the permanganate imparts a pink color to the solution. A few trials will enable the operator to ascertain this point with accuracy and rapidity.

This work was conducted more for the purpose of ascertaining the values of the methods when working with the rapidity which is required in actual practice, than for absolute accuracy, to 0.01 or 0.001 per cent. I have no doubt that Volhard's process can be made to check closer than 0.64 or 0.46 per cent. respectively, of the metallic content of an ore, but in practical metallurgical analyses, it is not always practicable to exercise the necessary precautions. The method is capable of wide application, and where rapidity is essential, is sufficiently accurate in most, if not all cases.

THE WET ASSAY FOR COPPER.

By R. S. Dulin.

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IT seems difficult for the metallurgical chemists of this country to settle upon a uniform method for the rapid determination of copper. We should have a standard method, applicable for all commercial work, which would be fairly accurate under as many possible varying conditions, so that results obtained from the same ore, by different chemists, should be substantially uniform. For about nine months past I have been engaged upon an extended series of experiments, having for their object a determination of the chief causes for variation and error in the methods most generally employed and for the purpose of finding a modification of common methods which would be an improvement upon those now used. At the same time I have made myself conversant with much of the current literature upon the subject and the observations herein offered, while based upon my individual experiments, are corroborated, in most part, by the published results of others.

There are at present three well-recognized methods employed in the United States for the determination of copper. Each method has its own advocates, and it is perfectly fair to say, that either method in the hands of a skilled chemist, thoroughly understanding the reactions of the methods, working with all due care, will yield substantially the same results. The methods referred to are :

1. The cyanide method. 2. The iodide. 3. The electrolytic. A colorimetric method is also employed for the determination of copper, when the percentages fall below two per cent. I have made no particular study of this method, and as it is only employed in special cases, I shall make no further reference to it.

The cyanide method depends upon the fact, that when a solution of potassium cyanide is run into an ammoniacal solution of copper the blue color is discharged. The reaction is as follows:

$$(NH_4)_2(NH_3)_2,CuO(NO_3)_2 + 4KCN + 3H_2O = K_2Cu(CN)_4 + 2KNO_3 + 4NH_4OH.$$

This method is fully described in Furman's Manual of Practical Assaying. The following precautions should always be carefully observed. 1. The bulk of the liquid titrated should always be uniform. By inattention to this an error of from two to three per cent. is possible. 2. The solution should always be cooled to the temperature of the laboratory before titrating, otherwise an error of about three per cent. is possible. 3. The amount of ammonia added should be nearly constant, otherwise the possible error may amount to as much as five per cent., or even more.

These precautions are general and must always be carefully observed, in every modification which may be made in the method. In the ordinary modification of the method, ferric hydroxide is almost certain to be precipitated, upon the addition of the ammonium hydroxide. If the amount be small, no error is apt to occur, but it should always be filtered off. If the amount be large, it is not easy to wash out all of the copper salt, thereby causing lower results, unless large quantities of wash-water are employed, thus increasing and varying the bulk. The error arising from increased bulk may be obviated, by taking, after mixing; an aliquot part of the solution ; if the solution be not thereby made very dilute, the error is so slight that it may be neglected. If salts of manganese are present, the end reaction cannot be determined, owing to the liquid first turning green, finally black. The presence of large quantities of calcium, I found, confused the end reaction, causing error of importance. Experiments made showed that magnesia did not interfere, and the presence of antimony and arsenic was found to cause no sensible variations.

Zinc, which is almost certain to be present in varying amount, is a possible source of great error. The following results were obtained from a large number of carefully conducted experiments. Only the averages are given and they are substantially the same as the extremes. In these experiments the bulk of the liquid varied from twenty-five to as much as fifty cc., thereby causing a slight error, for which no correction has been made. This error would not substantially change the results. Careful attention was paid to the precautions previously enumerated.

Weight of copper.	Weight of zinc.	Cyanide used.	Increase.
0.05	0.00	10.4 cc.	
0.05	0.01	11.0 "	0.6 cc.
0.05	0.02	11.7 "	1.3 "
0.05	0.03	12.3 "	1.9 "
0.05	0.04	12.9 "	2.5 "
0.05	0.05	14.0 "	3.6 "
0.05	0.06	16.1 "	5.7 "
0.05	0.07	18.9 "	8.5 "
0.05	0.08	21.6 "	11.2 "
0.05	0.09	24.3 "	13.9 "

These results show that there is a gradual increase of about six-tenths cc. in the amount of the cyanide solution required, until the amount of zinc present nearly equals the amount of copper, when the increase becomes variable, until the amount of zinc becomes greater than the amount of copper to the extent of twenty per cent., when the increase, though larger, about two and seven-tenths cc., again becomes regular.

The effects of cadmium are similar, as shown by the following results, which are also the averages of a large number of experiments, in which the extremes are farther removed from the mean than was found with zinc. As in the preceding experiments the precautions previously enumerated were very carefully observed, except in the case of bulk, in which the variations were identically the same as with the experiments with zinc.

Weight of copper.	Weight of cadmium	Cyanide used.	Increase.
0.05	0.00	10.4 cc.	
0.05	0.01	10.6 "	0.2 cc.
0.05	0.02	10.8 "	0.4 "
0.05	0.03	11.1 "	0.7 "
0.05	0.04	11.6 "	1.2 "
0.05	0.05	12.0 "	1.6 "
0.05	0.06	12.4 "	2.0 "
0.05	0.07	13.5 "	3.1 "
0.05	0.08	14.5 "	4.1 "

These results show that there is a gradually accumulating increase in the consumption of cyanide due to the presence of cadmium. As cadmium is a constituent usually found associated with copper, it must be removed, if reliable results be required. Silver also interferes, but in a regular way. If the amount of silver be known, by previous assay, it is best allowed for by calculation.

The following modification of the cyanide method has been thoroughly tested, under the immediate supervision of Prof. Seamon, and it is recommended as giving results equal in value to those obtained by the electrolytic method.

The ore is treated according to the method described on page 161 of Furman's Manual of Assaying. In this way a solution of the copper salt is obtained, practically free from lead and silver. This solution is boiled with strips of aluminum foil, resulting in the complete precipitation of the copper together with any silver which may remain in the solution, which is always so small as to be negligible, as I have demonstrated by a number of experiments upon different ores. If cadmium be present, it is only partially precipitated, beginning after the copper is thrown down. If care be taken to stop the boiling, immediately after the copper is precipitated, which can be determined with constant practice, by the eye, the amount of cadmium precipitated is so small as not to cause sensible error. The liquid is decanted from off the aluminum foil and copper, quickly washed several times with hot water, care being taken not to wash away any particles of the copper; three cc. of nitric acid are then added to the flask and boiled to dissolve the copper, the solution is then treated with ammonium hydroxide as in the usual way and titration is made with the usual solution of cyanide.

This method has been very carefully tested and the results were so satisfactory, and nearly uniform, that I recommend it as being as accurate as the electrolytic method, under the conditions in which the latter is usually employed.

The iodide method is most commonly employed in the Lake Superior district and in foreign countries, where it is regarded with much favor. Many chemists regard it as more accurate than the cyanide or electrolytic methods, and there is no doubt from my experiments that it is more accurate than the ordinary modification of the cyanide and equal to that of the electrolytic. The method depends upon the following reactions:

$$2CuSO_4 + 4KI = Cu_2I_2 + 2I + 2K_2SO_4$$
$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6$$

The best results are obtained when the copper is precipitated with aluminum foil, as previously described under the cyanide method. The method is fully described in Furman's Manual of Assaying, and I only desire to call attention to the necessity for attending to the following precautions:

1. The presence of iron in about equal amounts with the copper requires more "hypo," increasing the amount of copper to the extent of two to three per cent. 2. The solution should be titrated cold. 3. The presence of large amounts of alkaline salts, particularly sodium sulphate, decreases the amount of copper. 4. The presence of bismuth clouds the end reactions. My experience with the modification of this method, in which the copper is first precipitated with aluminum foil convinces me that with this change the results are as accurate as those obtained with the modified cyanide method; but it is not so rapid, owing to the time lost at various stages; this is an important factor in the adoption of any method for metallurgical work, when thirty and forty assays must be completed every day. The method is a little more difficult to manipulate than the cyanide method

The electrolytic method is perhaps the most highly favored in this country. It has the reputation for greatest accuracy. It requires more time than either of the other, but since it is easy to regulate the work, so that the battery will precipitate during the night, this is not of so much importance. In regular routine work after solution is effected, the copper should be precipitated with hydrogen sulphide, otherwise many interfering metals are apt to be present and deposited with the copper. I have found that errors from this source are largely, if not entirely, eliminated, if deposition be made from a solution containing a large amount of nitric acid. My best results were obtained when I added twenty cc. of strong nitric to about 150 cc. of solution. This holds up the other metals, but a stronger current is required to precipitate all of the copper and more attention must be paid to proper and rapid manipulation after precipitation. This method is much improved by previously precipitating the copper from its solution by boiling with aluminum foil and then redissolving the copper in nitric acid. The following results, obtained from the same sample, carefully prepared, obtained by the three methods, furnish a fair idea of the relative values of the several methods.

A copper matte, containing 20.15 per cent. of copper, as determined by a large number of analyses, made by several different assayers, and by different methods, was run by each method. The amount of copper in the second matte, determined from the same data, was found to be twenty-eight per cent., while the per cent. of copper in the ore was 30.18 per cent.

The results obtained by the cyanide method were respectively 20.15 per cent., 27.95 per cent., and 30.20 per cent. The copper was first precipitated with the aluminum foil. The same substances, with the iodide method, first precipitating with aluminum foil, gave, respectively, 20.25, 28.35, and 30.3 per cent. By the electrolytic method, the same substances gave, respectively, 20.045, 28.15, and 30.05 per cent.

These results justify the statement that the iodide method with the aluminum modification gives results usually one-tenth to three-tenths per cent. too high, while the electrolytic method is too high or too low, according to the amount of metallic substances present precipitable by the electric current; and the cyanide method gives results which are practically correct.

ON THE STANDARDIZATION OF SULPHURIC ACID.

By F. S. Shiver.

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M. WEINIG[1] has described a method for the standardization of sulphuric acid by means of weighing the $(NH_4)_2SO_4$ obtained by mixing an accurately measured quantity of the sulphuric acid solution with an excess of ammonia, evaporating, drying, and weighing. His method of procedure is as follows: To an accurately measured quantity of the sulphuric acid solution, ammonia in slight excess is added, the solution evaporated to dryness, dried for half an hour at 115°–

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[1] Ztschr. angew. Chem., *1892*, 204, 205; *J. Chem. Soc.*, 64, 2, 145.