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DETERMINATION OF ANTIMONY BY SUB- AND SUPER-EQUIVALENCE METHOD OF ISOTOPE DILUTION ANALYSIS

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Trace amount of antimony (0.45 ~ 0.28 μg/ml) has been determined by sub- and super-equivalence method in isotope dilution analysis. Substoichiometric amount of Sb(III) was oxidized to Sb(V) by potassium dichromate and separated by BPHA (in $CHCl_3$) extraction. It has been found that the determination can be performed within an accuracy of 2% in the wide region of acid concentration.

The method named sub- and super-equivalence method in isotope dilution analysis was proposed in 1974 by Klas et al.[1)] A few papers were reported with respect to the application of this method.[2-5)] Recently, trace amount of antimony was determined in our laboratory by means of redox substoichiometry in isotope dilution analysis[6,7)] (abbreviated as Redox Subst-IDA in this paper). In the present work, the sub- and super-equivalence method in isotope dilution analysis using a redox reaction (abbreviated as Redox SSE-IDA in this paper) was applied to the determination of antimony, and the results of the analysis were compared with those obtained by means of Redox Subst-IDA.

Principle ; First and second series are necessary for the determination of the sample. In the first series, each aliquot contains the same amount of the sample(X) labeled with isotope(A). In the second series, each aliquot contins a ξ times greater amount than first series. The first series are isotopically diluted by the addition of incremental amounts of carriers(Y_i). The second series are not. All aliquots of both series are brought to the same volume and acid concentration. The concentration of one of the aliquots of the first series is equal to that of the second series when the amount of the carrier was appropriately selected. The same amount of the reagent which reacts with the species to be analyzed are added to the all aliquots. The species produced by the reaction are separated and the activities are measured. M_i and M_o are the amounts of the species separated from the first and the second series, respectively. A_i and A_o are the activity of them. The specific activity is not changed before and after separation. Therefore,

The specific activity of the first series : $\dfrac{A}{X + Y_i} = \dfrac{A_i}{M_i}$ (1)

The specific activity of the second series : $$\frac{\xi A}{\xi X} = \frac{A_o}{M_o} \qquad (2)$$

From equations (1) and (2), equation (3) is obtained.

$$\frac{A_o}{A_i} = \frac{M_o}{M_i}\frac{1}{X}Y_i + \frac{M_o}{M_i} \qquad (3)$$

As the same concentration point exists in both series (in this case $X + Y_i = \xi X$), separated amounts are same at the point (in this case $M_i = M_o$) even if the spesies do not react with the reagent stoichiometrically. The activity ratio of the amounts separated from both series is equal to ξ at the same concentration point, hence the equation (3) can be reduced as follows.

$$X = \frac{Y_i}{\xi - 1} \qquad (4)$$

Accordingly, X is able to be obtained from the value of Y_i at the point ($A_o/A_i = \xi$) on the curve (A_o/A_i vs. Y_i) as shown in Fig. 1 (in this case $\xi = 2$)

Reagent : The antimony carrier used was prepared from reagent grade Sb_2O_3(99.999%). All chemicals used were of reagent grade.
Standard Sb(III) solution ; 11.9 μg Sb(III)/ml in 5.6N HCl was obtained by diluting 119 μg Sb(III)/ml in 5.6N HCl just before preparing a tracer solution.
Preparation of ^{125}Sb(III) tracer[8] ; 200 μl of ^{125}Sb (processed unit, ca. 1.3 μci/100 μl in 6N HCl) was mixed with 10 ml of conc. HCl and refluxed for 60 min in order to obtain ^{125}Sb(III). The ^{125}Sb(III) tracer solution (in 6N HCl) was always prepared just before labelling the sample solution. The labeled sample solution was stored in a brown-colored bottle and was kept in a dark place in order to avoid self- and photo-oxidation[8] of ^{125}Sb(III). The solution was stable for a week at the least for the analysis.

Procedure ; Two series of sample solutions were prepared for the analysis. (1) First series ; 0, 0.1, ---0.5 ml of inactive Sb(III) carrier solutions (11.9 μg Sb(III)/ml in 5.6N HCl) were placed in six brown-colored test tubes (30 ml) equiped with ground-in stoppers. Then, 0.5, 0.4, ---0 ml of 5.6N HCl were added to them. Thereafter, 0.3 ml of 5.8N HCl were added to them. Lastly aliquots (0.3 ml) of the sample to be analyzed (labeled with ^{125}Sb(III), in 5.8N HCl) were mixed with them. (2) Second series ; 0.5 ml of 5.6N HCl were placed in three test tubes in order to obtain three data for averaging, then 0.6 ml of the aliquots of the same labeled sample were mixed with them. (3) Oxidation and separation ; Acid concentrations of all solutions of both series were varied in the range of 0.52∼5.40N HCl (total volumes 12.2∼2.2 ml) by addition of the dil. HCl. After all the solutions of both series were brought to the same volume and acid concentration, $K_2Cr_2O_7$ solutions (5×10^{-4}N, 0.1 ml) were added, followed by standing for 15∼30 min to complete oxidation. The unreacted Sb(III) was extracted from all the aqueous solutions, which were adjusted to the same volume and to 0.8∼1.0N HCl concentration, with 0.05M BPHA[8] (N-benzoyl-N-phenylhydroxylamine) in $CHCl_3$.

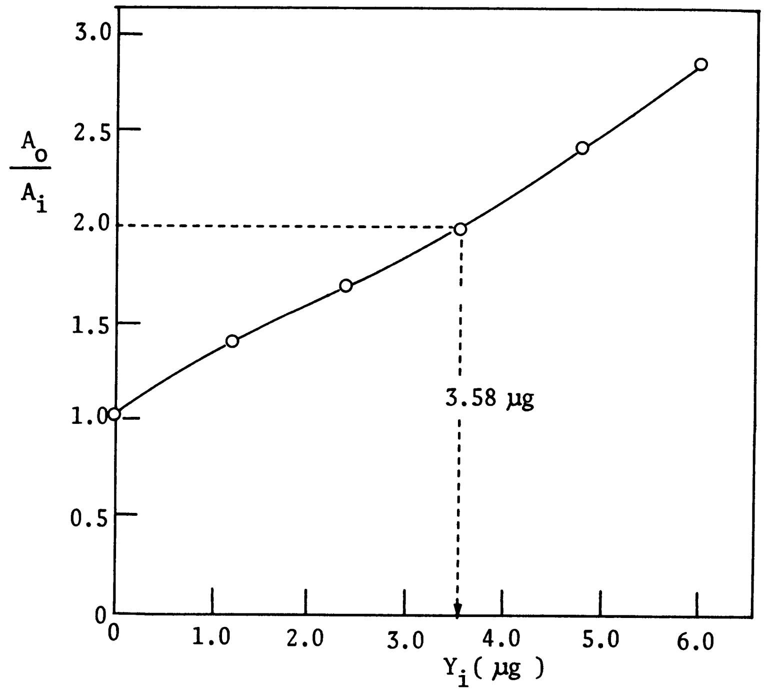

Fig. 1. Determination of Sb(III) by Redox SSE-IDA
[total Sb(III)=3.57 μg, [Sb(III)]=0.64~1.70 μg/ml
$[K_2Cr_2O_7]=5\times10^{-4}N$---0.1 ml, oxidized at 2.07N HCl]

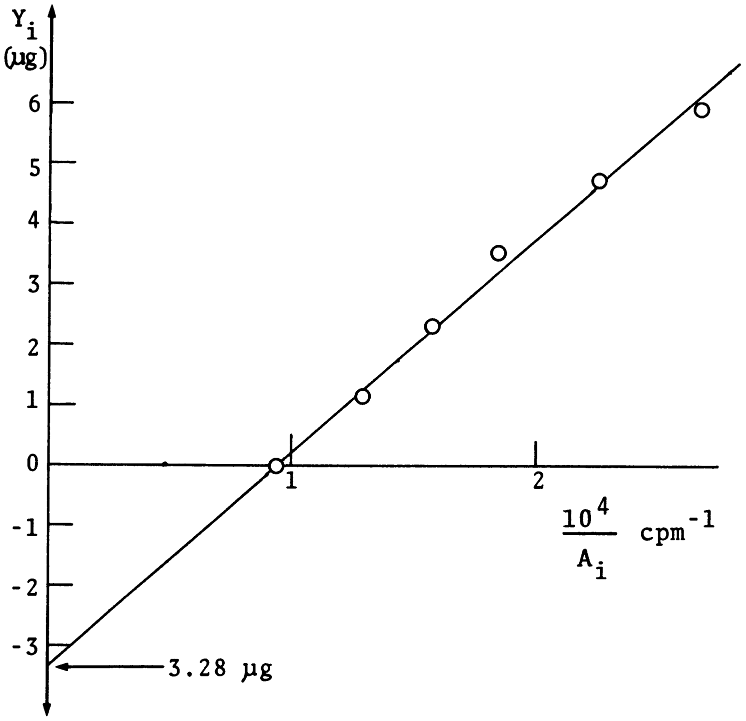

Fig. 2. Determination of Sb(III) by Redox Subst-IDA
[total Sb(III)=3.57 μg, [Sb(III)]=0.64~1.70 μg/ml
$[K_2Cr_2O_7]=5\times10^{-4}N$---0.1 ml, oxidized at 2.07N HCl]

Activity of definite volume of the aqueous phase of both series was measured by use of a NaI well-scintillation counter.

Fig. 1 shows an example of the determination of Sb(III) by Redox SSE-IDA. The determination of Sb(III) was also performed by the ordinary carrier variation method of Redox Subst-IDA, using the data of the first series (Fig. 2). As shown in two figures, it is possible to estimate X by the method in Fig. 1 even if the straight line is not obtained. However, the value of the intercept in Fig. 2 becomes erroneous when linearity was not observed. From the results listed in a Table. 1, it can be clearly seen that standard deviations of the analytical value obtained by Redox SSE-IDA are smaller than those obtained by Redox Subst-IDA. Fig. 3 shows the effects of hydrochloric acid concentration on radiometric titration[9]. The errors of SSE-IDA are smaller than 2% in a wide region of acid concentration, whereas the errors of redox radiometric titration exceed 5% in the region of the same acid concentration.

From these results obtained, it has been found that this method for antimony analysis can be applied in a wide region of acid concentration with high accuracy.

Table. 1. Results of Determination of Antimony by Redox SSE-IDA Method

HCl Concn. (N)	Amounts used for analysis** (μg)	Found (μg)	Standard Deviation (%)	Error (%)	Number of Determination
0.52	3.57	3.58	0.56	+0.28	3
0.77	〃	3.58	1.68	+0.28	5
0.99	〃	3.53 (3.68)*	0.84 (1.09)*	-1.12 (+3.08)*	5
2.07	〃	3.57 (3.44)*	0.84 (10.17)*	0.00 (-3.64)*	5
3.07	〃	3.63	1.65	+1.68	5
3.77	〃	3.63 (3.81)*	1.93 (12.86)*	+1.68 (+6.72)*	5
4.69	〃	3.54	1.69	-0.84	5
5.40	〃	3.58	2.50	+0.28	5

* : Carrier variation method of Redox Subst-IDA

** : Determined by $KMnO_4$, $KBrO_3$ titration

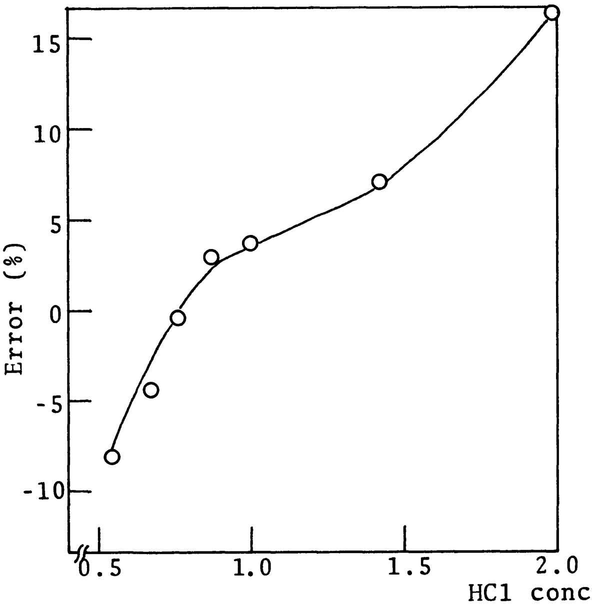

Fig. 3. Effect of HCl concn. on Redox Radiometric Titration.
[total Sb(III)=3.7 μg, [Sb(III)]=0.61 μg, $K_2Cr_2O_7$ (2~8x10^{-5}N, 1 ml)]

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