931. *A New Reagent for the Determination of Antimony.*

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Antimony can be determined gravimetrically by precipitation as dichlorobisethylenediaminocobaltic hexachlorostibnate which provides the favourable conversion factor of 0·2098. The effect of a selected number of other ions has been examined. Arsenic, copper, and zinc up to 200 mg., cadmium, iron, mercury, and tin up to 100 mg., and bismuth up to 10 mg. are without effect. Lead interferes even at a concentration of 0·5 mg. Satisfactory recoveries have been obtained over the range 1—50 mg. of antimony.

The two commonest forms in which antimony is ultimately weighed in analysis are the tetroxide and the trisulphide, but both involve unfavourable factors and it is necessary to use carefully controlled conditions to obtain products of correct stoicheiometric composition.

When *trans*-dichlorobisethylenediaminocobaltic chloride is added to a hydrochloric acid solution containing quinquevalent antimony, dichlorobisethylenediaminocobaltic hexachlorostibnate is precipitated (Pfeiffer and Tapauch, *Z. anorg. Chem.*, 1906, **49**, 438), which is insoluble in water and hydrochloric acid. The antimony content being only 20·98%, the compound is a convenient form in which to separate antimony if its formation is quantitative, and this we have found to be the case for 1—50 mg. of antimony. The effect of a number of selected metals has also been examined.

Effect of Standing-time and Volume of Solution.—The time of standing after precipitation and the final volume of the solution were varied in order to establish the most favourable conditions for quantitative precipitation. Complete precipitation is obtained in 2 hours

in a final volume of 50 ml., or after 6 hours in 100 ml., but we considered it preferable to standardise the method by use of the shorter time. Excess of reagent made no apparent difference to the recoveries; hence, a standard amount of 10 ml. of 2N-hydrochloric acid containing 0·2 g. of reagent was used for the range examined.

The precipitate was anhydrous and could be dried without loss or decomposition at 100°. Washing with an organic solvent followed by air-drying could not be used since the precipitate was very soluble in acetone and to a smaller extent in ethanol and ether.

Determination of Antimony in Solution.—Amounts of antimony ranging from 1 to 50 mg. were determined under the above conditions. The results (Table 1) show satisfactory recoveries over this range.

TABLE 1. *Recoveries of antimony (1—50 mg.) in 50 ml. of solution.*

Sb present (mg.)	1·19	2·37	5·94	11·87
Sb found (mg.)	1·12, 1·18	2·33, 2·37	5·95, 5·91	11·88, 11·84
Sb present (mg.)	23·74	47·48	59·35	
Sb found (mg.)	23·75, 23·69	47·50, 47·42	59·38, 59·32	

Effect of oxidising agents other than chlorine. In Pfeiffer and Tapauch's method (*loc. cit.*) for the preparation of the complex antimony compound, oxidation to quinquevalent antimony is effected by bubbling chlorine through the solution, this oxidant presumably being chosen to avoid dilution of the solution with concomitant reduction of acidity. We used this method, but also sought a more convenient oxidant; several were tried but only nitric acid yielded satisfactory results (see Table 2).

TABLE 2. *Recoveries in the presence of oxidants other than chlorine.*

Oxidant	Amount	Sb present (mg.)	Sb found (mg.)
H_2O_2 (100-vol.)	2 ml., 3 ml.	23·74	21·15, 21·00
MnO_2	100 mg., 200 mg.	23·74	19·97, 20·12
$KMnO_4$	100 mg., 200 mg.	23·74	21·04, 19·82
NaOCl (10% w/v of av. Cl_2)	2 ml., 3 ml.	23·74	18·46, 19·12
HNO_3, conc.	2 ml., 3 ml.	23·74	23·76, 23·68
,, ...	2 ml., 3 ml.	1·19	1·10, 1·17
,, ...	2 ml., 3 ml.	59·35	59·40, 59·32

TABLE 3. *Recoveries in the presence of other metals* (23·74 mg. of Sb present).

Metal	Wt., mg.	Sb found (mg.)	Metal	Wt., mg.	Sb found (mg.)	Metal	Wt., mg.	Sb found (mg.)
As	200 *	23·74, 23·68	Cd	100 †	23·77, 23·70	Hg	100 †	23·72, 23·78
Zn	200 *	23·70, 23·74	Fe	100 †	23·69, 23·75	Bi	10 ‡	23·78, 23·68
Cu	200 *	23·69, 23·75	Sn	100 †	23·76, 23·71	Pb	0·1 §	23·78, 23·76

* Highest amount examined. † Above 100 mg. coprecipitation occurred, and above 150 mg. a visible precipitate formed. ‡ Above 10 mg. coprecipitation occurred, and above 20 mg. a visible precipitate formed. § Coprecipitation occurred above this limit although no visible precipitate appeared immediately, even when moderate concentrations of lead were present alone. This precipitation of lead, however, is not quantitative.

Effect of other metals. The results in Table 3 show that arsenic, zinc, and copper up to 200 mg. (the highest amounts added), cadmium, iron, tin, and mercury up to 100 mg., and bismuth up to 10 mg. have no effect. Lead interferes at all concentrations. The reagent is therefore fairly selective.

Attempts to improve the limits of the interferences by addition of oxalate, tartrate, citrate, or fluoride ions failed. Ethylenediaminetetra-acetic acid could not be used as it is insoluble under the strongly acid conditions used for the precipitation. Accordingly, when metals are present in amounts likely to cause interference, a preliminary separation is necessary. The dithionite (hydrosulphite) method (Evans, *Analyst*, 1929, **54**, 395) appears suitable for this purpose since, of the metals it fails to separate, cadmium (in moderate amounts), arsenic, and copper are not precipitated by the reagent, and lead may be removed by a preliminary separation as the sulphate.

Applications of the method. Antimony was determined in a white metal having the certified composition: Cu, 4·30; Zn, 0·40; Sn, 83·7; Pb, 4·15; Sb, 7·45%. Before the dithionite procedure was applied to the alloy, the efficiency of the complete process

was checked on a standard solution containing only antimony. The separated metal was dissolved in hydrochloric acid containing a small quantity of nitric acid, and the deter-

TABLE 4. *Determination of antimony after precipitation with sodium dithionite.*

	Sb present	Sb found		Sb present	Sb found
Pure solution	23·74 mg.	23·70, 23·78 mg.	White metal	7·45%	7·41, 7·46%

mination completed by the standard procedure. The results were satisfactory (Table 4) and the white metal was then analysed by the same procedure. Satisfactory recoveries were obtained (Table 4).

EXPERIMENTAL

Preparation of Reagent.—*trans*-Dichlorobisethylenediaminocobaltic chloride hydrochloride was prepared by Bailar's method (*Inorg. Synth.*, 1946, **2**, 223), the heating to constant weight in an oven being omitted. The salt was purified by dissolving it in water, adding a large excess of concentrated hydrochloric acid, and evaporating until crystallisation started.

Recoveries.—A hydrochloric acid solution of antimony was prepared from trichloride which had been recrystallised several times. The antimony content was determined, after sulphur dioxide reduction to ensure that all was in the tervalent state, by oxidimetric titration, and found to be 2·374 mg. per ml.

A freshly prepared solution of the reagent (0·2 g. in 10 ml. of 2N-hydrochloric acid) was added to a measured volume of the antimony solution which had previously been saturated with chlorine by passage of the gas for about 15 minutes. After a suitable time, the precipitate was filtered off on a No. 4 sintered-glass crucible, washed with water until the washings were colourless, and dried at 100—110° to constant weight (an hour was ample).

Recommended Procedure.—The solution must consist of concentrated hydrochloric acid, and antimony of concentration 1—50 mg. per 50 ml. Chlorine, from a cylinder, was bubbled through the solution; or alternatively, about 3 ml. of concentrated nitric acid were added, and the solution warmed for a few minutes and cooled quickly. 10 Ml. of the above reagent solution were added, the mixture was set aside for 2 hours with occasional stirring, and the precipitate treated as in the preceding paragraph (factor, 0·2098).

Determination of Antimony in White Metal.—1·0 G. of the metal was dissolved in 8N-nitric acid (40 ml.), concentrated sulphuric acid (3 ml.) added, and the mixture evaporated to fuming in a porcelain basin and then cooled; the sides of the basin were washed down with distilled water and the evaporation was repeated. Distilled water (50 ml.) was added to the cooled mixture, which was stirred well and set aside for an hour. The lead sulphate was then filtered off on a sintered-glass crucible, washed with a little dilute sulphuric acid (1 : 20), and dissolved in concentrated ammonium acetate solution poured through the filter. Although no perceptible residue remained, the filter was then washed with concentrated hydrochloric acid (15 ml.) containing nitric acid (5 ml.), and the solution combined with the original solution and the lead sulphate washings. 20 Ml. of a citric acid solution (100 g. in 200 ml. of water) were added, and the mixture was made slightly alkaline with ammonia. A saturated solution of potassium cyanide (previously treated with bromine until it gave no violet colour with a solution of sodium nitroprusside) was added to the ammoniacal solution until the blue colour was discharged, followed by a further 30 ml.; 75 ml. of 20% ammonium chloride solution and sodium dithionite (10 g.) were added, and the solution heated just to boiling and kept on the steam-bath for an hour. More dithionite (5 g.) was added, the solution cooled in running water and filtered through a pulp filter, and the precipitated antimony washed with a cold solution containing 20 ml. of saturated potassium cyanide solution, 4 g. of ammonium chloride, and 2 g. of sodium dithionite in 400 ml. The filter was transferred to a beaker and covered with concentrated hydrochloric acid (100 ml.) containing some chlorine, and the pulp broken up and stirred till all the antimony had dissolved. The solution was filtered, and the antimony determined as described above.

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