XC.—*Separation of Cadmium from Zinc as Sulphide in the presence of Trichloroacetic Acid.*

By JOHN JACOB FOX.

THE usual quantitative methods of separating cadmium from zinc, other than electrolytic, depend on the use of mineral acids of strength sufficient to prevent the precipitation of zinc sulphide. The most convenient acids for this purpose are hydrochloric and sulphuric, but the quantity of these acids present must be limited to a maximum of about 1 gram of hydrogen chloride or 10 grams of sulphuric acid per 100 c.c. If these quantities are exceeded, some of the cadmium remains in solution and cannot be precipitated by hydrogen sulphide. Further, if the quantity of hydrogen chloride is less than 0.9 gram per 100 c.c., some zinc sulphide falls out of solution together with the cadmium sulphide. To ensure complete separation when much cadmium is present in a solution, three precipitations of the cadmium sulphide are necessary, and at the same time the amount of acid must be limited as mentioned above. For this purpose sulphuric acid is more convenient than hydrochloric, but there is considerable risk of keeping small amounts of cadmium in solution.

To avoid the inconvenience of several dissolutions and precipitations of the cadmium sulphide, an organic acid of the same order of strength as mineral acids was sought for, and finally trichloroacetic acid was selected. The strength of this acid as deduced from its degree of ionisation compared with hydrochloric acid, at a concentration of $1/32$ normal, is in the ratio of about 1 to 1.08. This ratio approaches equality at greater dilutions, and it may be assumed that at much greater concentrations than $1/32$ normal, trichloroacetic acid is still less dissociated than the corresponding equivalent of hydrochloric acid. The precipitation of zinc sulphide in presence of trichloroacetic acid bears this out. For if a solution containing about 1.0 gram of zinc and 6.1 grams of trichloroacetic acid per 100 c.c. is taken, a precipitate of zinc sulphide is formed on passing hydrogen sulphide, but the equivalent quantity of hydrochloric acid is sufficient under these conditions to prevent anything more than traces of zinc sulphide from being precipitated.

If, however, with the same concentration of zinc a solution is used containing 11 grams of trichloroacetic acid per 100 c.c., no precipitation of zinc sulphide results.

It is to be noticed in this connexion that the concentration of the zinc is also a determining factor in the precipitation of zinc sulphide. With solutions containing 0.1 gram of zinc per 100 c.c., as little as 4.5 grams of trichloroacetic acid, or 1 gram of hydrogen chloride, are sufficient to prevent the formation of zinc sulphide.

In general, concentrated solutions of trichloroacetic acid are not dissociated to the same extent as hydrochloric acid. This is of importance as regards the precipitation of cadmium sulphide, for strong solutions of trichloroacetic acid do not appear to exercise any effect in preventing the complete precipitation of cadmium sulphide, even when the concentration of the cadmium is small, as the following experiments show:

Volume of solution in c.c.	Grams of trichloroacetic acid present.	Gram of cadmium used.	Gram of cadmium obtained as cadmium sulphide.
15	6.70	0.0051	0.0050
55	16.74	0.0051	0.0050
105	33.48	0.0051	0.0050
200	34.12	0.1023	0.1024

To test the value of the reagent in the separation of zinc and cadmium, determinations were made on mixtures of solutions of zinc sulphate and cadmium chloride. It was found that when the proportion of zinc was large as compared with cadmium, and the concentration comparatively high, the separation of the two metals

was not quite complete, owing to some zinc being carried down with the cadmium sulphide if the amount of the latter were more than a few milligrams. On redissolving and reprecipitating, a complete separation resulted in all the cases examined.

	Vol. of solution in c.c.	Grams of zinc present.	Gram of cadmium present.	Grams of trichloroacetic acid present.	Gram of cadmium obtained.
1.	120	1.240	0.0512	13.4	0.0512
2.	250	4.552	0.0512	67.0	0.0510
3.	100	1.138	0.0512	12.2	0.0507
4.	200	0.124	0.2236	23.6	0.2245
5.	150	0.0552	0.0466	15.0	0.0466

Experiments 1, 2, and 3 needed two precipitations, experiments 4 and 5 one only.

In the ordinary examination of metals for cadmium, the addition of trichloroacetic acid would be objectionable for the separation of the sulphides of Group II., since it might interfere with the complete precipitation of Group III. metals. To avoid this, the first partial separation of cadmium and zinc may be effected by using 1 gram of hydrogen chloride per 100 c.c. of solution. Some zinc sulphide will be precipitated together with the Group II. sulphides. The second separation can then be effected by adding to the neutral solution of zinc and cadmium an amount of trichloroacetic acid sufficient to give a solution containing at least 10 grams of this acid per 100 c.c. A large excess of trichloroacetic acid above 10 per cent. may be used without interfering with the precipitation of cadmium sulphide (see experiments above). The zinc may be precipitated in the filtrate from the cadmium sulphide by adding ammonia and ammonium sulphide, the presence of ammonium trichloroacetate being without effect on the precipitation of zinc sulphide.

Thus, 50 grams of crystallised zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) corresponding to 11.380 grams of zinc, and 0.4128 gram of crystallised cadmium chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$) corresponding to 0.2116 gram of cadmium, were dissolved in water and diluted to 350 c.c., there being 1 per cent. of hydrogen chloride present. The sulphide precipitate obtained was redissolved and neutralised; 17.3 grams of trichloroacetic acid were added, and the whole diluted to 100 c.c. The cadmium obtained as cadmium sulphide was 0.2119 gram, and the filtrate from this gave 0.1546 gram of zinc.

Similar results were obtained when trichloroacetic acid was used for both precipitations of cadmium sulphide, but when the amount of zinc present was small compared with the cadmium, one treatment was sufficient for practically complete separation of the two metals.

In some experiments it was found that when the concentration of trichloroacetic acid was high (50 per cent. and more) the cadmium was not immediately precipitated on passing hydrogen sulphide. The precipitation was readily started in such cases by the addition of a few drops of a dilute solution of ammonia.

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