ON THE VOLUMETRIC DETERMINATION OF LEAD.

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FRESENIUS in the last edition of his Quantitative Analysis commenting on the volumetric determination of lead, says: "Although there is no lack of proposed methods for the volumetric estimation of lead, we are still without a really good method for practical purposes, that is, a method which can be generally employed, and which is simple and exact."

Among the methods which have been proposed, one which has been so much used is that of Schwartz,[1] briefly outlined. This depends upon precipitating the lead as chromate in a sodium acetate solution with a standard solution of potassium bichromate, the end point being determined by an outside indicator consisting of drops of a neutral solution of silver nitrate on a porcelain plate. It is exceedingly difficult to decide when the first red tinge makes its appearance in the indicator owing to the yellow color of the precipitated lead chromate. The end point is therefore frequently overrun. W. Diehle[2] modified the method by titrating the excess of bichromate in acid solution with sodium thiosulphate, the end point being indicated by the disappearance of the yellow color of the bichromate. In our experience this modification does not lessen the difficulty of determining accurately the end point, owing to the fact that the yellow color gradually shades off into a green in case a fair excess of bichromate has been added.

These considerations led us to endeavor to modify the original method in such a manner as to secure a simple and accurate means of determining the excess of bichromate present. This we accomplish by titrating the solution after filtering off the precipitated lead chromate, with a standardized solution of ammonio ferrous sulphate, using potassium ferricyanide as an outside indicator under exactly the same conditions observed in standardizing bichromate solutions. The bichromate solution is made up of convenient empirical strength, and standardized against a weighed amount of pure dried ammonio ferrous sulphate. Slightly more than the equivalent weight of the latter salt is then

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[1] Dingl. poly. Jour., 169, 284.

[2] *Ztschr. anal. Chem.*, *1880*, 306.

weighed out and dissolved in a liter of water with the addition of a few drops of sulphuric acid. The solution is transferred to a stock bottle into which is immediately poured a sufficient quantity of some light paraffin oil to form a layer over the solution, thus protecting it from oxidation. The stock bottle is fitted with a siphon tube and pinchcock so that the solution can be drawn out when needed. With this arrangement change in strength of the ammonio ferrous sulphate solution takes place very slowly, while as a few moments only are required to titrate it against the standard bichromate, its exact strength can be easily determined from day to day.

In order to test this modification, we decided to try it against other technical methods recently proposed, as well as against a standard gravimetric analysis. A well mixed sample of a crystallized galena containing only a little silica as impurity was first analyzed by the method of Rose as given in Fresenius, Quantitative Analysis. The lead is precipitated as the sulphide, with the proper precautions, the sulphide is then dried, ignited gently in a current of hydrogen, and weighed. The following results were obtained :

No.	Weight taken Grams.	Weight lead sulphide. Grams.	Lead sulphide. Per cent.	Lead. Per cent.
1	2.0000	1.9870	99.35	86.08
2	2.0000	1.9856	99.28	86.00
3	1.9988	1.9856	99.35	86.06

The next series of results were obtained by the method of Albert H. Low.[1] Briefly, the method consists in decomposing the ore with nitric and sulphuric acids, adding further an excess of sulphuric acid, dissolving the lead sulphate in a saturated solution of ammonium chloride and precipitating metallic lead by means of strips of aluminum. The precipitated lead sponge is scraped off, pressed into a button, dried and weighed. By this method the following results were obtained :

No.	Weight taken. Grams.	Weight lead. Grams.	Lead. Per cent.
1	0.5000	0.4341	86.82
2	0.5013	0.4311	86.00
3	0.4972	0.4313	86.64
4	0.5025	0.4371	86.98
5	0.5019	0.4351	86.25
6	0.5223	0.4540	86.92

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[1] *J. Anal. Appl. Chem.*, **6**, 12.

These figures show a general tendency to high results which is accounted for by the difficulty of washing the lead sponge free from ammonium chloride. In view of the fact, however, that one of these assays can be made in about twenty-five minutes, the results might be considered fair enough for some technical purposes.

The next method tried was Knight's[1] modification of Hempel's method. This consists essentially in the precipitation of the lead as oxalate, the decomposition of this salt by means of sulphuric acid and titration of the liberated oxalic acid, with potassium permanganate. This method did not yield concordant results in our hands and the percentages found were invariably low. As the method did not present any advantage over others either in points of accuracy or time, we discontinued work with it.

The modified Schwartz method we carry out as follows: About one gram of finely pulverized ore is digested in a casserole or evaporating dish with fifteen cc. of a mixture of two parts nitric and one part sulphuric acid until decomposition is complete. Ten cc. more of sulphuric acid are now added, and the liquid evaporated until it fumes freely. Cool, dilute with ten cc. of dilute sulphuric acid (1–10) and then add gradually forty cc. of water. Heat to boiling, filter and wash by decantation with dilute sulphuric acid (1–10) getting as little of the lead sulphate on the filter as possible. To the residue in the dish add twenty cc. of strong ammonia, then make slightly acid with acetic acid. Boil until the lead sulphate is dissolved, then pour the liquid through the filter, having first moistened the paper with ammonia. Wash the filter with water containing ammonium acetate in solution, and finally once or twice with hot water. Cool the filtrate and run in from a burette an excess of standard bichromate solution, stirring until the precipitate settles rapidly and the supernatant liquid has a yellow color. Allow to settle for a few minutes then filter, under pressure if possible, wash a few times and titrate the filtrate against the standard ammonio ferrous sulphate.

After a little practice the method can be carried out as above detailed in about thirty minutes. In case the ore is known to be

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[1] *J. Anal. Appl. Chem.*, 6, 11.

free from bismuth and antimony, the method can be materially shortened. Instead of bringing the ore into solution with a mixture of nitric and sulphuric acids, nitric acid alone is used. After solution, the acid is neutralized with an excess of ammonia and then made acid with acetic acid; this dissolves any lead sulphate that has been formed. This solution is then immediately titrated with the bichromate and ammonio ferrous sulphate solutions exactly as described above. The following table shows the agreement in the results obtained by this method:

No.	Weight taken. Grams.	Calculated weight lead found. Grams.	Lead per cent.
1	0.9983	0.8570	85.84
2	0.9987	0.8578	85.82
3	0.9997	0.8588	86.08
4	0.9806	0.8421	85.88
5	0.9996	0.8570	85.72
6	0.9971	0.8558	85.84
7	0.9975	0.8580	86.02
8	0.9936	0.8533	85.90

In general it may be said that the results are a trifle low. The mean of the amount of lead recovered in twenty determinations carried out by one of us was 99.6 per cent. of that taken.

We do not know that the modification as used by us has never before been tried, but our results appeared to possess sufficient value to warrant publication.

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REACTIONS BETWEEN COPPER AND CONCENTRATED SULPHURIC ACID.[1]

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ANDREWS[2] in writing on the "Assumption of a Special Nascent State," argued that the production of sulphur dioxide, as a result of the reaction between copper and concentrated sulphuric acid, was due not to nascent hydrogen, as is commonly considered, but to the deoxidation of sulphur trioxide by the copper with the production of copper oxide as a primary pro-

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[1] Read at the Springfield meeting.

[2] Chem. News, 70, 152.; Iowa Acad. of Sciences, Proc. p. 4.