the difference is negligible, but its use is not to be recommended where the alkalinity is over 100.

(3) A standard color is recommended for titrations with butter-yellow.

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A RAPID METHOD FOR THE ESTIMATION OF COPPER AND IRON.

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The insolubility of cuprous thiocyanate in dilute acid solutions has formed the basis for a number of methods for the estimation of copper. Without attempting to give complete references to the literature on this subject it may be pointed out that Rivot[1] and Van Name[2] have shown that the gravimetric estimation of copper as cuprous thiocyanate is accurate under properly regulated conditions, while Volhard,[3] Guess,[4] Jamieson,[5] and others, have based volumetric processes upon the same precipitation. The accuracy of the volumetric processes seems to be questioned by many reference books on analytical chemistry. Thus Low[6] states that cuprous thiocyanate is sufficiently soluble to necessitate the use of empirical tables in calculating the results of Guess's method, while Sutton[7] states that Volhard's method is inapplicable in the presence of iron. These statements seem to be contradicted by the results obtained by Van Name, Volhard, and by the results given in the present paper.

While engaged in the investigation of certain reactions of cuprous thiocyanate the writer was impressed by the simplicity and accuracy of the Volhard method, and carried out preliminary experiments which resulted in a modification of the Volhard procedure by which not only copper, but iron associated with it, may be rapidly and accurately estimated. The principles involved are as follows: (1) the copper is precipitated as cuprous thiocyanate and iron reduced to the ferrous state by the action of sulfur dioxide and standard NH_4CNS solution; (2) the excess of sulfur dioxide is removed by boiling, a current of carbon dioxide being passed into the solution meanwhile. The solution is then cooled and filtered; (3) the filtrate is treated with an excess of standard $AgNO_3$ solution, and is then titrated for iron with standard $KMnO_4$ solution; (4) the

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[1] *Compt. rend.*, **38**, 868 (1889).

[2] *Z. anorg. Chem.*, **26**, 230 (1901).

[3] *Z. anal. Chem.*, 18, 285 (1879).

[4] Low, "Techn. Meth. of Ore Analysis," 7th ed.

[5] This Journal, 30, 760 (1909).

[6] *Loc. cit.*

[7] "Vol. Meth. of Anal.," 10th ed., p. 200.

copper is then determined by titrating the silver present in excess in the solution with standard NH_4CNS.

The technique finally adopted is as follows: The solution containing copper and iron, together with some sulfuric acid, is nearly neutralized with NH_4OH or Na_2CO_3. It is then saturated with sulfur dioxide (either by passing the gas into the solution, or by adding a solution of the gas in water, or a solution of ammonium bisulfite) and heated to incipient boiling. At this point sufficient standard NH_4CNS solution is added from pipet or buret to precipitate all of the copper. With a little practice there is no difficulty in determining when an excess has been added. The iron is usually not completely reduced at this time, and the reddish color of ferric thiocyanate persisting for a few moments throughout the solution serves to show that the precipitation of copper is complete; or the precipitate may be allowed to settle a little, and the supernatant liquid tested with additional NH_4CNS. The solution is then boiled vigorously for ten minutes, a current of carbon dioxide being meanwhile passed into it. This serves to remove the last traces of sulfur dioxide, and the boiling serves to coagulate the precipitate and render it easily filtrable. After the boiling the flask containing the solution is placed in cold water to cool for a few minutes, the current of carbon dioxide being kept up in order to prevent the re-oxidation of the hot ferrous solution. The solution is now filtered through paper, or preferably through asbestos, and is washed with cold water. It shows no tendency whatever to run through the filter. The filtrate is treated with a few cc. of dilute sulfuric acid, and then there is added sufficient standard $AgNO_3$ solution to precipitate the excess of NH_4CNS. (If desired a little ferric sulfate may be added to show when precipitation is complete.) The solution is now titrated for iron with standard $KMnO_4$ solution in the usual way. When the end point is reached the color of the $KMnO_4$ is removed by the addition of a trace of ferrous sulfate, and the excess of silver present in the solution is at once determined by titration with standard NH_4CNS solution. If there is much iron present it will serve as indicator, otherwise ferric sulfate solution may be added for this purpose.

The iron is calculated in the usual way from the amount of $KMnO_4$ solution used; the copper is calculated from the difference between the total volume of ammonium thiocyanate and the volume equivalent of the silver nitrate (solution) added (1 cc. of 0.1 N NH_4CNS is equivalent to 0.006357 g. of Cu).

The whole determination requires practically no more time than that usually required for the estimation of copper alone, and in addition is highly accurate, as the results in Table I show.

The method is admirably adapted to the analysis of ores. In most cases the ore is decomposed with conc. HNO_3 and conc. HCl in the usual way. It is then heated with H_2SO_4 until all of the HNO_3 and HCl, and most of the H_2SO_4 has been removed. After diluting with water it is in most cases ready for treatment as described above, without even filtering off the insoluble residue. Of course in the case of ores not decomposable by the acid treatment, fusion methods may be adopted, the technique being thereafter modified accordingly. Silver, if present in sufficient quantity, must be removed as chloride by filtration, before evaporating with H_2SO_4.

TABLE I.

Standard solutions of copper sulfate and ferric alum were mixed in varying propor. tions, diluted to about 50 cc., and analyzed as described above.

No.	Cu taken. G.	Cu found. G.	Error Cu. G.	Fe taken. G.	Fe found. G.	Error Fe. G.	NH_4CNS[1] for titr. cc. $N/10 \times 1.3156$.	$KMnO_4$ cc. $N/10 \times 1.0024$.
1	0.0318	0.0318	±0.0000	....	....	....	1.40	...[2]
2	0.0318	0.0317	−0.0001	....	....	....	1.38	...[2]
3	0.0636	0.0635	−0.0001	....	....	....	5.19	...[2]
4	0.0636	0.0634	−0.0002	0.2464	0.2464	±0.0000	5.17	44.00[2]
5	0.0636	0.0635	−0.0001	0.1232	0.1233	+0.0001	5.19	22.02[2]
6	0.0318	0.0319	+0.0001	0.2464	0.2466	+0.0002	1.41	44.04[2]
7	0.0636	0.0635	−0.0001	0.0493	0.0493	±0.0000	5.18	8.80[3]
8	0.1589	0.1589	±0.0000	0.0246	0.0246	±0.0000	1.60	4.40[3]
9	0.0636	0.0635	−0.0001	0.1232	0.1231	−0.0001	5.19	21.98[3]
10	0.0636	0.0636	±0.0000	0.1232	0.1232	±0.0000	5.21	22.00[3]
11	0.0318	0.0318	±0.0000	0.1232	0.1234	+0.0002	1.39	22.04[2]
12	0.0636	0.0635	−0.0001	0.1232	0.1232	±0.0000	5.19	22.00[2]

In the writer's experience the method is much more rapid than the iodide process of Low[4] for copper, and gives the amount of iron present without an additional determination.

As an example of the applicability of the method to the rapid analysis of ores the following will serve:

An ore analyzed for copper by Low's method gave 13.05 and 13.07% Cu in two determinations. The same ore analyzed by the method proposed above gave 13.12 and 13.12% Cu, and 45.44 and 45.50% Fe in two determinations. The time required for determining both copper and iron by the new procedure was considerably less than that required for the determination of copper alone by the Low method.

Summary.

A modification of Volhard's method for the estimation of copper is suggested by which copper and iron may both be determined in the same

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[1] In Expt. 8, 25 cc. of NH_4CNS were used for precipitation of the CuCNS. In all of the others 10 cc. were used. In every experiment the excess of NH_4CNS was precipitated by the addition of 10 cc. of 0.1 *N* $AgNO_3$. The figures in Col. 7 refer to the final titration.

[2] Reduced with SO_2.

[3] Reduced with NH_4HSO_3.

[4] *Loc. cit.*

solution, the copper being precipitated as cuprous thiocyanate by standard NH_4CNS solution and the iron estimated by titration with standard $KMnO_4$ solution.

This method gives highly accurate results for both elements and requires a minimum of time for its completion.

The method is especially adapted to the rapid estimation of copper and iron in ores.

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NOTES.

Note on the Blackening of Yellow Phosphorus.—The sticks of yellow phosphorus in two laboratories in Colombo were found in time to become covered with a dull black coating. In one case the phosphorus had been kept in a stone jar and in the other in a glass bottle in a dark store-room. The experiments recorded below were undertaken with the object of discovering the nature and cause of the blackening.

A quantity of yellow phosphorus was purified by melting under a solution of potassium bichromate and concentrated sulfuric acid and leaving overnight; the still liquid phosphorus was then washed many times with distilled water and was solidified in the form of small globules by violent shaking.

Small quantities of the pure phosphorus were sealed up in glass tubes, two of which (A) contained distilled water and two (B) tap water (any oxygen in the small air space would soon be absorbed by the phosphorus). Small quantities were also placed in glass bottles loosely plugged with cotton wool to exclude dust and two of these bottles (C) contained tap water and two (D) distilled water.

One of each of the vessels A, B, C and D was placed in a dark cupboard and the remaining four were kept in the light. The contents were examined after seven months. The sealed tubes containing distilled and tap water which were kept in the dark, appeared to have undergone no change, while the corresponding tubes which had been kept in the light merely showed reddening due to the formation of red phosphorus. Another tube which contained melted phosphorus and distilled water and which had been kept in the light also, became covered on the surface with red phosphorus but still remained liquid at the end of seven months and only solidified on shaking vigorously; an interesting example of supercooling.

In the case of the vessel whose contents were exposed to air both those containing tap water showed slight blackening, while that containing distilled water and kept in the dark had a white coating, the nature of which is still being investigated; possibly the white coat is the suboxide P_4O, the existence of which has been asserted by Michaelis and Pitsch[1] and

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[1] *Ber.*, 32, 337 (1899).