Separation of Radioactive Arsenic from Germanium Irradiated with Protons

By Kazuo SAITO, Shigerô IKEDA and Makoto SAITO

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Concerning the preparation of radioactive arsenic including ^{70}As, ^{71}As, ^{72}As and ^{74}As, from a germanium target irradiated with protons, a little information is available. Green et al.[1] extracted germanium tetrachloride with benzene and left arsenic in the aqueous phase consisting of 11 N hydrochloric acid. Irvine[2] distilled off germanium tetrachloride in an oxidative atmosphere in the presence of carrier arsenic and hydrochloric acid. These reports, however, give only insufficient information on the preparation of radioactive arsenic of a very high specific activity (e. g. 1 mc in 0.05 ml. of aqueous solution containing less than 10 μg. of arsenic).

With the aims of measuring the accurate energy of the gamma rays of arsenic -74 by the internal conversion method and using the product for a tracer of a high specific activity, the present authors examined the separation of almost carrier-free arsenic by distillation with reference to the rate of distillation; they also applied the solvent extraction method[3] with diethyldithiocarbamate to the present purpose. Since commercial germanium of a high purity contains a very small amount of arsenic (e. g. less than 0.0001%), the product can not be called carrier-free. However this is regarded as practically carrier-free from either a nuclear spectroscopic or a radiochemical viewpoint; never-the-less the term "carrier-free" is not used in this paper.

It was elucidated that the distillation of arsenic trichloride in the absence of germanium, is completed within 5 min. (Table I.) and the

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[1] M. Green and J. A. Kafalas, *J. Chem. Phys.*, 22, 760 (1954).

[2] W. Irvine Jr., *J. Applied Phys.*, 13, 910 (1942).

[3] N. Stanford, P. F. Wyatt and F. G. Kershaw, *Analyst*, 70, 232 (1945).

distillate contains no appreciable amount of solute other than hydrogen chloride, hydrogen bromide and radioactive arsenic in an almost carrier-free state. It is often seen that the distillation of a substance is retarded on a micro scale, but this is not the case. It remains uncertain, however, whether the rapid distillation is due to the possible presence of a very small amount of carrier or to the fact that a large amount of hydrogen chloride simultaneously distils out. The distillate can be used as a tracer for arsenic. It was found, however, more convenient to extract arsenic into an organic phase and extract it back into an aqueous layer, for the product to be submitted to conversion electron measurement in a beta-ray spectrometer.

The extraction of diethyldithiocarbamate with carbon tetrachloride provides satisfactory results on such a micro scale, provided that a sufficient amount of the reagent is present. (Fig. 1) The use of an acetate buffer, which is generally involved in the analytical use of this reagent, was not found essential for a quantitative extraction, whenever the pH is duely adjusted. It appears as if the use of a buffer causes the presence of a salt-like substance in the final product, which vitiates the specific activity and hence the conversion electron spectrum. Although the presence of germanium does not interfere with the extraction, most satisfactory results were obtained by the application of the extraction method to the distillate of almost carrier-free arsenic trichloride. Retardation of the extraction, which is often involved in the case of carrier-free separation, was not recognized. The reason is uncertain, but it must be noticed that a large excess of diethyldithio carbamate is essential for a rapid extraction and that a very small amount of the reagent is extracted into the organic phase at the given pH.

When relatively short-lived arsenic-69, 70, 71, 72 and 76 decay after one week, the redioactivity consists of arsenic-74 (half-life, 17.5 days) and arsenic-73 (76 days); the latter gives only two gamma rays of 14 and 54 keV. and does not interfere with the measurement of gamma-rays of arsenic-74 having higher energies, by the scintillation method. Hence the product is satisfactorily used for the study of the decay scheme of ^{74}As and as a tracer of arsenic having an apparent half-life of 17.5 days. The result of the study of the decay scheme was published elsewhere[5]. A part of the spectrum is shown in Fig. 2, which clearly shows that the source is thin enough to give a resolution of ±0.8%. The amount of miscellaneous substances in the final product, including carrier arsenic is less than 10 μg. for 0.4 mc, the specific activity for ^{74}As being about 1 mc per 25 μg. immediately after preparation. The overall yield for ^{74}As is about 70%.

Experimental

Target and Irradiation.—Elementary germanium of a purity more than 99.99999999% (measured by the Hole effect) (possible chemical purity more than 99.999%) and germanium dioxide (purity more than 99.999%) were used as target. The germanium was placed on a water-cooled detachable stem and covered with a thin (20 μ) foil of aluminum. The oxide was mixed with a dilute solution of glycerin phthalate resin (glyptal) in ethylacetate, mounted on an aluminum plate and dried at 250°C; the plate was fixed on the head of the stem.

Irradiation was made in INS cyclotron (diameter of the magnet pole piece, 163 cm.) with protons of various energies ranging from 10 to 14 MeV. for 2 to 5 hr., the intensity of the beam current being 10 to 20 μA. The irradiated target was set aside in the vacuum chamber for 1 hr., the head of the stem taken out and the target submitted to chemical separation.

The irradiated unit contained arsenic-70, 71, 72, 73, 74 and 76, germanium-69 and 71 (produced by (p, pn) reaction) and probably a small amount of gallium-67, 68, 70 and 72 (produced by (p, 2p) and (p, α) reaction) as radioactive nuclides. The total amount of radioactive substance was of the order of several ten mc immediately after irradiation, when the beam current was 15 μA and the duration of irradiation was 5 hr.; the amount of arsenic-74 appeared to be 1 mc or a little less. Irradiation was made five times altogether. Chemical behavior of the produced nuclides was carefully checked. Essential parts are described as follows.

Distillation.—The elementaryger manium (10 g., in four pieces) was placed in a Clysen-type flask, dissolved in aqua regia (30 ml.) and germanium tetrachloride distilled in a current of chlorine with the addition of 6 N hydrochloric acid (50 ml.) until the volume of the residue is less than 1 ml. The addition of hydrochloric acid and the distillation were repeated three times. Germanium oxide taken off the plate was placed in the flask and similarly distilled. The remaining charred resin did not interfere with the subsequent distillation of arsenic. The removal of germanium was almost complete. The chlorine being removed in a current of nitrogen, the arsenic trichloride was distilled in the presence of 10 N hydrochloric acid (10 ml.) and 9 N hydrobromic acid (5 ml.), into an ice-cooled adapter containing water (10 ml.). The arsenic was found in the first a few milliliters' portion. This fact was clearly demonstrated by a small-scaled distillation

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[4] C. L. Luke, and M. E. Campbell, *Anal. Chem.*, 25, 1588 (1953); H. Goto and Y. Kakita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 77, 739 (1956).

[5] T. Yamazaki et al., *J. Phys. Soc. Japan*, in press. After the completion of the present study, the following two papers have appeared. They concern the decay scheme of ^{74}As, but not the chemical procedures. E. P. Gligoriev et al., *Izvestia Akad. Nauk, SSSR, Ser. Phys.*, 22, 831, (1958); D. J. Horen et al., *Phys. Rev.*, 113, 875 (1959).

TABLE I. DISTILLATION OF ARSENIC TRICHLORIDE*

Fraction	Distilled ml.	Time of distil. min.	Relative counting rate, c.p.m.	Remarks
1	5	5	10863	**
2	4	8	241	
3	5	13	88	
4	5	20	56	
5	5	24	45	
6	5	30	7	+HCl 10 ml. +HBr 5 ml.
7	5	35	23	
8	7	42	16	

* The amount of the radioactive As is much smaller than that in the practical separation, but the volume of the aq. soln. is almost the same.

** Initial vol. of the aq. soln. 0.5 ml.; the counting rate, 12100 c.p.m.

shown in Table I. The total recovery was about 94%; most of the remaining radioactive arsenic was found on the surface of the rubber stoppers.

Solvent Extraction.—The experimental procedure shown in the original paper[3] was followed.

Since this method has been examined for use in micro analysis of arsenic[4], the following experiments were centered around the rate of extraction on such an ultra-micro scale. The distillate was heated to dryness with sulfuric acid (1 N, 2 ml.) and nitric acid (15 N, 5 ml.), mixed with hydrochloric acid (12 N, 1 ml.) and water (15 ml.) and again heated to 50°C. The product is treated with potassium iodide solution (10%, 3 ml.) and sodium sulfite (1 g.), made pH 5 with sodium acetate (10%, 5 ml.) and aqueous ammonia solution and shaken with carbon tetrachloride for 1 min. (equal volume to the aqueous layer) in the presence of variable amounts of sodium diethyldithiocarbamate solution (0.1%, in water). The results are shown in Fig. 1.

It is clearly seen that the extraction largely depends on the amount of the reagent. No appreciable adsorption of radioactive arsenic was observed on the surface of the glass wares, not excepting the ground parts. A similar extraction curve was obtained in the presence of germanium. A satisfactory extraction of arsenic was also effected in the absence of any buffer, provided that the pH was duely adjusted. Back-extraction of radioactive arsenic was substantiated from the carbon tetrachloride solution, by the use of 8 N nitric acid, 6 N hydrochloric acid or aqueous ammonia solution. Single extraction suffices for the recovery of more than 90% of the radioactive arsenic.

Measurement of Radioactivity.—For checking the procedures for separation, a G. M. counter was used, the sample being placed at a reproducible geometry. Since one series of experiments is completed within a few hours, the radiochemical composition of the sample can be regarded as identical, although the sample solution contains, especially at the early stage of separation, several radioactive nuclides. Hence the counting rate was shown in c. p. m. on an arbitrary scale in the figures and tables.

For the measurement of the conversion electron spectrum, the back-extracted arsenic in nitric acid solution was mounted on a trace of insulin on a thin polyvinylchloride foil lined with a thin layer (several μg. per cm^2) of vacuum-evaporated aluminum, dried up under an infrared lamp or in vacuo and attached to a beta-ray spectrometer. (INS-III, $\rho=18$ cm.)

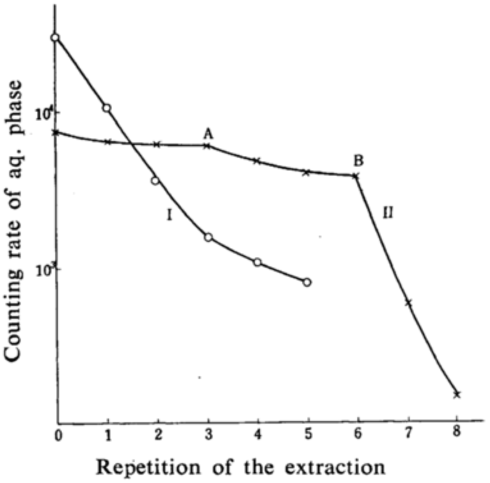

Fig. 1. Extraction of arsenic with carbontetrachloride in the presence of diethyldithiocarbamate.

Curve I. Extraction in the presence of 3 ml. of 0.1% reagent soln.; vol. of the aq. phase, 6 ml.; time of shaking 1 min. each.

Curve II. Extraction in the presence of a less amount of reagent; initial, 0.5 ml.; vol. of the aq. phase, 6 ml.; time of shaking, 1 min. At point A and B, 0.5 ml. and 1.0 ml. of 0.5% reagent soln. were respectively added.

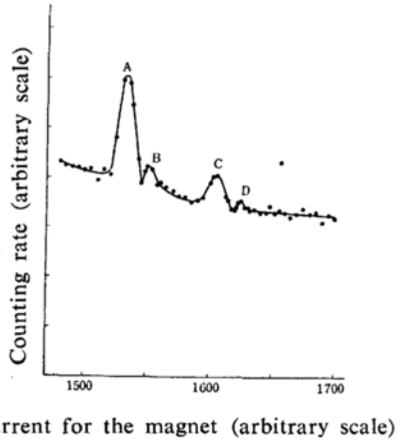

Fig. 2. Conversion electron spectrum of aresenic-74.

A, 596 keV.-K; B, 596 keV.-LM; C, 635 keV.-K; D, 635 keV.-LM.

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Institute for Nuclear Study
The University of Tokyo
Tanashi, Tokyo (K. S.)

Institute for Iron,
Steel and other Metals
Tohoku University
Katahira-cho, Sendai
(S. I. and M. S.)