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Improved Accountability Method for Measuring Enriched Uranium in H-Canyon Dissolver Solution at the Savannah River Site (U)

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by

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Abstract

At the Savannah River Site (SRS), accountability measurement of enriched uranium dissolved in H–Canyon is performed using isotope dilution mass spectrometry (IDMS). In the IDMS analytical method, a known quantity of uranium^{233} is added to the sample solution containing enriched uranium and fission products.The resulting uranium mixture must first be purified using a separation technique in the shielded analytical ("hot") cells to lower radioactivity levels by removing fission products. Following this purification, the sample is analyzed by mass spectrometry to determine the total uranium content and isotopic abundance. The magnitude of the response of each uranium isotope in the sample solution and the response of the U^{233} spike is measured. By ratioing these responses, relative to the known quantity of the U^{233} spike, the uranium content can be determined. A hexone solvent extraction technique, used for years at SRS to remove fission products prior to the mass spectrometry analysis of uranium, has several problems. The hexone method is tedious, requires additional sample clean–up after the purified sample is removed from the shielded cells and requires the use of Resource Conservation and Recovery Act (RCRA)–listed hazardous materials (hexone and chromium compounds). A new high speed separation method that enables a rapid removal of fission products in a shielded cells environment has been developed by the SRS Central Laboratory to replace the hexone method. The new high speed column extraction chromatography technique employs applied vacuum and columns containing tri (2–ethyl–hexyl) phosphate (TEHP) solvent coated on a small particle inert support (SM–7 Bio Beads). The new separation is rapid, user friendly, eliminates the use of the RCRA–listed hazardous chemicals and reduces the amount of solid waste generated by the separation method. In addition, the reduced cycle time represents a significant cost savings for each H–Canyon dissolver sample analyzed.

Introduction

Irradiated fuel from research reactor operators or their contract fuel service companies and fuel irradiated at the Savannah River Site (SRS) are processed in the SRS H–Canyon Separations Facility. The measurement of enriched uranium dissolved in the H–Canyon dissolver is a key accountability sampling point. Reliable, timely measurement of the uranium^{235} content in this highly radioactive solution is an essential component in the control and accountability of nuclear material in the H–Canyon facility. When offsite fuel is processed, the accurate measurement of uranium is critical to ensure good agreement with shipper estimates. Historically, shipper estimates and measured values at SRS have agreed very well.

Background

Accountability measurement of enriched uranium in the H–canyon dissolver is performed using an isotope dilution mass spectrometry (IDMS) method. In this technique, a known quantity of uranium^{233} isotope is added to the sample containing the enriched uranium and fission products. Prior to isotopic analysis, this mixture must be purified in the shielded ("hot") cells to remove the high levels of radioactivity. The purified solution is analyzed by thermal ionization – mass spectrometry to determine the ratio of the uranium^{233} signal to the uranium isotopes present in the sample. By comparing these isotopic responses with the known amount of uranium^{233} added, total uranium present is calculated. For years, the SRS Central Laboratory has used a hexone solvent extraction technique to purify the uranium mixture prior to analysis. The hexone method, however, has several drawbacks. Besides being time–consuming due to long stirring times, small volumes of hexone (difficult to see inside the shielded cells) must be carefully transferred using master–slave manipulator arms. Additional solvent scrubbing must be performed outside the shielded cells to lower radioactivity levels further. In addition, the hexone method uses RCRA–listed hazardous materials [hexone and a chromium compound (dichromate) used as an oxidant].

Uranium Separation Scheme

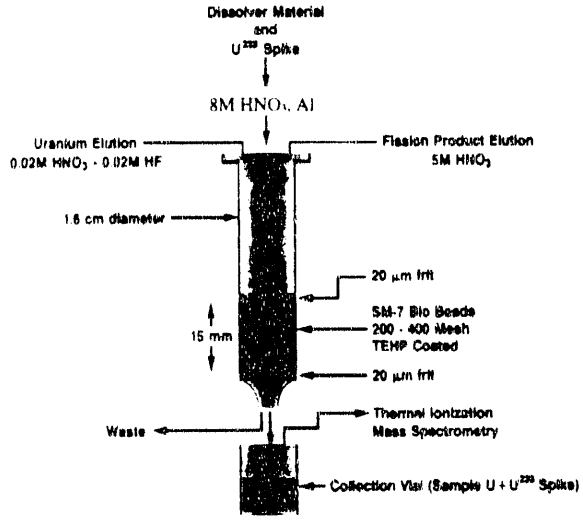

Figure 1. Uranium Separation Scheme

New Separation Method

A new high speed extraction chromatography technique has been developed by the SRS Central Laboratory to replace the hexone solvent extraction method. Since the mass spectrometer will still be used to perform the final uranium measurement, the accuracy and precision of the method will remain the same.The overall method is improved because the separation is streamlined, cycle times are reduced, the use of RCRA–listed compounds for this analysis is eliminated and the amount of solid waste generated during this analysis is reduced.

Sample Preparation

The new high speed column extraction chromatography technique employs applied vacuum and columns containing tri (2 ethylhexyl) phosphate (TEHP) solvent coated on a small particle hydrophobic support (SM–7 Bio Beads). Instead of using dichromate to ensure oxidation of the uranium^{233} spike and sample mixture to the uranium (VI) valence state, an oxidant such as cerium (IV) is used.

Shielded Cells

Figure 1 illustrates the sample preparation and column chromatography, which is performed in the shielded analytical cells using the apparatus shown in Figure 2. A quantity of U^{233} spike is added to a sample aliquot of approximately 0.5 g. Ten milliliters of 8 molar nitric acid containing 0.125 molar aluminum is added to the sample–spike mixture and 1 drop of a saturated cerium ammonium sulfate solution is added. Aluminum is added to complex any fluoride or sulfate present. After a wait step to ensure that all the uranium is oxidized to the U (VI) state, the solution is loaded onto a column containing SM–7 Bio Beads (200 to 400 mesh) coated with TEHP solvent. The column height is 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 40 milliliters of 5 molar nitric acid is added to remove fission products such as cesium^{137}, strontium^{90}, and cobalt^{60}. Because of the high flow rates, there is minimal delay due to the volume of rinse required.

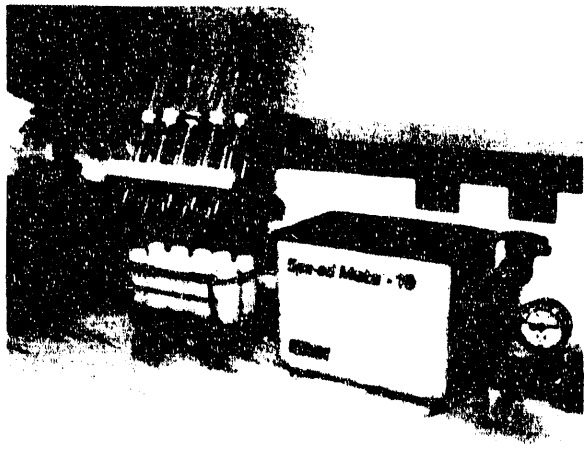

Figure 2. Column Extraction in Shielded Cells

Radiobench

The columns containing the purified uranium are transferred from the shielded cells to a radiobench. The uranium is stripped from the columns using the vacuum extraction system shown in Figure 3. The stainless steel walls of this extraction system have been coated with Teflon to prevent corrosion. The uranium is then 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 small volume of 1 molar nitric acid and a volume of sample that will give approximately 1 μg of uranium is plated on the thermal ionization filament using an evaporation technique.

Figure 3. Vaccum Extraction System in Radiobench

Comparison of TEHP and Hexone Sample Preparation Methods

The TEHP separation is rapid, efficient and easier to use inside the shielded cells than the hexone method. The stir time is less and there are no problems with phase separation, which occasionally has taken up to 30 minutes to separate fully. The shielded cell operators prefer the simpler column loading (by pouring) rather than the tedious slurring of a small layer of hexone after extraction. The TEHP column method effectively removes fission products without additional clean-up outside the shielded cells. The hexone method, in contrast, requires a second solvent scrub step in the radiobench using an aluminum nitrate–oxalic acid solution to lower fission product levels. This also generates additional solid waste for disposal. In addition, the hexone method generates contaminated liquid organic waste after the uranium is stripped from the hexone phase. The TEHP method also eliminates the use of the RCRA–listed hazardous compounds used in the hexone method.

A set of 2 samples and a standard can be prepared and purified in about 4 hours using the TEHP method. The hexone separation method, however, requires approximately 7 hours to perform the same number of analyses (including the time required for the radiobench scrub step).

Figure 4. Thermal Ionization Mass Spectrometer

Mass Spectrometry

A Finnigan MAT 260 thermal ionization mass spectrometer (Figure 4) is used to perform the uranium isotopic measurements. Normal instrument operational parameters were employed for the uranium isotopic measurements using a dual rhenium filament arrangement.

Verification Testing And Results

The method was tested using a 3.00 mg U/g standard. The goal of this testing was to ensure that the accuracy and precision of the current method are not adversely affected by the improved separation technique. Routine analytical results are bias – corrected based on the quality control standards analyzed along with the samples. Current quality control data for the hexone method showed a –.046% bias and a precision of 0.61% at the 95% confidence level. Tests using the TEHP column method show a bias of –0.27% and a precision of 0.80 % at the 95% confidence level. The results demonstrate that the new separation method has no adverse impact on the final isotopic results, since the precision and accuracy for both methods are very similar. Table 1 shows the results of verification measurements on a 3.00 mg/g standard.

Table 1. Standard Verification Data

Dup. Msmts Total U (mg/g)	Avg of Duplicates Total U (mg/g)	Avg of Duplicates U–235 (%)
2.989 2.988	2.989	58.837
2.985 2.990	2.988	58.830
3.031 3.002	3.017	58.764
2.998 2.990	2.994	58.854
2.988 2.995	2.992	58.854
2.990 2.990	2.990	58.882
2.988 2.966	2.977	58.891
	Mean = 2.992 Known Value = 3.000 Bias (%) = -0.27 RSD (%) = 0.4	Mean = 58.845 RSD (%) = 0.07

Comparison data showing results on offsite dissolver fuel by using the hexone–IDMS method and the TEHP–IDMS method are shown in Table 2. The results illustrate that the TEHP separation method effectively separates the uranium from a typical dissolver sample matrix. The average uranium^{235} values for measurements on a typical H–Canyon dissolver sample agree within approximately 0.2%.

Table 2. Comparison of Results on Typical Dissolver Sample

	Hexone Extraction Method	TEHP Column Extraction
Total U(mg/g)	0.497 0.506 0.502	0.503 0.503 0.503 0.504
	mean = 0.502 RSD (%) = 0.9	mean = 0.503 RSD (%) = 0.19
U–235 (%)	92.952 92.870 92.924	92.521 92.586 92.373 92.371
	mean = 92.915 RSD (%) = 0.04	mean = 92.463 RSD (%) = 0.12
U–235 (mg/g)	0.466	0.465 difference (%) = 0.2

Summary

The new high speed TEHP has been developed, tested and verified using quality control standards and crosschecks on dissolver samples from H–Canyon. The new method, which employs state of the art high speed extraction chromatography, is less tedious and more rapid than the hexone solvent extraction technique. It also eliminates the use of hexone and dichromate, RCRA–listed hazardous compounds. As a result, it has significantly improved the overall accountability method for the measurement of enriched uranium in H–Canyon dissolver solutions containing SRS or offsite fuel.

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