

The refraction method for the valuation of Chili niter gives results from one to one and one-half per cent. higher than those obtained by using the nitrometer and calculating the nitric oxide obtained as sodium nitrate. This is due to the almost unvarying presence of potassium nitrate, and the occasional presence of potassium perchlorate. The latter may be determined by fusing at a low temperature in the presence of powdered cupric oxide. The increase of chlorides after fusion is calculated as potassium perchlorate. The following is a complete analysis of one sample:

No. 471.	Per cent.
Moisture	2.2
Insoluble.....	0.1
Magnesium sulphate	0.2
Magnesium chloride.....	0.1
Sodium chloride.....	0.4
Potassium nitrate.....	3.6
Sodium nitrate	93.4
Potassium perchlorate.....	0.0
	100.0

The refraction method gave 96.8 per cent. of sodium nitrate by difference.

THE CALIFORNIA POWDER WORKS,
 PINOLE, CONTRA COSTA COUNTY,
 CALIFORNIA, January, 1899.

A MODIFICATION OF PIERCE'S METHOD FOR THE DETERMINATION OF ARSENIC IN ORES.

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Received February 20, 1899.

THERE are several methods for the estimation of arsenic in ores in current use, many of which, however, are defective or do not approach the accuracy required even in technical work.

Pierce's method¹ (one of the best of those in general use), with or without Canby's modification, on account of its simplicity, is largely employed in metallurgical works notwithstanding the fact that it is subject to a range of inaccuracy which renders it inadmissible where accurate results are required, and which can be reduced to a minimum only by the most careful execution.

It is my purpose, after having pointed out the defective points

¹ Proceedings of the Colorado Scientific Society, Vol. I.

in the above method, to present what is thought to be an improvement upon it, intended especially for the determination of arsenic in ores, together with the results of a number of experiments carried on with a view to determining its accuracy.

Pierce, after getting the arsenic into solution as an alkaline arsenate, expels carbonic acid by boiling with an excess of nitric acid and then very carefully neutralizes with ammonia and nitric acid, using litmus paper as an indicator. By Canby's modification the neutralization is effected by means of an emulsion of zinc oxide.

As to the first method, I have found it practically impossible, after making a large number of determinations, to secure concordant results, especially on high grade ores. This is due to the fact that the silver arsenate is highly soluble in a slight excess of either acid or alkali, and slightly soluble in an aqueous solution of ammonium nitrate; while the precipitate under the conditions that exist here, even after vigorous stirring, invariably passes through the filter. I believe it is practically impossible to secure a neutral solution by means of the above reagents and indicator. Litmus paper, as is well known, is not a good indicator under the conditions as they exist above and I have found it entirely inadequate for the purpose of securing the degree of neutralization which is here absolutely indispensable.

Canby's method is little better in this respect, as the neutralization is only partly effected, the acid becoming too weak to attack the oxide but remaining sufficiently strong to dissolve the arsenate. The method which I propose for eliminating the defective points as above mentioned, is based on the following considerations:

(1). "The addition of sodium acetate to a mixed solution of arsenic and nitric acid is sufficient to insure the immediate precipitation of silver arsenate when silver ammonio-nitrate is introduced."¹ Also, silver arsenate is only "more freely soluble in acetic acid than in solution of ammonium nitrate."²

(2). The use of phenolphthalein as indicator instead of litmus paper.

(3). The precipitation, as herewith proposed, renders the precipitate granular and as easily filtered as silver chloride.

¹ Every, in Crooke's "Select Methods," page 420.

² Graham, in Storer's Dictionary of Chemical Solubilities.

Under consideration (1), the precipitation might be effected in a nitric acid solution, but in order to eliminate any solvent action which the presence of nitric acid might have, the precipitation is effected in a sodium acetate solution slightly acid with acetic acid, as will be seen in the scheme which follows: The absence of ammonia salts, etc., permits the use of phenolphthalein as indicator, thereby securing the neutralization promptly and without the tedious delay due to the slow action of the litmus paper. It will be noticed that I state above on the authority of Graham, that silver arsenate is somewhat more soluble in acetic acid than in ammonium nitrate, while I precipitate in acetic acid solution. I will say, however, that the above is a fairly strong solution of acetic acid, while my solution contains only a sufficient excess of acetic acid to destroy the color of the phenolphthalein (a drop or two of dilute acetic acid in 100 cc. of solution), in which I have found the silver arsenate to be practically insoluble.

The method is as follows:

One-half gram of the finely powdered ore is mixed in a large porcelain crucible with from six to ten times its weight of a mixture of equal parts of sodium carbonate and potassium nitrate, preferably by mixing the ore with about two-thirds of the flux and using the balance as a cover. The mass is then heated gradually to complete fusion and kept so for a few minutes, cooled, and the soluble portion extracted with boiling hot water and filtered from the insoluble residue. The arsenic is in the filtrate as alkaline arsenate. Acidify filtrate strongly with acetic acid, cover and boil rapidly for a few minutes to expel carbonic acid; cool, add a few drops of a solution of phenolphthalein in alcohol, then a strong solution of sodium hydroxide to alkaline reaction; then one or two drops of acetic acid which will discharge the purple-red color if too much of the alkali has not been used. The solution should now consist of about 100 cc. Add, in slight excess, while violently agitating with a stirring rod, a neutral solution of silver nitrate, and allow to settle a few minutes, keeping out of direct sunlight. Pour the clear supernatant liquid through the filter, retaining the precipitate in the beaker, and wash once or twice by decantation with cold water. Finally throw the precipitate on the filter and wash

thoroughly with cold water. Now place the beaker in which the precipitation was made, under the funnel, fill the funnel full of water, and add twenty cc. strong nitric acid. When the filtrate has run through, wash filter thoroughly three or four times with cold water, make the filtrate up to about 100 cc., and titrate with a standard solution of potassium thiocyanate, according to Volhard;¹ or the silver may be determined by scorifying the filter and precipitate and cupelling. The former method must be adopted in the presence of chlorides.

Following are a few of a large number of determinations made to test the accuracy of this method :

Two hundred and fifty milligrams impure arsenic trisulphide (As_2S_3) were fused as above and the solution made up to 500 cc. Several portions of fifty cc., each containing 0.025 gram impure arsenic trisulphide, were taken and each portion treated as a separate determination from the point at which the filtrate is acidified strongly with acetic acid ; then scorified and cupelled. Results are as follows :

TABLE I.

No. of determination.	Weight of silver button. Gram.	Calculated amount of arsenic trisulphide found. Gram.
1	0.063915	0.02424
2	0.063240	0.02400
3	0.064720	0.02457
4	0.063450	0.02409
5	0.065075	0.02470
6	0.063675	0.02407

One-half gram impure arsenic trisulphide was fused and made up to 500 cc., and portions of 25 cc., containing 0.025 gram of arsenic trisulphide, were treated as above, except that the precipitate was dissolved in nitric acid and titrated with potassium thiocyanate (1 cc. = 0.02875 gram arsenic trisulphide) instead of scorifying and cupelling. Results are as follows :

TABLE 2.

No. of determination.	Standard solution of potassium thiocyanate. cc.	Arsenic trisulphide found. Gram.
1	8.6	0.024725
2	8.6	0.024725
3	8.3	0.023863
4	8.6	0.024725
5	8.6	0.024725
6	8.7	0.025013

¹ *Ann Chem.* (Liebig), 190, 1.

It will be noticed that the first table gave uniformly low results. This was attributed to the loss of silver in scorification and cupellation, and in order to correct this loss four assays were run containing 0.06512 gram pure silver each, corresponding to 0.024725 gram arsenic trisulphide (the amount found by titration in numbers 1, 2, 4, and 5 in Table 2). The average loss was found to be 0.001 gram silver, which, added to the amounts in Table 1, gave an average result agreeing very closely with those of the above numbers in Table 2.

Following is Table 1 corrected for loss of silver in scorification and cupellation :

TABLE 3.

No. of determination.	Silver found as per Table 1. Gram.	Silver after correction. Gram.	Calculated amount of arsenic trisulphide. Gram.
1	0.063915	0.064915	0.024648
2	0.06324	0.06424	0.024392
3	0.06472	0.06572	0.024954
4	0.06345	0.06445	0.024472
5	0.065075	0.066075	0.025089
6	0.063675	0.064675	0.024457

Average amount of arsenic trisulphide 0.024670

One gram of leucopyrite was fused and made up to 500 cc. Portions of fifty cc. were treated as above and titrated with potassium thiocyanate (1 cc. = 0.0017536 gram arsenic). Results were as follows :

TABLE 4.

No. of determination.	Standard solution of potassium thiocyanate. cc.	Arsenic found. Gram.	Arsenic in ore. Per cent.
1	7.0	0.012275	12.275
2	7.0	0.012275	12.275
3	7.0	0.012275	12.275
4	7.0	0.012275	12.275

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A SIMPLE VOLUMENOMETER.

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Received February 14, 1899.

MCKENNA¹ has recently described a "New Apparatus for the Determination of Volume," which resembles in several respects one which I have devised and have been using

¹ This Journal, 21, 50 (1899).