Quantitative Separation of Copper by Thiourea from Homogeneous Solution[1]

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It was reported by Y. Uzumasa and T. Okura[2], that on boiling alkaline solution containing the copper sub-group ions in the presence of thiourea, sulfides precipitate in crystalline and easily filterable form. These authors suggested that a new method of qualitative analysis without using hydrogen sulfide might be possible by the homogeneous precipitation with this reagent.

The author made, following this suggestion, a thorough study on the conditions for the complete precipitation of copper sulfide and for the quantitative separation of copper in the presence of other cations such as nickel, cobalt, zinc, manganese, calcium and magnesium. Finally the author found that the use of urea and ammonium chloride together with thiourea made this trial succeed. Urea[3] added to the acidified solution, when boiled, gradually diminishes the hydrogen ion concentration in the solution, owing to its hydrolytic decomposition, and the proper conditions for the complete precipitation of copper sulfide by thiourea are attained. Thus the satisfactory results were obtained in the case of copper alone, but the separation of copper is less satisfactory in the presence of other cations.

The selective reactions of thiourea against cations[4], or formation of metal sulfides are promoted with the increase of *p*H value in the solution. At a desirable high *p*H range, coprecipitation of some cations with copper sulfide occurs and unsatisfactory results as mentioned above are obtained. To avoid this, the increasing tendency of *p*H caused by the decomposition of these reagents should be controlled so as to be in the lower limit of *p*H value required for the formation of copper sulfide. The addition of ammonium chloride to the homogeneous solution containing these reagents successfully solves this problem. The realization of this optimum *p*H value is ascribed to the buffer action of urea and ammonium chloride.

Experimental

(A).—Complete precipitation of copper sulfide.

Materials.—Pure cupric oxide, ignited at 900°C., was dissolved in hydrochloric acid and the solution was diluted with water to a liter. The copper solution thus prepared was found to be

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[1] On September 26, 1952, part of this paper was read before the Meeting of the Hokkaido Section of the Chemical Society of Japan.

[2] Y. Uzumasa and T. Ôkura, This Bulletin, **23**, 163 (1950).

[3] The characteristic separation method from homogeneous solution by urea has been developed by H. H. Willard and others. H. H. Willard and N. K. Tang, *J. Am. Chem. Soc.*, **59**, 1190 (1937); H. H. Willard and N. K. Tang, *Ind. Eng. Chem., Anal. Ed.*, **9**, 357 (1937); H. H. Willard and J. L. Sheldon, *Anal. Chem.*, **22**, 1162 (1950); H. H. Willard, *Anal. Chem.*, **22**, 1372 (1950); L. Gordon, *Anal. Chem.*, **24**. 459 (1952).

[4] J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.*, **14**, 435 (1942).

free from other metallic ions. The concentration was determined as cupric oxide. Thiourea was recrystallized from water, while urea from ethanol.

Experimental Procedure.—Approximately 300 ml. of solution containing about 50 mg. of copper together with 2 grams of urea and one or more ml. of 10%thiourea solution, was placed in a 500 ml. Erlenmeyer flask. The solution was properly adjusted to give the desired initial *p*H value with diluted hydrochloric acid or alkali hydroxide solution. The homogeneous solution thus prepared was then heated to boiling point. A white turbidity first appeared, which gradually blackened upon the formation of copper sulfide. The solution was kept boiling, about thirty minutes later the black precipitate appeared, then it was cooled and kept at room temperature for one hour. The precipitate aggregated at the bottom of the flask was dense and not bulky.

The precipitate was filtered off, and washed with water. Unlike the precipitates formed by hydrogen sulfide, this precipitate was not oxidized by air, and no peptization was noticed during filtration and washing. The precipitate was ignited, and weighed as cupric oxide. *p*H values of the filtrates or solutions were measured with a glass electrode *p*H meter throughout this study.

(1). *Quantity of Thiourea Required.*—To find out the most suitable quantities of thiourea for precipitating copper, a series of experiments were conducted. The results obtained are given in Table 1. These results indicate that more than 1.7 of the mole ratio of thiourea added to copper are required to obtain accurate results. Although an excessive reagent seems to be harmless for the quantitative precipitation of copper, it is desirable to avoid an exceedingly excessive use, as it makes successive analytical procedures complicated. The proper amount required for 50 mg. of copper is 1 ml. of 10% solution of thiourea.

TABLE I

RELATION BETWEEN QUANTITY OF Cu AND THIOUREA ADDED (CuO Taken 62.6 mg.)

10% thiourea solution added,		CuO found,	Diff.
ml.	mole ratio to Cu	mg.	mg.
0.6	1.0	61.9	−0.7
0.8	1.3	62.7	+0.1
1.0	1.7	62.8	+0.2
2.0	3.4	62.9	+0.3
3.0	5.1	62.5	−0.1
4.0	6.8	62.8	+0.2

Initial *p*H of the solution is 4.0. Boiling duration is 30 min., and urea added is 2 g./300 ml. of the total volume.

(2). *Relation between Final pH Value, and Urea Added.*—As urea forms ammonia and carbon dioxide or ammonium carbonate gradually with hydrolysis, the resulting *p*H values of the solution depend on the molar concentrations of urea added. Table II shows the effect of varied quantities of urea on the final *p*H value. Final *p*H values of the solutions containing less than 1.5 g. of urea were low, and experimental errors were negative. It should be noted that copper is completely precipitated when *p*H is above 8.0 and the concentration of urea added is over 0.08 in molar concentration. As the length of time necessary for the appearance of copper sulfide precipitate was found to differ from each other, boiling should be continued for thirty minutes or more in each case.

TABLE II

RELATION BETWEEN FINAL *p*H, AND UREA ADDED (CuO taken 62.6 mg./300 ml.)

Urea added,		Final *p*H,	CuO found,	Diff.	Time elapsed from boiling to the appearance of black turbidity
g.	mol. $\times 10^2$/1.		mg.	mg.	min.
0.5	2.8	7.72	61.5	−1.1	15
1.0	5.6	7.85	61.9	−0.7	10
1.5	8.4	8.00	62.4	−0.2	7
2.0	11.2	8.48	62.6	±0.0	5
2.5	14.0	8.84	62.5	−0.1	5
3.0	16.8	9.00	62.6	±0.0	3

Initial *p*H of the solution is 4.0, thiourea added is 1 ml. of 10% solution. Boiling was continued for 30 min. or more after first black turbidity appeared.

(3). *Effect of Duration of Boiling.*—Table III gives the results for the various durations of boiling. The precipitation, at the urea content of 2.0 g., was found to be complete after thirty minutes from the appearance of black turbidity. Continuing the boiling, the precipitates coagulated and settled to the bottom of the flask. When the copper content is about 50 mg., boiling for forty minutes is ideal for practical purposes. Further experiments confirmed that sixty minutes of boiling is needed for 100 mg. of copper.

TABLE III

EFFECT OF BOILING DURATION (CuO taken 60.9 mg.)

Boiling duration	CuO found,	Diff.
min.	mg.	mg.
15	60.0	−0.9

30	60.8	−0.1
45	61.2	+0.3
60	60.7	−0.2
60	60.9	±0.0
60	61.1	+0.2

Initial *p*H of the solution is 4.0, urea added is 2.0 g./300 ml. of the total volume, and thiourea added is 1 ml. of 10% solution.

(4). *Effect of initial pH Value.*—Table IV shows that the amount of copper precipitated is affected by the initial *p*H of the homogeneous solution. As the hydroxyl ion evolved with the hydrolysis of urea neutralizes the hydrogen ion, resulting *p*H value of solutions with lower initial *p*H do not reach to the extent of complete precipitation. In the case of the initial *p*H 1.6, a white turbidity appeared after the solution began to boil, and took nearly thirty minutes till the black colored copper sulfide appeared. When the initial *p*H value was lower than 2.6, the coagulation of copper sulfide was incomplete. It is revealed that the precipitation is completely carried out when the initial *p*H value is regulated at 4.0 or more.

TABLE IV

EFFECT OF INITIAL *p*H VALUE (CuO taken 62.6 mg.).

Initial *p*H,	Final *p*H,	CuO found,	Diff.	Time elapsed from boiling to the appearance of black turbidity.
		mg.	mg.	min.
1.6	7.00	60.6	−2.0	30
2.0	7.24	60.9	−1.7	15
2.6	7.60	61.7	−0.9	7
3.4	8.00	62.3	−0.3	5
4.4	8.55	62.5	−0.1	5
5.2	8.80	62.4	−0.2	2

Urea added is 2 g./300 ml. of the total volume, and thiourea added is 1 ml. of 10% solution. Boiling was continued for 30 min. or more after first black turbidity appeared.

(B).—Separation of Copper From Other Metals.

(1) *Preliminary Investigation*:—Relation between final *p*H, and ammonium chloride.—

In order to ascertain the influence of the other cations, 50 mg. of copper was precipitated following the above mentioned procedure from the solution containing 0.5 g. of one of other cations respectively. The precipitates thus formed were ignited to constant weight, which compared with that obtained in the case where copper alone exists. It was found that calcium and magnesium had no affect, whereas the coprecipitated amounts of cobalt as well as nickel were 25%, while zinc and manganese were 70% and 1% respectively. Because of the interferences of these other cations, the procedure resulted in unsatisfactory separation of copper. To avoid these interferences, various amounts of ammonium chloride (from 0.5 to 4.0 g.) were added to the solution and boiling was continued to complete precipitation. Converse to the amount of ammonium chloride, the quantity of the coprecipitation gradually diminished, and satisfactory results were obtained by adding 2.0 g. of the salt.

To determine the influence of the amounts of ammonium chloride upon the final *p*H value and the precipitation of copper, two series of attempts were made in which various amounts of ammonium chloride were added to the solution containing 62.0 mg. of cupric oxide, and 2 g. of ammonium chloride was added to the solution containing various concentrations of copper. The former results are shown in Fig. 1, and the latter in Table V. Fig. 1 indicates that the final *p*H value of the solution decrease with the increase of ammonium chloride added, and the addition of more than 2 g. of it tends to make the precipitation less satisfactory. Table V indicates the relations between various concentrations of copper and the final *p*H. In order to guard against any reduction of the quantity of the precipitate, 2 g. of the salt is ideal, and in this state final *p*H is 8.0.

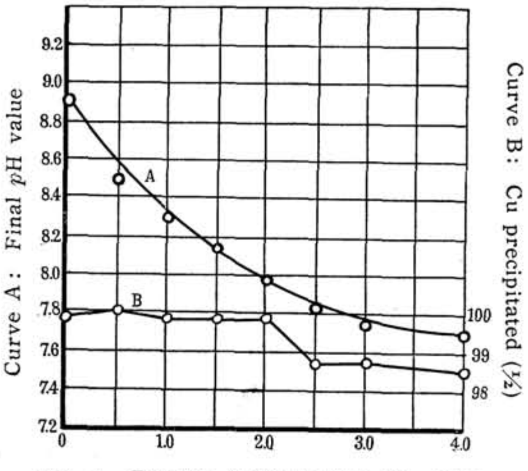

Fig. 1. Relation between final pH, quantity of copper precipitated, and amm. chloride added

Curve A. The final *p*H versus the amount of amm. chloride added.

Curve B. Percentages of precipitates versus the amounts of amm. chloride added.

Quantity of amm. chloride added (g./300ml.)

TABLE V

RELATION BETWEEN VARIOUS CONCENTRATIONS OF COPPER AND FINAL pH VALUE

Cu taken, g./300 ml.	Final pH,	Cu found, g.	Diff. mg.
0.0102	9.07	0.0102	±0.0
*0.0102	7.93	0.0102	±0.0
0.0204	9.00	0.0204	±0.0
*0.0204	7.94	0.0207	+0.3
0.0489	8.85	0.0492	+0.3
*0.0489	7.90	0.0489	±0.0
0.0978	8.60	0.0976	−0.2
*0.0978	7.85	0.0975	−0.3

indicate the solution to which 2 g. of amm. chloride was added.

(2) *Quantitative Separation of Copper from Various Kinds of Metal.*—Using the above procedure, copper was separated and determined from the solution containing various kinds of metal. In all cases, 2 g. of ammonium chloride were added, and the first precipitation was made from a volume of 300 ml. From the filtrate, a second precipitate was obtained and determination was performed as follows. Nickel was determined as nickel dimethylglyoxime. Cobalt was preicpitated by means of α-nitroso-β-naphthol, ignited and weighed as cobalto-cobaltic oxide. Zinc was precipitated as zinc ammonium phosphate, dried at 105°C. and weighed. Manganese was determined volumetrically by the bismuthate method as usual. Calcium was precipitated as oxalate and weighed as oxide. Magnesium was determined as magnesium hydroxyquinolate dihydrate.

Table VI indicates that approximately 10 to 100 mg. of copper can be satisfactorily separated from the above metals, provided that the metals exist at the following range: nickel, approx. 60 mg.; cobalt and zinc approx. 20 mg.; manganese, approx. 30 mg.; calcium and magnesium, allowable in a considerable amount. Fig. 2 indicates the interferences of cobalt, zinc, and manganese, of which the coexisting amount is larger than that taken above. It was found that errors in the case of zinc greatly depend upon the amounts of copper taken, but not so much in the case of manganese.

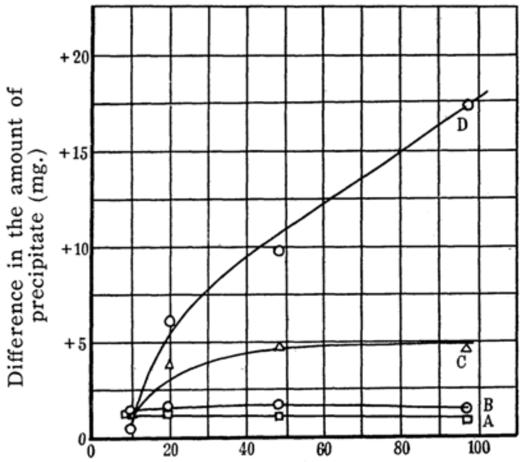

Fig. 2. Interferences of cobalt, zinc, and manganese
Curve A.—Cobalt added, 0.0260 g.
Curve B.—Cobalt added, 0.0444 g.
Curve C.—Manganese added, 0.0556 g.
Curve D.—Zinc added, 0.0390 g.
Concentration of copper (mg./300 ml.)

TABLE VI

DETERMINATION OF COPPER IN THE PRESENCE OF OTHER METALS

Copper taken,	Other metals added,	Diff.	
		Copper,	Other metals.
0.0102	0.0608 Ni	±0.0	−0.1
0.0204	”	+0.1	−0.2
0.0489	”	−0.1	−0.3
0.0978	”	−0.3	−0.1
0.0102	0.0133 Co	+0.3	+0.2
0.0204	”	±0.0	±0.0
0.0489	”	+0.6	±0.0
0.0978	”	+0.5	+0.1
0.0102	0.0195 Zn	±0.0	−0.1
0.0204	”	−0.2	±0.0
0.0489	”	+0.4	−0.3
0.0978	”	+0.7	−0.6
0.0102	0.0278 Mn	−0.1	±0.0
0.0204	”	+0.1	−0.1
0.0489	”	±0.0	−0.1
0.0978	”	−0.1	−0.3
0.0102	0.0673 Ca	+0.3	+0.2
0.0204	”	+0.2	−0.1
0.0489	”	±0.0	−0.2
0.0978	”	+0.3	+0.1
0.0102	0.1362 Ca	+0.3	−0.2
0.0204	”	+0.2	±0.0
0.0489	”	+0.1	+0.1
0.0978	”	+0.2	+0.3
0.0102	0.0347 Mg	+0.2	−0.1
0.0204	”	+0.2	−0.3
0.0489	”	−0.2	+0.1
0.0978	”	−0.2	−0.1
0.0102	0.0695 Mg	+0.3	−0.2
0.0204	”	+0.2	±0.0
0.0489	”	+0.2	+0.3
0.0978	”	±0.0	−0.3

Summary

Quantitative separation of copper as sulfide was made from homogeneous solution containing thiourea, together with urea and ammonium chloride. It was found, that with boiling, the solution adjusted to a pH 4.0 in forty minutes or more after the first appearance of black turbidity; the precipitate is obtained in an easily filterable and washable form. Addition of ammonium chloride was found very effective in the presence of some cations. The amount of 10 to 100 mg. of copper could be satisfactorily separated from calcium and magnesium, and the separabilities from nickel, cobalt, zinc, and manganese were examined in the presence of ammonium chloride, and their allowable amount of coexistence in quantitative separation was determined.

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