

ordinarily obtained, this mechanical loss is very apt to occur. The silica obtained by this method is, however, more difficult to decompose by treatment with hydrofluoric acid. It is much less hygroscopic and weighings are thus more accurately made.

For as many slags as have been investigated there is claimed for the above method (1) greater accuracy due to more complete dehydration of silicic acid, and thorough decomposition of certain slag constituents, and (2) greater rapidity and ease of execution than for other methods of about equal accuracy.

LABORATORY OF ANDOVER IRON CO.,
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THE DETERMINATION OF LEAD IN LEAD ORES.¹

BY RICHARD K. MEADE.

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IN the wet assay of lead ores, the general mode of procedure seems to be to precipitate the lead as a sulphate by dissolving the ore in a mixture of sulphuric and nitric acids and evaporating until the solution is free from the latter acid. The residue, consisting of the precipitated lead sulphate and gangue, is collected upon a filter paper and, after washing, is dissolved in either ammonium tartrate or acetate or in sodium thiosulphate; then precipitated as an oxalate or chromate and determined volumetrically, or precipitated as a sulphide and estimated gravimetrically. Another way is to ignite the residue of lead sulphate and gangue and weigh. Then treat with ammonium tartrate or acetate, and collecting whatever residue remains, ignite and weigh. The difference between these two weights is taken as lead sulphate.

Of these methods the first is rather inaccurate.² The third is rather slow, and both are inapplicable when calcium, barium, and strontium are present. The second is the most accurate of the three outlined above, but is also the slowest.

While recently working upon some specimens of galena, the writer thought of a simple method for determining the amount of lead in this mineral, and in lead ores in general. Like two of the above methods, it fails in accuracy when barium, strontium, and small amounts of calcium are present, since these

¹ Read at the meeting of the New York Section, March 5, 1897.

² See Sutton: "Systematic Handbook of Volumetric Analysis," Sec. 66, 1 and 2.

metals are precipitated by sulphuric acid, and would be weighed along with and calculated as lead, causing too high results. In detail the method is as follows :

Method.—Weigh one gram of the ore if rich, more if poor, into a platinum dish, cover with a watch-glass and add forty to fifty cc. of a mixture of one part sulphuric acid (1.84 sp. gr.) and three parts nitric acid (1.42 sp. gr.). Heat the covered dish on a hot plate, water-bath, or sand-bath until the action of the acids on the ore has apparently ceased. Then remove the watch-glass and rinse into the dish. Add ten to fifteen cc. hydrofluoric acid to the solution and evaporate until dense white fumes of sulphuric acid begin to come off. It is better to conduct the evaporation under a hood for obvious reasons. Remove the dish from the source of heat and cool. Dilute to about 100 cc. with water, digest until all soluble salts are in solution and filter, washing first with a two per cent. solution of sulphuric acid and then with alcohol. Dry, burn filter paper, and ignite precipitate separately. Weigh as lead sulphate and calculate per cent. of lead present in the ore.

To test the method several lead-bearing minerals were carefully assayed for lead by the method (A) outlined by Fresenius (*Quant. Anal.*, 213), and then by the above method (B), after ascertaining that calcium, barium, and strontium were absent, with the following results :

| | Method A. Per cent. lead. | Method B. Per cent. lead. |
|-------------------|------------------------------|------------------------------|
| Galenite..... | 77.34 | 77.46 |
| Pyromorphite..... | 75.26 | 75.35 |
| Cerussite..... | 76.46 | 76.53 |

To further test the method, and especially to see if any lead was lost by volatilization as a fluoride, a solution of lead nitrate was made. Twenty-five cc. of this solution, on evaporation with sulphuric acid, gave 0.4297 gram of lead sulphate as an average of six determinations.

The same quantity, on evaporation with sulphuric and hydrofluoric acids, gave 0.4280 gram of lead sulphate as an average of six determinations.

Twenty-five cc. of the solution, to which two-tenths gram of silica was added, on evaporation with hydrofluoric and sulphuric

acids, gave 0.4285 gram of lead sulphate as an average of six determinations.

Fearing that the stock solution might be too concentrated and that small errors in delivering exactly the same quantity each time from the pipette might be the cause of discrepancy in the results, a new and more dilute solution was made, and 100 cc. of this used in each experiment. Below are the results expressed in grams of lead sulphate :

| | On evaporating with sulphuric acid alone. | On evaporating with silica and sulphuric and hydrofluoric acids. |
|---------------|---|--|
| 1 | 0.4154 | 0.4131 |
| 2 | 0.4147 | 0.4136 |
| 3 | 0.4150 | 0.4142 |
| 4 | 0.4156 | 0.4136 |
| Average | 0.4151 | 0.4136 |

It will be seen that, in all experiments, the results are higher when sulphuric acid alone was used than when hydrofluoric acid was added. Thinking that there was a loss of lead by volatilization as a fluoride, one gram of pure lead sulphate was heated in a platinum crucible to drive off moisture, etc., and, after cooling, both crucible and contents were weighed. The crucible was then half filled with hydrofluoric acid, a few drops of sulphuric acid added, the whole placed over a lamp and the acid driven off. After being gently ignited and cooled, the crucible and contents were weighed, then ignited and weighed again until the weight was constant. The lead sulphate was found to have suffered no loss by volatilization as a fluoride ; for the crucible and contents weighed exactly the same after as before treatment with the acids. This experiment was repeated with identically the same results. We deemed these two experiments sufficient proof that no lead should be lost in this method by volatilization as a fluoride.

The possibility of the stock solution containing silica in solution, along with the lead nitrate, causing the higher results to be found in the left hand column, suggested itself. To ascertain if this was the case, two of the residues from the evaporation with sulphuric acid alone, were brushed into a beaker and treated with ammonium tartrate. They dissolved completely, the residue only weighing 0.0003 gram after the weight of the

filter ash had been subtracted. This experiment was also repeated with similar results, proving the purity from silica of the lead sulphate precipitate.

We believe the foregoing experiments test the method fairly and rigidly, and that chemists will be safe in using the above when they know metals precipitated by sulphuric acid as sulphates or oxidized by nitric acid to insoluble compounds are absent.

Barium and strontium are rarely found associated with lead. Calcium, when present in galena as calcite, may be gotten rid of by first treating the ore with hydrochloric acid and filtering. The filtrate will contain the calcium; the residue will hold the lead and may be treated with hydrofluoric, sulphuric, and nitric acids, and the process carried out as above.

When the ore contains calcium, in small quantities only, the latter may be hindered from interfering with accurate results by washing the precipitated lead sulphate four or five times by decantation and then thoroughly upon the filter with a two per cent. solution of sulphuric acid. The calcium sulphate, being slightly soluble in the acid solution, is carried off by the wash water. The writer has found it possible to remove as much as four per cent. of calcium sulphate by this means.

The analysis of a lead ore can be made very nearly as quickly by this method as volumetrically and much more satisfactorily.

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NOTE ON THE SEPARATION OF SILICIC AND TUNGSTIC ACIDS.

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Received March 20, 1897.

THE object of the present note is to call attention to an important observation made by Mr. Lawrence Dufty in reference to the determination of silicon in tungsten steel and ferrotungsten. A common method for making such determination is to dissolve the tungstic oxide on the filter by means of hot dilute ammonia and to so obtain the silica at once for determination. Karsten¹ had pointed out the solubility of freshly pre-

¹ *Ann. der Phys.* (Pogg.), 6, 357, 1826.