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Measurement of Trace Uranium-235 and Plutonium-239, 240 in Waste Tank Material at the Savannah River Site

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Abstract

At the Savannah River Site (SRS), large quantities of radioactive liquid waste are evaporated to reduce volume before eventual processing through the In-Tank Precipitation process (ITP). Actinides in the liquid waste are only slightly soluble in the highly alkaline waste solution. Since some of the actinide isotopes are fissionable, the quantities being processed through the evaporator system are of interest. To better quantify the concentration and mass of fissionable material entering the evaporator system and eventually deposited as salt, analysis of the actinide elements were necessary. The predominant fissionable actinide isotopes of interest are U^{235} and Pu^{239}. To enable the reliable measurement of these radionuclides, the Central Laboratory has developed high speed separation techniques to measure U^{235} content by Isotope Dilution Mass Spectrometry and $Pu^{239,240}$ by alpha spectrometry. Due to the high radioactivity levels in the samples all separations are performed in shielded analytical cells. Uranium is purified and concentrated using a high speed extraction chromatography technique that employs applied vacuum and columns containing tri (2-ethylhexyl) phosphate (TEHP) solvent coated on a small particle inert support (SM-7 BIO-BEADS™). The uranium method enables measurement of U^{235} concentrations to 1×10^{-4} g/L. Plutonium is purified and concentrated using a high speed anion exchange technique (BIO RAD™ AG MP-1 200-400 mesh resin). The Pu method enables measurements of $Pu^{239,240}$ to 2×10^{-6} g/L.

Introduction

The Savannah River Site stores approximately 35 million gallons of high level waste as sludge, saltcake, or salt solution. The salt solution is evaporated to reduce volume before the eventual processing through the In-Tank Precipitation process. A recent study at West Valley Nuclear Services showed that fissile material had accumulated in a waste evaporator. The SRS waste chemistry and evaporator design and operations are very different from those at West Valley. In particular, the SRS liquid waste is maintained at much higher hydroxide concentrations. This greatly reduces the solubility of the actinides in the salt solution. To address the questions associated with the West Valley issue, a reevaluation of the quantities of actinides entering the evaporator system was required, thus the need for the analysis of uranium and plutonium.

Background

At SRS, the mission of the Waste Management group over the past 30-35 years has been the safe storage and evaporation of high level liquid waste. In the near future, processing of this waste will occur which will remove the waste from the tanks, convert the waste to a glass form in the Defense Waste Processing Facility, and convert the decontaminated liquid as concrete in the Saltstone Facility. During the processing of this waste it is necessary to know the quantity of fissionable material being processed to assure criticality safety.

Separation Methods Developed

To enable the measurement of trace fissile material in high activity waste, rapid and versatile separations methods are required to separate the uranium and plutonium. High speed separation techniques were developed by the SRS Central Laboratory. Table 1 shows the typical composition of the liquid waste. The methods were developed so that samples can be analyzed over this wide range of varying sample

parameters without changing sample volumes or spike additions. The methods are rugged enough, for example, to accommodate a range of sodium hydroxide concentrations from 0.1 molar to 11 molar. A high speed extraction chromatography–isotope dilution mass spectrometry (IDMS) method was developed to measure fissile uranium. A high speed anion exchange–alpha spectrometry method was developed to measure trace plutonium. The level of detection required for the evaporator feed solution is less than 1×10^{-4} g/L for uranium and plutonium because of the low solubility of both in solution. To achieve these levels of detection, minimal dilution of the sample is required during the analyses. These methods provide minimal cycle times for the required analyses and generate no contaminated solvent waste. A set of four samples, in duplicate, along with quality control synthetics and blanks can be analyzed within a 12 hour shift.

Table 1. Typical Composition of SRS High–Activity Liquid Waste

Component	Wt %	Range (Molarity)
$NaNO_3$	48.8	0.1 – 4
$NaNO_2$	12.2	0.1 – 3
NaOH	13.3	0.1 – 11
Na_2CO_3	5.2	0.1 – 2
$NaAl(OH)_4$	11.1	0.1 – 2
Na_2SO_4	6.0	
NaF	0.2	
NaCl	0.4	
Na_2SiO_3	0.1	
Na_2CrO_4	0.2	

Gamma Radiation Levels: $10^7 - 10^{10}$ dpm/ml

Uranium Sample Preparation

The high speed column extraction chromatography technique employs applied vacuum and columns containing tri–2 ethyl–hexyl phosphate (TEHP) solvent coated on a small particle hydrophobic support (SM–7 BIO BEADS™). Figure 1 illustrates the sample preparation and column chromatography, which is performed in the shielded analytical cells. A known U^{233} spike is added to a sample aliquot of 5 milliliters. Twenty milliliters of 8 molar nitric acid containing 0.125 molar aluminum is added to the sample–spike mixture. The addition of strong nitric acid ensures complete oxidation of the uranium^{233} to the (VI) valence state. The additional aluminum is added to complex any ions that could potentially complex uranium and lower recoveries. After a wait step to ensure all the U^{233} is oxidized to the (VI) state, the solution is loaded onto a column containing SM–7 BIO BEADS™ (200 to 400 mesh) coated with TEHP solvent filled to 15 mm above the bottom 20 µm frit. Applied vacuum is maintained at 5 inches of mercury, controlling the flow rate to 5 to 10 milliliters per minute. Twenty milliliters of 5 molar nitric acid is added to remove fission products, mainly cesium^{137} and strontium^{90}. The columns containing the purified uranium are transferred to a radiobench and the uranium is removed using a modified Spe–ed Mate™ vacuum extraction system. The stainless steel walls of this extraction system have been coated with Teflon™ to prevent corrosion. The uranium is eluted with 10 milliliters of a mixture of 0.02 molar nitric acid and 0.02 molar hydrofluoric acid. The purified uranium solution is evaporated to dryness under a heat lamp, redissolved in a volume of acid that will yield approximately 1 µg of uranium, and evaporated onto a rhenium filament.

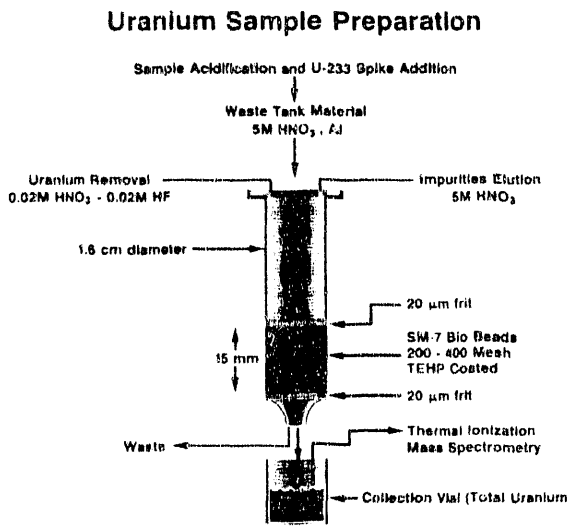

Figure 1. Uranium Sample Preparation

Plutonium Sample Preparation

The high speed column extraction chromatography technique employs applied vacuum and columns containing BIO RAD™ AG MP–1 200–400 mesh resin, nitrate form. Figure 2 illustrates the sample preparation and column chromatography, which is performed in the shielded analytical cells. A sample aliquot of 2 milliliter is used. The caustic waste samples are first acidified to less than 2 molar acid with 10 milliliters of 3 molar nitric acid. To ensure that all of the plutonium is in the (IV) valence state the plutonium is first reduced to the (III) valence state with 2 milliliters of 2 molar ferrous sulfamate. Ten milliliters of concentrated nitric acid are added to oxidize the plutonium to the (IV) valence state and adjust the final sample acidity to 8 molar. After a wait step to ensure all the plutonium is oxidized to

the Pu (IV) state, the solution is loaded onto a column containing AG MP–1 ion exchange resin filled to 15 mm above the bottom 20 µm frit. Applied vacuum is maintained at 5 inches of mercury, controlling the flow rate to 5 to 10 milliliters per minute. A total of 20 milliliters of 8 molar nitric acid is added to remove fission products. The columns containing the purified plutonium are transferred to a radiobench and the plutonium is removed using a modified Spe–ed Mate™ vacuum extraction system. The plutonium is eluted with 10 milliliters of a mixture of 0.02 molar nitric acid and 0.02 molar hydrofluoric acid. The purified plutonium solution is evaporated to dryness under a heat lamp, redissolved in 1 milliliter of 3 molar nitric acid. A 50 to 200 µL aliquot of sample is evaporated onto a plate for alpha spectrometric determination.

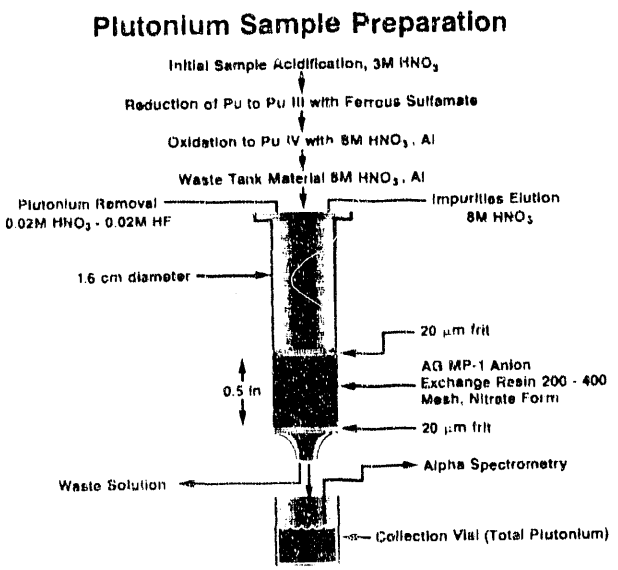

Figure 2. Plutonium Sample Preparation

Instrumental Analysis

A Finnigan MAT 260 thermal ionization mass spectrometer is used to perform the uranium isotopic measurements. Normal instrument operational parameters were employed for the uranium isotopic measurements using a rhenium filament arrangement.

Solid state silicon surface barrier alpha detectors were used for both the total alpha and alpha pulse height analyses.

Verification Testing and Results

The uranium method was tested on a simulated waste solution, holding the U^{233} spike concentration constant and varying the sample uranium concentration. The optimum spike to sample uranium ratio for the thermal ionization mass spectrometer used was determined to be no more than 10:1 for a spike to sample (or sample to spike) ratio. The method was tested at 15: 1 ratios over the expected sample uranium concentrations. The results are shown in Figure 3. The results show that total uranium can be measured accurately at the 1 x 10^{-4} g/L level. The U^{235} isotopic concentration can be determined at even lower levels.

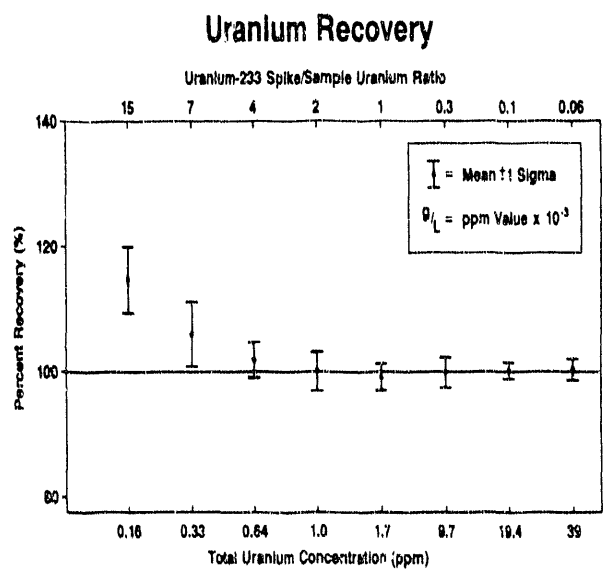

Figure 3. Uranium Recovery

The plutonium method was tested on a simulated waste solution with known plutonium standards. The results given in Table 2 showed an average standard recovery of 102%, with a standard deviation of 3.3 percent. The detection limit

for the plutonium method is approximately 100 disintegrations per minute per milliliter of solution (approximately 1 ppb).

Table 2. Plutonium Recovery

Known Value (dpm/mL)	Measured Value (dpm/mL)	Recovery (%)
5.01 E4	5.00 E4	99.8
5.01 E4	5.02 E4	100.2
5.01 E4	5.12 E4	102.2
5.01 E4	5.47 E4	109.2
5.01 E4	5.04 E4	100.6
5.01 E4	4.89 E4	97.6
5.01 E4	5.30 E4	105.8
5.01 E4	5.11 E4	102.1
5.01 E4	5.12 E4	102.2

Average Recovery = 102.2%

Std. Dev. = 3.3%

Summary

The high speed extraction chromatography techniques developed by the SRS Central Laboratory provide a rapid and reliable measurement of trace fissile uranium and plutonium in high activity liquid waste tank material. The methods have proven to be versatile, handling a wide range of varying sample characteristics, easy to use and generate no radioactive solvent waste. In the future these methods, with some modification, may be expanded to solutions associated with waste removal and processing.

Acknowledgements

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