ASSAYING WITH THE BLOWPIPE; LEAD, COPPER AND SILVER ORES

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Strictly speaking it cannot be said that the art of assaying with the blowpipe is a recent achievement. As early as 1827, while a student at Freiberg, Harkort conceived the idea of using the blowpipe for quantitative as well as for qualitative determinations and suggested a method for assaying silver ores. He had planned to work out methods for other metals but his early death prevented him from carrying on these investigations. His successor, Carl Friedrich Plattner, continued what Harkort had begun and extended the operations to include gold, lead, copper, bismuth, tin, nickel and cobalt.[1]

In all of these early attempts at quantitative work fusion was usually performed in a charcoal crucible which, by reason of its limited capacity and tendency to burn through, imposed certain hard and fast restrictions upon the assayer. The charge generally employed included only 100 mg. of the ore, which seems an unusually small amount for the successful operation of very lean ores. The time of fusion of necessity was short. Also the methods as outlined demanded considerable technique for the results obtained depended in no small measure upon the skill exercised by the operator in the manipulation of crucible and contents during the fusion period. To some or all of these objectionable features may be attributed the cause of the disuse of quantitative blowpipe methods in recent years. Finally, while results of a general quantitative character were no doubt obtained, no reference has been found where these determinations were checked against the results secured by other methods and their accuracy definitely established.

With the advent of the Fletcher Blowpipe furnace[2] a new impetus was given to blowpipe assaying. The size of the charge can easily be doubled and the effects of time of fusion or the influence of variation in flux can be more readily ascertained. Also, inasmuch as the general scheme employed is that of the

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[1] Plattner's Blowpipe Analysis; translated by Henry B. Cornwall. Eighth edition, revised. D. Van Nostrand, *New York*. 1902.

[2] Quantitative Assaying with the Blowpipe, E. L. Fletcher. John Wiley & Sons. *New York*. 1906. This will be found an extremely helpful text for those wishing to become proficient in this work.

ordinary fire assay, no manipulation is necessary during the fusion period, thereby reducing the personal technique to a minimum and making it possible for the average careful student to obtain very satisfactory results.

In the following brief survey I desire to record the experience and results obtained by a number of students working independently when instructed to assay ores of lead, copper and silver. The entire equipment required is of such a character as to render it equally serviceable in the field or laboratory. In every instance the metal content of the ores had been previously determined either by wet methods, as in the case of lead and copper, or by the regular fire assay in the case of silver ores. The student, however, was not informed in advance as to the approximate metal content, and it was only after his report had been received that this information was given in order that he might note his error and possibly benefit thereby.

ASSAY OF LEAD ORES. In order to carry out the operation successfully certain general chemical considerations must be kept clearly in mind.[3] The fire assay for lead is always less accurate than the wet method. It can, however, be of practical service in the field and if the ores are of the simpler types, furnish a fairly close approximation of the true value. The three chief reasons for the inaccuracy of the dry method for the determination of lead are (1) lead and lead sulfide are both volatile at moderate temperatures; (2) there is a tendency for lead and its compounds to enter the slag which is increased by the presence of arsenic, antimony and zinc; (3) other metals such as copper and silver would also be reduced with the lead and form a common button. It would seem, therefore, that the best results might be expected if the heat be moderate, the time of fusion short, and the slag easily fusible but not too acid in character. The ores investigated included both sulfide (galena) and carbonate (cerussite) ores. Because of the low fusibility of galena the sulfur cannot be volatilized by roasting but can be removed by inserting a 7/8 in. "wire brad" in the crucible. The role played by the iron in the removal of sulfur can be readily understood from the following equations: $4\ K_2CO_3+7\ PbS = 4\ Pb+3(K_2S.PbS)+K_2SO_4+4\ CO_2$. If iron were not present the double sulfide ($K_2S.PbS$) would enter the slag with resulting

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[3] Notes on Assaying, Richard W. Lodge. Third edition, 1911, p. 190. John Wiley & Sons. *New York.*

loss of lead. By adding iron we have: $(K_2S.PbS)+Fe=(K_2S.FeS)+Pb$.

The charge, weighed in a portable pocket assay balance, which gave the best results contained:

ore	200 mg.
sodium carbonate	150
potassium carbonate	100
borax	20–50
flour	100
iron peg	
salt cover	

The time of fusion varied from 4 to 5 minutes. With the richer ores better results were obtained by placing the ore at the bottom of the crucible with the mixed flux on top. Should there be a tendency for the crucible to burn through a small amount of powdered silica should be added. If borax is used in too large amounts the slag becomes too acid and the loss of lead is thereby increased. The same charge can also be used for carbonate ores with the omission of the iron peg.

The actual recovery compared with the true values can be seen from the following table.

Galena ores		Cerussite ores	
% of Pb(wet)	% of Pb(dry)	% of Pb (wet)	% of Pb(dry)
86.5	77.5–80	42.8	40 –41.5
35.0	28.5–32	22.9	20.5–21.0
25.6	23 –24	14.4	11 –12

From the above it will be seen that the sulfide ores offer more difficulty than carbonate ores, although sulfide ores running as low as 7½ to 8 % have been assayed. If the ore is very impure, containing a great deal of copper, antimony or arsenic, as would be the case of an intimate mixture of galena with tetrahedrite, no dry method could be recommended as the results would be unsatisfactory. But with the simpler types as indicated above fair approximations are possible.

Assay of Ores of Copper. As was the case in lead ores the dry assay of copper is not as accurate as any one of a number of wet methods. Still when the ores are of quite uniform grade and the character of the gangue known, satisfactory results can be obtained. These operations can also be adapted for field use where the facilities of a well stocked laboratory are absent. In general the slag should be as nearly neutral as possible, the amount of flux small and the temperature high in order that the operation may be completed in as short a time as possible.[4] Sulfide ores should be roasted in a clay crucible which removes not only the sulfur but arsenic and antimony which might also be present. The time of fusion should be restricted to about 4 minutes. This is an important consideration especially with ores containing both copper and iron. An increase of a minute or two in the fusion period may add several percent of iron to the copper button. The reports here recorded cover a number of determinations made on chalcopyrite and malachite ores. When these ores are rather high grade the following general charge may serve as a convenient guide.

ore	200 mg. (previously roasted if sulfide)
sodium carbonate	100
potassium carbonate	100
borax	100
flour	125
flour cover	

In some instances minor changes must be made depending upon the character of the gangue. Very lean and siliceous ores require 150 mg. each of Na_2CO_3 and K_2CO_3. The copper should collect in a single button at bottom of crucible and can be weighed after a short refinement with boracic acid to remove traces of iron. In case of lean ores a slight modification is necessary as the small particles of copper remain disseminated throughout the slag. To overcome this difficulty 125 mg. of PbO should be added to the original charge. The copper is then collected by the reduced lead as it slowly settles to the bottom. When litharge is added to the charge the refining is somewhat extended, as it is now necessary to remove all this lead as well as traces of iron before the copper can be weighed. It is also very desirable to dissolve the copper button and test for iron and lead to prove their absence as the mere copper red color is not sufficient.

The following results record the amount of copper recovered and the percentages obtained by a wet method.

Chalcopyrite ores		Malachite ores	
% of Cu(wet)	% of Cu(dry)	% of Cu(wet)	% of Cu(dry)
22.5	20–21	30.7	29–30.5
11.0	10	12.2	9.5–11

[4] Notes on Assaying, Richard W. Lodge. Third edition, 1911, p. 213. John Wiley & Sons. *New York.*

In the above PbO was added only to those containing less than 10% Cu. It will be noted that the agreement between the "wet" and "dry" determinations are much closer in the case of copper than lead.

ASSAY OF SILVER ORES. Due to the greater value of silver and its more limited distribution in the rocks, compared with lead and copper, certain modifications in procedure are necessary and greater skill required if satisfactory results are to be obtained. If the student is permitted to precede his silver assays by those of lead and copper he will have acquired the necessary experience to successfully undertake this determination. The resultant silver bead is usually too small to weigh accurately on the portable balance which is used for weighing the flux. The weight can, however, be determined by measuring the diameter of the bead on an ivory scale devised by Plattner. The scale is based on the principle that the weights of metallic spheres are proportional to the cubes of their diameters, and that these diameters can be measured by means of two fine converging lines between which the spheres are placed. Transverse lines indicate directly the weights of silver beads tangent to the converging lines at the various points of the scale. Knowing the weight the percent of silver present can be calculated. As a one percent ore is equivalent to 291.66 troy oz., the oz. per ton of any ore can be easily computed.

The successive steps in the assaying of silver ores by the blowpipe furnace method may be indicated as follows: (1) roasting of sulfide ores to eliminate S, As, and Sb; (2) fusion for 6-7 minutes in a clay crucible; (3) refining with borax to remove impurities; (4) scorification in a clay capsule to oxidize the greater portion of the lead and last traces of copper; (5) cupellation on bone ash to remove the balance of the lead; and (6) measuring of bead and computation in oz. per ton.

It is extremely difficult to describe the end points of some of the above stages but this knowledge is easily acquired with a little experience. The most accurate portion of the ivory scale is confined to the middle third section. It is desirable, therefore, in assaying ores high in silver, to subdivide the rich-lead (lead and silver) button and scorify and cupel these portions separately in order to bring the bead within this section of the scale. On the other hand, very low grade silver ores should have the rich-leads of a number of assays united to obtain the best results.

As the charge varies somewhat with the character of the ore and its associated gangue, the one given below may be designated as the initial trial charge for silver ores in general.[5]

ore	200 mg.
sodium carbonate	200
potassium carbonate	100
borax	100
litharge	500
flour	100
salt cover	

For rich silver ores high in cobalt the ore might be advantageously reduced to 100 mg. and the borax increased to 200 mg.

In the concluding table will be found the results obtained by both the blowpipe and regular fire assay methods.

REGULAR FIRE ASSAY	BLOWPIPE ASSAY
3470 oz. per T.	2900 –3500 oz. per T.
732.8	700 – 720
600	545 – 644
280	250 – 275
86	90 – 98
69	64 – 70
31.4	30 – 35
11	10 – 14

The variations in the figures listed in the right hand column represent the extreme values reported by different individuals. These ores might be considered typical, representing both lean and high grade types. Likewise, in some cases a great deal of impurity was encountered in the nature of copper, cobalt and nickel requiring repeated refining. In general it may be said that the average careful student, with some experience, should obtain results with silver ores easily within ± 10% of the values obtained by the regular fire assay. While it is not claimed that these methods will ever replace the regular fire assay, still for fairly close approximations in field or laboratory these methods seem eminently satisfactory.

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[5] To determine the amount of silver in argentiferous galena the charge to be recommended consists of: ore 600 mg., Na_2CO_3 300 mg., KNO_3 400 mg. and salt cover.