Preparation of Radioactive Antimony-120 of a High Specific Activity by the Irradiation of Tin with Protons

By Kazuo SAITO, Nobuo SUZUKI*, Kunio SETO** and Hidetsugu IKEGAMI

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This paper describes the separation of pure radioactive antimony from a tin target irradiated by protons, and the preparation of a radioactivity source suitable for an accurate study of the decay scheme by the measurement of the angular correlation of its γ-rays and of the conversion electron spectrum. Separation of a trace of antimony from tin has been studied by several workers[1-4]. Since solvent extraction from a hydrochloric acid solution[5] and cation exchange in a weakly acid solution containing tartaric acid[2] appeared to be most

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[*] Present address: Institute of Mineral Dressing and Metallurgy, Tohoku University, Nagamachi, Sendai.

[**] Present address: Faculty of Science, Tohoku University, Katahira-cho, Sendai.

[1] R. D. Maxwell, H. R. Haymond, W. M. Garrison and J. G. Hamilton, *J. Chem. Phys.*, **17**, 1340 (1949).

[2] F. Mylius and C. Hutter, *Ber.*, **44**, 1315 (1911).

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

[4] K. Kimura, N. Saito, H. Kakihana and T. Ishimori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 305 (1953).

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

suitable for our present purpose, these two methods were examined, with commercially-available radioisotope ^{124}Sb6). It was found that both methods require significant modification in order to be applied to the irradiated target, because the amount of irradiated tin is very large.

A great deal of difficulty is involved in the preparation of an activity source which satisfies the following demand. The sample for the measurement of angular correlation of γ-rays must be a liquid less than 0.05 ml. in volume and more than 200 μc. in intensity. Nevertheless, the presence of carrier antimony is permissible. The source for the measurement of the internal conversion electron spectrum, on the other hand, must be practically carrier-free and placed on a thin finlm; the presence of any material brings about confusion in angular correlation. Evaporation of an ethereal or esterial solution of antimony pentachloride and electrolytic deposition provide a useful source for the angular correlation and the conversion electron spectrum measurement, respectively.

Experimental and Results

Materials.—Metallic tin of a high purity (containing less than 8×10^{-4}% Sb) was kindly supplied by Dr. K. Itsuki of Mitsubishi Metal and Mining Co. The organic solvents were purified by the usual method. The other chemicals are of extra pure grade.

Irradiation.—Metallic tin was fused, poured into four square holes in an aluminum slab, which was fixed onto a water-cooled target holder, covered with aluminum foil (20 μ thick), and inserted into the vacuum chamber of INSJ cyclotron (diameter of the magnet polepiece, 165 cm.; maximum proton energy, 15 MeV.; maximum proton current intensity, 1 mamp.). The target was irradiated with 11.5 and 14 MeV. protons with a mean current, 15 μamp. A greater current density caused metallic tin to melt in the shallow hole. With a total bombardment of 120 μamp. hr., about 10 mc. of radioactive substances was produced altogether, including ca. 1 mc. of ^{120}Sb.

The head of the target holder was taken off out of the chamber after a few hours' cooling and subjected to chemical separation.

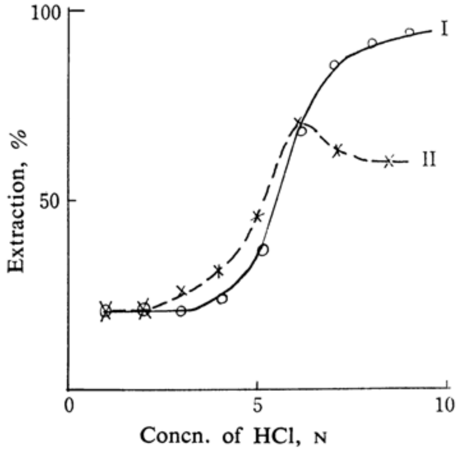

Fig. 1. Extraction of radioactive antimony-(V) from hydrochloric acid solution of irradiated tin.
vol. of the aq. phase, 100 ml.; vol. of org. phase, 30 ml.; I, amylacetate; II, ethylacetate.

Dissolution of the Target.—Tin was easily torn off from the aluminum plate, and each piece (2.5 g.) was either dissolved in 6 N hydrochloric acid (150 ml.) or in a mixture (100 ml.) of 6 N hydrochloric acid and concentrated nitric acid (3+1, v/v). In the former case, antimony remained in the tervalent state and was suitable for cation exchange separation from tin, but the time taken for dissolution was about 24 hr. In the latter case, dissolution was completed within 30 min.; the antimony was in the quinqui-valent state and extracted with organic solvent as shown below.

Solvent Extraction. — White et al. stated that the extraction of antimony with ethylacetate was best effected from 1 to 2 N hydrochloric acid solution in the presence of tartaric, acetic or oxalic acid. Our preliminary examination with ^{124}Sb disclosed that the extraction was facilitated by increased concentration of hydrochloric acid6). In a concentration greater than 6 N, however, the separation of the organic layer became incomplete, especially by the use of small quantity of the ester as compared with the volume of aqueous phase; hence, the extraction was less effective. By the use of amylacetate, such a defect was eliminated and the antimony, in both ter- and quinqui-valent state, was extracted almost quantitatively from more than 9 N hydrochloric acid. It appears as if the presence of organic acids little affects the extraction, when the antimony is in the quinqui-valent state. Nitric acid, used for the solution of the target, did not cause any interference. Tervalent antimony was extracted with less ease. A small amount of quadrivalent tin was extracted, because its concentration in the aqueous phase was great, but it was extracted back with 8 to 10 N hydrochloric acid. Only a negligible amount of antimony was transferred into the aqueous phase on the back extraction of tin. The amount of tin in the washed organic phase appears to be less than that of antimony coming from the impurity of the target metal. When antimony hydrolysed in too diluted an acid solution, solvent extraction was unsuccessful. Treatment with aqua regia, however, reverted the aged antimony to the ionic state

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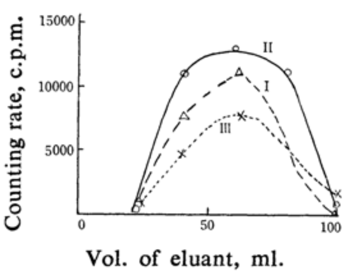

Fig. 2. Elution of radioactive antimony(III) from cation exchange resin with tartaric acid solution.

Resin column, 10 mm. in a diameter, 10 cm. in length, Dowex 50 X8, 100 to 200 mesh; concn. of tartaric acid, 0.4%; pH adjusted with HCl; I, pH, 0.4; II, pH, 0.6; III, pH, 1.6.

extractable with esters. The ester phase was evaporated and used for the γ-ray angular correlation measurement.

Ion Exchange. — Kimura et al. found that tervalent antimony in 0.4% tartaric acid of pH 1 passes through a column of cation exchange resin, bi-valent tin being quantitatively adsorbed on the resin[4]. Our re-examination made it clear that this method may satisfactorily be applied to the separation of radioactive antimony from a large amount of tin. However, it was also elucidated that the behavior of antimony was highly dependent on its state in the acid solution. So far as antimony(III) is not aged, the allowable pH range is rather wide, as is shown in Fig. 2. The tervalent antimony is apt to age in a dilute hydrochloric acid solution or in the presence of a less excess of hydrochloric acid. In the presence of tartaric acid, the aging was retarded in the cold, but not on boiling (see Fig. 3). When the antimony(III) was aged (perhaps by hydrolysis), its elution with a 0.4% tartaric acid solution of pH 1 was quite incomplete. It was partly eluted with 6 N hydrochloric acid, together with bivalent tin, but the remainder was eluted with great difficulty by the use of various agents including the following: 3 N hydrochloric acid containing 1% potassium chlorate, 3 N hydrochloric acid containing 5% (by volume) concentrated nitric acid, concentrated hydrochloric acid, 6 N hydrochloric acid containing various amounts of hydrogen iodide, and diluted hydrochloric acid containing various amounts of sodium bisulfite.

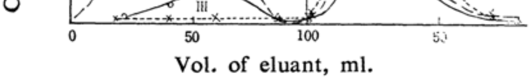

Fig. 3. Elution of radioactive antimony(III) after aging.

- I Irradiated Sn (0.3 g.) was dissolved in 6 N HCl (30 ml.) mixed with tartaric acid (0.1 g.), evaporated to ca. 1 ml., set aside overnight and diluted to ca. 25 ml. (pH, 0.6).
- II Prepared similarly to I; the tartric acid (1 g.) was added to the condensed soln., which was immediately diluted to ca. 25 ml. for ion exchange (pH, 0.6).
- III Prepared similarly to I; the condensed soln. (1 ml.) was set aside overnight, mixed with tartaric acid (0.1 g.) and diluted.

Electrolytic Deposition of Antimony.—Since the radioactive antimony consists of several kinds of nuclide, the scintillation spectrum is not resolving enough to enable an accurate study of the decay scheme. For the measurement of the internal conversion spectrum and the electron-gamma directional correlation, a source of a high specific activity is required. In order to minimize the scattering of electrons inside the source, the source thickness must be very small*. The lower the energy of electrons to be measured, the thinner the source should be. For the measurement in a rather high energy region, on the other hand, the influence of the scattering is less marked, and the conversion co-efficient is smaller. Hence, the demand for source thickness is less severe, but the intensity must be stronger.

The electrolysis of antimony is highly dependent on the state in the electrolytic solution. It is essential to avoid hydrolysis and to keep the antimony in an ionic state, either ter- or quinqui-valent. For this purpose, the radioactive antimony must be kept either in an organic solvent or in a hydrochloric acid solution more concentrated than 3 normal. When the organic solution is converted into an aqueous solution, care must be taken to maintain the acid concentration above this level. Aged antimony can be converted into an ionic state by boiling it with dilute aqua regia.

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* In this measurement the source should be embedded in a metallic lattice. This condition is imperative in this case, where the nuclear transition occurs through an electron capture or internal conversion. The electronic shell will be excited by these processes, and the excited electronic shell will give a time-dependent perturbation. In a metallic surrounding, however, the recovery time is much shorter than the mean lifetime of the nuclear intermediate state and, consequently, there will be no attenuation.

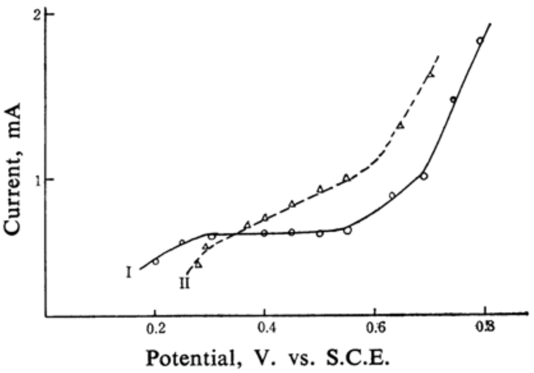

Fig. 4. Potential vs. current diagram for the electrolytic deposition of radioactive antimony in diluted hydrochloric acid.
I, in 1 N HCl; II, in 2.5 N HCl; 1% (w/v) hydroxylamine hydrochloride; 25°C; amount of Sb carrier < 2 μg.

Antimony was electrolytically deposited on a cathode (2×20 mm.) of silver or copper film (10 μg. per cm^2), which was evaporated in vacuo on a rubber hydrochloride film (0.25 mg. per cm^2), with platinum wire as anode. The potential-current diagram is shown in Fig. 4. About 70% of the radioactive antimony in ca. 1 N hydrochloric acid (ca. 10 ml.), containing 1% (w/v) hydroxylamine hydrochloride and less than 2 μg. of carrier antimony coming from the target, was deposited within 3 hr. with a terminal voltage 1.4 V. Under this condition the cathode potential vs. S.C.E. is -0.46 V. When the terminal voltage and the acid concentration were increased, the electrolysis was rather facilitated. However, an amorphous black substance appeared on the cathode surface, and the specific activity decreased. Such a black substance appeared even in the absence of antimony or by the use of pure carbon as anode. Spectrographic analysis indicated no other metal than the cathode metal. It appears as if the cathode is partly dissolved in the electrolytic solution owing to, e. g., local cell formation and then deposited again in the form of a very fine powder.

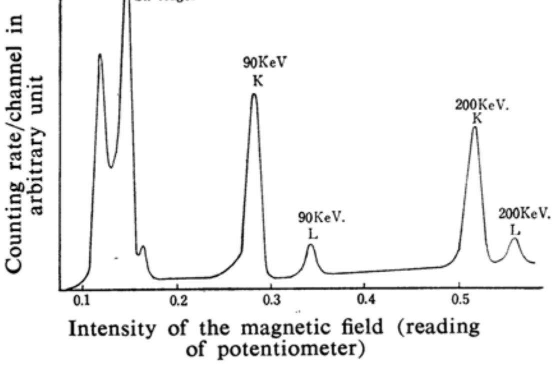

Fig. 5. Internal conversion electron spectrum of ^{120}Sb.

Measurement of the Internal Conversion Electron Spectrum. — Figure 5 illustrates the conversion electron spectrum in the lowest energy region; it clearly indicates that the source is so thin that the peaks corresponding to the Auger electron are distinctly separated. The form of the lines is symmetrical, indicating no source-scattering of low energy electrons.

Discussion

When tin with natural abundance ratio is irradiated with protons, radioactive antimony isotopes of mass numbers 115 to 124 are formed. Among these only Sb-119, 120 m and 124 survive after one day. The first gives only γ-rays of a low energy (23.8 keV.), and the last two are the main components of radioactive antimony. Although Sb-124 gives several γ-rays, they interfere neither with the accurate measurement of γ-ray energies by the conversion electron method nor with that of angular correlation of the γ-rays of Sb-120, because of the low abundance of ^{124}Sn.

Examination of solvent extraction, ion exchange and electrolysis of a micro amount of antimony disclosed that the procedures are satisfactorily effected so far as the antimony is not hydrolysed in the aqueous phase. Hence, care must be taken to avoid the hydrolysis especially in a rather low acid concentration. The recommended procedure is shown below.

The product is of so high a specific activity as to be more than 0.1 mc. per μg. of Sb. (The highest specific activity of Sb-124 produced in a reactor with a neutron flux of 10^{14} per cm^2 per sec. is ca. 0.01 μc. per μg. of Sb.) Figure 5 provides one of the rarest examples of low energy conversion electron spectra ever observed.

Recommended Procedure (*Separation by Solvent Extraction*).—Dissolve the target tin (4 g.) in a mixture (100 ml.) of 6 N hydrochloric and concentrated nitric acids (3+1 v/v), boil to decompose the nitric acid and treat it with concentrated hydrochloric acid to produce ca. 50 ml. of 8 N hydrochloric acid. Shake with amylacetate (25 ml.×2), and wash the ester layer with 8 N hydrochloric acid (20 ml.×2). Evaporate the organic phase almost to dryness with occasional addition of 8 N hydrochloric acid. Use the residual, rather viscous solution (ca. 0.1 ml. in volume) for γ-γ angular correlation study. Convert the residue into a 1 to 3 N hydrochloric acid solution (10 ml.) containing 1% (w/v) hydroxylamine hydrochloride and electrolyse antimony, using the apparatus illustrated in Fig. 6 of Ref. 7, upon an evaporated film of silver (thickness: 10 μg. per cm^2) on rubber hydrochloride (0.25 mg. per cm^2) with a terminal voltage, 1.4 V.

Summary

1) By irradiation of a tin target (antimony content, less than $8\times10^{-4}\%$) with 15 MeV. protons (120 μ amp. hr.), about 1 mc. of ^{120}Sb was produced, with a specific activity more than 30 μc. per μg. of antimony.

2) The radioactive antimony was either separated by extraction with amylacetate from more than 6 N hydrochloric acid containing tin(IV) or by cation exchange in a 0.4% tartaric acid solution of pH 0.6 to 1.6 containing tin(II).

3) ^{120}Sb is electrolytically deposited on an evaporated film of silver or copper from a 1 to 3 N hydrochloric acid solution containing 1% hydroxylamine hydrochloride with a yield of 70% within 3 hr.

4) Care should be taken to avoid hydrolytic aging of antimony in diluted hydrochloric acid, which vitiates the extraction, the ion exchange, and the electrolysis.

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Institute for Nuclear Study
The University of Tokyo
Tanashi, Tokyo

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