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Activation Analysis of Antimony in Tin Based on an Internal-Monitor Method using Thermal Neutrons

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An internal-monitor method proposed previously has been applied to the determination of trace amounts of antimony in tin by activation with thermal neutrons. After the antimony activity is chemically separated from the irradiated sample, the γ-ray spectrum corresponding to a mixture of ^{124}Sb and ^{125}Sb formed by the β^- decay of ^{125m,125}Sn is measured. Synthetic mixtures of antimony and tin with known weight ratios have been prepared to check the accuracy of the method. Good proportionality has been obtained between the ratios of the ^{124}Sb to ^{125}Sb activities and the ratios of the concentrations. By using this relationship, antimony analysis can easily be carried out. The content of antimony in a sample of tin down to 0.2 ppm can be determined with a relative error of $\pm 2\%$.

In cases of thermal neutron activation, where the atomic number of the element to be analyzed is higher by one unit than that of the matrix element and where the nuclear characteristics of the (n, γ) reaction product of the former and secondary β^- decay product from the latter are favorable for subsequent γ-ray spectrometric measurements, it is possible to determine the content of the element in question on the basis of the activity ratios of both radioactive species.

In a previous report,(1) the principles and applicability of this internal-monitor method to the determination of a trace amount of silver in palladium was described. By this method, errors which arise from neutron flux irregularities and self shielding effects can be avoided, and no corrections for chemical yield are neccessary. In the present work, this method was further applied to the determination of trace amounts of antimony in tin by means of thermal neutron activation.

Method of Determination

Antimony can be determined by γ-ray spectrometry through the induced ^{122}Sb or ^{124}Sb activity in an irradiated sample. Tin, on the other hand, gives nine radionuclides as (n, γ) reaction products: ^{113m}Sn, ^{113}Sn, ^{117m}Sn, ^{121m}Sn, ^{121}Sn, ^{123m}Sn, ^{125m}Sn and ^{125}Sn. However, radionuclides of present

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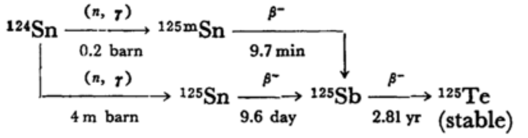
1) Y. Oka, T. Kato, H.-T. Tsai and K. Nomura, This Bulletin, **41**, 329 (1968).

importance are formed through the following reaction scheme:



When the antimony activity is separated from the irradiated sample, therefore, a composite γ-ray spectrum which corresponds to a mixture of the 2.8 day-^{122}Sb, the 60.9 day-^{124}Sb and the 2.81 yr-^{125}Sb as β^--decay products of ^{125m,125}Sn is measured. The marked difference in energy of γ-rays emitted from ^{124}Sb (1.69 MeV) and ^{125}Sb (0.427 MeV) permits a γ-ray spectrometric determination of antimony in tin. By applying the principles illustrated in the previous report,1) the following linear relationship is obtained between the ratio of the photopeak activities determined at identical times after each irradiation (R_{A_t}) and the ratio of the concentrations (R_W):

$$R_W = K R_{A_t}$$

The constant, K, can be determined by irradiating synthetic mixtures of antimony and tin with known compositions.

Experimental

Materials and Irradiation. A series of synthetic antimony-tin mixtures was prepared in the following manner. Tin powder 100 mg was weighed into a quartz tube with an internal diameter of 6 mm, and then known amounts of an aqua regia solution of antimony added. After evaporation to dryness, the tube was sealed.

The tin powder used was processed from tin(II) chloride of a guaranteed grade. After repeated recrystallization, the reagent was dissolved in hydrochloric acid. Tin was precipitated from this solution in the form of metallic powder by the addition of a concentrated sodium hydroxide solution with heating, repeatedly washed with water and dried in a vacuum.

The aqua regia solution of antimony was prepared through the dissolution of 99.9999% antimony metal. Proper dilution with water was made just before use. The hydrochloric acid, nitric acid and water were all redistilled. All other chemicals were of a guaranteed grade.

Commercial tin metal of a granular form and an electrolytic tin rod were tested for their antimony contents. From these samples, small pieces of approximately 60 mg were cut out and analyzed. The samples, a series of synthetic mixtures and 100 mg of the original tin powder were put together in an aluminum capsule for pile irradiation. Irradiation was performed for 180 hr in the JRR-2 reactor of the Japan Atomic Energy Research Institute. The reactor was operated at 10 MW, providing a thermal neutron flux of 2.0×10^{13} n/cm^2/sec at the irradiation site. After irradiation, the samples were cooled for 13 days and then subjected to the radiochemical procedure for the isolation of their antimony activities.

Radiochemical Procedure. Radioantimony was extracted from a hydrochloric acid solution of an irradiated tin target with isoamyl acetate. The irradiated sample was dissolved in a small amount of aqua regia, and made 8 N in hydrochloric acid to a volume of 25 m*l*. To this, 5 m*l* of isoamyl acetate was added and radioantimony extracted with 10 minutes' agitation. The organic extract was washed twice with 10 m*l* portions of 8 N hydrochloric acid, and drained into a polyethylene tube for γ-ray spectrometric measurements.

γ-Ray Measurement. For the γ-ray spectrometric measurement, a 1½″ϕ×1½″NaI(Tl) crystal connected to an 800-channel pulse-height analyzer made by the Tokyo Shibaura Electric Co., Ltd., Japan was used. The graphical subtraction method2) was employed to determine accurate photopeak areas from the γ-ray spectra obtained. Decay curve analyses have been performed for photopeak activities to confirm the radiochemical purity.

Results and Discussion

Isolation of Radioantimony. Penta-valent antimony is extractable from a hydrochloric acid solution with ethyl acetate, isoamyl acetate and other extractants,3-5) and these properties have been utilized for the separation of a trace amount of antimony from tin.6) To obtain the best procedure for the isolation of radioantimony from a large amount of tin, the extraction properties of both elements with isoamyl acetate have been examined further using ^{124}Sb and ^{113}Sn as tracers. Hydrochloric acid solution of varying concentrations containing definite amounts of either pentavalent antimony7) or quadrivalent tin8) was agitated with an equal volume of isoamyl acetate for 10 min. After agitation, both the organic and aqueous layers were γ-counted, and the percentage extraction was computed from the activity data. The extraction curves thus obtained are shown in Fig. 1. The extraction of antimony was best effected from a 7 to 8 N hydrochloric acid solution. Although up to about 20% of tin was accompanied by antimony, this could be completely removed by repeated backwashings with 8 N hydrochloric acid.

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2) W. S. Lyon, Jr., Ed., "Guide to Activation Analysis," D. Van Nostrand Co., Princeton, N. J. (1964), p. 104.

3) C. E. White and H. J. Rose, *Anal. Chem.*, **25**, 351 (1953).

4) G. K. Schweitzer and L. E. Storms, *Anal. Chim. Acta*, **19**, 154 (1958).

5) N. Suzuki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **81**, 437 (1960).

6) K. Saito, N. Suzuki, K. Seto and H. Ikegami, This Bulletin, **36**, 692 (1963).

7) The neutron irradiated antimony sample was dissolved in aqua regia, and used for the extraction experiment.

8) To prepare this solution, a known amount of irradiated tin was dissolved in aqua regia with heating. From this, tin(IV) hydroxide was precipitated by the addition of a dilute aqueous sodium hydroxide solution. The precipitate was dissolved in 8 N hydrochloric acid, and the antimony activity removed by isoamyl acetate extraction. An aliquot of the aqueous layer was used for the extraction experiment.

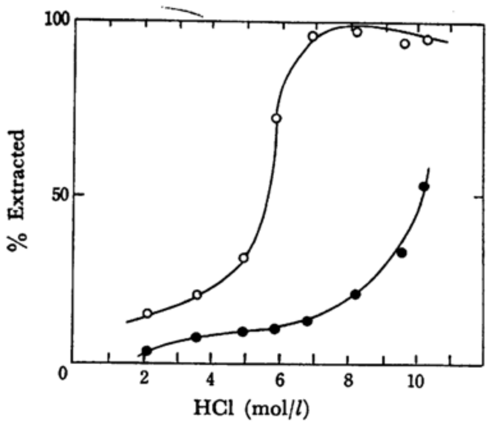

Fig. 1. Extraction curves of antimony(V) and tin(IV) from hydrochloric acid solution with isoamyl acetate.
○: Sb(V) 1.8 μg
●: Sn(IV) 2.6 mg
Org.: Aq. = 1:1 (5 ml)

When the irradiated antimony - tin mixture was subjected to the radiochemical procedure, a composite γ-ray spectrum was obtained in the final radioantimony fraction, which corresponds to a mixture of ^{122}Sb, ^{124}Sb and ^{125}Sb, as shown in Fig. 2-(1). Decontamination from other nuclides was successful.

R_W vs. R_{A_t} From the composite spectra obtained from the antimony - tin mixtures, photopeak areas were measured for 0.427 MeV γ-rays from ^{125}Sb, and for 1.69 MeV γ-ray from ^{124}Sb.

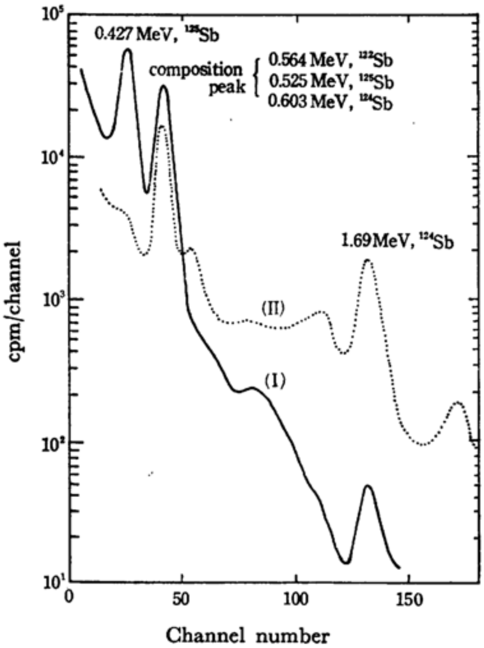

Fig. 2. γ-Ray spectra of radioantimony; (I) separated from irradiated tin - antimony mixture (Sn 101 mg+Sb 0.19 μg), 13 days after irradiation, (II) standard antimony sample.

The R_{A_t}'s were computed from the data thus obtained. At that time, the correction coefficient for ^{124}Sb arising from the original tin, α, was introduced in Eq. (1), obtaining

$$R_W = K\left(\frac{A_{^{124}\mathrm{Sb}}}{A_{^{125}\mathrm{Sb}}} - \alpha\right)_{t=13\ \mathrm{day}} \tag{2}$$

where

$$\alpha = \left(\frac{A_{^{124}\mathrm{Sb}}}{A_{^{125}\mathrm{Sb}}}\right)_{\mathrm{original}} \tag{3}$$

A's represent the photopeak activities. The α value obtained under the present conditions was 1.64×10^{-4}.⁹⁾ The reasons for this correction may arise from the antimony content in the original tin as an impurity and from the systematic second-order nuclear reactions as described later. Table 1 shows the relation between the weight ratios and the corrected photopeak activity ratios. Good proportionality was obtained between R_W and R_{A_t}. A relative standard deviation of ±1.2% was obtained under the present conditions. The present results show that an accurate determination can be expected using this relationship.

TABLE 1. R_W vs. R_{A_t} FOR TIN-ANTIMONY MIXTURES

R_W	R_{A_t} a)	R_W/R_{A_t}
8.67×10^{-6}	5.68×10^{-3}	1.52×10^{-3}
3.88×10^{-6}	2.59×10^{-3}	1.50×10^{-3}
1.85×10^{-6}	1.23×10^{-3}	1.50×10^{-3}
1.00×10^{-6}	6.80×10^{-4}	1.47×10^{-3}
3.13×10^{-7}	2.06×10^{-4}	1.52×10^{-3}
	Mean:	1.50×10^{-3}
	Std. dev.:	$0.01_8\times10^{-3}$ (±1.2%)

a) 13 days after the end of irradiation

When a minimum photopeak area of 50 cpm is selected as the limit of detection, an antimony content in tin down to about 0.2 ppm (0.02 μg in a 100 mg sample) can be determined with a relative error of ±2%.

Interference. Interference which arises from the tin matrix has been examined. In the present case, the effects of the (n, p) and the (n, α) reactions by fast neutrons give no trouble, but interference through second-order nuclear reactions must be considered which would produce additional amounts of radioactive antimony and thus cause a positive error. ^{124}Sb is formed from tin according to the reaction scheme:

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9) This corresponds to an antimony content of 0.25 ppm in the original tin. This can be attributed to the sum of antimony as an impurity and the apparent content produced by second-order reaction. The latter was computed to be 0.05 ppm as described later.

$$\begin{tikzcd}
 & \text{(I)} \arrow[r, "{(n,\gamma)}", "{0.16\ \text{barn}}"'] & {}^{123m}\text{Sn} \arrow[ddr, "\beta^-", "41\ \text{min}"'] & & \\
{}^{122}\text{Sn} & & & & \\
 & \text{(II)} \arrow[r, "{(n,\gamma)}", "{1\ \text{m barn}}"'] & {}^{123}\text{Sn} \arrow[r, "\beta^-", "129\ \text{day}"'] & {}^{123}\text{Sb} \arrow[r, "{(n,\gamma)}", "{2.5\ \text{barn}}"'] & {}^{124}\text{Sb}
\end{tikzcd}$$

The production rate of ^{124}Sb was computed using the Bateman equation.[10] Because of the small activation cross section for the $^{122}\text{Sn}(n,\gamma)^{123}\text{Sn}$ reaction and of the long half-life of the product, the production rate of ^{124}Sb through reaction path (II) can be excluded from the present calculation. Thus the scheme is simplified to successive reactions of the type:

$$N_1 \xrightarrow[\sigma_1]{\phi} \underset{A_1}{N_2} \xrightarrow{\lambda_2} N_3 \xrightarrow[\sigma_3]{\phi} \underset{A_4}{N_4} \xrightarrow{\lambda_4} N_5 \qquad (4)$$

where A's=activity; N's=number of atoms; λ's= disintegration constant; σ's=effective activation cross-section; and ϕ=effective neutron flux.

In order to compute the growth of the ^{124}Sb activity (A_4), a practical formula derived by De Neve *et al.*[11] was used in the present work. An apparent antimony concentration in ppb is defined by:

$$C_{\text{ppb}} = \frac{A_4(\text{for } 1\text{ g Sn})}{A_4'(\text{for } 10^{-9}\text{ g Sb})} \qquad (5)$$

For an irradiation time of t, this becomes:

$$C_{\text{ppb}} = \frac{N_1\sigma_1\phi}{N_4'(1-e^{-\lambda_4 t})}\left[t - \frac{\lambda_2+\lambda_4}{\lambda_2\lambda_4} + \frac{\lambda_2}{\lambda_4(\lambda_2-\lambda_4)}e^{-\lambda_4 t} - \frac{\lambda_4}{\lambda_2(\lambda_2-\lambda_4)}e^{-\lambda_2 t}\right] \qquad (6)$$

This apparent antimony content induced in the tin sample during 180 hr irradiation at a flux of 2.0×10^{13} n/cm²/sec was computed to be 52 ppb.[12] This value must be subtracted from the gross antimony concentration to obtain the true antimony content in a sample of tin.

Antimony Analysis. This method of antimony analysis was tested on both granular tin and an electrolytic tin rod. The results obtained are shown in Table 2. These data were corrected for the effect of second-order reactions. Good agreement for antimony content in granular tin was obtained. The results for electrolytic tin, however, show an irregularity over the range of 2—3 ppm. The reason for this behavior may be inhomogeneities involving antimony as an impurity in this sample.

TABLE 2. RESULTS OF ANTIMONY ANALYSES

Sample	R_{A_t}	Antimony content (ppm)	Average
Granular tin	1.38×10^{-2}	20.7	20.4 ± 0.3
	1.38×10^{-2}	20.7	
	1.34×10^{-2}	20.1	
	1.34×10^{-2}	20.1	
	1.37×10^{-2}	20.5	
Electrolytic tin rod	2.00×10^{-3}	2.9_5	$2.7_8\pm0.7_9$
	1.36×10^{-3}	1.9_9	
	1.98×10^{-3}	2.9_2	
	1.95×10^{-3}	2.8_8	
	2.16×10^{-3}	3.1_9	

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[10] G. Friedlander, J. W. Kennedy and J. M. Miller, "Nuclear and Radiochemistry," 2nd Ed., John Wiley & Sons Inc., New York (1964), p. 76.

[11] R. De Neve, D. De Soete and J. Hoste, *Anal. Chim. Acta*, **36**, 508 (1966).

[12] Nuclear data used for this calculation were those listed in the Nuclear Data Sheets.[13]

[13] Nuclear Data Sheets, Natl. Academy of Science-Natl. Research Council, Washington, D. C. (1961).