ART. XLIV.—*The Sulphocyanides of Copper and Silver in Gravimetric Analysis;* by R. G. VAN NAME.

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

Cuprous Sulphocyanide.

As early as 1854 attention was drawn by Rivot* to the possibility of estimating copper gravimetrically by weighing as cuprous sulphocyanide, and to the advantages which the process afforded in separating copper from other metals. Rivot's method of procedure consisted in dissolving the substance to be analyzed in hydrochloric acid, reducing the copper with hypophosphorous or sulphurous acid, and precipitating with potassium sulphocyanide. The precipitate dried at a moderate temperature was weighed as cuprous sulphocyanide and then as a control converted by ignition with sulphur into cuprous sulphide and weighed in that condition.

In his well known work upon quantitative analysis Fresenius in one place† denies the practicability of the direct weighing of copper as cuprous sulphocyanide on account of the tendency of the latter to hold water even when heated to the temperature of incipient decomposition. As authority for this statement he cites Claus,‡ who found 3 per cent of water in the precipitate after drying at 115°, and Meitzendorff, who gave the percentage of water under the same conditions as 1·54.

On a later page of the same volume,§ however, Fresenius, after a trial of the process which gave 99·66 per cent of the theory for copper, concludes that the method is practicable although apt to give low results, particularly in the presence of free acid.

The process was again recommended in 1878 by Busse,‖ who had employed it for the estimation of copper, both alone and in the presence of iron, nickel, zinc and arsenic, obtaining results very near the theory and plainly comparable with the figures obtained by afterwards igniting the cuprous sulphocyanide with sulphur in hydrogen.

In spite of the evident advantages for certain purposes of Rivot's method over other modes of determining copper, it has never come into general use. The chief reason for this has apparently been the difficulty and inaccuracy attendant upon the weighing of the precipitate upon dried paper filters, a process which can hardly be depended upon unless managed with extreme care.

* Comptes Rendus, xxxviii, 868.
‡ L. Gmelin Handb., iv, 472.
‖ Zeitschr. Anal. Chem., xvii, 53.
† Fresenius, 6th Aufl., i, 187.
§ 6th Aufl., i, 335.

In the experiments to be described this difficulty was avoided by performing the filtering and weighing upon asbestos in a perforated platinum crucible. The method of conducting a determination was as follows: A suitable quantity of a standard copper sulphate solution was run from a burette, diluted to a convenient volume, a few cubic centimeters of a saturated solution of ammonium bisulphite added, and the copper precipitated by an excess of ammonium sulphocyanide. The precipitate was allowed to settle, collected upon asbestos in a weighed crucible, washed with cold water and dried at 110° until no further loss of weight took place.

In Table I are given the results of a number of determinations made in this way. The copper sulphate solution was made up exactly decinormal and the standard confirmed electrolytically. As the ammonium sulphocyanide solution was slightly above decinormal, 13^{cm^3} represent a small excess (about one cubic centimeter) above the amount theoretically required to precipitate 25^{cm^3} of the copper sulphate solution. The ammonium bisulphite, which had been recently prepared by saturating aqueous ammonia with sulphur dioxide, was always used in sufficient quantity to give the liquid a strong and permanent odor of the latter.

TABLE I.

25^{cm^3} of N/10 $CuSO_4$ solution, equivalent to 0·0795 grm. Cu, taken for each experiment.

	H_2SO_4 concentrated. cm^3.	HNH_4SO_3 sat. sol. cm^3.	NH_4SCN approx. N/10. cm^3.	Final volume. cm^3.	Time of standing. hours.	Cu found. grm.	Error grm.
1.	none	5	13	68	¼	0·0795	0·0000
2.	"	3	13	66	48	0·0793	−0·0002
3.	"	3	25	78	½	0·0796	+0·0001
4.	"	3	25	78	12	0·0796	+0·0001
5.	1·5	10	13	85	12	0·0792	−0·0003
6.	1·5	8	13	105	48	0·0785	−0·0010
7.	1·5	3	25	85	4	0·0783	−0·0012
8.	1·5	5	25	85	21	0·0795	0·0000
9.	5	5	25	85	3	0·0797	+0·0002
10.	15	10	25	115	21	0·0793	−0·0002
	HCl concentrated cm^3.						
11.	10	5	25	100	20	0·0795	0·0000
12.	25	10	25	100	28	0·0784	−0·0011

When there is no free acid present the time of standing before filtration and the amount of the excess of ammonium sulphocyanide are practically without effect, as experiments 1 to 4 of the table show.

Experiments 5 to 10 were carried out in the presence of various amounts of free sulphuric acid up to 12 per cent of the total volume of liquid. The acid, at least within this limit, does not exert a sufficient solvent effect upon the cuprous sulphocyanide to interfere materially with the accuracy of the process, but it retards the precipitation, making it necessary to increase the time of standing before filtering in proportion to the amount of acid present. In several of these determinations the precipitation was visibly incomplete even after several hours standing. This effect of the acid, however, hardly shows in the results of the table because the standing was always prolonged until the copper appeared to be all down before filtering.

The low results of No. 7 was probably due chiefly to incomplete precipitation, although No. 9 shows that even with a much larger amount of acid precipitation may be complete within three hours. In general, however, it is safer to allow ample time (twelve hours or more) for the precipitation when there is much free acid present.

Comparison of Nos. 5 and 6, for which only a bare excess of ammonium sulphocyanide was used, with Nos. 7 to 12 shows an apparent advantage in the larger excess in the presence of acid. Hydrochloric acid, judging from the results of No. 11 and 12, has no greater disturbing influence than sulphuric acid, although in No. 12, where the concentrated acid constituted one-fourth of the entire volume, there was apparently a slight solvent action. The filtrate from this determination when concentrated to about 25$^{cm^3}$ and treated with potassium ferrocyanide gave a strong test for copper, as did also the filtrate from No. 6. Several of the other filtrates were tested in the same way, but none showed more than an insignificant trace of copper. No. 7, however, was not tested.

Table II contains the results of a series of experiments conducted as before, except that larger amounts of copper were

TABLE II.

	Cu taken. grm.	H_2SO_4 conc. cm^3.	NH_4SCN approx. N/10. cm^3.	Final volume. cm^3.	$Cu_2S_2(CN)_2$ found calc. as Cu. grm.	Error. grm.	Cu in filtrate.
1.	·3175	none	60	500	·3176	+0·0001	none
2.	·3175	"	60	500	·3177	+0·0002	"
3.	·3175	"	60	500	·3176	+0·0001	"
4.	·3175	10 HCl conc. cm^3.	100	500	·3175	0·0000	"
5.	·3175	20	100	500	·3165	−0·0010	distinct

employed. The copper sulphate solution was approximately N/5 and standardized by the battery. The solution of ammonium sulphocyanide was the same previously used and a considerable excess was employed in every determination. More than twice the amount theoretically required was used in every case where free acid was present, and at least twenty hours were allowed for the precipitation, which was made in cold, and as the table shows, rather dilute solutions. If the solution is too concentrated the copper is apt to be thrown down in a finely divided condition, making it hard to filter.

The time required to dry the cuprous sulphocyanide at 110° is in general from two to three hours. Heating much longer than this is not to be recommended, as a gradual increase in weight begins to take place, as is shown by the following example, which gives a series of weights of the same precipitate at different stages.

	$Cu_2S_2(CN)_2$. grm.	Calculated as Cu. grm.
After 2 hours at 110°	·6060	·3167
" 4 " " "	·6059	·3167
" 19 " " "	·6067	·3171
" 23 " " "	·6069	·3172

This tendency to increase in weight is, however, usually less marked than in the above example, and in any case need not interfere materially with the accuracy of the process unless the drying is prolonged far beyond the necessary length of time.

The method is easily handled and as the results of Tables I and II show is capable of considerable accuracy. From the nature of the process it is evident that it is much less likely to be interfered with by the presence of other metals than the other gravimetric methods for copper, and may therefore be directly applied with good results in many cases where the use of the electrolytic or the oxide method would involve a previous separation.

Silver Sulphocyanide.

The sulphocyanide of silver, unlike that of copper, is soluble in an excess of ammonium or alkali sulphocyanides and this fact prevents the use of the latter to precipitate silver for gravimetric estimation. The reverse process, however, the precipitation of a soluble sulphocyanide by an excess of silver nitrate, as will be shown by the experiments to be described, furnishes a convenient means of standardizing sulphocyanide solutions and in general for estimating thiocyanic acid.

When freshly precipitated the sulphocyanide of silver resembles the chloride in appearance, but when allowed to

stand a few hours becomes finely granular and is very easily filtered and washed. It may be safely dried to a constant weight upon an asbestos filter at 110°–120° but at a somewhat higher temperature is decomposed, leaving a residue of silver sulphide.

The determinations which are tabulated below were made as follows. Portions of 25^{cm^3} of an approximately decinormal solution of ammonium sulphocyanide were measured from a burette, diluted with 100^{cm^3} of water and silver nitrate added in excess. The precipitate was collected upon asbestos in a platinum crucible, washed with cold water and dried to a constant weight at 115° the drying requiring usually between two and three hours.

The filtering is facilitated by allowing a few hours for the precipitate to settle; but this is by no means essential, as it is easy with a little care to obtain a clear filtrate even when the filtering is performed at once.

The solution of ammonium sulphocyanide was prepared from a pure salt, especially tested and found free from choride. This point is of importance, as chlorine is a common impurity and its presence in any considerable quantity will vitiate the results.

TABLE III.

Final volume of liquid 150^{cm^3}

25^{cm^3} of NH_4SCN sol. equivalent to $25{\cdot}15^{cm^3}$ of $AgNO_3$ sol.

	NH_4SCN cm^3	$AgNO_3$ cm^3	Excess of $AgNO_3$ cm^3	AgSCN found. grm.
1.	25	25·3	0·15	.4372
2.	25	25·3	0·15	·4376
3.	25	25·4	0·25	·4373
4.	25	25·4	0·25	·4375
5.	25	30·4	5·25	·4382
6.	25	Rough excess.		·4366
7.	25	"		·4381
8.	25	"		·4373
9.	25	"		·4372
10.	25	"		·4369

In order that the effect of varying the excess of silver might be investigated, an approximately decinormal solution of silver nitrate was titrated against the ammonium sulphocyanide and the ratio between the two solutions determined. This silver nitrate solution was used for the first five determinations of Table III. For the rest the quantity of silver nitrate was not measured but regulated by the eye alone, thus making

the conditions the same as would be the case in practical use of the method.

These results are as uniform as could be expected considering the variations which would be produced by even very small errors in measuring out 25^{cm^3} of decinormal sulphocyanide solution. It is moreover clearly shown that there is no difference in the results whether a bare excess or a moderately large excess of the silver nitrate is used.

The mean of the values in the last column is ·4374, which is equivalent to ·2006 grm. of ammonium sulphocyanide for every 25^{cm^3} of the solution.

The standard of the sulphocyanide solution was also determined volumetrically by Volhard's process. The mean of four titrations carried out with great care against a standard silver nitrate solution gave as the standard ·2003 grm of ammonium sulphocyanide for 25^{cm^3} of solution. This difference between the standards as determined by the two methods (one part in 670) is much less than the variations which frequently appear between successive determinations by Volhard's method, under like conditions as to strength of solutions and amounts used. It is about equal to the error that would be produced in a single volumetric determination by a mistake of one drop in measuring one of the solutions, or of one half drop in the same direction on each.

It is therefore evident that the standard of a sulphocyanide solution obtained in the above way may be applied directly to the estimation of unknown amounts of silver by Volhard's method without sensible error.

To remove a possible doubt as to whether the silver sulphocyanide dried at 115° was entirely free from water, a number of electrolytic determinations of the silver contained in the previously weighed precipitates of Table III were made in the following way.

The perforated platinum crucible containing the silver sulphocyanide and asbestos was hung in a loop of heavy platinum wire and served as the anode. For the cathode a deep platinum dish of about 200^{cm^3} capacity was used. An ammonical solution of potassium cyanide was employed as the electrolyte and gave the best results when made up by dissolving 2 grams of potassium cyanide in 15^{cm^3} of strong ammonia and 15^{cm^3} of water. The crucible which served as the anode was filled with this solution in full strength, and the remainder was put into the platinum dish and diluted to the required volume with water. In this medium the silver sulphocyanide is slowly dissolved and diffuses through the asbestos felt into the space between the electrodes where the silver is deposited in the usual way. This diffusion is, however, aided but little if at

all by the current, and there is a tendency for traces of the silver to remain behind in the crucible. The current density employed was about ·0012 ampére per square centimeter of cathode surface and the time about twelve hours. After weighing the silver deposited, it was dissolved in nitric acid, precipitated by hydrochloric acid and weighed again as the chloride, giving a check upon the results.

Seven of the ten determinations of Table III were thus treated, but owing to the imperfections of the process the results were all slightly low, the worst showing a deficiency of ·0025 grm. of silver, an error of less than 0·9 per cent. The results of the two best of these determinations given below are, however, sufficient to prove the point in question, namely that the silver sulphocyanide dried at 115° has the theoretical constitution and contains no water. The numbers are those under which the determinations appear in Table III.

	AgSCN taken grm.	Calc. as Ag. grm.	Ag found by battery. grm.	Error. grm.	Weighed as AgCl. grm.	Calc. as Ag. grm.	Error. grm.
4.	·4375	·2844	·2839	—0·0005	·3765	·2834	—0·0010
10.	·4369	·2840	·2838	—0·0002	·3761	·2831	—0·0009

It is clear therefore that the estimation of sulphocyanides by precipitation with silver nitrate and direct weighing of the precipitate is wholly permissible. The method is extremely simple and, as has been shown, the results are quite accurate.

In conclusion I wish to thank Prof. F. A. Gooch for many valuable suggestions given during the course of this investigation.