regulating the furnace doors.
I will mention that I recommend cold cupellation on buttons when their weights are between 18 & 40 gms. I have had no occasion to cupel buttons without these ages.

Special Experiments

1. In running an arsenic or flue dust the by crucible, there is usually a deposit formed that sticks to the top of the lead button. This may be thrown away for analysis shows it contains none of the silver & gold they having presumably alloyed with the lead. This deposit should be discarded because it interferes with the subsequent cupellation.

2. HCN reduces PbO in the presence of an reducing agent and oxidizes it.

Eqn. PbO + Na_2CO_3 + 1 gm flour = 7.88 gm Pb

PbO + Na_2CO_3 + 1 gm flour + 2 gm HCN = 10.2 gm Pb

40 gms Pb + 2 gm HCN = 38.2 gm Pb

3. Haile can reducing to Oxide and Carbonate as well as Sulphide and Silicate ores.

4. Nitre varies in the amount of its action as an oxidizer in the same compounds.

5. Impure litharge (Pb_3O_4 + PbO) oxidizes Silver in the absence of an reducing agent but has little or no effect in a crucible assay where reducing agents are present.

Ex: Ten grams pure silver in each and cupelled hot all at same heat and time.

1.	Pure PbO gave	.98 [illegible] grams
2.	Impure PbO (Red litharge) gave	.9746
3.	" " with flour	.974
4.	" " " "	.9722
5.	Pure Ag cupelled with pure Pt	.834

Report submitted for the class by E. H. Grove 4th June 1894.