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**Cyclotron production, separation  
and quality control of  $^{73}\text{As}$**

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## Abstract

The isotope  $^{73}\text{As}$  has been produced on the AIC-144 cyclotron via the  $^{\text{nat}}\text{Ge}(\text{p},\text{xn})^{73}\text{As}$  nuclear reaction. The high purity germanium target of natural isotopic abundance was bombarded by the internal proton beam. The target was dissolved in aqua regia, and the As isotopes were separated on the Dowex-1 ion-exchange resin. The contaminant  $^{74}\text{As}$  was let to decay. Traces of stable germanium in the final product were determined spectrophotometrically and by the internal tracer method. The  $^{69}\text{Ge}$  tracer was produced on the same cyclotron in the  $\text{Zn}(\alpha,\text{xn})^{69}\text{Ge}$  reactions. The isotope  $^{69}\text{Ge}$  as well as its contaminants  $^{66}\text{Ga}$  and  $^{67}\text{Ga}$ , produced in  $\text{Zn}(\alpha,\text{pxn})^{66,67}\text{Ga}$  reactions, were separated from Zn by solvent extraction from 7M HCl. The resultant carrier-free  $^{73}\text{As}$  was of high radionuclide purity and did not contain detectable traces of the target material.

## Introduction

The isotopes  $^{73}\text{As}$  and  $^{74}\text{As}$  (especially the longer-living  $^{73}\text{As}$ ) are valuable tracers for toxicology studies. As such,  $^{73}\text{As}$  was recently produced in our Institute for the IAEA Marine Laboratory in Monaco and for the Institute of Nuclear Chemistry and Technology in Warsaw. Both As isotopes can be obtained either in  $\text{Ge}(\text{d},\text{xn})$  [1, 2, 3] or in  $\text{Ge}(\text{p},\text{xn})$  reactions [4], and  $^{74}\text{As}$  also in the  $^{71}\text{Ga}(\alpha,\text{n})$  reaction [5]. Each of these reactions can be carried out on the AIC-144 cyclotron of our Institute. In this work,  $^{73}\text{As}$  was produced in the proton-induced reaction on germanium, which we considered the most convenient.

To assess the effectiveness of chemical separation of As isotopes from the target material, we applied the internal tracer method. Owing to versatility of the AIC-144 cyclotron, the radioactive  $^{69}\text{Ge}$  tracer could be also produced in the Institute.

Independently, it was important to find an alternative method for checking chemical purity of  $^{73}\text{As}$  if the  $^{69}\text{Ge}$  tracer is not readily available. For such situation we tested the spectrophotometric method for determination of germanium.

The nuclear properties of the isotopes of study are listed in Table 1.

Isotope	$t_{1/2}$	Decay mode	Branching ratio	$E_{\gamma}$ keV	Intensity %
$^{73}\text{As}$	80.3 d	EC	100%	53	10
$^{74}\text{As}$	17.77 d	$\beta^+$	29 %	595.9	59.22
		EC	39 %		
		$\beta^-$	32 %		
$^{69}\text{Ge}$	39.2 h	$\beta^+$	33 %	573.9	14
		EC	67 %	871.7	13
				1106.4	32.4

Table 1. Nuclear properties of  $^{73}\text{As}$ ,  $^{74}\text{As}$ , and  $^{69}\text{Ge}$ .

## Experimental

### *Target preparation and irradiations*

The targets for  $^{73}\text{As}$  production were prepared from scraps of high-purity germanium of natural isotopic abundance, supplied by the laboratory of semiconductor detectors of this Institute. Portions of about 200 mg of germanium were fixed on the indirectly cooled aluminium support and covered with the aluminium foil ( $2 \text{ mg cm}^{-2} \text{ Al}$ ). In a few subsequent experiments the targets were bombarded during 5-8 hours with the internal proton beam of the AIC-144 cyclotron. The beam current was 0.5 to  $1 \mu\text{A}$ , and the incident proton energy was always 30 MeV.

The tracer  $^{69}\text{Ge}$  was also produced at the internal beam of the same cyclotron. The targets were made of zinc of natural isotopic abundance, electrochemically deposited on copper supports. Each 450 ml portion of the electrolyzed solution contained 8.2 g of  $\text{ZnCl}_2$ , 2 ml of hydrazine and 35 ml of concentrated HCl [6]. The electrolysis was carried out from the starting pH=3, during 30 min at the current of 0.5 A. The obtained targets, about  $20 \text{ mg cm}^{-2}$  thick, were irradiated with 20 MeV alpha particles at  $1 \mu\text{A}$  during 3 hours.

### *Gamma spectrometry*

All radioactive products were identified by gamma spectrometry. The spectra were recorded using a HPGe co-axial detector ( $35 \text{ cm}^3$ , made in this Institute) coupled with a multichannel analyser (Silena, Milano, Italy).

## *Chemical separation*

### *As isotopes*

The irradiated germanium targets were stored during 3-4 weeks to get rid of the short-lived isotopes, and partially of  $^{74}\text{As}$ . Then, the target was dissolved in 2-3 portions of aqua regia (concentrated  $\text{HNO}_3$  + concentrated  $\text{HCl}$ , 1 + 3, v/v), 3-4 ml each. The portions were mixed together and evaporated to dryness. To avoid losses of volatile arsenic, the evaporation was carried out very slowly (several days) at the temperature not higher than  $55^\circ\text{C}$ . The dry residue was re-dissolved in 3 ml of the concentrated  $\text{HCl}$  and doped with  $100\ \mu\text{l}$  of the concentrated  $\text{HNO}_3$  to oxidate As to 5+. The resultant solution was put on the anion-exchange separation column Dowex-1X8, mesh 200.

The freshly prepared column was pre-conditioned with concentrated  $\text{HCl}$ , and its free volume was determined. The As isotopes were passing through the column along with concentrated  $\text{HCl}$ , and germanium was eluted later with 0.5 M  $\text{HCl}$ . Finally, the column was washed with water. Each fraction of the effluent and of the eluate was measured by gamma spectrometry.

The separated As(V) was again evaporated to dryness and converted to a desired chemical form by adding to it either 0.05 M  $\text{NaOH}$  {→ sodium arsenate(V)} or 0.05 M  $\text{HCl}$  {→ arsenic(V) chloride}.

### *Ge and Ga isotopes*

The freshly irradiated Zn targets were dissolved in 6 M  $\text{HCl}$ . The activation products were identified by measuring  $10\ \mu\text{l}$  samples of the resultant solution by gamma spectrometry. Then, germanium and gallium were extracted with di-isopropyl ether from  $\text{HCl}$  adjusted to 7 M [7], back extracted into water, evaporated, dissolved in concentrated  $\text{HCl}$ , and put on the same separation column. The radioactive isotopes of Ga and Ge were eluted from the column with a sequence of 5 M  $\text{HCl}$  and 0.5 M  $\text{HCl}$ . As before, all fractions of the eluate were measured by gamma spectrometry.

### *Spectrophotometric determination of Ge*

Independently, fractions of stable Ge eluted with 0.5 M  $\text{HCl}$  from the same column and at the same conditions at which As was separated, were measured by UV-VIS spectroscopy using phenylfluorone (9-phenyl-2,3,7-trihydroxy-6-fluorone) as a complexing agent for Ge.

The standard germanium solution was prepared by dissolving 0,19035 g of Ge in aqua regia, transferring it quantitatively into a volumetric flask and filling up to 100 ml with double-distilled water.

The aliquots containing: 0.18, 1.8, 7.5, 9.4, and 18.0  $\mu\text{g}$  of germanium were transferred into volumetric flasks into which the following substances were added: 10 ml of the double-distilled water, 1 ml of 6% w/w gelatine in water, 5 ml of 0.01% w/w phenylfluorone (for synthesis, Merck, Germany) in methanol, 5 ml of pure methanol, and 1 ml of acetate buffer in water. Then, the volume was adjusted to 25 ml with diluted HCl (1 + 4, v/v).

The absorbance was measured on a Helios-Alpha UV-VIS spectrometer in the 400 to 600 nm range against a blank solution containing all reagents except germanium [8]. (Fig. 1.)

## Results

### *Radionuclide purity*

After appropriate waiting period, the proton-irradiated germanium targets contained only measurable quantities of  $^{73}\text{As}$  and  $^{74}\text{As}$ , and so did the corresponding eluate fractions. At the day of shipment to the customers, only traces of  $^{74}\text{As}$  were detected in the  $^{73}\text{As}$  preparations.

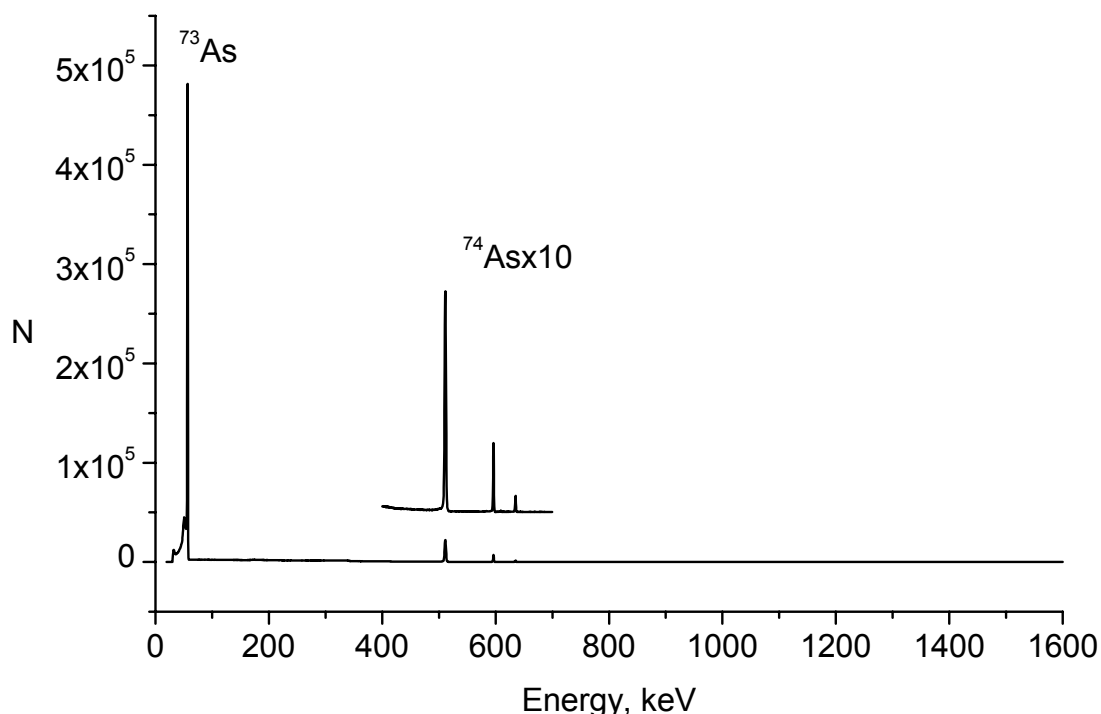


Fig. 1. Gamma spectrum of the irradiated germanium after 4 months from EOB.

Data acquisition time: 1 h.

The freshly irradiated zinc targets contained  $^{69}\text{Ge}$  produced in the  $\text{Zn}(\alpha, \text{xn})^{69}\text{Ge}$  reaction, and two isotopes of gallium, produced in the  $\text{Zn}(\alpha, \text{pxn})^{66}\text{Ga}$  and  $\text{Zn}(\alpha, \text{pxn})^{67}\text{Ga}$  reactions. Other irradiation products were not detectable.

### *Chemical purity of As*

The free volume of the ion-exchange column was determined as 7.8 ml. In concentrated HCl, the target material was retained on the column whereas arsenic(V) was passing through, and almost equal activities of As were detected in the effluent fractions corresponding to the 4<sup>th</sup> and 5<sup>th</sup> free volume. Starting from the 6<sup>th</sup> free volume, activity of As in the effluent was dropping rapidly. After recuperation of the whole As(V), germanium was eluted from the column with 0.5 M HCl. Such separation of As from Ge was possible only if arsenic was in 5+ oxidation state. Otherwise, the trivalent As was retained in the upper part of the column and could be removed only with 0.5 M HCl.

### *Separation of Ge from Ga*

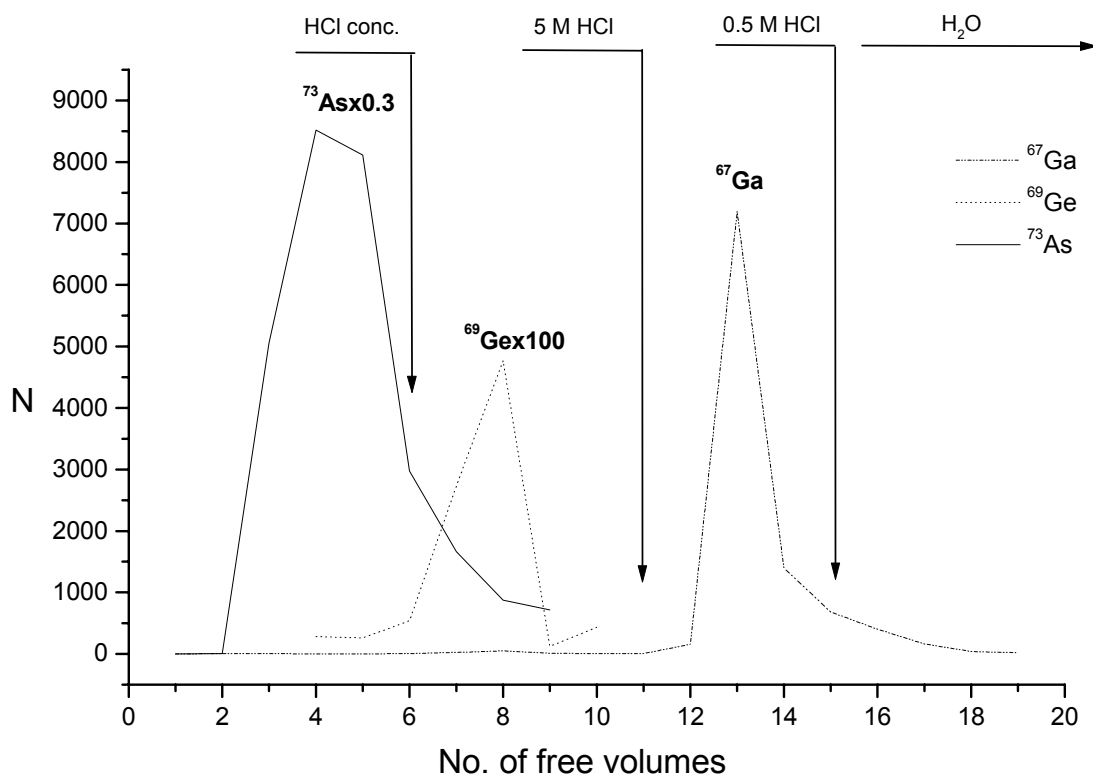


Fig. 2. Separation of  $^{73}\text{As}$  from Ge and of  $^{69}\text{Ge}$  from  $^{67}\text{Ga}$  on the Dowex-1 column (curves from two independent experiments).

The blank tests (without As isotopes) have shown that if a mixture of  $^{67}\text{Ga}$  and  $^{69}\text{Ge}$  in concentrated HCl was put on the same column, both tracers were retained and both could be eluted with HCl. The best separation was achieved if  $^{69}\text{Ge}$  was eluted first with 5 M HCl, after which  $^{67}\text{Ga}$  was eluted with 0.5 M HCl.

The combination of the elution curves for  $^{73}\text{As}$ ,  $^{69}\text{Ge}$  and  $^{67}\text{Ga}$  is shown in Fig. 2. It has to be noted that the experiments for  $^{73}\text{As}$  and for  $^{69}\text{Ge}$  and  $^{67}\text{Ga}$  were carried out independently. In the case of arsenic separation, elution of Ge was not started until the whole As was collected for further processing.

### *Spectrophotometry*

The UV-VIS spectra of the germanium-phenylfluorone complex in aqueous solutions are shown in Fig. 3. The detection limit for spectrophotometric determination of germanium was  $2 \times 10^{-6} \text{ mol dm}^{-3}$  ( $1.4 \times 10^{-4} \text{ g dm}^{-3}$ ). Within this sensitivity, no traces of the target material were detected in the simulated As fraction of the eluate (1<sup>st</sup> to 12<sup>th</sup> free volumes collected from the concentrated HCl).

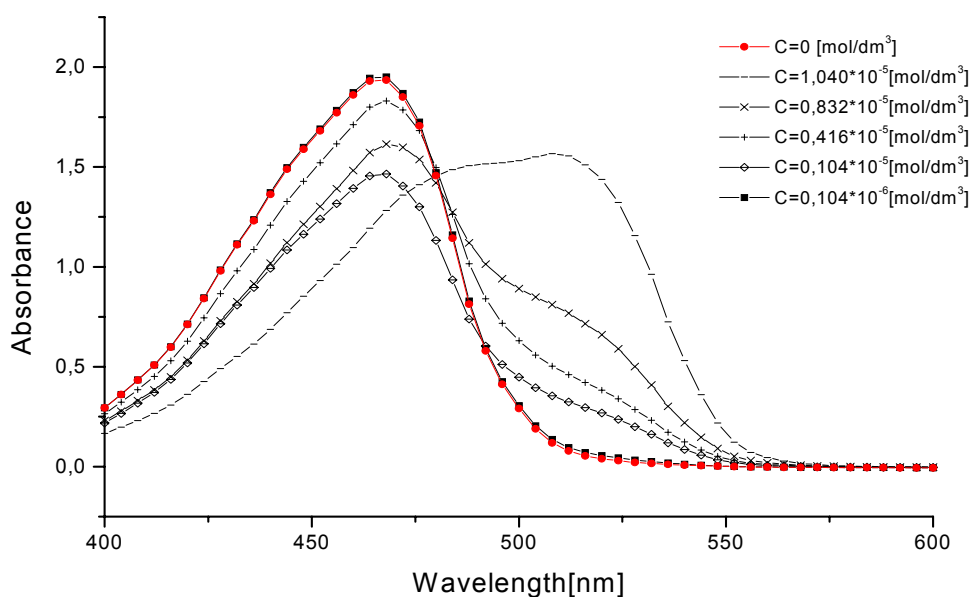


Fig. 3. Changes of the UV/VIS spectra of the germanium-phenylfluorone complex. Solutions containing: 0,  $1.04 \times 10^{-5}$ ,  $0.832 \times 10^{-5}$ ,  $0.416 \times 10^{-5}$ ,  $0.104 \times 10^{-5}$ , and  $0.104 \times 10^{-6} \text{ mol dm}^{-3}$  of germanium.

## Conclusions

- Under the conditions described above, the separation of As from Ge (as well as separation of Ge from Ga) is very good.
- The 5+ oxidation state of As is essential for its separation from Ge on the ion-exchange column.
- If the radiometric method of detecting germanium is not available, chemical purity of the As fraction can be determined spectrophotometrically with the detection limit of  $1.4 \times 10^{-4}$  g dm<sup>-3</sup> of Ge.

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## References

1. M.Green, J.A.Kaflas, *Journal of Chemical Physics*, 22(1954) 760.
2. U.Schindewolf, J.W.Irvine, Jr. Preparation of carrier-free vanadium, scandium, and arsenic from cyclotron targets by ion exchange. *Analytical Chemistry*, 30 (1958) 706-708.
3. I.J.Gruverman, P.Kruger. Cyclotron-produced carrier-free radioisotopes. *International Journal of Applied Radiation and Isotopes*, 5 (1959) 21-31.
4. D.Basile, C.Birattari, M.Bonardi, L.Geots, E.Sabbioni, A.Salomone. Excitation functions and production of arsenic radioisotopes for environmental toxicology and biomedical purposes. *International Journal of Applied Radiation and Isotopes*, 32 (1981) 403-410.
5. M.Ismail. Measurement and analysis of the excitation function for alpha-induced reactions on Ga and Sb isotopes. *Physical Review C*, 41 (1990) 87-108.
6. G.deBacker, P.van den Winkel, Vrije Universitet Brussels, private communication (1997).
7. I.A.Sheka, I.S.Chaus, T.T. Mityureva, *The chemistry of gallium* (Topics in Inorganic and General Chemistry, Monograph 5) Amsterdam / London / New York: Elsevier Publishing Co. Ltd. 1966, p. 225.
8. Z.Marczenko, M.Balcerzak. *Spectrophotometric methods in inorganic analysis* (in Polish: *Spektrofotometryczne metody w analizie nieorganicznej*). ISBN: 83-01-12612-4, PWN, Warszawa, 1998.