[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF COPPER.

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THE average analyst is often deterred from the use of a volumetric method by the necessity of making and standardizing a special solution. In many cases it takes nearly as much time to ascertain the strength of the required solution as it does to make the analysis itself, and the standardization and analysis together render the volumetric method frequently as slow, if not slower, and vastly more troublesome than the gravimetric determination.

Volumetric analysis, therefore, becomes more and more an ideal method of quantitative determination as it approaches the requirement of a single standard solution, capable of having its strength accurately determined by simple means, giving a single, definite, clear end-reaction.

In iron and steel laboratories permanganate is fast coming to the front as a help to rapid analysis. Iron, phosphorus, manganese, sulphur (Payne's iodine solution is prepared by adding standard permanganate to potassium iodide) and calcium can all be quickly determined by the use of one standard solution. While it may never be possible to supplant other standard solutions by permanganate, still the sphere of its usefulness is a large one and is constantly enlarging.

For a year or more I have been experimenting upon a new method for the determination of copper by permanganate, which seems to possess many points of superiority over the old one of reduction by grape sugar. In general it is as follows: The copper is brought into solution as a sulphate, either by dissolving it in sulphuric acid or evaporation of its solution with sulphuric acid. The greater part of the free acid is neutralized by ammonia, the solution warmed, sulphurous acid added until the solution smells strongly of the reagent, and then a slight excess of ammonium or potassium thiocyanate.[1] The copper

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[1] Rivot: *Compt. rend.*, **38**, 868; and Busse: *Ztschr. anal. Chem.*, *1878*, 55.

is immediately precipitated as cuprous thiocyanate. Stirring and warming renders the precipitate heavy and easily handled. The solution is filtered through asbestos, using the pump, and well washed. The precipitate and filter are thrown into the beaker in which the precipitation was made and heated with a solution of caustic soda or caustic potash. Double substitution takes place. Hydrated cuprous oxide and potassium or sodium thiocyanate result.

$$2CuSCN + 2KOH = Cu_2(OH)_2 + 2KSCN.$$

The oxide is filtered on asbestos and washed well with hot water. The precipitate and filter are again placed in the same beaker and an excess of ferric chloride or ferric sulphate (free from nitric acid, free chlorine or ferrous salts) together with a little dilute sulphuric acid added. The copper oxide reduces a corresponding amount of iron from the ferric to the ferrous condition.

$$Cu_2O + Fe_2Cl_6 + 2HCl = 2CuCl_2 + 2FeCl_2 + H_2O.$$

The beaker is warmed and stirred until all the copper oxide is dissolved. The solution is then poured through a perforated platinum disk and the asbestos which stays behind upon it washed with water, to which has been added a little sulphuric acid and a little ferric chloride or sulphate. The solution is then titrated with permanganate. The iron equivalent to the permanganate used multiplied by 1.125 gives the weight of copper in the sample.

Instead of sulphurous acid, ammonium or sodium bisulphite may be used to reduce the copper. A solution of equal weights of sodium bisulphite and potassium thiocyanate answers well as a reagent for the precipitation of the metal. Since copper is the only metal precipitated by an alkaline thiocyanate from an acid solution, the presence of arsenic, antimony, bismuth, zinc, and other materials which render the electrolytic, the cyanide, and the iodine method inaccurate, will not affect the results.

The caustic alkali solution, used to convert the cuprous thiocyanate into cuprous hydroxide, must not be too strong or some of the metal will go into solution, coloring the liquid blue. I have used about a half normal solution of caustic potash, made by dissolving twenty-eight grams of the salt in a liter of water. Either ferric sulphate or ferric chloride may be used to dissolve the cuprous oxide. The former is probably the safest, but the latter appears to dissolve the precipitate the more readily of the two.

As a test of the accuracy of the method four grams of pure electrolytic copper were dissolved in nitric acid and the solution evaporated with sulphuric acid until the nitric acid was expelled. The solution was cooled and diluted to one liter. The copper contained in fifty cc. was then determined electrolytically with the following result:

	Gram.
1	0.2003
2	0.2003
3	0.2000
4	0.1997
Average	0.2001

The copper in fifty cc. was next determined by the thiocyanate-permanganate method outlined above. The permanganate solution used was made by dissolving 5.02 grams of pure crystallized potassium permanganate in water and diluting after standing twenty-four hours to two liters. Its strength was determined by titration against iron wire and against ferrous ammonium sulphate.

Against ferrous ammonium sulphate:

Gram iron.
1. One cc. = 0.004455
2. One cc. = 0.004456

Against iron wire:

Gram iron.
3. One cc. = 0.004460
4. One cc. = 0.004449

Average one cc. = 0.004455

One cc. = 0.004455 × 1.125 = 0.005012 gram copper.

Below are the results on fifty cc. of the copper solution containing 0.2001 gram copper by the thiocyanate-permanganate method:

No.	Permanganate. cc.	Copper. Gram.
1	39.6	0.1985
2	39.5	0.1980
3	39.6	0.1985
4	39.7	0.1990
5	40.0	0.2004
6	39.8	0.1995

In determinations numbers 1, 5, and 6, ferric chloride was used to dissolve the cuprous oxide; in numbers 2, 3, and 4, ferric sulphate was used.

As a further and more practical test of the method, the copper in some samples of copper ore was carefully determined by the electrolytic, and then by the thiocyanate-permanganate method. Below are the comparative results:

Sample.	Weight of sample. Gram.	Permanganate. cc.	Copper by thiocyanate-permanganate method. Per cent.	Copper by electrolytic method. Per cent.
1. Chalcopyrite I	1.0	39.6	19.85	19.95
2. "	1.0	39.3	19.70	19.86
3. Chalcopyrite II	2.0	24.6	6.16	6.37
4. "	2.0	24.8	6.21	6.30
5. Malachite	1.0	72.2	36.19	36.10
6. "	1.0	72.2	36.19	36.15
7. Tetrahedrite	1.0	42.0	21.05	21.06
8. "	1.0	41.7	20.90	21.18

It will be seen by the above results that the method is accurate enough for ordinary commercial purposes. In spite of its three filtrations, the method is quite rapid. Not counting the time required for the solution of the ore, duplicate analyses can be easily made in from a half to three-quarters of an hour.

In the writer's opinion the process is superior to both the iodine and the cyanide method. It requires the use of no rapidly changing solutions, but one which every analyst has on hand nearly all the time. The end-reaction is clear, distinct, and familiar to all chemists. The method is applicable to any ore, matte or alloys. It is as rapid as the cyanide, except in certain cases favorable to the latter, and more rapid than the iodine method. Finally, not the least of its points of advantage is that it is more accurate than either of the two.

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