

**MEETING OF FEBRUARY 5th, 1883.**

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*On the Estimation of Arsenic*, BY RICHARD PEARCE.

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I have long felt the need of a rapid and reliable method for the estimation of arsenic in ores and metallurgical products, and more particularly in copper ores and copper smelting products. The copper ores of Montana, Utah and Colorado are so abundantly associated with arsenic that it is a matter of importance to copper smelters to be able to determine with some sort of rapidity and fair accuracy the amount of arsenic present in any given sample.

After a great many experiments in different directions the following scheme, depending upon the insolubility under certain conditions of silver arseniate in neutral solutions, has been found to work well.

The finely powdered substance for analysis is mixed in a platinum crucible with from six to ten times its weight of a mixture of equal parts of carbonate of sodium and nitrate of potassium. The mass is then heated with gradually increasing temperature to fusion, and kept for a few minutes in that state. It is then allowed to cool (this may be hastened by dipping the outside of the crucible in cold water), and the soluble portion is extracted by warming with water in the crucible and filtering from the insoluble residue when disintegration is complete. The arsenic is in the filtrate as alkaline arseniate. The solution is acidified with nitric acid, and boiled to expel carbonic acid and nitrous fumes. It is then cooled to the ordinary temperature and almost exactly neutralized as follows: Place a small piece of litmus paper in the liquid; it should show an acid reaction. Now gradually add strong ammonia till the litmus turns blue, avoiding a great excess. Again make slightly acid with a drop or two of strong nitric acid, and then, by means of very dilute ammonia and nitric acid added drop by drop from a pipette, bring the solution to such a condition that the litmus paper, after having previously been reddened, will in the course of a half minute begin to show signs of alkalinity. The solution, if tolerably clear, is ready for the addition of nitrate of silver. If the neutralization has caused much of a precipitate (alumina, etc.) it is

best to filter it off at once, to render the subsequent filtration and washing of the arseniate of silver easier. If this filtration is unnecessary, the litmus paper is drawn up the sides of the beaker, leaving a portion, however, still immersed in the liquid. A neutral solution of nitrate of silver is now added in slight excess, and after stirring a moment the color of the immersed portion of the litmus paper is observed, and, if necessary, the neutralization is repeated.\*

The precipitated arseniate of silver, which is of a brick red color, is finally collected on a filter and well washed with cold water. As a further precaution the filtrate may be tested with nitrate of silver, dilute nitric acid and ammonia to see that the precipitation is complete.

The object is now to determine the amount of silver in the precipitated arseniate of silver and from this to calculate the arsenic. To accomplish this it was originally proposed to subject the arseniate of silver to scorification or fusion with lead and subsequent cupellation, and to weigh the button of silver obtained, but as this would necessitate the removal earlier in the process of any soluble chloride present, and would require additional time, another and shorter method was finally adopted.

This was simply to dissolve the arseniate of silver on the filter with dilute nitric acid (which leaves undissolved any chloride of silver) and titrate the filtrate after addition of ferric nitrate or sulphate with sulphocyanate of ammonium. About five cubic centimeters of a saturated solution of ferric ammonium sulphate are added, and the standardized sulphocyanate solution (about five grams to the litre) run in till a faint red tinge is obtained, which remains after considerable shaking. The shaking breaks up any clots of sulphocyanate of silver; and frees any solution held mechanically.

From the formula  $3\text{Ag}_2\text{O}, \text{As}_2\text{O}_5$ , we find that 648 parts silver represent 150 parts arsenic, or 108 parts of silver 25 of arsenic.

One-tenth of a gram of sample enargite tested by this method gave . . . . . As, per cent  
19.03

\* This second neutralization is always necessary when the amount of arsenic present is large, as nitric acid is set free in the reaction between the alkaline arseniate and nitrate of silver according to one or both of the following equations, or those of the corresponding potassium salts:

$$3\text{AgNO}_3 + \text{NaH}_2\text{AsO}_4 = \text{Ag}_3\text{AsO}_4 + \text{NaNO}_3 + 2\text{HNO}_3; 3\text{AgNO}_3 + \text{Na}_2\text{HAsO}_4 = \text{Ag}_3\text{AsO}_4 + 2\text{NaNO}_3 + \text{HNO}_3.$$

	As, per cent
A second trial showed . . . . .	19.09
To try the effect of antimony 1-10th of a gram of the enargite was mixed with an equal weight of stibnite and tested: the result was	19.13
The arsenic in the enargite determined by the arseniate of magnesia and ammonia method showed . . . . .	19.44
A sample of copper glance was tested and found free from arsenic. This was then mixed with a sufficient quantity of enargite to produce a mixture calculated to contain	0.37
0.55 gram was taken for analysis and showed	0.38
A test on 1-20th of a gram of pure proustite gave . . . . .	15.08
Theoretical . . . . .	15.15
A sample of copper matte gave on first trial	0.47
Second trial . . . . .	0.46
Another sample of copper matte gave on first trial . . . . .	0.28
Second trial . . . . .	0.284
A sample of pimple metal gave . . . . .	0.458
Repeated . . . . .	0.459

Additional experiments have been made with samples of speiss, and alloys of copper and arsenic, with equally satisfactory results.

In determining arsenic in ores very rich in arsenic, such as arsenopyrite niccolite, etc., it is perhaps desirable to add a few drops of fuming nitric acid to the weighed sample in the platinum crucible prior to the usual fusion. This oxidizes the arsenic and sulphur present and prevents subsequent loss by deflagration; this precaution should also be adopted in the determination of arsenic in sulphide of arsenic obtained in the ordinary course of analysis.

Substances such as molybdic and phosphoric acids, which may behave similarly to arsenic under this treatment, interfere of course with the method. Antimony, by forming antimoniate of sodium, remains practically insoluble and without effect.

It is quite probable that the method could be adopted for the estimation of phosphorus in commercial iron and steel; but beyond a few preliminary experiments nothing has been attempted in this direction.

As an example of the rapidity of the process I may state that a correct determination of arsenic in a sample of

copper ore was made by Mr. A. H. Low, in the laboratory of the Boston and Colorado Smelting Co., at Argo, where the details of the process were worked out, in twenty-two minutes.

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*Technical Estimation of Copper*, BY A. H. LOW.

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The present paper is intended to outline the scheme for the technical estimation of copper as developed by the writer, now in use at the works of the Boston and Colorado Smelting Company at Argo, Colorado. This scheme is essentially that of Dr. Steinbeck, but so modified as to save considerable time, while ensuring equal if not greater accuracy. Omitting the discussion of the details, the method is as follows:—

Treat one gramme of the pulverized ore in a small, (250 c. c.) flat-bottomed glass flask with seven cubic centimetres of commercial nitric acid and five cubic centimetres of commercial sulphuric acid. Heat strongly till the nitric acid is all expelled and the sulphuric acid is boiling freely. Sulphur, if present, is usually partially, sometimes entirely volatilized, a portion recondensing on the neck of the flask. What remains in the bottom of the flask should be melted into globules which are yellow when cold, and free from copper. Allow the flask and contents to cool sufficiently and add 25 c. c. of water and six grammes of commercial sheet zinc cut into small slips. Shake the zinc about in the flask a little to break up any cake formed in the bottom, and allow to stand five minutes. Now add 50 c. c. of water and 20 c. c. of sulphuric acid to rapidly dissolve the excess of zinc, which usually takes about five minutes more. When solution is complete, fill the flask up to the neck with water, allow to settle, and decant the clear, supernatant liquid. This may be tested for copper if desired, with sulphuretted hydrogen water, bearing in mind that antimony, bismuth etc., may be present and give tints or discolorations likely to be mistaken for copper. As a rule, no discoloration whatever, or only an extremely faint one will be observed, and consequently the test is usually omitted. Fill up and decant twice more. The residue in the flask may consist of gangue and copper, besides various other constituents of the ore and the impure reagents used, such as silver, gold,