III.—*On a new Volumetric Method for the Determination of Copper.*

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A SERIES of experiments conducted by Mr. Abel in connection with the manufacture of bronze guns, involved the analysis of a large number of samples of gun metal, with which I was entrusted by him; and the much greater rapidity with which copper can be estimated by volumetric methods than by precipitation as oxide, led in the first instance to the selection of the method of Pelouze for adoption in these experiments, as the one of that class most likely to furnish trustworthy results.

The process in question, as originally described by Pelouze, is as follows:—

1 gramme of copper is dissolved in 5 or 6 grammes of commercial nitric acid, with the addition of a little water, if necessary; this solution is then mixed with 40 or 50 cubic centimetres of concentrated ammonia, raised to the boiling point, and a standard solution of sulphide of sodium added, until the blue colour disappears. During the whole of the operation, the liquid is kept in a state of gentle ebullition, fresh quantities of ammonia being added from time to time, to make up for the loss by evaporation. The use of the large quantity of ammonia keeps the boiling point of the liquid below the temperature of 80° C., beyond which it is not to be allowed to rise. The precipitate produced is expressed by the formula $\text{CuO}, 5\text{CuS}$; but it is stated to have a different composition, if the liquid, at the time of precipitation, is at a higher temperature than that above stated.

Following these directions as closely as possible, an attempt was made to standardize a solution of sulphide of sodium by means of electrotyped copper. The results are given in the following table:—

Quantity of Copper taken.	Measures of Sulphide of Sodium taken.	Calculated for 10 grains of Copper.
9.10	82.5	90.6
9.10	82.8	90.9
9.10	82.2	90.3
9.10	82.5	90.6
14.48	136.0	93.9
13.29	121.5	91.4
13.21	121.8	92.2

It will be observed that there is little discrepancy between some of these numbers, and it is necessary therefore to notice, that when this is the case, the same quantities of copper were employed, and especial care was taken that the operation should be conducted in a precisely similar manner. In those instances in which there was any material difference in the amount of copper taken, and the quantity of sulphide of sodium necessary to obtain corresponding results was consequently unknown, the numbers obtained exhibit but little similarity. It should also be remarked, that whenever the contents of the flask were not shaken, but only agitated by boiling, a smaller amount of sulphide of sodium was required.

Considerable difficulty was experienced in deciding on the exact point at which the blue colour disappeared; since it was found, on agitating the liquid a short time after decoloration, that the colour was restored, and this continued to be the case for a considerable period after its first disappearance. Finding that little dependence could be placed on the disappearance of the blue colour, and observing that on reaching this point, the sulphide of sodium still gave a copious black precipitate, the addition of the sulphide of sodium was continued, until the copper was completely precipitated, and the following results were obtained:—

Quantity of Copper taken.	Measures of Sulphide of Sodium taken.	Calculated for 10 grains of Copper.
9·10	88·3	97·0
9·10	89·4	98·2
9·10	88·6	97·3
9·10	88·4	97·1
12·42	123·0	99·0
13·06	127·0	97·2

The same remarks apply to these determinations as to the former series.

The wide difference which exists between these numbers and the quantity of sulphide of sodium required, after the disappearance of the blue colour, to precipitate the whole of the copper, naturally led to the inference, that some chemical change, not hitherto noticed, had taken place.

The following experiments were consequently made:—

1st. A small quantity of a solution of sulphate of copper was diluted with 2 oz. of water containing a considerable excess of

ammonia, and the solution, which was of a light blue colour, was then boiled; on adding a drop of sulphide of sodium, a precipitate was produced, which was almost immediately redissolved, the solution changing to a greenish-brown. A second drop of sulphide of sodium produced a similar effect. On allowing the solution to stand five minutes, it became perfectly clear, its original blue colour being restored.

2nd. To a solution of copper, in all respects similar to the last, 3 drops of sulphide of sodium were added with the same effect as before. On the addition of the fourth drop, the precipitate ceased to redissolve and subsided in a few seconds, leaving the solution still of a brown colour, but of a lighter shade. The three next drops of sulphide of sodium each produced the same effect, after which it was found that the whole of the copper had been entirely precipitated.

3rd. A solution of copper was taken, similar to the last, but of double the strength. Two drops of sulphide of sodium produced no permanent precipitate, the solution retaining its original blue colour. The third drop changed the blue colour to a brown. No permanent precipitate was, however, produced till after the seventh drop, but only a darkening of the brown colour. On the addition of the seventh drop, a precipitate appeared, which, after much agitation of the liquid, gradually subsided, leaving the solution nearly colourless. The eighth drop again darkened the colour of the liquid, this effect also disappearing on violent agitation. The ninth drop produced no effect, the whole of the copper having been precipitated.

4th. To a similar solution of copper, but of four times the original strength, four drops of sulphide of sodium were added without changing the blue colour of the solution, the precipitate redissolving as soon as formed. The fifth drop produced a greenish-brown tint; but on allowing the solution to stand about half a minute, the original blue colour was restored. After the lapse of two or three minutes, a sixth drop was added; the precipitate redissolved, leaving the solution still brown. On the addition of the seventh drop the greenish-brown tint again made its appearance, gradually becoming darker with each successive drop until the fourteenth, when a permanent precipitate was first produced.

5th. To a solution of copper prepared as before, but eight times the original strength, eight drops of sulphide of sodium were

added before the blue colour changed to a brown, and a permanent precipitate was first obtained after adding fourteen drops.

In order to ascertain whether the amount of ammonia present influenced the solubility of the oxysulphide of copper, these experiments were repeated with a much larger, as well as with a smaller quantity of ammonia than usual, but with the same results.

From these results it is evident that the first quantities of oxysulphide of copper formed, are redissolved in the ammoniacal sulphate of copper, and that the amount so dissolved depends on the quantity of copper in solution.

The following experiment was then made in order to ascertain whether the oxysulphide of copper dissolved without undergoing any change :—

To an ammoniacal solution of copper, sulphide of sodium was added so long as the precipitate produced was redissolved ; the solution was then boiled, and a drop of chloride of mercury added, which produced a white precipitate, showing that no sulphide existed in the solution.

It is evident, therefore, that oxidation of the sulphur must have taken place, which was proved to be the case by the following experiment :—

Sulphide of sodium was added to an ammoniacal solution of copper, until the blue colour was destroyed ; the liquid was then agitated by boiling and the clear liquid decanted off : it was then acidified with sulphuric acid ; and on boiling, a brown precipitate of sulphide of copper made its appearance, rendering it highly probable that the sulphur had passed into the state of hyposulphurous acid, or some of the lower oxides of sulphur.

It would appear that the oxysulphide of copper was oxidised at the expense of the protoxide of copper in solution, the suboxide being produced ; whilst the repeated restoration of the blue colour on agitation of the liquid, as already described, clearly shows that suboxide of copper exists in solution. This is also further proved by the fact, that on filtering an ammoniacal solution of copper, to which sulphide of sodium has been added till the blue colour is destroyed, the blue tint immediately reappears in the filtrate, from oxidation of the suboxide having taken place in its passage through the pores of the filter.

In order to show still more clearly that the changes above mentioned take place, the following experiment was made :—

Sulphide of sodium was added to an ammoniacal solution of copper until the blue colour disappeared. After allowing the precipitate to subside, the colourless liquid was decanted off and divided into two portions, one of which was acidulated with sulphuric acid and boiled, when the brown precipitate, before mentioned, made its appearance. The other portion was passed through a filter, when it was observed that the blue colour immediately reappeared, and on acidifying no precipitate was produced; showing that in the latter case, by passing through the pores of the filter (which may be considered equivalent to a lengthened agitation), the sulphur had passed from the lower into the higher oxides, and the suboxide of copper into the protoxide.

Throughout these experiments, the ammoniacal solution of copper was boiled, previous to adding the sulphide of sodium.

The standard solution of sulphide of sodium used was made by dissolving 2 oz. of caustic soda in 1 quart of water. This solution was then divided into two equal parts, one of which was saturated with sulphuretted hydrogen; after mixing this saturated portion with the remainder of the solution of caustic soda, the whole was placed in a vessel capable of holding one gallon, which was then filled with distilled water.

It appears, therefore, that in determining copper by this method, the following changes take place:—

1st. That a portion of the oxysulphide of copper is oxidised at the expense of the salt of copper in solution, the latter being reduced to the state of suboxide, and consequently that a considerable quantity of copper must exist in the solution after the disappearance of the blue colour. From the great affinity of an ammoniacal solution of suboxide of copper for oxygen, it necessarily follows that agitation of the liquid must give rise to a constant reproduction of protoxide of copper.

2nd. That the sulphur of the sulphide of sodium also passes into solution in the form of hyposulphurous acid or some other low oxide of sulphur, thereby lessening the effect which the sulphide of sodium would otherwise produce.

It should also be remarked, that in adding sulphide of sodium to a solution of suboxide of copper, a smaller quantity of sulphur is required for a given amount of copper than in precipitating the protoxide.

These changes, in addition to the different composition of the oxysulphide of copper produced, according to the temperature of

the liquid at the time of precipitation, as stated by Pelouze, sufficiently explain the difficulty experienced in obtaining accurate results by the use of this method.

The conclusion to be drawn from the above results appears to be, that the method of determining copper by means of sulphide of sodium cannot be considered as chemically correct, inasmuch as an equivalent of sulphur does not precipitate a constant amount of copper; although it is evident from the great number of determinations detailed by Pelouze, that by long practice and skilful manipulation, considerable accuracy may, be attained, as, by adhering closely to the same mode of operating in all cases, the errors in each must necessarily be nearly alike.

A trial was next made of the method proposed by Parkes, which is thus described in Mitchell's Manual of Assaying.

"Take a given quantity of pure copper (say 10 grains), place it in a flask, and dissolve it in nitric acid, add ammonia in excess, and then make it into a bulk of 2500 grs. by measure (about 1-third of a pint) by the addition of water, although this is not absolutely necessary. Dissolve 1 ounce (avoirdupois) of pure cyanide of potassium, free from ferrocyanide or sulphide of potassium, in 6 oz. by measure of water; filter if necessary, and place the solution in a well-stoppered bottle till required for use. I then ascertain the quantity of this solution of cyanide of potassium required to decolorize the solution of copper by taking a given quantity in any graduated vessel—as a burette—and pour it by degrees into the solution of copper, adding the last quantity drop by drop until it is decolorized. This is very easily perceived, as there is no precipitate to interfere, and the operation is conducted at the ordinary atmospheric temperature."

In the course of the experiments made by this method, it was observed that the bleaching effect of the cyanide of potassium was gradual in its operation; and it was found that on allowing an ammoniacal solution of copper, to which cyanide of potassium had been added (but not sufficient to destroy the blue colour) to stand for a short time, it became completely bleached; the quantity of cyanide of potassium necessary to produce complete decoloration being in proportion to the length of time taken in the operation.

Under these circumstances, the point at which the addition of the cyanide of potassium should cease became a matter of great uncertainty, and as this method did not promise more accurate

results than those obtained by sulphide of sodium, it was not pursued further.

In the course of a number of experiments made with the view of obtaining some other method of determining copper with greater certainty than either of the preceding, the reaction of iodide of potassium upon a salt of copper, which results in the production of subiodide of copper and free iodine, appeared likely to be available for this purpose.

Knowing with what accuracy iodine may be determined by means of sulphurous acid, according to the method proposed by Bunsen, it seemed reasonable to expect, that by determining the amount of iodine liberated by the action of iodide of potassium upon a salt of copper, an equal degree of accuracy could be attained in the estimation of copper.

Bunsen's method for the determination of iodine, is to add an excess of a very dilute solution of sulphurous acid of known strength, and to estimate the amount of sulphurous acid unacted upon, by a standard solution of iodine. On calculating the amount of S O_2 in this state of dilution, required for the determination of 10 grs. of copper, I found the quantity would be inconveniently large, and that the use of a stronger solution was not practicable. Whilst endeavouring to obviate this difficulty, it occurred to me that the reaction of hyposulphurous acid on iodine, which results in the formation of hydriodic and tetrathionic acids, might be substituted for that of sulphurous acid; and a number of experiments were instituted to ascertain whether this was the case, the results of which proved that iodine may be determined by means of hyposulphurous acid with as great a degree of accuracy as by Bunsen's method, and moreover, with the advantage of requiring only one standard solution instead of two, and that of a more stable character than a solution of sulphurous acid.

The method finally adopted for determining copper is as follows :—

Ten grains of copper are dissolved in dilute nitric acid, and the solution boiled until free from nitrous acid; it is then diluted with about an ounce of water, and carbonate of soda added until a portion of the copper is precipitated. Pure acetic acid is then added in excess, and the solution poured into a flask capable of holding about 12 oz. About 60 grains of iodide of potassium are then thrown into the flask, and sufficient time having been allowed for the crystals to dissolve, a standard solution of hypo-

sulphite of soda is added until the greater part of the iodine has disappeared, which is indicated by the liquid changing from a brown to a yellow colour. A little clear solution of starch is then added, and the addition of the hyposulphite of soda cautiously continued until no further effect is produced.

The bleaching effected by the last portions of hyposulphite of soda may be best seen by allowing the drops to fall into the centre of the flask whilst the liquid is in motion, when streaks of a lighter colour will be produced so long as any iodine remains.

When the quantity of iodide of potassium employed was less than six times the weight of the copper to be determined, satisfactory results were not obtained.

Care must be taken that the iodide of potassium employed is free from iodate of potash, and that the acetic acid contains no sulphurous acid.

The solution of starch should be made by boiling with a large quantity of water, any undissolved portions allowed to subside, and the clear liquid only used.

A solution of hyposulphite of soda obtained by dissolving about 4000 grains of the salt in two gallons of water, was standardized by means of electrotyped copper. The burette employed was capable of holding 1500 grains of solution, each drop corresponding to about 0.006 of a grain of copper.

The numbers obtained were as follows:—

Grns. of Copper taken.	Measures of Standard used.	Calculated to 10 grs. of Copper.
8.02	124.6	155.3
7.44	115.7	155.4
7.67	119.2	155.4
8.32	129.4	155.5

Another quantity of standard solution gave the following:—

8.38	131.4	156.8
8.78	137.5	156.7

Several experiments were made in order to ascertain to what extent the results obtained by this process were liable to error from irregular manipulation or changes of temperature, the same amount of copper (9.10 grains) being used in each experiment.

In the first, the directions above given were strictly observed; the quantity of standard solution required was 134.4 measures.

In the second, time was not allowed for the crystals of iodide of potassium to dissolve before beginning to add the hyposulphite of soda ; the number of measures required was 134·3.

In the third, the solution of copper was diluted with as much water as could be conveniently contained in the flask ; the number of measures required was 134·5.

In the fourth, the solution of copper was as concentrated as possible ; the number of measures required was 134·4.

In the fifth, after adding the crystals of iodide of potassium, the solution was shaken up and allowed to stand for a quarter of an hour before proceeding with the hyposulphite of soda ; the number of measures required was 134·3.

In the sixth, the operation was conducted at 150° F. ; the number of measures required was 131·2. The flask in this experiment was observed to be filled with the vapour of iodine.

In the seventh, the operation was conducted at the temperature of 90° F. ; the number of measures required was 134·0.

From these experiments it is evident that slight differences in the mode of manipulating do not in any way affect the results so long as the solution is not heated.

The presence of tin, lead, iron, or zinc in small quantities, is also immaterial.

When the alloy in which the copper is to be determined contains a large proportion of lead or iron, these metals should be separated previous to the determination of the copper, since the yellow precipitate of iodide of lead and the red colour of the acetate of iron render it difficult to distinguish the effect produced by the last quantities of hyposulphite of soda.

The following determinations of copper in a number of specimens of gun-metal, taken from castings at the Royal Gun Factory at Woolwich, will serve to show the accuracy which may be obtained by this method :—

Grs. of Metal taken.	Measures of Standard used.	Per centage of Copper in alloy.
10·13	139·7	90·79
9·99	137·7	90·66
10·54	145·0	90·59
10·46	144·1	90·68
10·09	139·3	90·90
10·52	145·5	91·09

Grs. of Metal taken.	Measures of Standard used.	Per centage of Copper in alloy.
10·23	141·9	91·32
10·15	140·6	91·23
10·52	146·7	91·79
10·40	144·9	91·75
9·93	136·4	90·48
10·14	139·3	90·42
10·19	141·1	91·21
10·26	142·3	91·36
9·79	136·6	89·17
9·82	137·0	89·19
9·96	142·7	90·78
10·05	144·2	90·72
10·00	144·6	91·60
10·10	146·2	91·52

It may, therefore, be safely stated that copper can be estimated with ease and certainty by this method to within $\frac{1}{100}$ or $\frac{2}{100}$ per cent., and that the method possesses the advantage over those hitherto used of being likely to give similar results in the hands of different manipulators.