



Rapid separation method for ^{237}Np and Pu isotopes in large soil samples

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ABSTRACT

A new rapid method for the determination of ^{237}Np and Pu isotopes in soil and sediment samples has been developed at the Savannah River Site Environmental Lab (Aiken, SC, USA) that can be used for large soil samples. The new soil method utilizes an acid leaching method, iron/titanium hydroxide precipitation, a lanthanum fluoride soil matrix removal step, and a rapid column separation process with TEVA Resin. The large soil matrix is removed easily and rapidly using these two simple precipitations with high chemical recoveries and effective removal of interferences. Vacuum box technology and rapid flow rates are used to reduce analytical time.

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1. Introduction

There are a number of analytical methods reported that use ion exchange/extraction chromatography plus alpha spectrometry to determine actinides in soil. Hou et al. (2009) surveyed a wide range of separation methods for Pu in waters and environmental solid samples. Methods included varied combinations of ion exchange and/or extraction chromatographic techniques. Chemical recoveries for Pu typically varied between 40% and 85%.

Vajda et al. (2009) reported an interesting method for actinides in soil in which 0.5 g soil samples were fused using lithium metaborate. After preconcentration of actinides using calcium fluoride precipitation, a TRU Resin separation was performed. Tests on IAEA soil standards showed very good results, but tracer recoveries showed some significant variation, as high as 80% for plutonium, but notably as low as 20–30% for uranium. The method could, however, be completed rapidly, but still required ~24 h. The overall results were very good relative to soil reference values, however, two of the IAEA soil samples tested showed relatively low chemical recoveries for Pu and U. The authors concluded that the lower chemical recoveries were caused by the soil matrix. This may have resulted from the use of only 1 ml of TRU Resin to recover all the actinides from the soil sample, even though the soil aliquot was only 0.5 g.

Wang et al. (2004) reported a sequential method to determine actinides and strontium in soil samples. The samples were digested in nitric acid and hydrogen peroxide, and redissolved in a large volume of 3 M nitric acid. A large anion resin column (Dowex 1 × 8)

was used to collect and separate Pu and Th. The rinse fractions from the anion resin were treated further and processed individually for Am, U, and Sr. Several sequential precipitations were carried out. An oxalate precipitation was performed at pH 4.2 on the anion resin rinse solution followed by a Sr Resin separation. A separate oxalate precipitation at pH 1.5 was performed on the supernatant after the first oxalate precipitation to recover Am and separate on TRU Resin. The supernatant from the second oxalate precipitation was passed through a large amount of Chelex 100 resin to collect and purify uranium. Strontium was counted using Čerenkov counting, while all actinide fractions were electrodeposited for counting by alpha spectrometry. The chemical recoveries using this method on NRIP (National Institute of Standards and Technology [NIST] Radiochemistry Intercomparison Program) soil were as follows: plutonium (60–76%), americium (40–59%), uranium (57–76%), and strontium (63–77%). A large number of sequential steps were required, but the accuracy of the actinide and strontium results versus the NIST reference values was very good.

Eikenberg et al. (2009) compared three different separation methods to determine actinides in soil samples. Samples were leached in 8 M nitric acid, filtered and a calcium oxalate precipitation technique that settles overnight was used to pre-concentrate actinides. One of the separation methods tested was anion resin (AG-1 × 2) plus DGA Resin (Eichrom Technologies, Lyle, IL, USA). Am, Cm, and U were collected on DGA Resin, which has a k' of approximately 30,000 for Am (Horwitz et al., 2005). The sample was loaded in 3 M nitric acid, and uranium was eluted in 0.25 M nitric acid, prior to stripping Am and Cm with 0.2 M HCL. It was not clear what the uranium tracer recoveries were for these samples, but DGA resin is not typically used to recover and purify uranium because the k' in 3 M HNO_3 for U on DGA Resin is only

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about 20. Electrodeposition was used to prepare alpha sources for measurement by alpha spectrometry.

Ageyev et al. (2005) reported a method for environmental samples including soil samples. After ashing the samples at 550 °C the samples were leached with 8 M nitric acid, followed by calcium oxalate precipitation, furnace heating of oxalates, redissolution in hydrochloric acid, iron hydroxide precipitation, and a lanthanum precipitation of plutonium, americium, and curium. Carbonate, chromate, and iron hydroxide precipitations were performed to prepare strontium. Plutonium was separated using Dowex 1 anion resin loaded under reduced atmosphere. Am and Cm were precipitated as LaOH_3 , redissolved in dilute hydrochloric acid, separated on Dowex 50 cation resin loaded under reduced pressure. A gradient elution separation of Am and Cm with rare earths was performed using α -hydroxy-isobutyric acid. Actinides were electrodeposited for alpha counting. Chemical yields were respectable as follows: Pu 60–70%, Am and Cm 50–65%, and Sr 50–70%. The method is, however, relatively complex and would not be considered a rapid method.

Tavčar et al. (2005) reported a method to determine actinides in soil. Soil and sediment samples up to 10 g were leached using strong nitric acid, filtration, evaporation, and the residue was redissolved in 1 M HNO_3 . The valence adjustment was performed using hydroxylamine hydrochloride to reduce Pu to Pu^{+3} , followed by sodium nitrite to oxidize Pu to Pu^{+4} . The acid concentration was increased to 8 M HNO_3 and the samples were loaded onto Dowex 1 \times 8 resin. Pu was eluted using 9 M HCl with iodide ion present and Np was eluted with 4 M HCl. The chemical yields were ~60% and the Np yields were ~40%. The low Np yields were attributed to poor valence control of Np^{+4} .

We have previously used TEVA Resin plus TRU resin plus DGA Resin in the SRS (Savannah River Site) Environmental Laboratory to determine Pu and Am isotopes in 5–10 g soil samples. TRU Resin was used in tandem with DGA Resin to effectively recover uranium and provide very high chemical recoveries for Am and Cm. The method first uses nitric acid–hydrofluoric acid to digest samples and remove silica, then uses an alkaline fusion to digest the samples, an iron hydroxide precipitation, followed by a cerium fluoride preconcentration step to remove the sample matrix and preconcentrate the actinides (Maxwell and Culligan, 2006). A version of this method to determine Pu and Am in 200 g soil samples using acid leaching only was also reported (Maxwell and Culligan, 2008), but a fusion of the soil leachate was still used in this process.

A new method has been developed in the SRS Environmental Lab (Aiken, SC, USA) that allows the separation of Pu isotopes and ^{237}Np in large soil samples with high yields and effective separation. The Pu and Np in soil method utilizes an acid leaching method, iron/titanium hydroxide precipitation, a lanthanum fluoride soil matrix removal step, and a rapid column separation process with TEVA Resin. This series of rapid precipitations enables high yields and effective removal of interferences. The final precipitate, due to the selectivity of lanthanum fluoride, is very small and easily dissolved in a small column load solution. This work is simpler and more rapid than previously published work from this laboratory with large soil samples because no fusion step is required. In addition, Np, which was not included in the previous work, is also recovered effectively along with Pu due to rigorous valence control of Np as Np^{+4} using Ti(III) reductant during the iron/titanium hydroxide and lanthanum fluoride precipitations.

2. Experimental

2.1. Reagents

TEVA Resin[®] (Aliquat[™]336), available from Eichrom Technologies, Inc., (Lisle, Illinois, USA). Nitric, hydrochloric, and hydrofluoric

acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2[™] water purification system. All other materials were ACS reagent grade. Radiochemical isotope tracer ^{236}Pu was obtained from the National Physical Laboratory (Teddington, UK) to enable yield corrections. ^{239}Pu , ^{238}Pu , and ^{237}Np standards were obtained from Eckert and Ziegler Analytics, Inc. (Atlanta, GA, USA). MAPEP 20 and MAPEP 21 soil standards (Mixed Analyte Performance Evaluation Program) were obtained from Department of Energy (DOE)—Radiological and Environmental Sciences Laboratory (RESL), Idaho Falls, ID, USA.

2.2. Procedures

2.2.1. Column preparation

TEVA Resin was obtained as cartridges containing 2 ml of each resin from Eichrom Technologies, Inc. Small particle size (50–100 μm) resin was employed, along with a vacuum extraction system (Eichrom Technologies). Flow rates of 1–2 ml min^{-1} were typically used for this work.

2.2.2. Sample preparation

Soil samples obtained from a location near the Savannah River Site (Aiken, SC, USA) were dried at 110 °C and blended prior to taking sample aliquots. Eight 20 g soil samples, six 30 g samples, and three 50 g soil sample aliquots were analyzed. Samples were aliquoted into large glass beakers. To all but two of the 20 g soil samples, 1 g MAPEP 21 soil standard was added. ^{237}Np (37 mBq) was added to each sample since MAPEP standards do not contain ^{237}Np .

Fig. 1 provides a flow chart of the sample preparation method. ^{236}Pu tracer (46.2 mBq) was added to each sample. The first two 20 g soil samples were analyzed without MAPEP 21 soil standard to determine the Pu content of the soil. The assumption was made that the ^{237}Np activity in this soil was negligible compared with the 37 mBq ^{237}Np added.

Acid leach volumes were adjusted slightly for sample size. For 20 g soil samples, 30 ml concentrated nitric acid and 10 ml concentrated hydrochloric acid were added to each beaker and samples were heated to dryness on a hot plate. For 30 and 50 g soil samples, the nitric acid and hydrochloric acid volumes were increased proportionally. For 20 and 30 g soil samples, 30 ml of concentrated nitric acid were added to each sample (50 ml for 50 g samples). The beakers were warmed on a hot plate and the leachate and some of the solids were transferred to a 225 ml centrifuge tube.

The residual solids were rinsed two more times. Fifteen to twenty-five milliliters of concentrated nitric acid were added to each beaker, warmed on a hot plate and the leachate plus additional solids were transferred to the centrifuge tube. The centrifuge tubes were centrifuged at 3500 rpm for 10 min. The leachate was transferred to a 600 ml beaker, heated on a hot plate to evaporate the leachate to dryness. Fifteen to twenty-five milliliters of concentrated nitric acid were added to each beaker with residual solids to rinse the solids. This rinse solution plus additional solids was transferred to the centrifuge tube. The centrifuge tubes were centrifuged at 3500 rpm for 10 min and the rinsed solution was transferred to the evaporating leachate. The leachate solutions were evaporated to dryness on a hot plate on low to medium heat as needed to prevent splattering.

To each evaporated leachate, 15–20 ml 1 M hydrochloric acid was added and warmed on a hot plate to easily dissolve the residue. This solution was transferred to 225 ml centrifuge tube and 5 mg La as lanthanum nitrate was added to each tube. To each 20 g sample, 125 mg Fe was added as ferric nitrate. For the 30 and 50 g samples, the 125 mg Fe was not added since large amounts

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