

1870

A New Volumetric Assay for Lead Ores

There are two different methods now in use for determining the amount of lead in an ore; namely the fire assay in which the ore is smelted in an iron or clay crucible either with or without a flux, and the wet assay which does not differ essentially from a gravimetric analysis. The fire assay is almost universally used at lead-smelting establishments, because although it is not at all accurate, the error being sometimes ten per cent, yet when the furnace and crucibles are once prepared the assay can be quickly performed and does not require much chemical knowledge or nice manipulation. I think that the only smelting works at which the gravimetric assay is used are those at Bleiberg.

A good volumetric method combines the advantages of both the dry and gravimetric assays; for it can usually be performed as quickly as the fire assay and at less expense and is nearly as accurate as the gravimetric method.

A large number of volumetric processes have been proposed for determining lead but according to Percy and Fresenius none of them are satisfactory. The following methods have been proposed.

Domonte precipitates the lead from an alkaline solution with a standard solution of sulphide of sodium, which is added as long as a precipitate is formed.

Margueritte adds permanganate of potassium to the alkaline lead solution until a green color is produced; the lead is converted into binoxide.

Pappenheim adds a standard solution of sulphate of potassium until a drop of the lead solution produces no yellow spot of iodide of lead with iodide of potassium.

Streng oxidizes the lead with "chloride of lime"; the binoxide of lead produced is treated with a known quantity of

protochloride of tin in excess and this excess being determined by bichromate of potassium the amount of lead can be calculated. Hempel precipitates the lead as oxalate which is then dissolved in nitric acid, sulphuric acid added, the oxalic acid determined with a solution of permanganate of potassium and the lead calculated from the quantity required.

Schwarz precipitates the lead as chromate, which is then dissolved in hydrochloric acid, a known quantity of ferrous chloride added in excess and permanganate of potassium added until the excess is converted into ferric chloride; the quantity of lead can be calculated from the amount of permanganate used.

According to a later method Schwarz adds bichromate of potassium to a solution of lead in acetic acid until a drop produces a red coloration with nitrate of silver.

The methods of Hempel, Streng and Schwarz's first method give quite accurate results but they are so long that it is usually preferable to make a gravimetric analysis instead. Schwarz's second method is simple enough but the end reaction is not sufficiently delicate and an error of several milligrammes in the quantity of lead present is likely to occur.

This last method was so satisfactory in all respects except the end reaction that I endeavored to find some more delicate test for bichromate of potassium than nitrate of silver. I wished to apply the process to the determination of lead in galena. For this purpose I treated about half a gramme of the finely pulverized galena in a beaker with a quantity of strong nitric acid and the application of a gentle heat. Nitrous fumes were given off in abundance and

in from a quarter to half an hour the whole of the galena was converted into sulphate and nitrate of lead with the separation of a little free sulphur, which as it separated in globules which <sup>appeared</sup> to be free from foreign substances were washed and thrown away. The sulphate of lead was dissolved in a concentrated solution of acetate and nitrate of ammonium by the aid of heat. To the lead solution thus obtained was added a solution of bichromate of potassium of known strength, until a drop of nitrate of silver added to a drop of the lead solution on a porcelain plate showed ~~a~~ red coloration. The amount of lead was calculated from the quantity of bichromate of potassium used.

I obtained pretty fair results by this method, for instance 85. 83.6 and 87.7 per cent instead of 86.6 which is calculated from the formula PbS. The galena used was a pure specimen from Missouri.

Not being satisfied with the delicacy of the final reaction I made a number of experiments and found that a solution of bichromate of potassium acidified by one of the common mineral acids turned a mixture of starch paste and iodide of potassium blue, even when only a minute quantity of chromate was present. I also found that chromate of lead gave a blue color when treated in the same manner. The blue color in this reaction is perhaps due to <sup>the</sup> ozone, which is formed by the action of acids on bichromate of potassium; as chromic acid is an ozonide. The ozone formed displaces the iodine in the iodide of potassium and the free iodine colors the starch paste blue.

To make this reaction of bichromate of potassium on starch paste and iodide of potassium of any use in the present case it was necessary to find some

acid which would cause bichromate of potassium to act on iodide of potassium but which would have no action on chromate of lead. After trying nitric hydrochloric, sulphuric, oxalic, acetic tartaric, citric, malic, succinic, benzoic and other acids of various degrees of concentration, a solution of one part by weight of citric acid and six of water was found to be the best adapted to object in view. When a highly dilute solution of bichromate of potassium was added to a mixture of thin starch paste, iodide of potassium and the before mentioned citric acid solution a fine blue color was at once produced; while chromate of lead added to the same mixture gave a perceptible color only after standing four or five minutes. Now that a delicate end reaction had been found the process seemed to be capable of giving as accurate results as could be desired; but on attempting to determine



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the lead in a solution of galena made as before described the results obtained were not as good as the former ones; the end reaction not being nearly as delicate as was anticipated. A number of experiments were then made with pure nitrate of lead to see if the process really was valuable. The solution of bichromate of potassium used contained 7.13 grammes of the dry salt to the litre; that is one cubic centimetre of the solution corresponded to one hundredth of a gramme of lead; for one equivalent of bichromate of potassium <sup>(295.18)</sup> corresponds to two equivalents of lead (414); therefore  $\frac{7.13}{295.18 \div 414} = 10$  nearly = the quantity of lead that the litre of bichromate solution was equivalent to. A lead solution was made containing 0.00574 gramme of lead in a cubic centimetre of the solution, by dissolving 5.392 grammes of pure nitrate of lead in 500 cubic centimetres of water. 20 cubic centimetres of this lead solution were placed in a beaker, water and a little acetic

acid added, the solution heated nearly to boiling and the standard solution of bichromate of potassium added until a drop of the liquid in the beaker gave a blue color with starch paste, iodide of potassium and citric acid.

The 20 cubic centimetres of the lead solution required the following number of cubic centimetres of the bichromate solution to produce a blue color,

1 <sup>st</sup> Experiment-	13.4	2 <sup>nd</sup> Experiment-	13.3
3 <sup>d</sup>	"	4 <sup>th</sup>	"
5 <sup>th</sup>	"	6 <sup>th</sup>	"

13.4 cubic centimetres of lead solution required 13.9 c.c. of bichromate, or 20 c.c. lead required 13.5 c.c. bichromate. In the 7<sup>th</sup> experiment a gramme of sulphate of ammonium was added to the nitrate of lead in the beaker and then 13 c.c. of bichromate solution were sufficient to produce a dark blue color; in another experiment a still less quantity of bichromate solution was required, the end reaction not being

as distinct- as when no sulphate of am-  
 monium was present. By calculation the  
 quantity of lead present- in the 20 c.c. should  
 be 0.1348 gramme =  $0.00674 \times 20$ ; the quantity  
 of lead present- reckoned from the bichromate  
 used was 0.133 gramme, 13.3 cc being the  
 mean of the bichromate solution used.

These experiments showed that the process  
 was an excellent one for pure nitrate of lead  
 and it- also showed that sulphate of am-  
 monium prevented part- of the lead from  
 being precipitated as chromate.

Some qualitative experiments were then  
 made to see if ammonia or acetic acid  
 had any influence on the reaction. A con-  
 siderable quantity of ammonia water was  
 added to a very dilute solution of bichro-  
 mate of potassium which alone would give  
 a decided blue color to an acid solution of  
 iodide of potassium and starch paste.  
 After the addition of the ammonia no blue  
 color was produced when the solution was  
 acidified and added to the iodide of

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potassium and starch. Acetic acid hindered the reaction but not as much as ammonia. These experiments in connection with the fact that sulphate of ammonium prevents all the lead from being converted into chromate are sufficient to account for the discordant results which I obtained with the method; for the sulphate of ammonium would make the result too low and the ammonia and acetic acid would tend to bring it too high: the varying amounts of these reagents would make the results vary as was found to be the case. Another method of treating the galena was then tried, in which the large excess of ammoniacal salts was avoided. The galena was treated as before with nitric acid, but the resulting sulphate and nitrate of lead instead of being dissolved was treated with a large excess of bicarbonate of sodium and the mixture left in a warm place several hours. At the end of this time the sulphate of lead seemed to be wholly converted into carbonate, sulphate of sodium

being formed. The carbonate of lead, which is nearly insoluble in a solution of carbonate of sodium, was separated by filtration from the sulphate of sodium. After the carbonate of lead had been washed it was dissolved, on the filter, in as small a quantity of nitric acid as could be conveniently used and, the solution having been neutralized with ammonia and a small excess of acetic acid added, the lead was determined by titrating the solution with bichromate. I made only a few determinations by this method as it was rather long. My results were uniformly too low being from 83 to 85 per cent instead of 86.6. The probable cause of the error in the determinations was that the carbonate of lead was not washed enough to remove all the sulphuric acid which prevented all the lead from being converted into chromate. The excess of nitric acid ought also to have been neutralized with carbonate of sodium instead of ammonia as the last has been shown to have an injurious effect on the determination.

The method would undoubtedly have

given good results but as it was rather long I tried to find a shorter way of converting the lead of the galena into nitrate. Professor Storer had just devised a method of decomposing galena by means of zinc and an acid: with chlorhydric acid the reaction being

$$PbS + 2HCl + Zn = Pb + H_2S + ZnCl_2.$$

In employing his method I treated about half a gramme of galena in a beaker with chlorhydric acid, diluted with twice its volume of water, and about a gramme of pure zinc, the reaction being hastened by means of a gentle heat. The decomposition was complete when no more sulphuretted hydrogen was given off, usually in from five to ten minutes; the lead separated as a gray spongy mass adhering to the zinc. The excess of acid was then decanted, the mass washed and the lead removed from the zinc; the last traces being removed by concentrated nitric acid. The remainder of the lead was then dissolved in dilute nitric acid, the small excess being neutralized by ammonia, and the solution of nitrate of lead

titrated with bichromate of potassium.

There was one difficulty with the process: on dissolving the lead in nitric acid a small white residue remained; but as the residue was probably either chloride of lead, and could be removed by washing, or sulphate of lead, and was occasioned by the chemicals employed containing sulphuric acid, it could be readily prevented.

I had time to make only a few experiments with this last method before the term closed and I have had no time to take it up again.

If the method will give accurate results, and there seems to be no reason why it should not, it ought to come into general use in cases where a large number of assays of galena have to be made. After the solution of bichromate of potassium has been made and standardized and a little practice acquired an assay can be made in half an hour from the time of weighing out the sample. Bismuth is the only metal which would affect the assay and that seldom occurs with lead ores.

# Thesis

by

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Class of '70