Radiometric Determination of Small Amounts of Antimony

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Dichlorobisethylenediamine cobaltic hexachlorostibinate, the insoluble precipitate obtained by adding *trans*-dichlorobisethylenediamine cobaltic chloride to a hydrochloric acid solution of quinquevalent antimony, was reported first by Pfeiffer and Tapauch[1] in 1906. The reaction can be written as

$$\underset{\left\{\substack{\textit{trans}\text{-Dichlorobisethylene-}\\ \text{diamine cobaltic chloride}}\right.}{[Co(en)_2Cl_2]Cl}+(Sb^{V}Cl_6)^- \longrightarrow \underset{\left\{\substack{\text{Dichlorobisetylenediamine}\\ \text{cobaltic hexachlorostibinate}}\right.}{[Co(en)_2Cl_2]\ (Sb^{V}Cl_6)}+Cl^-$$

Recently Belcher and Gibbons[2] succeeded in gravimetric determination of antimony by means of the above-mentioned reaction. The scheme of the method is given in Table Ia. According to their paper, the lower limit of determinable amount is 1mg. antimony, and the determination is interfered with seriously with a very small amount of lead.

In the present paper, a radiometric method of determination of $(1-0.06)$ mg. antimony by radioactive *trans*-dichlorobisethylenediamine cobaltic chloride labelled with cobalt-60 is described. The present method consists of the precipitation of antimony and the washing with water according to the procedure given by Belcher et al. and the dissolution of the precipitate into acetone followed by the measurement of radioactivity. (Table Ib). Owing to the treatment with acetone in which antimony and lead salts are separated, this method is not disturbed

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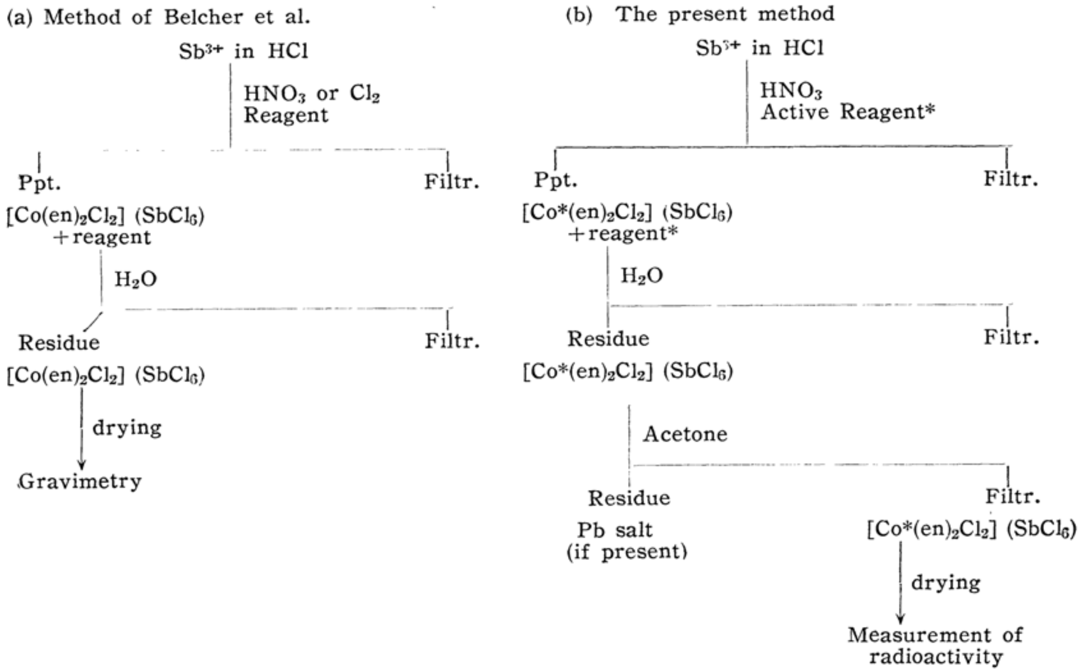
[1] P. Pfeiffer und M. Tapauch, *Z. anorg. Chem.*, **49**, 438 (1906).

[2] R. Belcher and D. Gibbons, *J. Chem. Soc.*, **1952**, 4775.

TABLE I
SCHEMES OF DETERMINATION OF ANTIMONY



even in the presence of small amounts of lead.

(1) Selection of Washing Solution and Solvent.—Before beginning the radiometric study, nonactive dichlorobisethylenediamine cobaltic chloride,[3] antimony and lead salts[4] of the complex are prepared and their behaviors against some kinds of organic solvents or mineral acids are checked.

The results are summarized in Table II.

TABLE II
BEHAVIORS AGAINST ORGANIC SOLVENTS AND MINERAL ACIDS

	Reagent	Sb salt	Pb salt
water	soluble	insoluble	partial decomposition
conc. HCl.	slightly soluble	insoluble	slightly soluble
hot dil. HNO_3	—	—	soluble with decomposition
acetone	insoluble	soluble	insoluble
ethyl alcohol	insoluble	slightly soluble	insoluble
ethyl ether	insoluble	slightly soluble	insoluble
chloroform	insoluble	slightly soluble	insoluble

As can be seen from the table, the washing with water is suitable in separating precipitant and its antimony salt, and acetone is available to dissolve the antimony salt leaving the lead salt undissolved. These different behaviors against water and acetone are used as the basis of the following procedure.

(2) Radiometric Determination of (1—0.06) mg. Antimony.—Various amounts of antimony are taken and radioactive $[Co^*(en)_2Cl_2]$ $(SbCl_6)$ is precipitated; this is dissolved in acetone according to the following procedure. The relation between the relative intensity of the radioactivity of the residue of acetone extracts and the amounts of antimony taken is investigated.

(a) Preparation of the Radioactive Reagent.—Radioactive precipitant $[Co^*(en)_2Cl_2]Cl$ is prepared from radioactive cobalt chloride (about 0.2 milli curie Co^{60}/g. $CoCl_26H_2O$) according to the usual method[3], the heating to constant weight in an oven being omitted. This reagent is reserved in solid state to prevent the decomposition in an aqueous solution.

(b) Procedure.—1.5 cc. of the sample solution is taken in a microbeaker. The solution must be concentrated hydrochloric acid containing 1 to 0.06 mg. antimony. Three drops of concentrated nitric acid are added, and the solution is warmed for a few minutes and cooled quickly. In this treatment anti-

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[3] W. C. Fernelius, "Inorganic Synthesis", Vol. II, McGraw-Hill Book Company, New York, N. Y. (1946), p. 222; Tupizina, dissertation, Zürich, 1912.

[4] The antimony salt is prepared according to Belcher's method. The lead salt is prepared similarly from a saturated hydrochloric acid solution of lead nitrate. The composition of the lead salt is not known.

mony is oxidized to the quinquevalent state. 0.23 to 0.3 cc. Of a freshly prepared solution of the radioactive reagent (0.02 g. in 1 cc. of 2 N-hydrochloric acid) are added, and the mixture is set aside over night with occasional stirring. The precipitate is filtered off with a filter tube, washed with three or four portions of water until the washings become colorless, and dissolved in acetone. The acetone solution is transferred to a glass dish and evaporated under an infra-red lamp.

The radioactivity of the residue is measured by a Lauritsen electroscope, made by the Scientific Research Institute, Tokyo, and compared with that of a standard of cobalt-60.

TABLE III

RESULTS OF (2)

microg. Sb (taken)	Relative Intensity of Radioactivity, $(d/m)/(d/m)_s$	$(d/m)/(d/m)_s$ / microg. Sb.	% Deviation
0.0	0.000	—	—
67.0	0.180	2.69	−2.53
136.0	0.369	2.71	−1.81
199.9	0.527	2.64	−4.35
268.0	0.756	2.82	2.17
334.5	0.935	2.80	1.45
342.5	0.973	2.84	2.80
469.0	1.340	2.86	3.62
670.0	1.780	2.66	−3.62
682.0	1.910	2.80	1.45
945.0	2.660	2.81	1.81
	Mean	2.76	±2.57

The activity of the standard, $(d/m)_s$, is about $14d/m$. It shows slight variations according to the daily variation of the sensitivity of the Lauritsen electroscope.

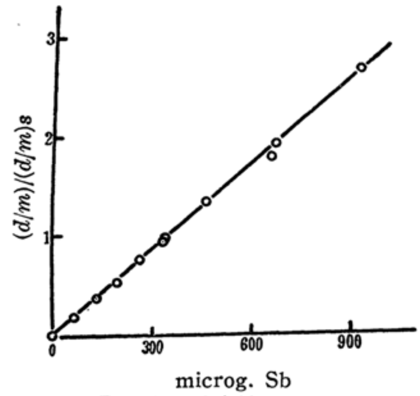

Fig. 1. Results of (2b).

(c) **Results Obtained.**—The results of experiments are shown in Table III and Fig. 1. The strictly linear relationship between the relative radioactivity and the amount of antimony taken is shown in Fig. 1, so we can conclude that 1 to 0.06 mg. antimony is determinable according to the above procedure.

If the reagent with much stronger specific activity is used, the determination of much smaller amounts of antimony may be successful. However it is so dangerous to handle the reagent of such high specific activity in solid state (as described above the reagent must be dissolved just before use). that we gave up such experiments.

(3) **Determination of Antimony in the Presence of Lead.**—Solutions which contain antimony as well as lead, are treated according to the procedure given in (2b). As can be seen from the results given in Table IV, the presence of a small amount of lead does not disturb the determination unless the ratio of lead to antimony is much less than one. However the errors are always negative and tend to increase as the ratio increases. Finally in two determinations in which the ratios are about one or more than one, errors become seriously negative.

TABLE IV

DETERMINATION OF ANTIMONY IN THE PRESENCE OF LEAD

microg. Pb (present)	microg. Sb (taken)	microg. Sb (found)	% Error
22.9	201	198	−1.5
22.9	201	199	−1.0
34.4	201	193	−3.9
114.5	397	394	−0.8
114.5	268	258	−3.7
114.5	130	95	−26.7
229	271	263	−2.9
229	268	261	−2.7
229	131	80	−39.1

Negative errors will be caused by the coprecipitated lead salt which prevents complete dissolution of antimony salt in acetone.

Roughly speaking, the present radiometric method is available in determining antimony in the presence of an almost equal amount of lead, while Belcher's gravimetric method is disturbed by 0.1 mg. lead in the determination of 23.74 mg. antimony.

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