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Age determination of a ^{75}Se gamma radiography source for nuclear forensics

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Abstract

Two methods were used to evaluate the age of ^{75}Se sealed source material. Both methods utilized gamma spectroscopy to determine the quantity of parent ^{75}Se present, but they differed in the technique used to determine the quantity of daughter ^{75}As. In one method, ^{75}As was quantified using inductively coupled plasma-mass spectrometry (ICP-MS) after using chromatographic techniques to separate the parent and daughter isotopes. In the other method, total As was measured using optical emission spectroscopy (OES), which did not require separation prior to measurement. The OES method was faster and gave slightly lower uncertainties, but required more daughter material to be present because of higher concentration requirements, making it unsuitable for young material. Both methods are hampered by the monoisotopic nature of As, but still gave reasonable model ages that were in agreement with each other.

Keywords

Nuclear forensics; radiological material; Se-75; extraction chromatography

Introduction

A radioactive material's age is one of the primary parameters of interest to the field of nuclear forensics because it can provide unique insights to the material's origin and history.[1] In a single parent/daughter pair relationship in which the daughter is stable, the equation for determining the time since last purification (age) takes the form of:

$$t = ln\left(1 + \frac{N_D}{N_P}\right) \times \frac{1}{\lambda} \quad (1)$$

in which t is the time elapsed since purification, N_D is the number of atoms of the daughter, N_P is the number of atoms of the parent, and λ is the decay constant of the parent.[2]

Radiological materials can be especially tricky to determine an age for, as they often are composed of isobaric parent/daughter couples with the daughter nuclide being stable.[3] Because mass spectrometry is generally the analysis method of choice for nuclear forensics when measuring isotopes with half-lives longer than ~100 years, it is critical to ensure clean separation of the parent and daughter nuclides and to prevent the cross-contamination of the sample with environmental material when the daughter is naturally occurring.

One such radiological material is ^{75}Se. Selenium-75 sealed sources are relatively recent additions to the radiological material portfolio of most manufacturers. In recent years, they have been developed to replace the much more common ^{192}Ir sealed sources used in certain gamma radiography applications. The former has several advantages, including a longer half-life of 119.8 ± 0.05 d (^{192}Ir $t_{1/2}$ = 73.8 d).[4] This results in decreased dose to the end-users because sources need not be changed out nearly as often. In addition, ^{75}Se has softer gamma ray energies at 265, 136, 280 and 121 keV (> 0.10 gamma/decay) when compared to the ^{192}Ir gamma ray energies at 317, 468, 309, and 296 keV (> 0.10 gamma/decay), which can be advantageous when performing radiography on thin-walled or less-dense materials.[4]

Generally, ^{75}Se is produced either by bombarding ^{75}As targets with protons or by bombarding targets enriched in ^{74}Se with neutrons. The former method has the advantage of using naturally mono-isotopic ^{75}As and producing carrier-free ^{75}Se. This is the production method of choice when the ^{75}Se will be used in medical applications or as a radiotracer. The latter method has the advantage of an order of magnitude larger thermal

neutron cross section, and is the method of choice when very large activities of ^{75}Se are required, such as with gamma radiography.[5,6] This is fortunate, as it means that ^{75}As is not present in the target material is true, barring any trace contamination, and that equation (1) can still be used to determine when a radiography source was produced.

As advanced construction materials become lighter-weight and less dense, the importance of ^{75}Se as a gamma radiography source material could increase dramatically. Unfortunately, selenium has a relatively high volatility (relative to other sealed source materials like iridium and cobalt) and is toxic in small amounts. In addition to these drawbacks, ^{75}Se decays to stable arsenic, which is extremely toxic in small amounts and requires even depleted sources be handled carefully. These combined factors make ^{75}Se a concerning material when considering possible radiological dispersal device (RDD) scenarios. As a result, an effort has been put forth to develop a procedure to determine the age of a ^{75}Se source using radiochronometry.

Experimental

Materials

Anion and cation exchange chromatography resins were used to effect the cleanup of the source material and to separate ^{75}Se from the stable daughter ^{75}As. The cation exchange resin used in this work was AG 50W-X8, 100-200 mesh. The anion exchange resin used was AG 1-X8, 100-200 mesh. Both ion exchange resins were obtained from Bio-Rad Laboratories, Inc. Columns of each resin were prepared by slurrying the resin with de-ionized water (DIW) and packing it into a 1 mL Bio-Scale Mini Cartridge made of polypropylene with a height of 38 mm and an inner diameter of 6 mm. Optima grade nitric acid, hydrochloric acid, and 30% hydrogen peroxide solutions were obtained from Fisher Scientific. Sodium bicarbonate was ACS Grade (99.7+%) obtained from Acros Organics. All solutions used in this work were prepared using DIW from a Thermo Scientific™ Barnstead™ MicroPure™ water purification system.

All calibration standards and internal standard solutions were prepared using certified elemental standards of selenium, arsenic, vanadium, and scandium. The certified density of each standard was exploited to determine its concentration in terms of μg g^{-1} of solution. This allowed for mass-based dilutions, which reduce random and systematic errors. A depleted ^{75}Se gamma radiography source was acquired from the Idaho National Laboratory (INL) and dismantled to obtain the active source material for these experiments. Once the source was removed from its encapsulation, it was dissolved using optima grade mineral acids. Further serial dilutions were performed in an analytical chemistry fume hood using DIW, which produced the solutions used in this work. Prior to separation, samples were gently evaporated to dryness and reconstituted twice in 0.1 M HCl to ensure the material was in the appropriate matrix to begin the separation process. The source was acquired by INL in 2017 with an activity of roughly 18.8 mCi, and based on decay calculations had an approximate activity of 345 μCi at the time of dismantlement.

Measurements

Elemental and isotopic concentrations of Se, As, and Sc were measured using either inductively coupled plasma optical emission spectroscopy or mass spectrometry (ICP-OES or ICP-MS, respectively). A Perkin-Elmer/SCIEX™ ELAN DRC-II® quadrupole ICP-MS equipped with a SC-2-DX auto sampling system and discrete dynode detector was used for MS measurements, while a Perkin-Elmer Optima 8000 ICP-OES was used for OES measurements. Gamma spectroscopy was carried out using an Ortec GEM-35190 high purity germanium detector (HPGe) in a lead-shielded canyon. The detector was calibrated at various distances with an Eckert & Ziegler multi-nuclide NIST-traceable gamma standard for energy and efficiency. GammaVision version 7.02.01 software was used to capture, analyze, and report the results from the collected spectra.

Procedure

Two methods were tested for measuring stable As in solution. The first was relatively straightforward and involved measuring As directly from the initial dissolver solution using ICP-OES. This type of measurement is often avoided in nuclear forensics due to the lack of isotopic information that can be gleaned from this instrument. In this case, though,

the daughter, ^{75}As, is also the only stable isotope of arsenic, which means that there is no way to account for environmental As contamination using either this method or ICP-MS, the usual tool for radiochronometry. The OES analysis method also circumvents the need for performing a separation, as As can be measured at the 188.98 nm emission line, which does not suffer interference from Se, common alloying material (used to raise the boiling point of Se during irradiation), or common encapsulation materials.[7] The main drawback of this method is that it has a higher detection limit that ICP-MS. Given that the age of a relatively young source could feasibly be desired as part of an investigation, a separation and ICP-MS measurement method was also pursued in this work.

The separations utilized in this work were derived from *Wycoff et al.* in which a solution containing Se and As is neutralized with $NaHCO_3$ then oxidized using 30% H_2O_2 to ensure the two analytes are in the +6 and +5 oxidation states, respectively. For this work, excess H_2O_2 was pipetted into previously neutralized load solutions and refluxed at 95°C for varying lengths of time to determine the minimum reflux time required for complete oxidation. This was determined by observing how much Se was in the As fraction, as incomplete oxidation will result in co-elution of As and Se.

Once completely oxidized, the solution was then loaded onto a chloride form anion exchange column, after which As was eluted with 0.03 M HNO_3 and then Se was eluted with 0.6 M HNO_3.[8] Unfortunately, the chloride displaced from the column during elution could combine with Ar in the instrument plasma to create Ar-Cl, which interferes with the quantification of m/z 75. This can be corrected for by either use of a reaction cell or by mathematically correcting the signal intensity based on the measurement of other mass numbers. For this research, it was elected to correct the signal instead of develop and optimize a reaction cell protocol. Equation (2), in which I denotes the measured signal intensity for ^{75}As or a specified m/z, was used to correct the excess Cl signal at m/z 75.

$$I^{As-75} = I^{75} - 3.127[I^{77} - (0.874 * I^{82})] \quad (2)$$

To use this equation, m/z 82 is measured to determine how much natural Se is present in the sample. This is then used to subtract ^{77}Se signal from m/z 77, leaving only contributions

from Ar-Cl (^{40}Ar, ^{37}Cl) which is then used to subtract the extra Ar-Cl (^{40}Ar, ^{35}Cl) signal from m/z 75, leaving only contributions from ^{75}As.

All separations took place at room temperature, with columns loaded at a rate of 0.5 mL min^{-1} and eluted at a rate of 1 mL min^{-1}. The column setup was described previously in *McLain et al.* [3] The anion exchange columns were prepared by conditioning them with 5 mL of 0.1 M HCl before being used. Following this conditioning, the neutralized, oxidized solution was loaded and eluted as described in *Wycoff et al*.[8] During testing, it was also noted that V is often used as either the inner encapsulation or an alloying material for the ^{75}Se source (or both) due to its low neutron capture cross section and high melting point.[9-11] For this reason, V was added to the solutions used to test the method. Initially, method development was carried out using dilutions of stable certified spectroscopic standards. Following initial development, separations and measurements were carried out on a commercial ^{75}Se radiography source that had been retired at the end of its service life. This source had an initial activity certification date of January 21, 2015. Uncertainties reported for age calculations were evaluated as described in *Cummings et al.*[12]

Results and discussion

Method Development

The separation of Se and As using anion exchange resin relies on the difference in first dissociation constant values for arsenic acid (H_3AsO_4, pKa1 = 2.26) and selenic acid (H_2SeO_4, pKa1 = strong).[13] If Se is not completely oxidized, it will be present as selenous acid (H_2SeO_3, pKa1 = 2.62) and elute along with As in 0.03 M HNO_3.[13,8] Tests evaluating the minimum reflux time to completely oxidize Se and As showed incomplete oxidation until 2 hours, as evidenced by the presence of Se elution peaks in the 0.03 M HNO_3 elution fractions in Fig. 1. At 0, 1, and 2 hr oxidation times, roughly 100, 85, and 4 % of the Se was found in the collected fractions. Although 4 % of the Se was still present in the collected fractions, no distinct peak was seen which indicated the detected Se was likely due to background noise. This elevated noise was possibly due to the presence of an inconsistent amount of HCl in the collected fractions, which would have been eluted due

to the replacement of Cl^- ions on the column with NO_3^- with the introduction of dilute nitric acid to the column.

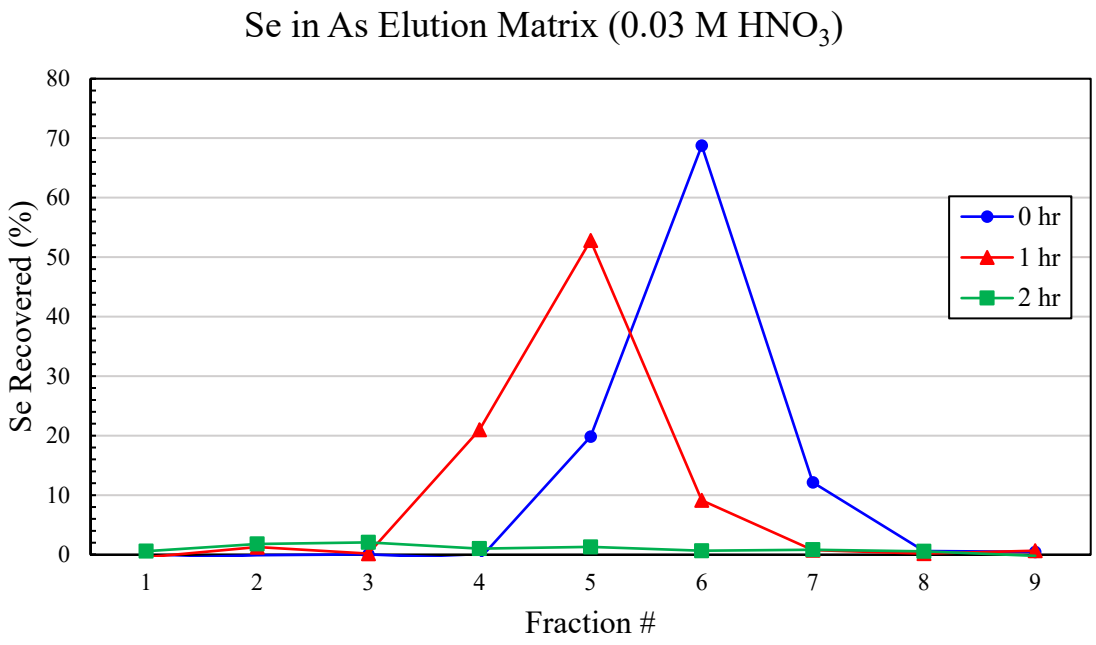
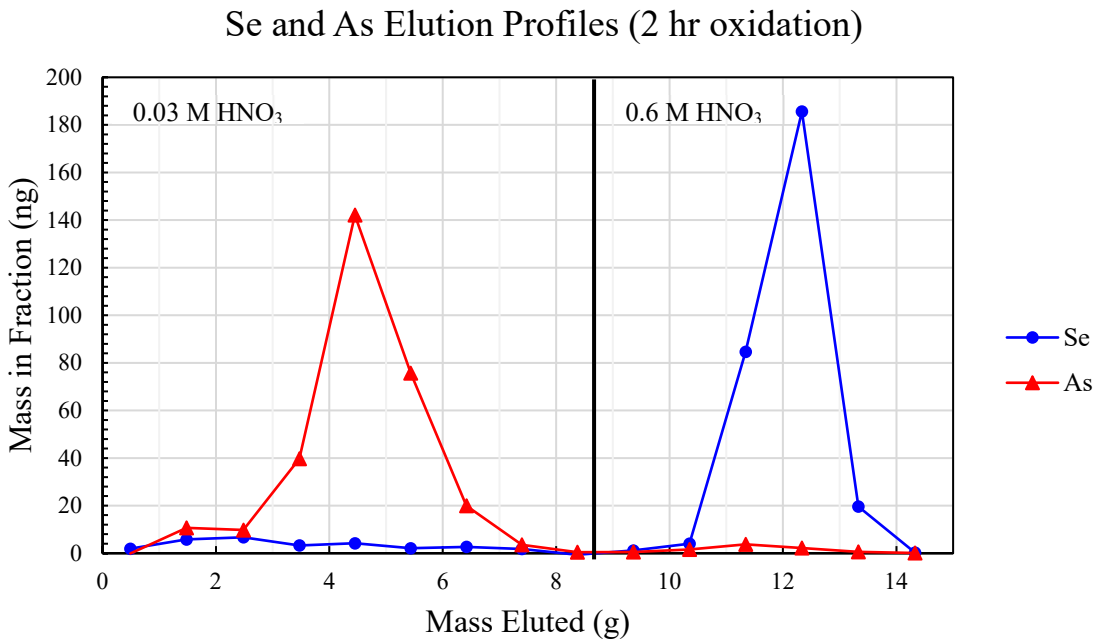


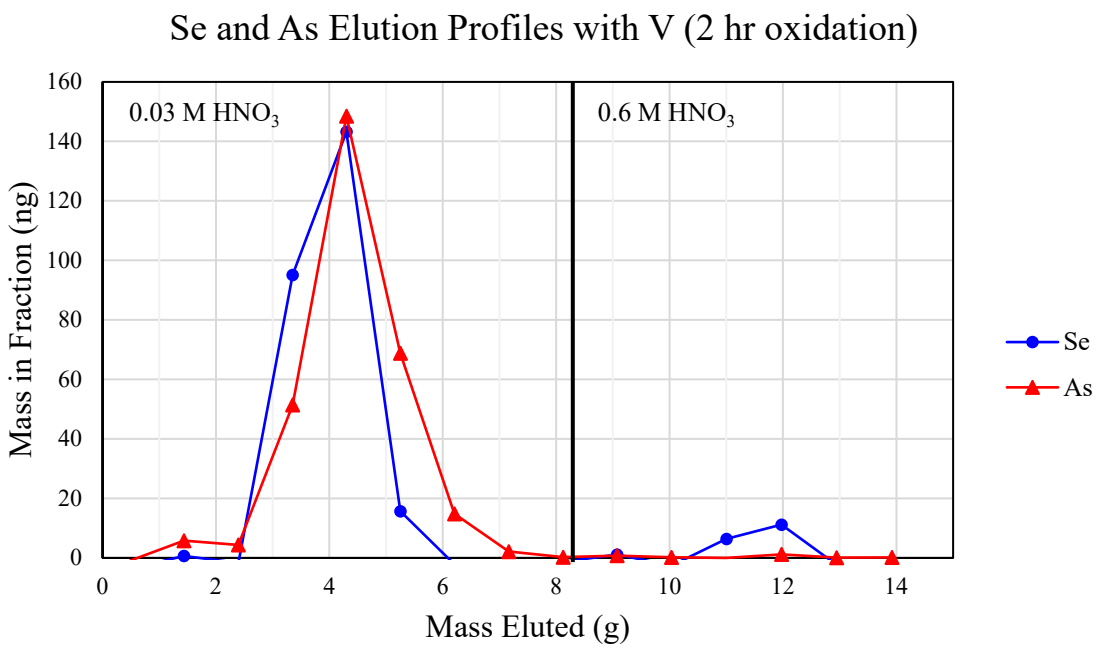
Fig. 1: Selenium found in collected As elution fractions for a 1 mL column. Each fraction was roughly 1 mL.

Fig. 2 shows the clean separation of Se and As associated with the complete oxidation achieved with a 2 hr reflux time. The vertical line at 8.4 g eluted indicates the demarcation between the As fraction (0.03 M HNO_3) and the Se fraction (0.6 M HNO_3). Prior to attempting the separation on real source material, V was added to the solution to simulate matrix effects from contamination by potential source capsule materials. When the same 2 hr reflux time was used in the presence of this V, very little oxidation of Se occurred, as evidenced by the large mass of Se in the As fraction and the small Se peak in the Se fraction at 11-13 g eluted in Fig. 3. Because it was unclear how much V might be present in a real source and it seemed likely that the aqueous conversion of VO^{+2} to VO_2^+ was both using up the oxidative power of H_2O_2 and re-reducing any oxidized Se^{6+} back to the Se^{4+} state (see equations (3)-(6)[14]), it was decided to remove the V prior to the Se/As separation using a cation exchange column.



187

188 *Fig. 2:* Selenium (circles) and As (tirangles) elution profiles from a 1 mL column of AG 1X8 anion exchange resin after
189 2 hr oxidation.



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191 *Fig. 3:* Selenium (circles) and As (tirangles) elution profiles from a 1 mL column of AG 1X8 anion exchange resin after
192 2 hr oxidation in the presence of V.

193 $$VO_2^+ + 2H^+ + e^- \rightleftarrows VO^{2+} + H_2O + 1.00eV \quad (3)$$

$$HSeO_4^- + 3H^+ + 2e^- \rightleftarrows H_2SeO_3 + H_2O + 1.15eV \quad (4)$$

$$H_3AsO_4 + 2H^+ + 2e^- \rightleftarrows H_3AsO_3 + H_2O + 0.575eV \quad (5)$$

$$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O + 1.78eV \quad (6)$$

To remove V from the solution, a 1 mL column of AG 50W-X8 was prepared as described above and conditioned with 5 mL 0.1 M HCl. A solution of Se, As, and V in 0.1M HCl was then loaded on the column and 10 mL 0.01 M HCl was used to elute the column. The V stayed on the column, while Se and As were eluted in the first 4 mL of solution with ≥ 95% recovery. After this column was implemented as a clean-up step, the 2 hr reflux was once again sufficient to oxidize all of the Se and As to their highest states, and complete separation was achieved, which is illustrated in Fig. 4. Though Se recovery was somewhat low (~ 40%), it was suspected that this was due to an abbreviated Se elution volume. Ultimately, the ^{75}Se will be quantified using gamma spectroscopy on the solution prior to separation, so complete recovery of the Se was unimportant. Recovery of As was excellent (91 ± 3 %), with very little material lost to either of the column separations or the oxidation step. These results indicate this separation strategy would work well in performing radiochronometry on ^{75}Se source material.

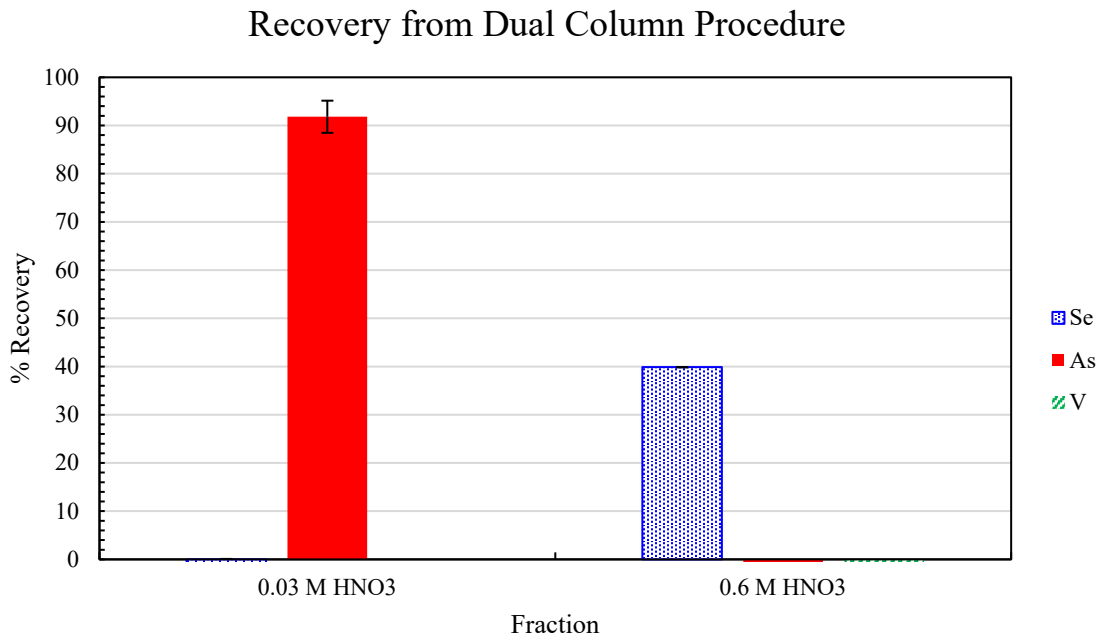

Fig. 4: Recovery of As, Se, and V when using the cation column clean-up followed by neutralization, oxidation, and anion column separation.

Age Determination of a ^{75}Se Source

A 6:50 dilution of the original dissolved source solution was prepared and used for all of these analyses. Gamma spectroscopy was carried out on a 1 g aliquot, in which the sample was counted for 5 days followed by a 5-day background count. The results of this analysis indicated an activity concentration of 1.66 ± 0.14 µCi/g at the 95% confidence level on the day of analysis (Nov 27, 2019). Analysis of the same 6:50 solution via ICP-OES indicated the As concentration was 62.96 ± 0.51 µg/g when analyzed 47 days later. Decay correcting the gamma activity information to the time of ICP-OES analysis and applying equation (1) results in a model purification date of 8/18/2013 ± 30 days (k = 2). Though natural As contamination in the source could not be directly quantified, an un-irradiated target from the same source manufacturer was obtained, dissolved in the same manner, and characterized for As content. This data was used to estimate the amount of natural As contained in the initial target, and was subtracted from the total As measured in the source material. The coinciding age adjustment was roughly 1 day younger.

The separation procedure that was developed as part of this work, which is summarized in Fig. 5, was used on a 1 mL aliquot of the 6:50 dilution prior to making measurements via ICP-MS. During sample processing, As recovery was determined using 7.4 μCi of ^{73}As as a radiotracer.

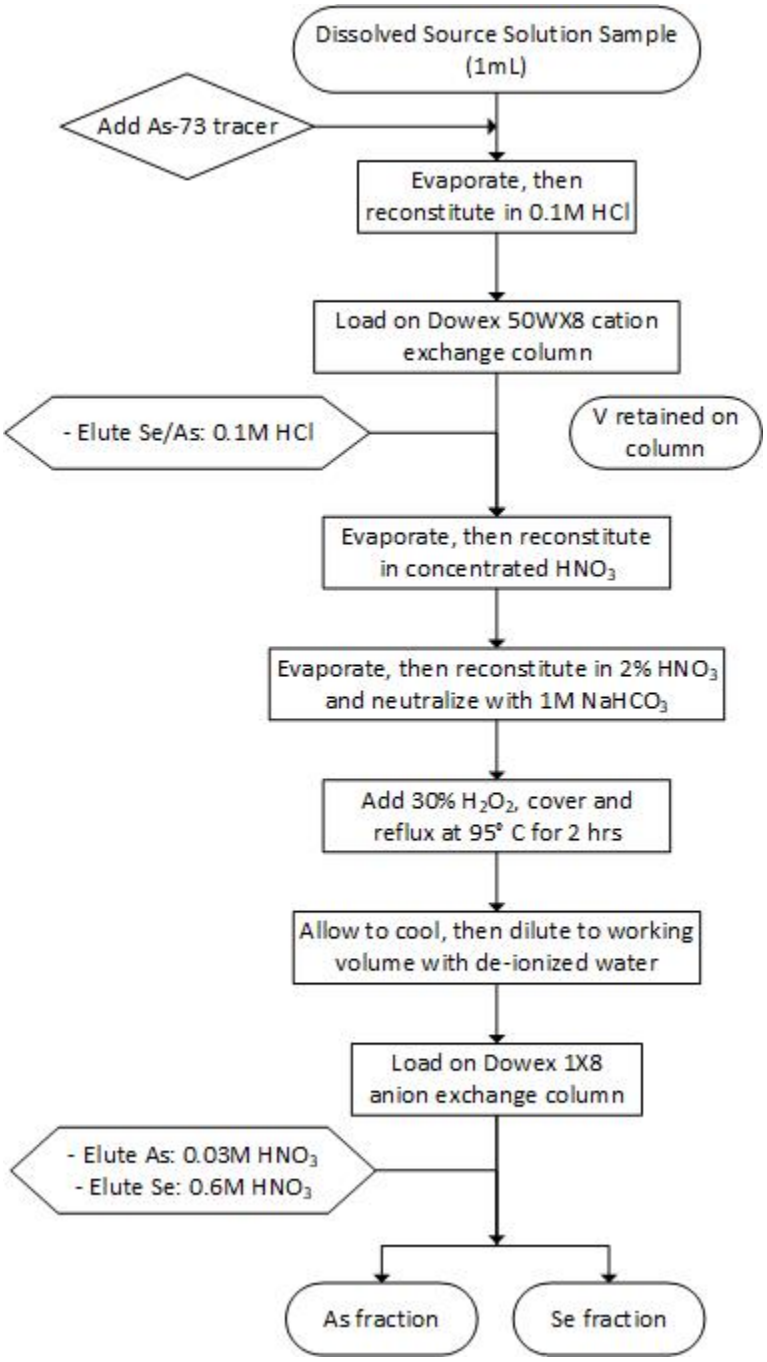

Fig. 5: Flow chart for the processing procedure used on the ^{75}Se source material

Analysis of the separated fractions indicated that the As recovery was 93.7 ± 5.7%, and that the As concentration in the 6:50 dilution solution was 51.0 ± 3.1 µg/g, as analyzed on Aug 3, 2020. Gamma spectroscopy carried out on the remainder of the working solution used to perform the separation indicated that the initial ^{75}Se content was 0.519 ± 0.035 µCi/g at the 95% confidence interval on the day of analysis (Aug 20, 2020). Using this data, a model purification date of 11/11/2013 ± 60 days was calculated.

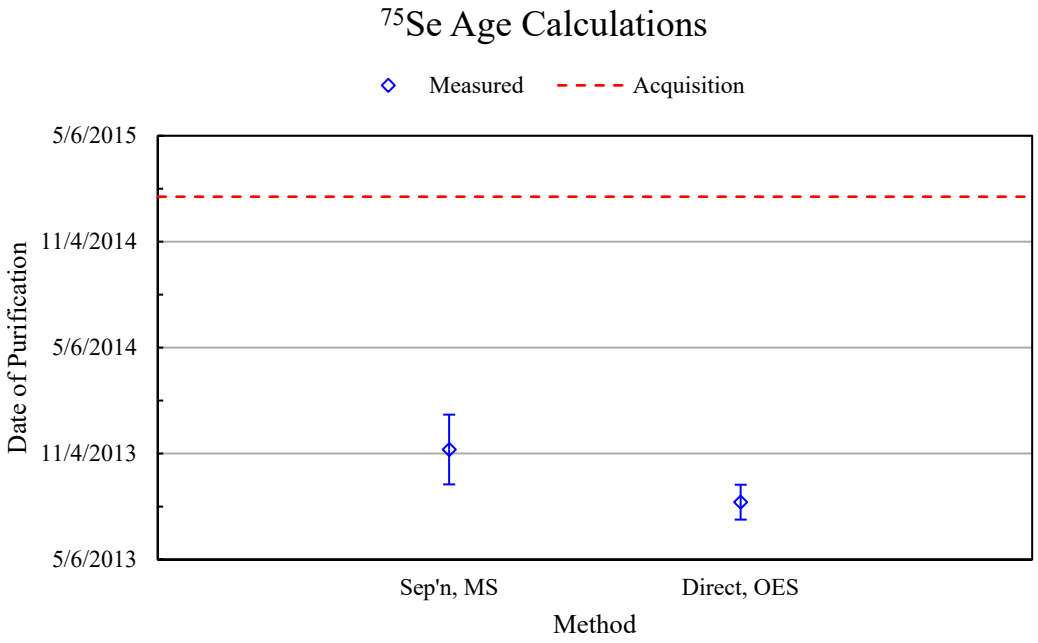

Fig. 6: Model ages obtained for the dissolved ^{75}Se sealed source material when measuring ^{75}As via ICP-MS after separation and when directly measuring the total As via ICP-OES, along with the date the depleted source was acquired by INL.

Fig. 6 shows the results of the two analyses, as well as the known acquisition date by INL. The two model ages indicate the source is much older than the acquisition date, and are in good agreement with each other, despite using two different methods for their determination. These results are promising and indicate that a model age can be determined for dissolved ^{75}Se material by simply analyzing it via gamma spectroscopy and ICP-OES without separating the isobaric parent and daughter first.

Conclusions

Radiochronometry methods were developed for determining the model age of ^{75}Se source material. It was found that direct measurement of an aqueous solution containing ^{75}Se and its stable daughter, ^{75}As, using a combination of gamma spectroscopy and ICP-OES techniques could be used to determine a model age. Further, it was found that this method was in good agreement with a more time-consuming method that was developed over the course of this work, in which gamma spectroscopy was used to quantify the parent isotope while the daughter isotope was quantified using ICP-MS after separating it from the parent using ion exchange chromatography. The separation method, based on previous work by *Wycoff et al.*, worked well but required the addition of a clean-up step using cation exchange resin to remove vanadium that interfered with a crucial oxidation step that facilitated the separation of parent and daughter. Further efforts would have to be undertaken using a source with a known age and pedigree to validate these techniques, but these preliminary analyses indicate they should be effective.

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