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Advances in ^{79}Se Analyses on Savannah River Site Radioactive Waste Matrices

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Waste cleanup efforts underway at the United States Department of Energy's (DOE) Savannah River Site (SRS) in South Carolina, as well as other DOE nuclear sites, have created a need to characterize ^{79}Se in radioactive waste inventories. Successful analysis of ^{79}Se in high activity waste matrices is challenging for a variety of reasons. As a result of these unique challenges, the successful quantification of ^{79}Se in the types of matrices present at SRS requires an extremely efficient **and** selective separation of ^{79}Se from high levels of interfering radionuclides.

A robust ^{79}Se radiochemical separation method has been developed at the Savannah River National Laboratory (SRNL) which is routinely capable of successfully purifying ^{79}Se from a wide range of interfering radioactive species. In addition to a dramatic improvements in the K_d, ease, and reproducibility of the analysis, the laboratory time has been reduced from several days to only 6 hours.

Introduction

^{79}Se is a pure beta-emitter (E_{max}=151keV) with a radiological half-life of $2.95 \bullet 10^5$ years. At the Savannah River Site, the isotope was produced as a by-product of the plutonium production operation. Due to its relatively long half-life, as well as its mobility in the environment, ^{79}Se is an isotope of particular concern in Site inventories. It has, therefore, been an issue for waste characterization and disposition. While currently representing only a small fraction of the activity in the various Sites' radioactive waste inventories, the isotope will eventually represent a more significant portion of the inventories due to its relatively long half-life.

SRS wastes fall primarily into three categories: High Level Waste (HLW) tank supernate, a salt-cake formation, and a sludge layer on the bottom of the tank. It was originally unclear which of these categories contained ^{79}Se. Unaltered by waste treatment, the ^{79}Se inventory would exist at 6-7 orders below the total ^{137}Cs inventory in any of the categories. Both the supernate and the more concentrated salt-cake are comprised predominately of ^{137}Cs in terms of radiological distribution. Supernate ^{137}Cs activities are typically in the 10^{12} dpm/L range. Other fission products (i.e., ^{125}Sb, ^{126}Sn, the shorter lived ^{106}Ru, etc.) exist at still lower levels, while ^{90}Sr, the actinides, and the lanthanides exist at trace levels. The sludge radiological inventory is primarily made up of hydroxides of Sr, the actinides and the lanthanides with gross activities in the range of 10^{10} dpm/g. ^{137}Cs and isotopes such as ^{99}Tc exist at substantially lower relative levels in the sludge.

Successful analysis of ^{79}Se in high activity waste matrices is challenging for a variety of reasons:

- Required detection limit requirements for ^{79}Se are quite low.
- ^{79}Se is typically present in very small concentrations relative to the other radioactive species present in waste inventories.

- ^{79}Se is a pure beta emitter with a relatively low average energy, so it is highly susceptible to spectral interference during the counting processes.

Waste Acceptance Criteria at various repositories often require ^{79}Se measurements which are 8 orders of magnitude lower than the concentration of interfering radioactive species, necessitating an extremely efficient **and** selective separation of ^{79}Se from high levels of interfering radionuclides. SRNL's traditional ^{79}Se radiochemical method was loosely based upon a method published in the DOE Methods[1]. The separation methodology relied upon repetitive purifications by precipitation of selenium as a metal, decontamination of the selenium with a mixed bed resin, and purification of the selenium using distillation. The method was very labor intensive (requiring several days to complete) and yields were so variable that numerous re-analyses were required to meet target detection limits.

In response to the need for a more efficient and more reliable separation, a robust ^{79}Se radiochemical separation method has been developed at SRNL which is routinely capable of successfully purifying ^{79}Se from a wide range of interfering radioactive species (K_d ~E10). In addition to dramatic improvements in K_d, ease, and reproducibility, the laboratory time has been reduced from several days to only 6 hours.

Experimental

Initial Separation and Analysis Method

The method initially utilized for ^{79}Se separations was based on a publication in DOE Methods. Stable Se tracer was added to an aliquot of sample, and the Se was then precipitated via reduction with hydroxylamine hydrochloride and heat. The precipitate was collected via centrifugation, washed, and dissolved using concentrated HNO_3. At this point, the Se was decontaminated from interfering nuclides via oxidation with Br_2 to form H_2SeO_3. This solution was decontaminated using a batch addition of mixed-bed resin followed by filtration. The filtrate was treated with concentrated HBr and reduced with hydroxylamine hydrochloride. The Se/hydroxylamine hydrochloride mixture was heated to precipitate Se metal. The precipitate was collected via centrifugation, washed, and dissolved using concentrated HNO_3. The concentrated HNO_3 containing the purified Se was neutralized by the addition of caustic and aliquots of the neutralized solution were analyzed by liquid scintillation counting (LSC) for ^{79}Se quantification and atomic absorption spectroscopy (AA) to determine tracer recovery.

Evaluation Strategy

The method just described was labor intensive, time consuming, technique dependent, and produced marginal results. The decontamination of Se from interfering nuclides was insufficient for typical samples, the tracer recoveries were extremely low, and the overall outcome of the method was too analyst-dependent for routine use.

Various studies were carried out to evaluate decontamination efficacy and Se losses throughout the method. The outcome of each of the studies will be presented.

Rapid Recovery Determination

Tracer recoveries were monitored using several different approaches: AA was initially used, but this was not efficient since the AA laboratory was independent of the radiochemistry laboratory. To facilitate rapid method development, and provide almost immediate feedback on tracer recovery during step-wise evaluations, the SRNL ^{252}Cf neutron activation analysis (NAA) facility, which is part of the radiochemistry laboratory, was used[2]. The NAA facility was used to provide neutron activation analysis on sample fractions spiked with stable selenium (^{76}Se(n,γ)^{77m}Se, $t_{½}$ 17.4s, 162 keV γ-ray). The NAA facility was also used to activate stable Se to ^{75}Se, a convenient spike easily quantified by gamma pulse height analysis (^{74}Se(n,γ)^{75}Se, $t_{½}$ 119.8d, 265 keV γ-ray).

Evaluation of Hydroxylamine HCl Precipitation

Substantial losses of Se were observed during each hydroxylamine hydrochloride precipitation step. The addition of titanium chloride with ascorbic acid along with the hydroxylamine hydrochloride during reduction dramatically improved recovery. The combination of all three of these reducing agents was required to obtain improved recovery; combinations of 2 of the 3 did not prove as effective.

Evaluation of Se Loss During Large-Volume Decontamination Rinses

Substantial losses of Se were observed during centrifugation and precipitate washing. The use of filtration rather than centrifugation facilitated rapid large-volume rinses. Successive rinses using 20mL 1.0N HNO_3, 50mL DI water, 100mL 0.1N HNO_3, and 100mL 2.0N HNO_3 were evaluated and no measurable loss of Se was observed.

Evaluation of Se Loss during Concentration Steps

Losses of Se during concentration steps were significant. Concentration by heating in HCl or HBr resulted in significant losses. However, it was determined that Se in the presence of HNO_3 could be successfully concentrated using oven temperatures as high as 170º C.

Evaluation of Se Losses with Various Resins

Selenium losses were evaluated with a variety of different resins typically used during decontamination: Bio-Rad ammonium molybdophosphate AMP-1 (for Cs-137 decontamination), Eichrom Actinide Resin (for actinides and lanthanides), Eichrom Sr Resin (for Sr-90), Bio-Rad AG 50W-X8 (for cations), Bio-Rad anion exchange resin (for anions), and Eichrom TEVA® (for Tc-99 at low acid strengths or tetravalent ions at high acid strength). No significant Se losses due to retention were observed for any of these resins.

Evaluation of Se Loss During Final Preparation for Liquid Scintillation Analysis

When utilizing the DOE-based methodology, the final form of the isolated Se (concentrated HNO_3 solution) was incompatible with Ultima Gold AB liquid scintillation cocktail. Neutralization to a cocktail-compatible pH resulted in significant losses.

Revised ^{79}Se Separation Method

Based on observations discussed in previous paragraphs, a revised methodology for ^{79}Se separation was attempted on HLW samples. Stable Se tracer and concentrated HNO_3 were added to an aliquot of HLW, which was then reduced to dryness in a 170º C oven. The dried material was re-dissolved in 0.5N HCl, at which point Se metal was precipitated by the addition of hydroxylamine hydrochloride, titanium chloride, and ascorbic acid. The precipitate was filtered and successively rinsed with DI water, 0.1N HNO_3, 1.0N HNO_3, and 2.0N HNO_3. The rinsed precipitate was dissolved in concentrated HNO_3 followed by dilution to an acid strength of 0.6N prior to resin decontamination steps.

Decontamination steps were carried out using batch addition of a mixture of AMP-1, anion exchange resin, and AG 50W-X8 followed by filtration through a TEVA® disc. This process was carried out 3 times. The decontaminated Se-containing filtrate was concentrated to near dryness and diluted with DI water to a final volume of 3mL.

Aliquots of this purified and concentrated Se-containing fraction were analyzed by liquid scintillation counting for ^{79}Se quantification. Separate aliquots of the Se-containing fraction were analyzed by neutron activation analysis to determine tracer recovery.

Results of Revised ^{79}Se Separation Method

Se losses, traced using ^{75}Se, were substantial during several steps: the re-dissolution of Se metal in concentrated HNO_3 and the pH adjustments prior to resin decontamination and liquid scintillation counting. This revised method, while more rapid than the original, still required 2-3 days.

A Different Approach

A completely different approach to Se separation was attempted due to the still lengthy laboratory steps and inconsistent, sometimes terrible recoveries. A separation of Se from Te using tributyl phosphate (TBP) was described by Y.C. Hoh et. al.[3] This approach involved the extraction of tetravalent Se as $SeCl_4$ using 30% TBP in kerosene. Based on this article, and the routine use of tetravalent extraction chromatography already established in the radiochemistry laboratory, the feasibility of extraction chromatography on Se(IV) was evaluated using the following Eichrom resins: RE, UTEVA®, Actinide, and TEVA®.

Results from initial studies utilizing HCl (to form $SeCl_4$) were sporadic. The use of HBr (to form $SeBr_4$) was evaluated. The Se solution was dissolved with concentrated HBr and then diluted to 9N HBr for column loading. The presence of $SeBr_4$ was visible on the columns as a dark band.

The RE and UTEVA® resins provided superior results relative to TEVA® and Actinide resins. Unfortunately, all of the resins demonstrated Se elution during rinsing with less than one column-volume of 9N HBr. Se was eluted with 1 column-volume of DI water. Unfortunately, some interfering species ^{126}Sn (as $SnBr_4$) and ^{125}Sb (as $SbBr_3$, with RE) were retained and eluted along with Se.

The method utilizing the extraction of tetravalent Se was carried out as follows for the two most promising resins (UTEVA® and RE). Selenium tracer was added to an aliquot of sample which was nitrated through the addition of concentrated HNO_3. The solution was reduced to dryness using a 170º C oven. The Se was reconstituted in 0.5N HCl and Se metal was precipitated by the addition of hydroxylamine hydrochloride, titanium chloride, and ascorbic acid. The precipitate was filtered, rinsed successively with DI water, 0.1N HNO_3, 1.0N HNO_3, and 2.0N HNO_3. The rinsed precipitate was dissolved in 5mL concentrated HBr to form $SeBr_4$. The $SeBr_4$ solution was diluted to 9N HBr using DI water and subsequently loaded onto either UTEVA® or RE columns. The columns were rinsed with 1mL 9N HBr. The dark brown band of $SeBr_4$ was mobile, necessitating this small rinse volume. The Se was then eluted from the columns using 3mL DI water, followed by 2mL concentrated HNO_3.

The Se-containing eluate was further decontaminated. It was evaporated to dryness and reconstituted in 0.5mL 8N HNO_3. The sample was diluted to a total volume of 4.5mL using DI water, and then subjected to several batch treatments with Bio-Rad AMP, actinide resin, and AG 50W-X8. The slurry was filtered using a 0.45µm cellulose filter. Aliquots of the purified and concentrated Se-containing filtrate were analyzed by liquid scintillation counting for ^{79}Se quantification. Separate aliquots of the Se-containing fraction were analyzed by NAA for tracer recovery determination. It is noteworthy that the final state of this method is a small volume of DI water, which is easily added to LSC cocktail and NAA rabbits for analysis-thus eliminating the loss-prone concentration and pH adjustment steps.

The results from this approach indicated weak retention of Se on the columns, precluding thorough rinsing of the columns and reducing the decontamination effectiveness. The yields for this method were still very dependent upon laboratory technique.

Tributyl Phosphate and n-Paraffin Extraction of Se

At this point, the solid phase resin extraction method of tetravalent Se was replaced with solvent-solvent extraction using a 30% tributyl phosphate/n-paraffin system. This method was less dependent on laboratory technique than the resin technique and was more robust due to increased active extraction sites. It also facilitated simple preparation for LSC and NAA since small volumes of DI water were used for back-extraction of Se. The solvent-solvent extraction provided significantly higher decontamination factors than the solid phase resin extraction techniques, enabling the elimination of the time consuming and loss-prone decontamination and rinsing steps. However, it was found the selectivity for Se was not sufficient to preclude co-extraction of the interfering radionuclide ^{125}Sb.

The Final Method-The Best of Both Approaches

Since interfering nuclides were co-extracted using the solvent-solvent system, both methods of extracting Se(IV) were combined. The poor affinity for $SeCl_4$ coupled with the excellent affinity for $SbCl_4$ in the RE system were utilized to improve ^{125}Sb decontamination during ^{79}Se analyses. The RE system, coupled with the solvent-solvent extraction provided a robust, efficient, relatively rapid method for ^{79}Se separation and analysis (Fig 1).

Sample was spiked with Se tracer and the solution was acidified to 6M HCl. The solution was treated with a batch addition of AMP (to extract ^{137}Cs), and the slurry was added to a RE column (to extract ^{125}Sb). The column was rinsed with 2mL 6N HCl. The Se-containing eluate/rinse was diluted with DI water to 1N HCl. Se metal was precipitated from this solution by the addition of hydroxylamine hydrochloride, titanium chloride, and ascorbic acid. The precipitate was filtered, rinsed with 20mL 2N HNO_3 and 20mL 1N HNO_3. The washed precipitate was dissolved in concentrated HBr and diluted to 9N HBr with DI water. The $SeBr_4$ was extracted with 30% TBP/n-paraffin (4:1 v/v). The organic layer was back-extracted with DI water (1:2 v/v). Aliquots of the aqueous extract, which needed no concentration of pH adjustment, were analyzed by LSC and NAA.

Apparatus

LSC analyses were carried out using Packard Ultima Gold AB liquid scintillation cocktail with a Packard Instruments 2550 AB, a PI 2750 AB, or a PI 3150 AB equipped with a bismuth germanate gamma-ray guard.

Gamma analyses carried out to determine tracer recoveries were conducted on a high purity germanium detector (for ^{75}Se) or a NaI well detector (for ^{77m}Se). The MCA software used for the gamma measurements was Canberra's Genie 2K spectroscopy package.

Results and Discussion

Numerous experiments were carried out to study ^{79}Se separations. Results from each set of experiments were used to optimize the methodology currently used in the laboratory. Concentrations steps were carried out in nitrate solutions to minimize losses. Decontamination by solid-phase extraction using both AMP-1 and RE were optimized using HCl solutions to remove interferences such as ^{137}Cs and ^{125}Sb. The Se was reduced and precipitated using the combination of hydroxylamine hydrochloride, titanium chloride, and ascorbic acid.

The feasibility of extracting Se(IV) as $SeBr_4$ using commercially available extraction-based chromatographic resins was explored. Decontamination factors were not high enough for any of the resins to provide a useful decontamination step.

Solvent-solvent extraction was explored using 30% TBP/n-paraffin and was found to be substantially more robust than the solid phase extraction methodology. Solvent-solvent extraction, which did not provide adequate decontamination factors of ^{79}Se from other radioactive species by itself, offered considerable time saving synergies to decontamination steps already in place.

Ultimately, a combination of the most promising methods is currently utilized: removal of many interferences using solid-phase extraction resins followed by purification of Se by extraction as $SeBr_4$ in a TBP/n-paraffin solvent-solvent system. Data on the activity levels of radionuclides present in an SRS waste tank sample run through this protocol in triplicate are provided in Figure 2. No other radioactive species were observed in this sample other than Se-79. Selenium carrier recoveries for the analyses typically are around 50%. The relative percent standard deviation for the Se-79 set of data depicted in Figure 2 was 6.1%.

Conclusions

A robust ^{79}Se radiochemical separation method was devised which is capable of purifying Se from a wide range of interfering radioactive species with decontamination factors approaching 10 orders of magnitude. The laboratory time for this method was drastically improved from several days to 6 hours.

References

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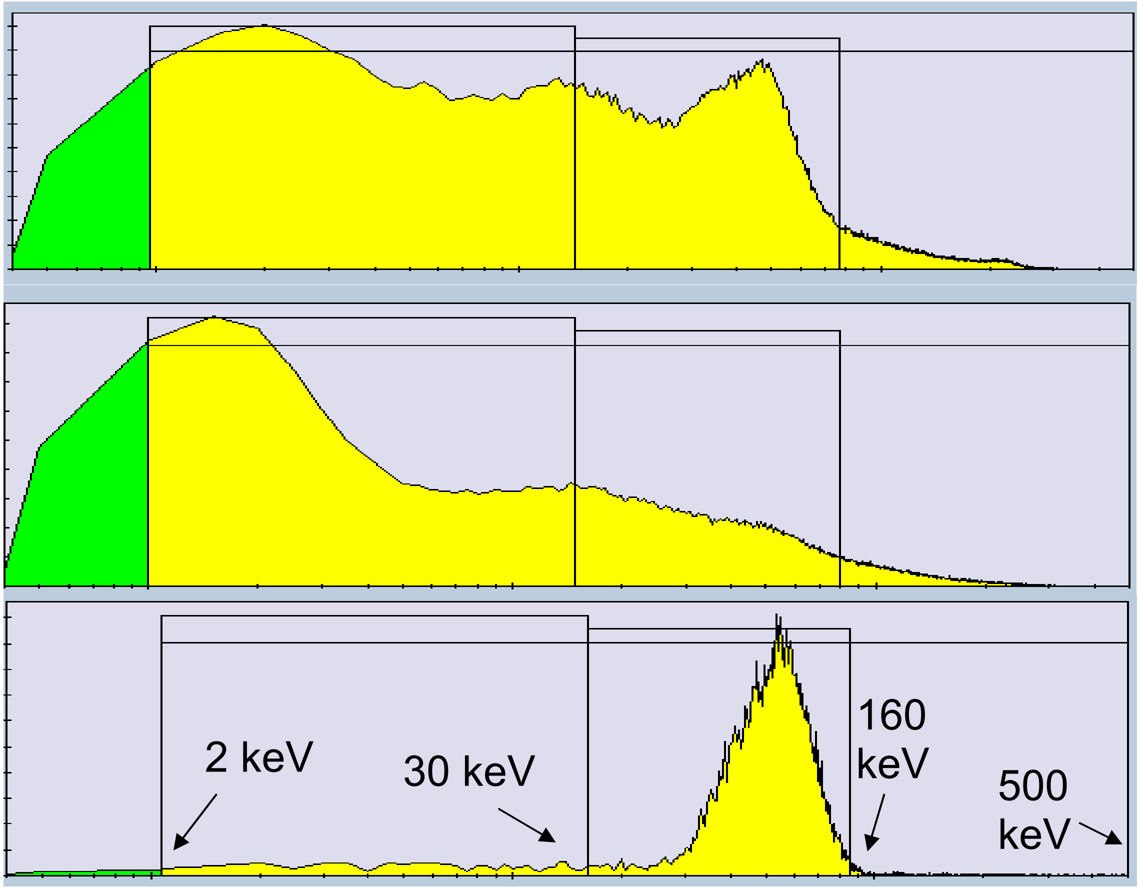
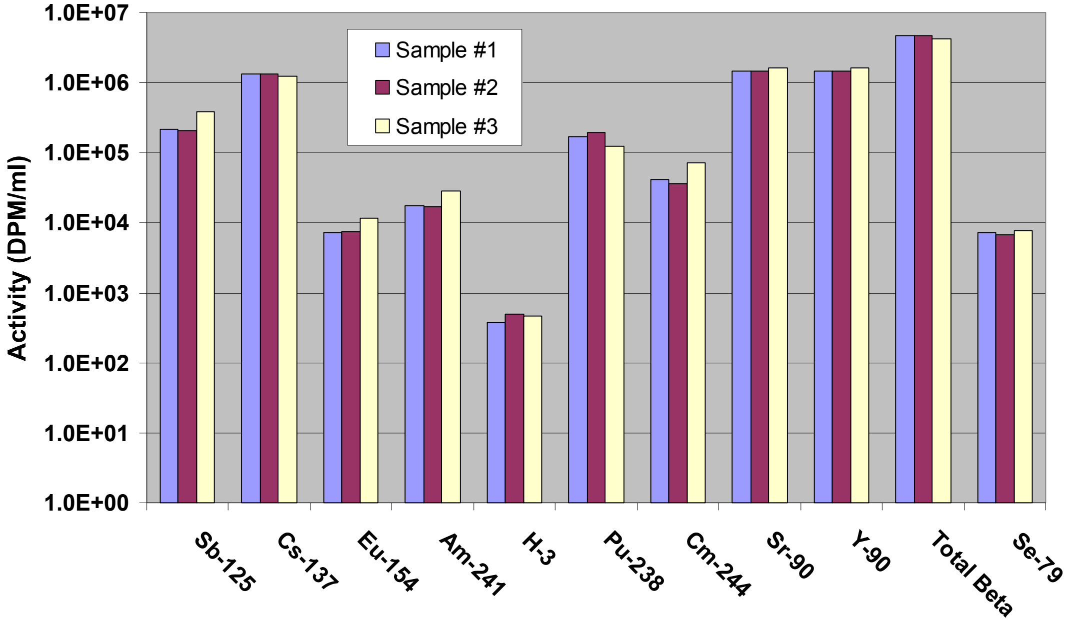
Figure 1. Top liquid scintillation spectrum displays an SRS waste tank slurry sample run through the Se-79 protocol before the addition of the RE column clean-up step. A composite of a Sb-125 beta spectrum and a Se-79 beta spectrum are present. The middle spectrum was taken from a filtered sample run of the same waste tank run through the same procedure as the slurry sample, the Se-79 bearing solids had been filtered out, only Sb-125 is present. The bottom spectrum resulted from the waste tank slurry sample run through the final method, with only Se-79 beta present.

Figure 2. Activities of various isotopes separated from Se-79 in an SRS waste tank sample


2 keV
30 keV
160 keV
500 keV


1.0E+07
1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.0E+00
Activity (DPM/ml)
Sample #1
Sample #2
Sample #3
Sb-125
Cs-137
Eu-154
Am-241
H-3
Pu-238
Cm-244
Sr-90
Y-90
Total Beta
Se-79