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Precipitation of Cuprous Thiocyanate from Homogeneous Solution

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A method for precipitating cuprous thiocyanate from homogeneous solution is described, in which the character of the precipitate is governed by the rate of the reduction of cupric ions to the cuprous state. The method is simple and accurate; its main advantages over conventional methods are an over-all reduction in the time required for the determination, and the production of a precipitate that is easy to manipulate and to collect by filtration.

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The insolubility of cuprous thiocyanate and the relatively high solubilities of the thiocyanates of many other metals provides a selective method for quantitatively separating copper from a solution containing other metals, as well as providing a gravimetric method for its determination. Consequently, since its introduction by Rivot in 1854,[1] the quantitative precipitation of cuprous thiocyanate has been widely applied.

Rivot[1] precipitated cuprous thiocyanate from hydrochloric acid solution with potassium thiocyanate, after reduction of cupric copper to the cuprous state with sulphite. He applied the method to the determination of copper in bronzes, but gave few practical details.

This method was used by van Name[2,3,4] for determining copper in coinage metals. He reported that only a small amount of free acid should be present during precipitation and that the precipitate should be set aside for 20 hours before filtration. Precipitation of tin, arsenic, antimony and bismuth was prevented by adding tartaric acid.

Kolthoff and van der Meene[5] studied in detail the conditions for precipitating cuprous thiocyanate. They concluded that the concentration of free acid should not exceed 0·5 N and that the concentration of the excess of thiocyanate precipitant should be less than 0·05 N. Reduction of cupric ions with sulphite was best performed in boiling solution.

Similar conclusions on the maximum permissible concentrations of acid and excess of precipitant were reported by Belcher and West,[6] who used ammonium ferrous sulphate as the reductant in the cuprous thiocyanate method.

Most workers consider it necessary to age the precipitated cuprous thiocyanate before filtration, although there are disagreements about the recommended time periods. Thus 2,[7] 6,[6,8] 20,[2,3,4] 24[5] and "several"[9] hours have been specified.

Stathis[10] used ascorbic acid to reduce cupric ions in the thiocyanate method. Whereas previous workers[2,5] had found that oxidising agents must be excluded, Stathis obtained quantitative precipitation of cuprous thiocyanate from nitric acid solutions of copper alloys. Moreover, the time period between precipitation and filtration was reduced to 30 minutes.

Experimental

The main disadvantage of the cuprous thiocyanate method is that the rather fine precipitate generally produced may clog or even pass through the filter. It has a marked tendency to "creep" with consequent risk of loss in transferring it to the filter and difficulty during washing. Heating the solution, even to boiling, with constant stirring, improves the granularity of the wetted precipitate, but is only partly effective in dealing with the precipitate that has crept up the walls of the container.

The work described here was undertaken to produce cuprous thiocyanate with good filtration characteristics and that does not require ageing before filtration.

The technique of precipitation from homogeneous solution[11] depends on the production of one of the reactants in the presence of the others at a rate such that a controlled growth of the crystals of the insoluble product results.

To achieve homogeneous precipitation of cuprous thiocyanate, it was decided to control the rate of production of cuprous ions. Three methods of approach can be envisaged for achieving this, namely, (1) the slow liberation of cupric ions from a complex compound

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into a reducing medium, (2) the generation of a reducing agent in a solution containing cupric ions and (3) the production of conditions under which the reaction of cupric ions with a reducing agent is delayed.

Successful precipitation of cuprous thiocyanate from homogeneous solution was achieved by using each of these three approaches. Thus, it was possible to precipitate cuprous thiocyanate from homogeneous solutions containing amminocupric ions. Ammonia solution was added to cupric sulphate solution until the cupric hydroxide precipitate redissolved. The solution remained clear when ammonium thiocyanate and sodium sulphite were added, but when the solution was heated ammonia was expelled and cuprous thiocyanate was precipitated. This procedure would, however, have no practical value for determining copper in the presence of metals having insoluble hydroxides.

The controlled generation of a reducing agent was obtained by the hydrolysis of sucrose. Sucrose was added to slightly acidic solutions containing cupric and thiocyanate ions. The solutions remained clear at room temperature, but when they were heated precipitation of cuprous thiocyanate began after a few minutes. The cupric ions were reduced by the glucose and fructose produced by hydrolysis of the sucrose. In this way highly crystalline cuprous thiocyanate with excellent filtration characteristics was produced. Unfortunately, it was impossible to precipitate the copper quantitatively in less than 4 hours, and strict control of pH was necessary. Solutions having acidities in excess of 0·03 N in hydrochloric or sulphuric acid gave darkened precipitates, and the supernatant liquid developed an opalescence and a sulphurous odour. This was attributed to further reaction of cuprous thiocyanate with fructose to produce cuprous sulphide. Nevertheless, with proper control of the conditions, successful gravimetric determinations of copper were made, but this method was abandoned because of practical difficulties.

Delayed reduction of the cupric ion was reported by Davis[12] in the homogeneous precipitation of cuprous tetraphenylborate. Ascorbic acid was added to acid solutions containing cupric and tetraphenylborate ions, and precipitation did not occur until about half a minute had elapsed. This method was not applicable to cuprous thiocyanate; immediate precipitation occurred under a wide range of temperature and acidity conditions when ascorbic acid was added to solutions containing cupric and thiocyanate ions.

With hydroxyammonium chloride, which is a milder reducing agent than ascorbic acid, delayed reduction of cupric ions was achieved by temperature control. A solution of hydroxyammonium chloride was added to a solution of cupric and thiocyanate ions, with an acidity of about 0·2 N, without precipitation occurring. When this solution was heated on a steam-bath, precipitation of cuprous thiocyanate began within a few minutes and appeared to be complete within about half an hour. The cuprous thiocyanate produced in this way was granular and had excellent filtration properties. A study of the conditions for precipitation resulted in the development of an accurate method for the gravimetric determination of copper.

Investigation of precipitation conditions—

An investigation of the reaction variables was carried out to find conditions under which precipitation of copper was complete within the limits of good gravimetric accuracy. These conditions were then applied to gravimetric determinations on solutions containing known amounts of copper, to check the procedure.

Preliminary experiments were performed in which completeness of precipitation was judged visually. When ammonium or potassium thiocyanate is added to a solution of a cupric salt, a green colour is produced, presumably due to the formation of a complex between cupric and thiocyanate ions. The disappearance of this colour when the complex is treated with hydroxyammonium chloride and heated is a good indication that precipitation is complete. These experiments led to the adoption of the reagents used in the subsequent tests. It was found expedient to use a colorimetric micro-titration procedure for determining the amount of copper remaining in the filtrate after precipitation of the cuprous thiocyanate.

Portions (50 ml) of a 1 per cent. solution of cupric sulphate were transferred to separate 150-ml Phillips beakers. To each solution were added in the stated order the amounts of hydrochloric acid, sp.gr. 1·18, 3·5 per cent. ammonium thiocyanate solution and 3 per cent. hydroxyammonium chloride solution specified in Table I, the solutions being stirred after each addition. The solutions were heated on a steam-bath for 30 minutes, cooled to room temperature and set aside for 10 minutes.

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After filtration through No. 4 porosity sintered-glass crucibles, 5 ml of each filtrate were transferred to a separating funnel containing 8 ml of water and 2 ml of 5 N sulphuric acid, and treated as described below.

Five millilitres of a 0·1 per cent. solution of diethylammonium diethyldithiocarbamate were added, and the mixture was shaken vigorously for 2 minutes and allowed to separate. Any copper remaining in the 5-ml portion of filtrate was extracted into the organic layer as the intense yellow copper dithiocarbamate. A blank solution, containing 50 ml of water in place of the cupric sulphate solution, was prepared, and, with each test, 5 ml were taken through the procedure described above.

The blank solution was titrated from a 2-ml burette with dilute standard cupric sulphate solution (1 ml $\equiv$ 10 μg of copper), the mixture being shaken vigorously after each increment and allowed to separate. This was continued until the colour of the organic layer of the blank matched that of the test. The volume of titrant required was therefore a measure of the amount of copper in 5 ml of filtrate.

RESULTS—

Results obtained in this way are shown in Table I. The last column shows the calculated negative error due to the amount of copper remaining in the whole filtrate.

TABLE I

EFFECTS OF DIFFERENT CONCENTRATIONS OF THE REAGENTS

Hydrochloric acid added, ml	Ammonium thiocyanate solution added, ml	Hydroxyammonium chloride solution added, ml	Copper in filtrate, %
1·0	7·5	15	0·17
1·0	10	15	0·06
1·0	12·5	15	0·05
1·0	15	15	0·03
1·0	20	15	0·05
1·0	15	5	0·13
1·0	15	10	0·04
1·0	15	15	0·03
1·0	15	20	0·03
0·5	15	15	0·03
1·0	15	15	0·03
1·5	15	15	0·03
1·8	15	15	0·09
2·0	15	15	0·25

DISCUSSION OF RESULTS—

The optimum conditions derived from the results shown in Table I require 15 ml each of ammonium thiocyanate solution and hydroxyammonium chloride solution, and about 1 ml of hydrochloric acid. The concentration of acid should not exceed 0·3 N, and the concentration of the excess of ammonium thiocyanate should not exceed 0·07 M. Similar results were obtained by using a 4·5 per cent. solution of potassium thiocyanate ($\equiv$ 3·5 per cent. ammonium thiocyanate) and with sulphuric or perchloric acid instead of hydrochloric acid. It was also found that nitric acid in concentrations less than 0·1 N did not affect the results.

When the optimum reagent concentrations were used it was found that 20 minutes' heating was insufficient (error 0·33 per cent.), but that heating for longer than 30 minutes was unnecessary.

METHOD FOR THE GRAVIMETRIC DETERMINATION OF COPPER

The precipitation conditions derived were applied to the gravimetric determination of copper in solutions prepared from pure electrolytic copper foil and copper-bearing alloys. After the cuprous thiocyanate had been precipitated and collected, it was washed first with a dilute solution of ammonium thiocyanate containing a little ascorbic acid (to maintain reducing conditions) and finally with dilute ethanol to remove any excess of ammonium thiocyanate.

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PROCEDURE—

Transfer 50 ml of acidified copper solution, containing about 125 mg of copper and having an acid concentration of less than 0·3 N, to a clean unscratched 150-ml Phillips beaker. Add, with mixing, 15 ml of ammonium thiocyanate solution and 15 ml of hydroxyammonium chloride solution. Heat the solution on a steam-bath for 30 minutes, cool it to room temperature, and set aside for 10 minutes. Collect the precipitate on a previously dried and weighed No. 4 porosity sintered-glass crucible, and use the wash solution to complete the transfer of the precipitate. Wash the precipitate a few times with wash solution and finally with dilute ethanol. Dry the crucible and its contents for 2 hours at 110° C, set aside to cool, and weigh.

1 g of cuprous thiocyanate ≡ 0·5226 g of copper.

APPLICATION OF THE METHOD TO COPPER METAL

Pure electrolytic copper foil (2·4395 g), freshly de-greased and washed with dilute nitric acid, was dissolved in 3 ml of nitric acid, sp.gr. 1·42, and 3 ml of water. When dissolution was complete, 5 ml of sulphuric acid, sp.gr. 1·84, were added, and the mixture was evaporated to small volume to expel nitric acid. When it was cool, the mixture was diluted with 20 ml of water and again evaporated to small volume; this treatment was repeated twice. The solution was then transferred with water to a 1-litre calibrated flask and diluted to the mark with water at 20° C.

This solution was about 0·18 N in sulphuric acid, and 50 ml contained 0·1220 g of copper. Twelve 50·0-ml portions were tested by the method described above, and the weights of copper calculated from the weights of cuprous thiocyanate obtained lay within the range 0·1219 to 0·1221 g with a mean value of 0·1220 g. By assuming the copper to be 100·0 per cent. pure, the recoveries were thus 100·0 per cent. to within ±0·08 per cent. The standard deviation was 0·067 per cent.

APPLICATION OF THE METHOD TO COPPER ALLOYS

Four British Chemical Standard alloys of copper were analysed by this method. Two solutions, one in sulphuric acid and the other in perchloric acid, were prepared from two of the alloys and one solution was prepared from each of the other alloys.

Preparation of Alloy Solutions

CUPRO-NICKEL 180/1—

In sulphuric acid—A 0·9299-g sample of the alloy was placed in a 150-ml Kjeldahl flask, and 3 ml each of water and nitric acid, sp.gr. 1·42, were added. After the metal had dissolved, 1·5 ml of sulphuric acid, sp.gr. 1·84, were added, and the solution was evaporated to small volume to expel the nitric acid. The solution was then cooled, diluted with 50 ml of water, and neutralised to pH 4 with ammonia solution, sp.gr. 0·89. It was then transferred with water to a 250-ml calibrated flask, 15 ml of 5 N sulphuric acid were added, and the solution was made up to the mark at 20° C with water.

In perchloric acid—A 0·9301-g sample of the alloy was weighed into a tall 150-ml beaker and heated with 7·5 ml of perchloric acid, sp.gr. 1·54, until it dissolved. When cool, the solution was transferred with water to a 250-ml calibrated flask, and the solution was diluted to the mark with water.

MANGANESE-BRASS "B" 179—

In sulphuric acid—A 1·0601-g sample of the alloy was weighed into a 150-ml Kjeldahl flask, 4 ml each of water and nitric acid were added, and occasional heating was applied until dissolution was complete. Two millilitres of sulphuric acid were added, and the solution was heated to fumes for 5 minutes. When cool, the solution was diluted with about 20 ml of water, and again heated to fumes for 5 minutes. It was then cooled and diluted with 50 ml of water. The turbid solution produced was filtered through a Whatman No. 42 filter-paper into a 250-ml flask, and the filter was washed with water. The filtrate and washings were diluted to the mark with water.

In perchloric acid—A 1·0727-g sample was transferred to a tall 150-ml beaker and dissolved, with warming, in 9·5 ml of perchloric acid. When cool, the solution was diluted with 50 ml of water and filtered through paper into a 250-ml calibrated flask. The filter was washed with water, and the filtrate and washings were diluted to the mark with water.

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BRONZE 183/1—

A 0·7301-g sample was dissolved in a mixture of 8 ml of water and 12 ml of nitric acid contained in a 150-ml beaker. The solution was evaporated by heating on a steam-bath to reduce the volume to between 5 and 10 ml. It was then diluted with 50 ml of hot water, and digested on the steam-bath for a further 15 minutes. The precipitate of metastannic acid was removed by filtration through a No. 42 filter-paper, and the filter was washed 10 times with a few millilitres of dilute nitric acid (1 + 20). The filtrate and washings were evaporated to small volume (but not to dryness); the concentrated solution was then diluted with 50 ml of water, and neutralised to pH 4 with ammonia solution. The solution was transferred to a 250-ml calibrated flask, acidified with 5 ml of perchloric acid, and diluted to the mark with water.

BRONZE "C" 207—

A 0·7302-g sample was heated in a tall 150-ml beaker with 9 ml of perchloric acid and 1·5 ml of nitric acid. The solution was then heated to fumes until colourless, diluted with 50 ml of hot water, and digested for 15 minutes on a steam-bath. It was then filtered through No. 42 filter-paper (to remove the metastannic acid precipitate) into a 250-ml calibrated flask. The filter was washed with 100 ml of water containing 1 ml of perchloric acid, and the filtrate and washings were diluted to the mark with water.

Procedure

Copper was determined in three 50-ml portions of each solution by the method described, except that 0·5 g of sodium hydrogen tartrate was added to each portion of the solution prepared from Bronze 183/1 before the other reagents were added. This alloy contained 0·24 per cent. of antimony and 0·14 per cent. of arsenic, both of which produce precipitates under the conditions of the test unless tartrate is added to complex them. The results obtained are shown in Table II and are compared with the certified copper contents.

TABLE II

RESULTS OBTAINED WITH COPPER ALLOYS

Alloy	B.C.S. reference number	Method of preparing solution	Copper found, %	Mean copper found, %	Certified copper value, %	Range of copper values certified, %
Cupro-nickel	180/1	In H_2SO_4	67·35 67·35 67·32	67·34	67·36	67·32 to 67·40
		In $HClO_4$	67·33 67·30 67·36	67·33		
Manganese brass "B"	179	In H_2SO_4	58·73 58·71 58·75	58·73	58·8	58·6 to 59·06
		In $HClO_4$	58·70 58·73 58·67	58·70		
Bronze	183/1	—	84·68 84·68 84·76	84·71	84·8	84·75 to 84·95
Bronze "C"	207	—	86·76 86·76 86·84	86·79	86·84	86·65 to 87·00

RESULTS

All the results obtained are in good agreement with the certified copper contents, and the replicate determinations on each alloy agree well. The other constituents of the alloys do not, therefore, interfere in the determination. The certified amounts of the other metals are shown in Table III.

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TABLE III

OTHER CONSTITUENTS OF THE ALLOYS

Alloy	Constituents other than copper
Cupro-nickel 180/1	30·85 per cent. of Ni; 0·82 per cent. of Fe; 0·81 per cent. of Mn
Manganese brass "B" 179 ..	33·9 per cent. of Zn; 1·03 per cent. of Mn; 0·91 per cent. of Fe; 1·62 per cent. of Al; 1·75 per cent. of Sn; 0·78 per cent. of Pb; 1·01 per cent. of Ni
Bronze 183/1	5·17 per cent. of Zn; 5.01 per cent. of Sn; 3·51 per cent. of Pb; 0·51 per cent. of P; 0·51 per cent. of Ni; 0·24 per cent. of Sb; 0·14 per cent. of As
Bronze "C" 207	9·80 per cent. of Sn; 2·53 per cent. of Zn; 0·41 per cent. of Pb

CONCLUSIONS

Precipitation of cuprous thiocyanate from homogeneous solution by controlled reduction of cupric ions to cuprous with hydroxyammonium chloride provides a quick, simple, accurate and specific method for the determination of copper. The precipitates produced by this method have good filtration characteristics and in this respect are far superior to those produced by the classical heterogeneous precipitation procedures, notably in that they do not produce the fine suspension of cuprous thiocyanate that displays the phenomenon of creeping up the sides of apparatus in which it is handled.

Precipitation of copper in this way also provides a practicable alternative to electrolysis for removing copper from solutions before certain other metals are determined. It has been used for separating large amounts of copper from small amounts of iron, for the determination of traces of iron in analytical-reagent grade copper salts. It is hoped that this will form the basis of a further communication.

REFERENCES

1. Rivot, L. E., *Compt. Rend.*, 1854, **38**, 868.
2. van Name, R. G., *Amer. J. Sci.*, 1900, **10**, 451.
3. ——, *Ibid.*, 1902, **13**, 20.
4. ——, *Ibid.*, 1902, **13**, 138.
5. Kolthoff, I. M., and van der Meene, G. H. P., *Z. anal. Chem.*, 1927, **72**, 337.
6. Belcher, R., and West, T. S., *Anal. Chim. Acta*, 1952, **6**, 337.
7. Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," Third Edition, The Macmillan Company, New York, 1952, p. 671.
8. Wilson, C. L., and Wilson, D. W., *Editors*, "Comprehensive Analytical Chemistry," Elsevier Publishing Co., Amsterdam and New York, 1962, Volume IC, p. 370.
9. Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis," Second Edition, Longmans, Green and Co. Ltd., London, 1951, p. 431.
10. Stathis, E. C., *Anal. Chim. Acta*, 1957, **16**, 21.
11. Gordon, L., Salutsky, M. L., and Willard, H. H., "Precipitation from Homogeneous Solution," John Wiley and Sons Inc., New York, 1959.
12. Davis, D. G., *Anal. Chem.*, 1960, **32**, 1321.

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