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Determination of ^{237}Np and Pu isotopes in large soil samples by inductively coupled plasma mass spectrometry

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ABSTRACT

A new method for the determination of ^{237}Np and Pu isotopes in large soil samples has been developed that provides enhanced uranium removal to facilitate assay by inductively coupled plasma mass spectrometry (ICP-MS). This method allows rapid preconcentration and separation of plutonium and neptunium in large soil samples for the measurement of ^{237}Np and Pu isotopes by ICP-MS. ^{238}U can interfere with ^{239}Pu measurement by ICP-MS as $^{238}UH^+$ mass overlap and ^{237}Np via ^{238}U peak tailing. The method provides enhanced removal of uranium by separating Pu and Np initially on TEVA Resin, then transferring Pu to DGA resin for additional purification. The decontamination factor for removal of uranium from plutonium for this method is greater than 1×10^6. Alpha spectrometry can also be applied so that the shorter-lived ^{238}Pu isotope can be measured successfully. ^{239}Pu, ^{242}Pu and ^{237}Np were measured by ICP-MS, while ^{236}Pu and ^{238}Pu were measured by alpha spectrometry.

1. Introduction

Inductively coupled plasma mass spectrometry is a powerful tool for the analysis of plutonium isotopes and ^{237}Np in environmental samples. The measurement time for sequential assay by ICP-MS is typically shorter than alpha spectrometry, although the alpha spectrometry measurements may be performed simultaneously with large numbers of detectors. ICP-MS can, however, be hampered by isobaric, polyatomic interferences and signal suppression and have limited effectiveness for relatively short-lived actinide isotopes at low concentrations, for example, ^{238}Pu [1].

For soil samples in particular, which can contain large amounts of ^{238}U, the measurement of ^{239}Pu can be hampered significantly due to $^{238}UH^+$ hydride formation and ^{238}U peak tailing. To a lesser extent, ^{238}U can also interfere with ^{237}Np via peak tailing. Both alpha spectrometry and ICP-MS techniques may require separation of sample matrix interferences to determine ^{237}Np and Pu isotopes accurately, depending on the sample matrix and the detection limit required. Kim et al. [2] noted that the ^{238}U level in the purified solutions should be less than 100 pg mL^{-1} to minimize spectral interference in the quantitative analysis of ^{239}Pu and ^{237}Np.

There are a number of analytical methods reported that use ion exchange/extraction chromatography to determine actinides in soil. Hou et al. [3] surveyed a wide range of separation methods for Pu in environmental samples. Methods included varied combinations of ion exchange and/or extraction chromatographic techniques. Chemical recoveries for Pu typically varied between 40 and 85%, often ~60% or less even for smaller sample sizes. When a soil matrix removal/preconcentration step for larger soil samples is not used, lower actinide yields can occur. Mellado et al. [4] reported an analytical method for 2–5 g marine sediment samples using TRU Resin® to separate the actinides. While the overall Pu isotope results for IAEA soil standard were very good, the average chemical yield was only about 40%.

Qiao et al. [5] described an interesting method for the determination of plutonium isotopes in soil samples using sequential injection chromatography and ICP-MS. Chemical yields were good for 10 g samples (99.9% ± 12.6 at 1SD) and 100 g samples (77% ± 12.6 at 1SD), with decontamination factors of 6.4×10^4 and 3.8×10^4 for ^{238}U, respectively. The method used aqua regia leaching, iron hydroxide precipitation to remove much of the soil matrix, and acid conversion from HCl to HNO_3. This work reported some difficulty reducing Pu to Pu^{3+} using ascorbic acid, thus the use of potassium disulfite instead. This difficulty may have been the result of adding only 200 mg of ascorbic acid, which may not have been enough reductant to reduce the amount of Fe^{3+} ions present in large soil samples to Fe^{2+}. In addition, sulfamic acid, often used in concert with ascorbic acid, was not added to scavenge nitrite ions present in nitric acid, which would also have interfered with the reduction step. The potassium disulfite reduction step worked well, but interestingly a more time-consuming ferrous hydroxide precipitation was integrated into this valence adjustment. Though taking addi-

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tional time, further sample matrix removal likely helped improve chemical yields. A 2 M HCl solution containing $NH_2OH–HCl$ reductant was employed to facilitate Pu stripping from TEVA Resin, and the final eluant solution had to evaporated and redissolved prior to measurement.

Röllin et al. [6] reported a method for Pu and Np analyses in soil using ICP-MS. Following a lithium borate fusion of 5 g samples, samples were redissolved in 4.5 M HNO_3 and PEG (polyethylene glycol) was used to precipitate the silicates, which were removed by filtering. The method employed large rinse volumes relative to the 2 mL TEVA Resin used, including a 100 mL 3 M HNO_3–0.1 mM Fe^{2+} rinse solution. Use of Fe^{2+} reductant in 3 M HNO_3 is normally applied only when reduction of Pu to unretained Pu^{3+} is desired so that Np can be separated from Pu. The use of 3 M HNO_3–0.1 mM Fe^{2+} rinse solution and Fe^{2+} in the column load solution without subsequent addition of an oxidant is perplexing. The use of such a low concentration of Fe^{2+} in 3 M HNO_3 without the presence of ascorbic acid may have accounted for the apparent lack of reduction of Pu to unretained Pu^{3+}. The Pu and Np were eluted using a dilute HNO_3–HF mixture, which included 0.01 mM Fe^{2+} reductant. Chemical yields were 50–80%, with Np yields 75–80% of the Pu yields. This is likely due to the lower retention of Np^{4+} vs. Pu^{4+} on TEVA Resin and the large volume of rinse utilized. Plutonium yields may have also been adversely affected to a slight extent by the use of Fe^{2+} reductant during column load and rinse steps. A decontamination factor of ~20,000 from uranium was achieved.

Tavčar et al. [7] 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 × 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 reported a method in the SRS (Savannah River Site) Environmental Laboratory to determine Pu and Am isotopes in 100–200 g soil samples using alpha spectrometry, but a fusion of the soil leachate was used in this process and ^{237}Np was not investigated in this work [8].

A new method has been developed that allows the separation of Pu isotopes and ^{237}Np in large soil samples with very good chemical yields and enhanced removal of uranium to allow accurate measurement by ICP-MS. This 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 [9]. Np is also recovered effectively along with Pu due to rigorous valence control of Np as Np^{4+} using Ti^{3+} reductant during the iron/titanium hydroxide and lanthanum fluoride precipitations. The rapid separation method uses a TEVA cartridge (2 mL) to separate plutonium and neptunium initially, followed by additional decontamination of Pu from ^{238}U using DGA Resin. ^{239}Pu, ^{242}Pu, ^{237}Np were measured by ICP-MS, while ^{236}Pu and ^{238}Pu were measured by alpha spectrometry. No correction for ^{238}U interference was necessary because of the high decontamination factors achieved.

2. Experimental

2.1. Reagents

The extraction chromatography resins employed in this work are TEVA Resin® (Aliquat™ 336) and DGA Resin® (N,N,N′,N′ tetraoctyldiglycolamide), available from Eichrom Technologies, Inc. (Lisle, IL, USA). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc., Pittsburgh, PA, USA). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS reagent grade and were used as received. Radiochemical isotopes ^{239}Pu, ^{242}Pu, ^{237}Np, ^{238}Pu were obtained from Eckert & Ziegler Analytics, Inc. (Atlanta, GA, USA) and diluted to the appropriate levels. ^{236}Pu was obtained from the National Physical Laboratory (Teddington, UK). A 1000 mg L^{-1} uranium standard was obtained from SpexCertiprep, Inc., Metuchen, NJ, 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).

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. The soil was heated in a furnace at 550 °C to remove any organics present. Six 20 g soil samples (soil A), six 50 g samples (soil B) and four 75 g soil sample aliquots (soil B) were analyzed. Samples were aliquoted into large glass beakers

Known amounts of ^{237}Np and Pu isotopes were pipetted into each 20 g soil sample to demonstrate performance for both neptunium and plutonium analysis using this method. Uranium removal is particularly important when analyzing for ^{239}Pu. To perform additional uranium removal testing with even larger amounts of ^{238}U present, 50 g and 75 g soil samples were also analyzed, but these samples were spiked only with Pu isotopes. ^{236}Pu (46.2 mBq) and ^{242}Pu (298 mBq) tracers were added to each sample. The uncertainties associated with the known values of ^{237}Np and Pu isotopes added is ~1% at the 95% confidence level.

Fig. 1 provides a flow chart of the soil sample preparation method, which was previously been reported for analysis of ^{237}Np and Pu isotopes by alpha spectrometry [9]. This method utilizes iron/titanium hydroxide and lanthanum fluoride precipitations to remove the soil matrix and preconcentrate ^{237}Np and Pu isotopes. Valence adjustment of the column load solution was performed by adding 0.5 mL 1.5 M sulfamic acid, 0.4 mL of 5 mg mL^{-1} Fe as ferric nitrate and 1.25 mL 1.5 M ascorbic acid with a three minute wait step to reduce plutonium to Pu^{3+}. The iron added, which is converted to Fe^{2+} by ascorbic acid, was added to facilitate rapid ^{237}Np reduction to Np^{4+}. Experience in this laboratory has shown this reduction/oxidation sequence and times used to be very effective for adjustment to Pu^{4+} and Np^{4+}, giving essentially quantitative recoveries of plutonium and neptunium without correction for chemical yield [10]. To oxidize plutonium to Pu^{4+}, 1 mL 3.5 M sodium nitrite was added to each sample solution. The kinetics of oxidation of Np to Np^{5+} in the presence of sodium nitrite, are negligible at room temperature.

2.3. Column separation

Fig. 2 provides a flow chart of the rapid column separation method. After the valence adjustment, the sample solution was loaded onto the TEVA column at approximately ~1 drop per second. After the sample was loaded, a beaker rinse of ~3 mL 3 M HNO_3 was transferred to the TEVA column and allowed to pass through the resin at ~2 drops per second. Although the TEVA Resin separation is similar to previous work reported, additional steps were applied to maximize uranium removal. The column reservoirs were changed