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THE DETERMINATION OF COPPER—A MODIFICATION OF THE IODIDE METHOD.

By E. C. KENDALL.

For the determination of copper the most important methods are the electrolytic, the iodide, and the cyanide. As the determination by means of the electrolytic method requires a considerable amount of time and apparatus, the only methods for the rapid estimation of copper are the iodide and the cyanide.

Upon an examination of the two volumetric methods mentioned it is apparent that in respect to the amount of time and attention required for a determination the cyanide has a great advantage over the iodide method. However, in respect to the accuracy of the results obtained the iodide method is conceded to be by far the more accurate of the two. As every consideration would be in favor of the iodide method if it could be modified in such a way as to make it as rapid and easy of manipulation as the cyanide method, an attempt was made to make such a modification.

In the determination of copper by the iodide method the copper may be originally present as copper, copper oxide, or sulfide. The first step is to obtain the copper in solution. Practically the only way to do this is to dissolve it in nitric acid. The solution of the copper with nitric acid produces nitrous acid in the solution, and it is the removal of this which causes the delay in the estimation of the copper. As the method is described in the literature, the nitrous acid is destroyed with bromine, the excess of bromine being removed by boiling; or the nitrous acid is removed by evaporating to dryness.

The modification of the iodide method as described in this paper consists in the destruction of the nitrous acid without boiling. This is accomplished by the addition of a small amount of sodium hypochlorite. The addition of sodium hypochlorite to a nitric acid solution produces hypochlorous acid. The interaction of hypochlorous acid and nitrous acid results in the oxidation of the nitrous acid and the formation of hydrochloric acid, and the reaction between hypochlorous and hydrochloric acid results in the destruction of the hypochlorous acid and the formation of free chlorine and water. As the solution of sodium hypochlorite contains small amounts of chlorides, hydrochloric acid will always be present when the solution is acidified, thus insuring the destruction of the hypochlorous acid and the formation of free chlorine. We thus see that the effect of adding sodium hypochlorite to the solution is the complete destruction of the nitrous acid and the formation of free chlorine.

To remove the free chlorine in solution some compound must be added which will take up the chlorine, but will not affect subsequent operations. Such a compound is found in phenol. Under the conditions of the determination, phenol will add chlorine directly to the benzene ring, but is not affected by iodine or any of the other compounds in the solution. Chlorophenol not being ionized removes all traces of free chlorine.

This modification of the method greatly reduces the time and attention required for a determination, and, in addition, the copper solution is prepared in such a way that iodine can be liberated by copper alone.

In the determination, the copper, copper oxide, or sulfide is dissolved in nitric acid. After the addition of the sodium hypochlorite and phenol, which requires but a moment, the solution is made slightly alkaline with sodium hydroxide, and is then made acid with acetic acid, when the solution is ready for titration. Potassium iodide and starch are added, and the titration is made to the disappearance of the starch iodide color. There is never any fear of the blue color "flashing back," and the solutions will remain colorless indefinitly after the titration. As the ionization constant for acetic acid is too low to allow nitrates to liberate iodine, the amount of nitric acid in solution is immaterial. Even 20 cc. of concentrated nitric acid will not affect the titration. However, too great an acidity is to be avoided, as nitrophenol will be formed. The presence of nitrophenol prevents the determination of copper, but there is no danger of its formation even in the presence of a large amount of acid if the solution is neutralized soon after the addition of the phenol. If a large amount of nitric acid is used to dissolve the copper, it should therefore be partly neutralized before addition of the phenol.

As chlorine easily oxidizes phenol to compounds which prevent the determination of copper it is essential that all of the phenol be added quickly to the solution. Under these conditions the chlorine adds directly to the benzene ring, but if the phenol is added drop by drop the chlorine will oxidize it, producing colored compounds in solution.

In order to add the phenol quickly enough to the solution it may be poured in from a beaker, or, a more convenient way, from a pipet from which the tip has been removed so that the delivery is from an opening which is of the same bore as the rest of the tube. By forcing the phenol out of such a pipet with the breath the entire volume is added very quickly and at the same time the phenol is well mixed with the contents of the flask.

After addition of the phenol the chlorine gas which is in the flask above the liquid is removed by blowing it out with the breath, and the sides of the flask are washed with a jet of water from a wash bottle. There should be no odor of chlorine just before the solution is made alkaline.

It should be remembered that the end point of the titration is not pure white. Cuprous iodide has a cream color, and when a large amount of copper is present the cuprous iodide gives a decided tint to the solution. When the end point is nearly reached a drop of the thiosulfate is allowed to fall into the center of the flask. If a change of color occurs the solution is given a slight rotary motion and after the solution is again quiet another drop of the thiosulfate is added. This "spot test" is easily recognized and gives a very accurate end point.

The speed of reaction of the copper with potassium iodide varies with the volume. In a small volume the action is rapid and all of the iodine is liberated at once, but in a large volume an appreciable time may be required for all of the copper to react. This is especially noticeable when a small amount of copper is present. A high concentration of potassium iodide greatly assists the liberation of the iodine. Accurate results can not be obtained unless at least 3 grams of potassium iodide are added, irrespective of the amount of copper present, up to 500 mg. of copper.

The solutions required are:[1]

A. *The Sodium Hypochlorite* solution is made by boiling together a mixture of 112 grams of calcium hypochlorite and 100 grams of anhydrous sodium carbonate in 1200 cc. of water. After the calcium is precipitated as carbonate, the solution is filtered and its strength found as follows: 5 cc. of the hypochlorite solution are added to 100 cc. of water containing 5 cc. of 30 per cent. potassium iodide solution, and a few cc. of dilute hydrochloric acid are added. The liberated iodine is titrated with 0.1 N sodium thiosulfate. The volume of the solution is now adjusted so that 5 cc. of the hypochlorite solution are equivalent to 30 cc. of 0.1 N sodium thiosulfate.

B. *Phenol.*—A 5 per cent. colorless solution of phenol.

C. *Sodium Hydroxide.*—A 20 per cent. solution.

D. *Acetic Acid*, 50 per cent.

E. *Potassium Iodide.*—A convenient way to use this is to prepare a solution which contains 30 grams per 100 cc. of solution. Then 10 cc. will contain 3 grams, which is the amount needed for a determination.

F. *Sodium Thiosulfate.*—For the accurate titration of the liberated iodine two solutions are used. One strong solution, 1 cc. of which equals 6 mg. of copper, and a weak solution, 1 cc. of which equals 1 mg. of copper. The strong solution is run in until the iodine liberated by the copper gives a light straw color to the solution. Starch is then added and the titration is finished with the weak solution.

[1] The weights given here are for calcium hypochlorite having 35 per cent. or more available chlorine.

As a thiosulfate solution loses strength, it should be restandardized from time to time. A convenient way to do this is as follows: A solution of sodium thiosulfate, approximately 0.1 N, is made by dissolving 24 grams of the crystallized salt per liter of water. After the solution has stood at least twenty-four hours it is standardized against copper by the method described below. Pure electrolytic copper which has been cleaned with emery paper should be used. After dissolving 150 to 200 mg. of the copper in 6 to 8 cc. of 50 per cent. nitric acid the solution is treated as described below and the thiosulfate is then standardized with this known weight of copper. The most convenient means of restandardizing the thiosulfate is to use a solution of acid potassium iodate. Acid potassium iodate has the formula $KIO_3.HIO_3$, so that a normal solution has one-twelfth the molecular weight in grams per liter. A 0.1 N solution is prepared by dissolving 3.249 grams of the salt in 1 liter of water, and it is standardized against a known strength of thiosulfate as follows: Add 10 cc. of the acid iodate solution to 150 cc. of water containing 0.5 to 1 cc. of hydrochloric acid. Upon the addition of potassium iodide, iodine will be liberated according to the equation

$$HIO_3 + 5HI = + 3H_2O + 6I.$$
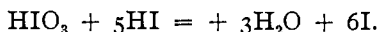
Starch is added and the titration is made to a colorless solution. From this titration the weight of copper to which 20 cc. of this solution are equivalent is accurately determined. A 20 cc. pipet is passed through a one-hole stopper and is allowed to remain in the acid iodate bottle. The end of the pipet is closed with a small rubber stopper. The exact copper equivalent of a thiosulfate solution is now easily found by titrating 20 cc. of the acid iodate solution whose copper equivalent is known with the thiosulfate as described above. The acid iodate remains constant indefinitly.

G. *Starch for Indicator.*—The best preparation for this purpose is a 0.5 per cent. solution of Kahlbaum's soluble starch. This is prepared as ordinary starch, but gives a perfectly clear solution which is very sensitive with iodine. If ordinary starch must be used it should be free from all cloudiness.

Detailed Description of the Method.

If the copper to be determined is present as metallic copper, 200–300 mg. are placed in a 300 cc. flask and dissolved in 5–10 cc. of 50 per cent nitric acid.

If the copper is present as cuprous oxide, it is filtered on a Gooch crucible through asbestos. The cuprous oxide is then dissolved through the Gooch crucible with 10–15 cc. of 30 per cent. nitric acid into a 300 cc. Erlenmeyer flask.

If the copper is in the form of sulfide, it is filtered on a Gooch crucible which has a layer of asbestos one-eighth inch in thickness. The crucible is then placed in a small beaker of 50 cc. capacity, and 10 cc. of 50 per cent. nitric acid are added. The beaker is placed on a hot plate, and the nitric acid allowed to boil until all the black sulfide has gone into solution. The crucible is then washed off, and the solution transferred to a 300 cc. Erlenmeyer flask. The presence of the asbestos in the solution does not interfere with the titration of the copper.

If the copper to be determined is already in solution as sulfate, chloride, or other salt, sufficient solution is taken to give 100 to 300 mg. of copper.

Having obtained the copper in solution, preferably in a 300 cc. Erlenmeyer flask, the volume being between 50 and 60 cc., the acidity is adjusted to equal 4 to 5 cc. of concentrated nitric acid. A greater volume or acidity is to be avoided. The temperature should not be above 25°. Five cc. of the hypochlorite solution are now added to the copper solution, which is well mixed with a rotary motion. As soon as the color of the copper solution changes from a clear blue to a greenish tint, sufficient hypochlorite has been added. Another indication of a sufficient amount of hypochlorite is the liberation of chlorine. For weights of copper up to 200 mg., 2–3 cc. of the hypochlorite are sufficient. For larger amounts of copper more hypochlorite may be needed, but 5 cc. will be sufficient for any amount of copper which would be determined by this method. The reactions between the hypochlorous and nitrous acid require an appreciable time and the best results are obtained by allowing the solution to stand about 2 minutes before the addition of the phenol. This, however, is not essential. Ten cc. of the phenol solution are now added as quickly as possible, by blowing the solution from a pipet from which the tip has been removed.

The chlorine gas which remains in the flask above the liquid is removed by blowing into the flask and the sides are washed down with a jet of water. If the solution is allowed to stand at this point, nitrophenol will slowly form. Sodium hydroxide is therefore added until a very slight precipitate is obtained. The solution is now made acid with acetic acid; only a few drops should be required to dissolve the precipitate. Ten cc. of the potassium iodide are added and the titration made with the standardized thiosulfate. If great accuracy is required the titration is finished with a weak solution of thiosulfate.

The following are some results obtained by the method described above. The milligrams found and the error are calculated only to a point which is within the degree of accuracy of the apparatus used.

DETERMINATION OF COPPER.

Copper taken. Mg.	Copper found. Mg.	Error. Mg.	Error. Per cent.
20.00	20.01	+0.01	+0.05
20.00	19.99	—0.01	—0.05
20.00	20.00	0.00	0.00
30.00	29.99	—0.01	—0.03
30.00	30.00	0.00	0.00
40.00	39.98	—0.02	—0.05
40.00	39.96	—0.04	—0.10
60.00	60.01	+0.01	+0.02
60.00	60.01	+0.01	+0.02
80.00	80.12	+0.12	+0.15
80.00	80.03	+0.03	+0.04
80.00	79.98	—0.02	—0.02
80.00	79.98	—0.02	—0.02
100.00	100.00	0.00	0.00
100.00	99.99	—0.01	—0.01
120.00	119.95	—0.05	—0.04
140.00	140.00	0.00	0.00
160.00	160.00	0.00	0.00
160.00	160.00	0.00	0.00
180.00	180.00	0.00	0.00
180.00	180.00	0.00	0.00
200.00	200.00	0.00	0.00
200.00	199.9	—0.1	—0.05
203.2	203.2	0.00	0.00
220.2	220.1	—0.1	—0.05
240.0	240.0	0.00	0.00
240.0	240.2	+0.2	+0.08
261.6	261.6	0.00	0.00
280.0	280.0	0.00	0.00
280.0	280.3	+0.3	+0.10
300.0	300.1	+0.1	+0.03
320.0	319.9	—0.1	—0.03
320.0	319.9	—0.1	—0.03
340.0	340.0	0.00	0.00

NOTE.—The sum of the + and — errors very nearly equals zero.

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THE OCCURRENCE OF POTASSIUM NITRATE IN WESTERN AMERICA.

BY ROBERT STEWART.

About one year ago a sample of material was received at this laboratory for chemical analysis. The material was almost completely soluble in water and the analysis showed that it contained 12.79 per cent. of nitric