

ART. XII.—*The Estimation of Copper as Cuprous Sulphocyanide in the Presence of Bismuth, Antimony, Tin and Arsenic*; by R. G. VAN NAME.

[Contributions from the Kent Chemical Laboratory of Yale University,—CVI.]

It has long been known that copper may be quantitatively separated from a number of other metals by precipitation as cuprous sulphocyanide. The additional fact that this salt is suitable for direct weighing as a means of estimating copper was mentioned, apparently for the first time by Rivot\* in 1854, and was confirmed a quarter of a century later by the experiments of Busse,† who employed the process for determining copper not only alone but also in the presence of iron, nickel, zinc and arsenic. Recent work by the present writer‡ has shown that, with the sole modification of filtering and weighing upon asbestos, Rivot's method is accurate and satisfactory.

In view of the tendency of bismuth, antimony and tin to form insoluble basic chlorides in solutions containing only a slight excess of hydrochloric acid, and the difficulty of obtaining a complete precipitation of cuprous sulphocyanide in strongly acid solutions, the estimation of copper by the above method in the presence of these metals seemed to present some difficulties. The following investigation, in which arsenic was also included on account of its close relationship with the above metals, was accordingly undertaken.

The first series of experiments yielded the results given in Table I, the method being as follows: A convenient quantity of a copper sulphate solution of about  $\frac{1}{8}$  normal strength was measured from a burette, diluted, and acidified with a definite amount of hydrochloric or sulphuric acid. If tartaric acid was employed it was added at this point, after which the solution of arsenic, bismuth or antimony was introduced and the copper finally precipitated by ammonium bisulphite and ammonium sulphocyanide. Of the last a uniform amount, 70<sup>cm</sup>³ of a decinormal solution, was used for each experiment. The ammonium bisulphite solution was prepared in the usual way by passing sulphur dioxide into strong ammonia.

Arsenic was introduced in the form of measured portions of a standard arsenious acid solution which were made faintly acid to litmus just before addition. Bismuth and antimony were taken in the form of solutions of the chlorides in dilute hydrochloric acid, the amount of acid thus introduced into the determination being in all cases taken into account.

\* Compt. Rend., xxxviii, 868.

† Zeitschr. anal. Chem., xvii, 53.

‡ This Journal, vol. x, 451.

All the determinations were allowed to stand fifteen hours or more before filtering to insure completeness of precipitation. The filtering was performed upon asbestos in a perforated crucible, the precipitate thoroughly washed with cold water, dried at 105° to a constant weight, and weighed as cuprous sulphocyanide.

TABLE I.

Final volume 500<sup>cm</sup>³.

70<sup>cm</sup>³ of approximately decinormal NH<sub>4</sub>SCN used for each experiment.

Cu taken gram.	As taken as H <sub>3</sub> O <sub>3</sub> As gram.	H <sub>2</sub> SO <sub>4</sub> cm <sup>3</sup> .	Tartaric acid. gram.	HNH <sub>4</sub> SO <sub>3</sub> sat. sol. cm <sup>3</sup> .	Cu <sub>2</sub> S <sub>2</sub> (CN) <sub>2</sub> found. gram.	Calcu- lated as Cu. gram.	Error. gram.
1. .3144	0.2	5		5	.5889	.3078	-.0066
2. "	0.2	"		10	.5978	.3124	-.0020
3. "	0.05	"		10	.5919	.3091	-.0053
4. "	0.2	"		15	.6020	.3146	+ .0002
			HCl sp. gr. about 1.17 cm <sup>3</sup> .				
5. "	0.4	15		10	.5969	.3120	-.0024
6. "	0.05	"		"	.5995	.3133	-.0011
7. "	0.6	10	1	"	.6035	.3154	+ .0010
8. "	0.5	"	1	"	.6032	.3153	+ .0009
9. "	0.4	"		"	.6015	.3144	.0000
10. "	0.2	"		"	.6024	.3148	+ .0004
11. "	0.1	"		"	.6017	.3145	+ .0001
12. "	0.1	9	1	"	.6029	.3151	+ .0007
13. "	0.01	10		"	.6022	.3147	+ .0003

The negative errors of experiments 1 to 3 of Table I are plainly due to the large amount of acid present, for they disappear when the bisulphite is sufficiently increased (experiment 4), and the deficiencies in nos. 5 and 6 may be ascribed to the same cause, for they are not found in the subsequent experiments with arsenic where less acid was used. Tartaric acid was added in three of the above determinations, but its use in separations from arsenic is obviously unnecessary.

From these results it is evident that the estimation of copper in the presence of arsenic by this method is entirely practicable in either sulphuric or hydrochloric acid solution.

When bismuth is present a much closer adjustment of conditions is necessary. Experiments 14 to 19 show the effect of attempting to keep the bismuth in solution with hydrochloric

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TABLE I (continued).

Final volume 500 <sup>cm</sup> ³.								
Cu taken.	Bi taken as BiCl <sub>3</sub> + HCl.	HCl	Tartaric acid.	HNH <sub>4</sub> SO <sub>3</sub> sat. sol.	Cu <sub>2</sub> S <sub>2</sub> (CN) <sub>2</sub> found.	Calculated as Cu.	Error.	
gram.	gram.	cm <sup>3</sup> .	gram.	cm <sup>3</sup> .	gram.	gram.	gram.	
14.	·3144	0·5	20	10	·6534	·3415	+·0271	
15.	"	0·4	25	"	·5933	·3101	-·0043	
16.	"	0·2	20	5	·5932	·3101	-·0043	
17.	"	0·2	"	10	·6014	·3143	-·0001	
18.	"	0·1	"	"	·5977	·3124	-·0020	
19.	"	0·05	"	"	·5998	·3135	-·0009	
Final volume 300 <sup>cm</sup> ³.								
20.	"	0·5	10	1	5	·6007	·3139	-·0005
21.	"	0·4	"	"	"	·6018	·3145	+·0001
22.	"	0·2	"	"	"	·6003	·3137	-·0007
23.	"	0·1	7	"	"	·6033	·3153	+·0009
24.	·3163	0·1	10	"	"	·6033	·3153	-·0010
25.	"	0·1	8	"	"	·6056	·3165	+·0002

acid, using no tartaric acid. In experiment 14 the free acid present during the precipitation of the copper did not suffice to hold up all the bismuth. In the others, with the exception of no. 17, the acid prevented the complete precipitation of the copper.

For experiments 20 to 25 the quantities of hydrochloric acid required were materially diminished by the addition of tartaric acid, and by reducing the total volume from 500<sup>cm</sup>³ to 300<sup>cm</sup>³. The quantities of tartaric and hydrochloric acids required were previously determined by a series of blank tests and both kept as low as possible.

The results fall fairly near the theory but average a trifle low, and the filtrates of all, even those which show positive errors, gave decided tests for copper when concentrated and treated with potassium ferrocyanide. Moreover, a slight variation in the conditions would allow some of the bismuth to be precipitated. The results therefore are hardly satisfactory.

TABLE I (continued).

Final volume 500 <sup>cm</sup> ³.								
Cu taken.	Sb taken as SbCl <sub>3</sub> + HCl.	HCl	Tartaric acid.	HNH <sub>4</sub> SO <sub>3</sub> sat. sol.	Cu <sub>2</sub> S <sub>2</sub> (CN) <sub>2</sub> found.	Calculated as Cu.	Error.	
gram.	gram.	cm <sup>3</sup> .	gram.	cm <sup>3</sup> .	gram.	gram.	gram.	
26.	·3163	0·5	10	2	5	·6024	·3148	-·0015
27.	"	0·4	8	"	"	·6043	·3158	-·0005
28.	"	0·3	"	"	"	·6044	·3159	-·0004
29.	"	0·5	5	"	"	·6046	·3160	-·0003
30.	"	0·4	"	"	"	·6054	·3164	+·0001
31.	"	0·2	"	"	"	·6058	·3166	+·0003

Antimony is affected to a much greater extent than bismuth by the presence of the tartaric acid, so that if enough of the latter is present, relatively little hydrochloric acid is required to hold the antimony in solution. As the amount of the tartaric acid is practically without effect upon the precipitation of the copper, these conditions are favorable for the process. Experiments 26 to 31 give the results obtained in the presence of antimony, which show that the process is practicable.

In all the experiments thus far described the excess of ammonium sulphocyanide above the amount theoretically required has been comparatively small, 70<sup>cm<sup>3</sup></sup> of the decinormal solution having been employed where the theory called for about 50<sup>cm<sup>3</sup></sup>. It has been elsewhere shown\* that increase in the amount of the sulphocyanide diminishes the effect of the hydrochloric acid present. This fact has an important application in the separation of copper from bismuth, because it is possible, even when the solution contains an excess of hydrochloric and tartaric acid above the amount required to keep the bismuth in solution, to precipitate the copper completely by employing a sufficient quantity of ammonium sulphocyanide. By working in this way in solutions more strongly acid than would otherwise be consistent with accuracy, an additional advantage is gained because the consequent retardation of the precipitation produces precipitates which can be more easily filtered than those obtained from neutral or less acid solutions.

For the experiments of Table II the precipitation was carried out in the manner just described, and as the quantity of copper employed in the previous determinations had proved rather too large to be conveniently filtered and washed in a crucible of the ordinary size, a smaller amount was taken. A new copper sulphate solution of about  $\frac{1}{10}$  normal strength was employed, the other solutions being the same previously used.

The results obtained with bismuth are given in experiments 1 to 8. For this amount of copper the theory requires about 12.5<sup>cm<sup>3</sup></sup> of the decinormal ammonium sulphocyanide, but owing to the amount of acid present the results are low until about 125<sup>cm<sup>3</sup></sup> are added, beyond which point further increase produces no effect. Carried out in this way the separation from bismuth is satisfactory and the results accurate.

Tin in the higher condition of oxidation may be successfully treated in the same manner as experiments 9 to 11 show. Tartaric acid is of material assistance in reducing the amount of hydrochloric acid necessary to hold the tin in solution, whether in the stannic or stannous state.

The estimation of copper in the presence of tin in the

\* This Journal, vol. xiii, p. 23.

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TABLE II.

	Cu taken. gram.	Bi. gram.	Final volume 200 <sup>cm</sup> ³.			Cu <sub>2</sub> S <sub>2</sub> (CN) <sub>2</sub> found. gram.	Calcu- lated as Cu. gram.	Error. gram.	
			HCl sp. gr. about 1·17. cm <sup>3</sup> .	Tar- taric acid. gram.	HNH <sub>4</sub> SO <sub>3</sub> sat. sol. cm <sup>3</sup> .				NH <sub>4</sub> SCN approx. n/10. cm <sup>3</sup> .
1.	·0793	0·2	6	1	2	15	·1329	·0695	—·0098
2.	“	0·2	“	“	“	35	·1479	·0773	—·0020
3.	“	0·2	“	“	“	60	·1504	·0786	—·0007
4.	“	0·1	“	“	“	100	·1512	·0790	—·0003
5.	“	0·3	“	“	“	125	·1515	·0792	—·0001
6.	“	0·2	“	“	“	“	·1518	·0793	·0000
7.	“	0·2	“	“	“	“	·1519	·0794	+·0001
8.*	“	0·2	“	“	“	230	·1519	·0794	+·0001
Sn taken as SnCl <sub>4</sub> + HCl. gram.									
9.	“	0·2	5	“	“	40	·1502	·0785	—·0008
10.	“	0·2	6	“	“	125	·1514	·0791	—·0002
11.	“	0·2	5	“	“	130	·1516	·0792	—·0001
taken as SnCl <sub>2</sub> + HCl. gram.									
12.	“	0·2	6	“	“	125	·1529	·0799	+·0006
As. gram.									
13.	“	0·2	“	“	“	“	·1523	·0796	+·0003
Sb. gram.									
14.	“	0·2	“	2	“	“	·1518	·0793	·0000
As, Bi, Sb, Sn of each gram.									
15.	·0795	0·1	“	“	“	130	·1523	·0796	+·0001
16.	“	0·1	“	“	“	“	·1525	·0797	+·0002

stannous condition requires some care, because the bisulphite is often acted upon by a solution of stannous chloride, and a slight precipitate of sulphur thrown down from a mixture of these solutions upon standing. Unless, however, the amount of tin present is more than equivalent to the copper, it may be readily oxidized to the stannic state by merely adding the sulphocyanide before the bisulphite. The tin then acts as the reducing agent and a corresponding amount of copper is thrown down, after which bisulphite may safely be added and the rest

\* Final volume 300<sup>cm</sup>³.

of the copper precipitated. Determination 12 of the table was treated in this way, but as the tin present was much more than equivalent to the copper, some precipitation of sulphur probably took place, as the high result would indicate. In all such cases it would be better to convert the tin into the higher condition by some suitable oxidizing agent before precipitating the copper. Where the weight of copper present is not desired, but merely a separation between the copper and tin, this precaution is of course unnecessary.

Experiments 13 and 14, with arsenic and antimony respectively, show that for these metals the conditions which gave good results with bismuth and tin are equally favorable.

In experiments 15 and 16 arsenic, bismuth, antimony and tin were all present to the extent of 0.1 grm. of each metal, and the results for copper are still accurate.

If cuprous sulphocyanide is precipitated in the presence of a moderate amount of free acid, using a decided excess of ammonium sulphocyanide, as was done in the experiments of Table II, the tendency of the precipitate to pass through the filter during the washing may be almost completely overcome. It is, however, more likely to appear the more rapidly the precipitation has taken place, that is, the smaller the effective amount of acid present. This tendency, in the experience of the writer, need not greatly interfere with the accuracy of the determination. If only a light pressure of the filter pump is used, the washing may generally be completed and the small quantity of copper thus lost disregarded. A very distinct cloudiness in the filtrate may be caused by an amount of copper not greater than one or two tenths of a milligram, and the loss from this cause will seldom exceed this limit. Although, on the other hand, by precipitating in strongly acid solutions cuprous sulphocyanide can be thrown down in a form that filters well, the losses from incomplete precipitation may be many times greater.

The filtrates from determinations 15 and 16, the first of which showed a distinct cloudiness, were treated with great care for the recovery and estimation of the trace of copper present. The colorimetric method described in a previous article\* was used in determining the copper, and the amounts found were respectively 0.00034 and 0.00020 grm., these figures representing the sum of the mechanical loss with that due to the solubility of the precipitate in the acid solution.

Under the conditions of Table II, the estimation of copper in the presence of arsenic, bismuth, antimony and tin, either separately or in any combination, is obviously possible. To

\* This Journal, vol. xiii, 22.

separate copper from unknown quantities of bismuth, or from mixtures containing bismuth, the procedure would be as follows: Having the copper and bismuth in hydrochloric acid solution, add tartaric acid and, after diluting if necessary, determine by blank tests with small aliquot portions of the solution how much ammonium bisulphite can be added to the whole without precipitating the bismuth. Then keeping the bisulphite well within this limit, carry out the precipitation of the copper as already described, using a considerable excess of ammonium sulphocyanide. Where bismuth is absent, antimony and tin could be treated in the same way, but the latitude possible in the adjustment of the conditions is so much greater with these metals that preliminary tests would usually not be needed. For the separation from arsenic no precautions are required beyond a reasonable degree of acidity of the solution.

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