



## Novel radiochemical separation of arsenic from selenium for $^{72}\text{Se}/^{72}\text{As}$ generator

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### ARTICLE INFO

#### Article history:

Received 30 June 2011

Received in revised form

14 January 2012

Accepted 22 January 2012

Available online 1 February 2012

#### Keywords:

Selenium

Arsenic

Separation

Extraction chromatography

Positron emission tomography

### ABSTRACT

A new radiochemical separation scheme based on extraction chromatography has been proposed for isolation of arsenic from selenium. The distribution coefficients of As and Se on prepared sorbents: (selected aromatic o-diamines supported on polystyrene adsorbents) were determined in order to find the best condition for separation of both the elements. Batch experiments were verified by column studies. This work, together with earlier results from this Laboratory, enabled to elaborate a new separation scheme for selective and quantitative separation of arsenic from selenium. Proposed approach insures high selectivity and radionuclide purity of separated arsenic fraction; it is also characterized by high elution efficiency ( $> 95\%$ ) using small volume (2 mL) of 0.9% NaCl with very low breakthrough ( $< 0.01\%$ ) of selenium.

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### 1. Introduction

Due to its nuclear and physical properties,  $^{72}\text{As}$  is a potentially attractive radionuclide for nuclear medicine, in particular in positron emission tomography (PET) [1,2]. It has the positron emission rate of 88% with  $E_{\beta^+ \text{max}} = 2.5$  MeV. Its relatively long half-life of 26 h can provide  $^{72}\text{As}$  as a PET radionuclide of choice for the quantitative imaging of biochemical and physiological processes with longer biological half-lives, e.g. immunoimaging and receptor mapping [3–5]. Arsenic-containing bone, brain and tumor seeking species already exist. The versatile chemistry of arsenic will permit the synthesis of many potentially valuable PET radiopharmaceuticals. Compounds such as arsenic analogs of phenothiazines could be useful in PET technique. An organic arsenite has been shown to cross the blood–brain barrier, thus permitting imaging of cerebral tumors and trauma [2]. Methods are being developed to label monoclonal antibodies with arsenic so that tumor-specific PET imaging can be accomplished [6]. It is believed that the use of  $^{72}\text{As}$  will permit early detection of lung cancer by allowing very small tumors to be shown on PET images. One of the ways for obtaining  $^{72}\text{As}$  is using radionuclide generator where arsenic is formed by the radioactive decay of  $^{72}\text{Se}$ . The 8.4 day half-life of  $^{72}\text{Se}$  makes the  $^{72}\text{Se}$ – $^{72}\text{As}$  pair ideal for a radioisotope generator from which  $^{72}\text{As}$  can be obtained within about a month. Different As–Se separation strategies based on ion-exchange [7],

electrodeposition [8], distillation [9] or solid phase extraction [10,11] have been described for radionuclide generators during last 30 years. The methods proposed have some limitations: insufficient radionuclide purity of isolated arsenic, poor elution efficiency, difficult automation, etc. The aim of the present work was to develop a suitable radiochemical method for separation of  $^{72}\text{As}$  from  $^{72}\text{Se}$  with improved radiochemical yield, separation efficiency and radiochemical purity. The present investigation provided separation scheme based on extraction chromatography, which can be used for designing a new  $^{72}\text{Se}/^{72}\text{As}$  generator.

### 2. Experimental

#### 2.1. Reagents, ion-exchange resins, standards, radioactive tracers

2,3-Diaminonaphthalene (Sigma) and 3,3'-diaminobenzidine (Fluka) were used as received. Two resin supports were used: Amberlite XAD 4, 20–50 mesh (Rohm and Haas) was ground and sieved to obtain a fraction of particle size of 0.10 mm to 0.12 mm, whereas Bio-Beads SM-2, 200–400 mesh (Bio-Rad Laboratories), was used as received. The column filling for extraction chromatography was prepared by suspending the chosen support in the solution of appropriate o-diamine in water–ethanol mixture (1:1) and evaporating the solution at ca. 60 °C, with occasional stirring to obtain dry colored powder. The ratio of amine mass/sorbent mass  $R$  was 0.15.

For this study, all experiments were carried out using radioactive tracers of selenium-75 ( $T_{1/2} = 120$  d), arsenic-76 ( $T_{1/2} = 1.05$  d), and arsenic-73 ( $T_{1/2} = 80$  d), as the analogs of Se-72 and As-72.

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Radiotracers of  $^{75}\text{Se}$  and  $^{76}\text{As}$  were prepared by neutron irradiation of spectrally pure oxides or salts in the nuclear reactor MARIA at Świerk, Poland (neutron flux  $\sim 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ ).  $^{73}\text{As}$  was produced by  $^{nat}\text{Ge}(p,xn)^{73-75}\text{As}$  reaction at the AIC-144 cyclotron in Institute of Nuclear Physics in Cracow. All reagents were of the highest grade commercially available. High purity water (18 M $\Omega$  cm) from Milli-ORG Millipore Co. system was used throughout.

## 2.2. Apparatus

High pressure microwave system (Plazmatronika, Poland) was used to reduce Se(VI) to Se(IV).

The following spectrometers were used to perform gamma-ray spectroscopic measurements:

- 180 cm<sup>3</sup> HPGe well-type detector (Canberra) with associated electronics (Ortec) (resolution 2.09 keV for 1332 keV  $^{60}\text{Co}$  line, efficiency ca. 30%), coupled to the multichannel analyzer TUKAN (The Andrzej Soltan Institute for Nuclear Studies, Świerk, Poland),
- 255 cm<sup>3</sup> HPGe well type detector (Canberra) with associated electronic (Canberra) (resolution 2.15 keV for 1332 keV  $^{60}\text{Co}$  line, efficiency ca. 50%), coupled to the multichannel analyzer and spectroscopy software Genie-2000 (Canberra).

## 2.3. Procedures

### 2.3.1. Batch experiments

Mass distribution coefficients  $K_d$  (the ratio of the amount of a given species per 1 g of dry sorbent to that per 1 mL of the solution) were determined by batch equilibration at room temperature  $22 \pm 2$  °C. Known amounts of prepared sorbent (ca. 200 mg) were brought in contact (for 24 h with shaking) with 10 mL of a solution of appropriate composition, containing radioactive tracers. After 24 h the sorbent was filtered off and the concentration of individual tracer was determined in the aliquots of the solution by  $\gamma$ -ray spectrometry, and then compared with that of standard solution (without the resin). The distribution coefficients were calculated from the relation:

$$K_d = \frac{A_0 - A_s}{A_s} \times \frac{V}{m_j} \quad (1)$$

where  $A_0$  is the concentration of individual tracer in the standard solution,  $A_s$  is the concentration of individual tracer in an aliquot of the solution, after equilibration with the resin, loaded with a given extractant,  $V$  is the volume of the solution (mL) and  $m_j$  is the mass of dry resin (g).

In order to find potential separation possibilities for arsenic from selenium, their extraction behavior were investigated by batch equilibration technique in the systems: HCl ( $C_{\text{HCl}} = 0.05\text{--}0.5 \text{ mol L}^{-1}$ ) and NaCl solution (0.5–5%)—with an appropriate column filling.

### 2.3.2. Column studies

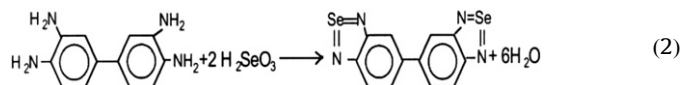
Column experiments were performed using the glass columns of 3–5 mm I.D., containing the resin bed of the height 3–4 cm, supported on a quartz wool plug or fritted glass disk. Arsenic and selenium radiotracers were introduced into the top of the column in a small volume of initial solution (depending on experiment), and then the remaining volume of the mobile phase was added. All of the column investigations were carried out at room temperature ( $22 \pm 2$  °C). The effluent was collected in fractions of several drops by means of a fraction collector, and measured using HPGe detector. The count rate measurements of respective

fractions were done with counting times in a live-time mode varying between 1 min and 15 min.

To verify the stability of the sorbent prepared in respect to retention of selenium within six weeks, repeated elution processes were carried out every week. 20 mL of 0.9% NaCl or 20 mL 0.1 M HCL were used as eluents. Each fraction from the column was measured for 20000 s.

## 3. Results and discussion

As well known, aromatic o-diamines are selective organic reagents for selenium. In acidic solutions, selenium(IV) forms stable, colored complex piaszelenol [12,13], according to Eq. (2):



Taking into account that extraction chromatography combines the selectivity of liquid–liquid extraction with the rapidity of chromatographic methods [14], selected orto-diamines: 3,3'-diaminobenzidine (DAB) and 2,3-diaminonaphtalene (DAN) (Fig. 1) were loaded on the two adsorbents Bio Beads-SM2 and Amberlite XAD4. Earlier work from this Laboratory have shown that selenium can be quantitatively retained on the prepared sorbents from acidic solutions [15,16]. In the earlier paper we described the process of reduction of Se(VI) to Se(IV), and the influence of the ratio  $R = m_{\text{ekstr}}/m_{\text{sorb}}$  on retaining of selenium traces [15]. Table 1 lists mass distribution coefficients for Se and As at various HCl concentrations. Both prepared sorbents have a very low affinity for As, its  $K_d$  values are less than 5 in all cases. Contrary, the  $K_d$  values for selenium are sufficiently high to ensure its quantitative retaining on the sorbents. A similar behavior is observed for NaCl solution (Table 2). The above conclusions were verified by the series of column experiments. In  $^{72}\text{Se}/^{72}\text{As}$  generator systems used for medical purposes, very important assumption is that arsenic fraction should be free from  $^{72}\text{Se}$ , as well as that it should be eluted with solution which can be easily used without any unnecessary chemical operation. Figs. 2 and 3 show the results obtained for two eluents: 0.9% NaCl and 2.5% NaCl for two sorbents: SM-2—2,3-diaminonaphtalene and SM-2—3,3'-diaminobenzidine. With the 2.5% NaCl, over 95% of total amount of arsenic is eluted in the first 5 mL fraction. In the case of 0.9% NaCl; over 95% of total amount of arsenic appeared in the 2 mL fraction of effluent. Figs. 4 and 5 illustrate elution curves of As in NaCl solutions from the sorbents: XAD 4—2,3-diaminonaphtalene and XAD 4—3,3'-diaminobenzidine. Similar elution profiles were obtained for dilute hydrochloric acid. Taking into account potential usage of described separation scheme for designing arsenic generator system and labeling appropriate biomolecules by  $^{72}\text{As}$ , the more convenient eluent is 0.9% NaCl solution.

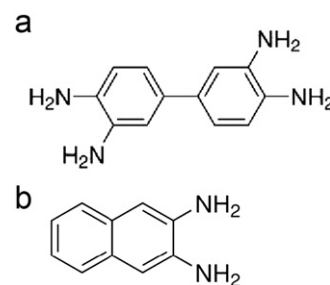


Fig. 1. Aromatic orto-diamines used for the preparation of stationary phases used in this work: (a) 3,3'-diaminobenzidine and (b) 2,3-diaminonaphtalene.

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