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Determination of Trace Radionuclides in SRS Depleted Uranium (U)

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Executive Summary

Prior to final dispositioning of Savannah River Site (SRS) residual depleted uranium (DU) following reactor irradiation the amount of contamination from other radionuclides must be determined. The Nonproliferation Technology Section (NTS) was requested by the SRS Nuclear Materials Management Division (NMMD) to analyze a number of samples in the SRTC/NTS clean labs. The requested analytes were Am-241, Np-237, Ra-226, Cs-137, I-129, Tc-99, Sr-90 and the plutonium isotopes from 238 through 242. The NTS routinely analyzes all types of samples for trace plutonium by mass spectrometry. The other analytes are routinely analyzed only in environmental samples. This report documents the analytical data and the analysis methods developed and used for these analyses. All requested analytes were determined to be less than one tenth of the waste acceptance criteria in all samples analyzed.

All the analytes required chemical separation from the bulk uranium matrix prior to quantification. After separation from uranium and its Th-234 daughter by anion exchange, Am-241, Ra-226 and Cs-137 were determined by gamma spectrometry in the NTS Ultra-Low Level Counting Facility (ULLCF). The maximum activity found for Am-241 was 25 pCi/g, Ra-226 was 600 pCi/g and Cs-137 was 21 pCi/g. The Sr-90 was counted on a gas flow proportional counter. All the samples contained less than 440 pCi/g of Sr-90 per gram of DU. Technetium-99 was counted by liquid scintillation spectrometry; a maximum activity of 94 nCi/g was determined. Mass spectrometry analysis for Pu-239, Pu-240, Pu-241 and Pu-242 and alpha spectrometry analysis for Pu-238 resulted in a total plutonium activity (sum of all isotopes) of less than 25 pCi/g. Np-237 was quantified by alpha spectrometry and found to be less than 35 pCi/g. Iodine-129 had a maximum activity of less than 35 pCi/g. The uranium isotopic depletion was confirmed by alpha spectrometry, with some of the samples being analyzed by mass spectrometry. Mass spectrometry is required to distinguish U-233 from U-234 and U-235 from U-236.

List of Acronyms

cpm	counts per minute
DL	detection limit
DOE-EML	Department of Energy’s Environmental Measurements Laboratory in New York City
DU	depleted uranium
MDA	minimum detectable activity
NIST	National Institute of Standards and Technology
NMMD	Nuclear Material Management Division
NTS	Nonproliferation Technology Section
QAP	Quality Assurance Program run by DOE-EML
QC	quality control
RCO	Radiation Control Officer
SRS	Savannah River Site
SRTC	Savannah River Technology Center
TIMS	thermal ionization mass spectrometry
ULLCF	Ultra-Low Level Counting Facility
WAC	waste acceptance criteria
WSRC	Westinghouse Savannah River Co.

Introduction

The Nonproliferation Technology Section of the Savannah River Technology Center operates ultra low-level research and development facilities for the determination of trace radionuclides in a variety of sample types. Included in these facilities are a mass spectrometric laboratory for the determination of plutonium and uranium isotopic radionuclides and several low-level counting facilities for the determination of gamma, alpha and beta emitting radioisotopes. Typical sample sizes for the determination of plutonium are a few picogram (pg; 10^{-12} gram) and a few nanogram (ng; 10^{-9} gram) for uranium. For most of the other radionuclides typical limits of detection are a few picoCurie (pCi) down to several femtoCuries (fCi; 10^{-15} Curie). The routine sample type analyzed by the NTS is environmental samples (water, soil and atmospheric particles); however, the NTS does have the experience to determine most radionuclides in any matrix. The NTS does operate one high-level laboratory for the preparation of samples that exceed radioactivity limits set for direct introduction into the low-level analytical facilities.

The NMMD is tasked with managing the DU at the SRS. As part of that task they needed 3300 barrels of material to be characterized prior to off-site shipment for disposal. It was decided to analyze 33 barrels (1%) for contaminants of concern. The NTS was requested to analyze these samples for the following radionuclides: Tc-99, I-129, Np-237, Pu-238, Pu-239, Pu-240, Pu-242, Am-241, Pu-241, Ra-226, Sr-90, Cs-137, U-233, U-234, U-235, U-236, U-238. The requested limits of detection (DL), about one tenth of the waste acceptance criteria (WAC), are shown in Table 1.

Table 1. Requested Detection Limits

Constituent	WAC Limit	Required DL
Alpha emitting TRU with $t_{½}$ >5 years	10 nCi/g	0.1 nCi/g for each isotope
Pu-241	350 nCi/g	35 nCi/g
Ra-226	10 nCi/g	1 nCi/g
Sr-90	0.04 Ci/m^3	1.5 nCi/g
Cs-137	1.0 Ci/m^3	40 nCi/g
Tc-99	0.3 Ci/m^3	10 nCi/g
I-129	0.008 Ci/m^3	0.3 nCi/g

The NTS was requested to use the best possible method to provide the lowest limit of detection rather than just screening the samples to prove they were below the acceptance limits. Although the NTS had previously analyzed SRS DU for plutonium, methods had to be validated for the other radionuclides. The analytical methods used and sample results are individually discussed below.

All the samples were initially separated in the NTS high-level lab. Only one customer's sample set is handled at a time in this lab. The containment units are cleaned and cleared between the introduction of each new sample type. This ensures minimal cross contamination potential from previous samples. To stay below SRTC reportable limits for DU, only one gram of each sample was submitted to the NTS for analysis. After separation and purification of the analyte of interest the samples were cleared by WSRC Radiation Control Officers (RCO) to be moved into the NTS low-level analytical facilities.

Technetium-99

Approximately 0.1 gram of the DU was weighed into a tared plastic vial. About 5 mL of 8M nitric acid was added to the vial to start the dissolution. A blank was prepared with each batch of samples; 5 mL of the same acid was placed into a vial with no sample. Technetium has no naturally occurring isotopes; other isotopes of technetium are not readily available for use as chemical yield monitors. Typically, technetium chemical yield is monitored by a batch yield method whereby one sample in the batch is spiked with Tc-99 in excess of that expected to be present. The chemical yield of that sample is assumed to be that of all samples in the batch. One sample per batch was weighed out in duplicate and spiked with 16 nCi of Tc-99 to serve as the yield monitor.

The samples were transferred to a glass beaker with additional nitric acid and placed on a hot plate. The nitric acid was evaporated and the samples converted to hydrochloric media. Columns were prepared containing 10-mL of BioRad AG 1X8 analytical grade anion exchange resin. The columns were conditioned with 8M hydrochloric acid. Under these conditions the resin retains the uranium while the technetium passes right through. The sample was loaded onto the column and the technetium washed through with additional 8M HCl. The load and wash solution (containing the Tc) was collected in a clean beaker and taken to dryness. It was then brought up in DI water and loaded onto an EIChroM Industries, Inc. TEVA® extraction chromatography resin column. This column contained approximately 2-mL of TEVA® resin wetted with DI water. Technetium is selectively retained by the TEVA® resin under neutral to slightly acidic conditions while any remaining uranium and thorium will pass through the column. The column was washed with DI water. Finally the resin containing the technetium was extruded into a 20-mL liquid scintillation vial with a minimum of water. Fifteen milliliters of liquid scintillation cocktail was added to the vial and the samples counted on a liquid scintillation counter.

The samples were each counted three times for 10 minutes per count. The detector background was determined by placing a vial containing 5-mL of DI water and 15-mL of cocktail in position 1 of the counter. The detector efficiency was determined by placing 16 nCi of Tc-99 in a vial containing 2-mL of TEVA® resin and 15-mL of cocktail. The average of the three sample counts was used to calculate the sample activity. The average net count rate was divided by the detector efficiency and the DU sample weight to calculate the activity of Tc-99 per gram of DU oxide. The average chemical yield was near 100% thus no correction was made for chemical recovery. The results of the blanks and spikes are shown in Table 2 and 3, respectively. The sample results are shown in Table 4, the error is the counting error only. Sample activities varied from 15 to 94 nCi Tc-99 per gram of DU oxide. Technetium is known to follow uranium in the purification process following irradiation and therefore this result is not unexpected. The results are all below the acceptance limits shown in Table 1.

Table 2. ^{99}Tc Blank Results

	nCi/g UO3
blank-1	0.21
blank-2	0.03
blank-3	0.06
blank-4	0.14

Table 3. ^{99}Tc Spike Results

	% recovery
spike-1	101.4
spike-2	99.9
spike-3	98.2
spike-4	94.0

Table 4. ^{99}Tc Results for SRS DU Samples

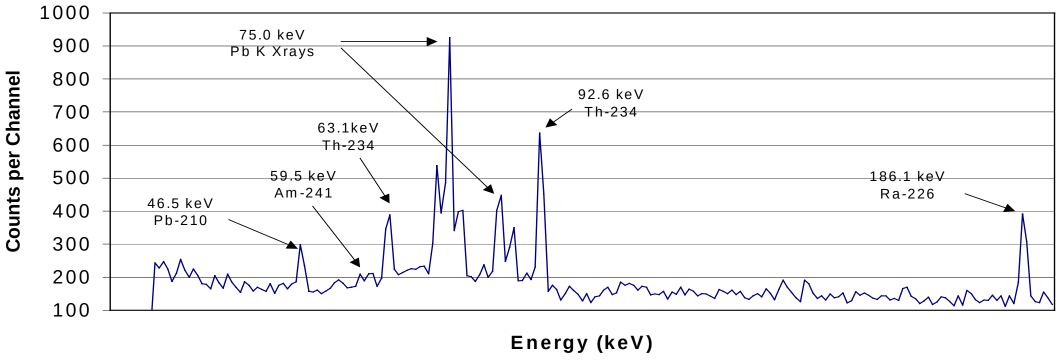
spl #	nCi/g UO3	2s error
1	44.2	1.0
2	57.5	1.5
3	21.2	0.6
4	33.3	0.4
5	15.7	0.4
6	19.1	0.3
7	18.5	0.4
8	24.5	0.5
9	90.2	2.6
10	79.7	1.6
11	89.8	1.6
12	79.7	2.8
13	37.5	0.9
14	75.3	1.5
15	34.2	0.7
16	74.2	1.7
17	41.4	1.0
18	64.7	1.6
19	16.1	0.3
20	14.9	0.4
21	27.2	0.4
22	8.1	0.2
23	15.7	0.3
24	9.0	0.2
25	93.8	2.1
26	92.7	2.5
27	32.5	0.7
28	55.3	1.1
29	53.8	0.8
30	88.5	2.4
31	93.7	1.4
32	54.3	1.2
33	73.0	2.2

Amercium-241, Radium-226 and Cesium-137

Concentrations of Am-241, Ra-226 and Cs-137 were measured in the DU by low-level gamma-ray spectrometry in the ULLCF. The uranium matrix was separated from these isotopes by trapping ~100 mg of U on an anion column from 9M HCl (similar to the Tc-99 first column above). The Th-234/Pa-234^m daughter activity (~50,000 to 100,000 dpm per sample) in the effluent from the first column was removed with a second anion column from 8M HNO_3. The Am, Ra and Cs cations passed through the columns and were quantitatively recovered in the combined effluent/wash solutions. Second aliquots from four of the samples were spiked with known amounts of the three nuclides; these served to monitor the chemical yield similarly to the Tc-99 spiked duplicates above. These spikes and four reagent blanks were processed through the chemical separations with the actual samples.

The solutions from each sample, spiked sample and reagent blank were measured on one of three identical Ge spectrometers in the NTS ULLCF. Samples were counted ~ 24 hours or longer. Raw spectra were archived and then analyzed by the Grabgam code developed by the NTS for the analysis of low-level gamma emitters in environmental samples. The detectors have ~25% efficiencies (relative to Co-60 @ 1332 keV) and have extended low energy sensitivities down to ~ 20 keV. The electronics for the three spectrometers were tuned to give optimum performance in the 40 to 100 keV regions to resolve the 59.5 keV gamma-ray of Am-241 from the 63.1 keV line of Th-234 which is also present in the detector background spectra. The low energy portion of the spectrum from one of the DU samples is shown in Figure 1.

Figure #1: Low Energy Gamma-ray Spectrum of DU Sample 29



The detector calibrations had been checked in July 2002 with a multi-line, gamma-ray reference standard (NIST traceable as defined in ANSI N42.22-1995). Acceptable values were obtained with these detectors on the Environmental Measurements Laboratory's Quality Assurance Program Sample QAP-56 in June 2002. The results for the "blind" round robin, water sample are shown in Figure 2. The ULLCF Cs-134 is biased about 10% low due to over-correction for coincidence summing in this nuclide in the tight geometry used to achieve high sensitivities.

Recoveries from the four spiked samples were compared with an aliquot of the standard solution (Table 5) and found to be quantitative (100 +/- 5%) within the experimental uncertainty. The four blanks were measured and shown to be essentially identical with detector backgrounds (Table 6).

No net activity above background was detected for any of the three isotopes in the DU samples. Minimum detectable activities (MDA) were calculated for each of the three nuclides of interest. For Am-241 and Cs-137 they were less than ~ 1pCi per sample. For Ra-226 the MDA was less than ~ 30-60 pCi per sample since the 186 keV transition used in its analysis has a relatively low intensity ($I\gamma$ = ~3.5%) and there is net activity in the background spectra at this energy. Uncertainties and MDA's quoted are at the 95% confidence level. Net weights of uranium oxide processed for each sample were used to calculate MDA's in terms of pCi per gram of uranium oxide. These values are listed in Table 7.

Figure 2: EML QAP-56 (6/02) Matrix: Water Gamma-ray Spectrometry

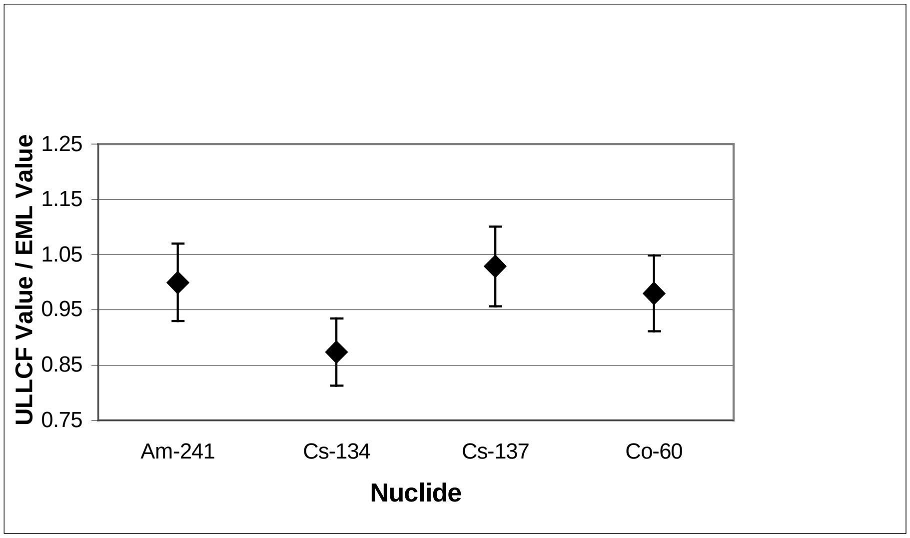


Table 5. Gamma Spectrometry Spike Results

	Am-241		Ra-226		Cs-137	
	pCi	1s error	pCi	1s error	pCi	1s error
spike	312	16	210	15	48	1
#4+spike	340	17	217	16	50	1
#9+spike	306	15	220	11	48	1
#24+spike	309	15	227	10	46	1
#29+spike	332	16	241	13	48	1

Table 6. Gamma Spectrometry Reagent Blank Results

	Am-241 pCi	Ra-226 pCi	Cs-137 pCi
Det. Bkgd	<1.2	<29	<1.0
Blank #1	<2.3	<45	<1.8
Blank #2	<1.1	<30	<1.0
Blank #3	<1.2	<27	<0.96
Blank #4	<1.2	<25	<1.1
Det. Bkgd	<1.1	<28	<1.1

Table 7. Activity in DU Samples, pCi/g DU

sample #	Am-241	Ra-226	Cs-137
1	<6	<120	<6
2	<24	<500	<19
3	<21	<450	<17
4	<17	<330	<14
5	<25	<600	<20
6	<20	<390	<15
7	<16	<314	<13
8	<16	<310	<12
9	<10	<240	<9
10	<21	<470	<19
11	<16	<370	<14
12	<11	<250	<10
13	<11	<260	<10
14	<13	<340	<12
15	<17	<360	<13
16	<12	<300	<11
17	<11	<230	<10
18	<11	<230	<8
19	<10	<210	<7
20	<6	<170	<5
21	<14	<300	<13
22	<9	<250	<8
23	<18	<380	<15
24	<16	<340	<13
25	<13	<280	<11
26	<9	<250	<9
27	<10	<280	<10
28	<25	<550	<21
29	<16	<410	<14
30	<10	<190	<10
31	<16	<350	<15
32	<9	<190	<7
33	<9	<240	<9

Strontium-90

The concentration of Sr-90 was measured in the DU by low-level beta proportional counting in the ULLCF. Sample fractions from the gamma-ray analyses of Am-241, Ra-226 and Cs-137 had the uranium matrix and Th-234 activity removed by two ion exchange column treatments. Inactive strontium carrier (~10 mg) had been added prior to these treatments. Strontium-90/Y-90 was co-precipitated from each sample as $SrCO_3$ from basic solution. The $SrCO_3$ fractions were filtered and dried. Chemical recovery was measured by weight and averaged ~85%. The samples were mounted for beta proportional counting.

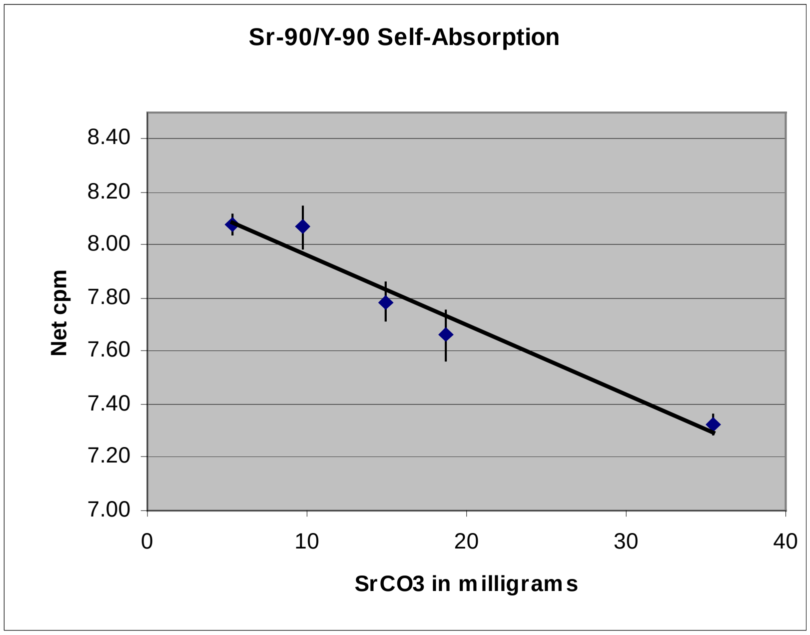
The eight beta proportional counters used have detector backgrounds in the range of 0.25 to 0.40 counts per minute (cpm). Four reagent blanks were processed through the entire chemistry and measured on the detectors. They had backgrounds of about 1.0 cpm (Table 8).

Table 8. Sr-90 Reagent Blank Results

		cpm	1 sigma
Blank #1		1.19	0.04
Blank #2		1.14	0.03
Blank #3		0.96	0.03
Blank #4		1.01	0.01

Five strontium spike samples containing ~ 4 pCi of Sr-90 and 5 to 35 mg of $SrCO_3$ were also processed to determine the detector efficiencies as a function of sample weight. The self-absorption corrections were generally 5 to 10% (Figure 3).

Figure 3: Sr-90 Spiked Samples



The measured count rates were corrected for chemical recovery, self-absorption and detector efficiencies. The "net" Sr-90 activities per gram of UO_3 dissolved are listed in Table 9. The values are expressed as minimum detectable activities since the chemical purification was not sufficient to exclude traces of Ra-226 and Th-234 in the samples. All Sr-90 values were below the acceptance criteria.

Table 9: Activity in DU Samples, pCi/g

Sample		**Sr-90**
1		< 8.6
2		< 5.9
3		< 3.4
4		< 6.7
5		< 7.2
6		< 14.0
7		< 8.0
8		< 7.7
9		< 50.7
10		< 32.7
11		< 23.4
12		< 29.3
13		< 46.6
14		< 31.2
15		< 40.0
16		< 68.2
17		< 28.4
18		< 38.3
19		< 51.0
20		< 45.6
21		< 27.1
22		< 28.6
23		< 45.7
24		< 26.9
25		< 45.7
26		< 100.5
27		< 59.1
28		< 28.0
29		< 57.9
30		< 32.9
31		< 78.9
32		< 438.2
33		< 35.8

Iodine-129

I-129 was measured by radiochemical separation of the iodine combined with photon counting of its low energy X-rays. Samples of the DU weighing ~0.1 g were dissolved in nitric acid, neutralized with sodium hydroxide and made strongly basic with sodium carbonate. About 20 mg of non-radioactive iodine carrier (as I^-) was added to the solution and oxidized to periodate (IO_4^-) with sodium hypochlorite. The solution was acidified and the iodine selectively reduced to I_2 with hydroxlyamine hydrochloride. The I_2 was separated from the uranium and other impurities by solvent extraction into xylene. The organic phase was separated and the I_2 back extracted into an aqueous phase as I^- by reduction with sodium bisulfite. Iodine was separated by precipitation and filtration as $PdI_2{\cdot}H_2O$. The chemical recovery was measured gravimetrically. After weighing the $PdI_2{\cdot}H_2O$ deposit, the filter pad (~ 1 cm in diameter) was quantitatively transferred into a 4-ml volume polypropylene vial for counting.

The concentration of I-129 was measured in each sample by low-level photon counting of the 30-34 keV Xe K X-rays in a Ge well detector in the ULLCF. The detector has a low background cryostat with a high purity Cu endcap and a very high purity Al well lining. The photon counting efficiency at 30 keV is about 50%. Figure 4 shows a low energy photon spectrum of 5 pCi of I-129 in the counter. The small peak above the X-ray multiplet is the 40 keV gamma ray with a rather low abundance. The net activity in the X-ray complex was used in these analyses. The self-absorption of the 30 keV X-rays by the $PdI_2{\cdot}H_2O$ was measured by precipitating 50 pCi aliquots of I-129 with various weights of $PdI_2{\cdot}H_2O$. Figure 5 is the self-absorption curve showing the relative count rate versus sample weight. Counting times for the samples ranged from 2,000 to 50,000 seconds. A long count on sample #2 is shown in Figure 6.

Figure 4. Low-Energy Photon Spectrum of I-129 in ULLCF Ge Well Detector

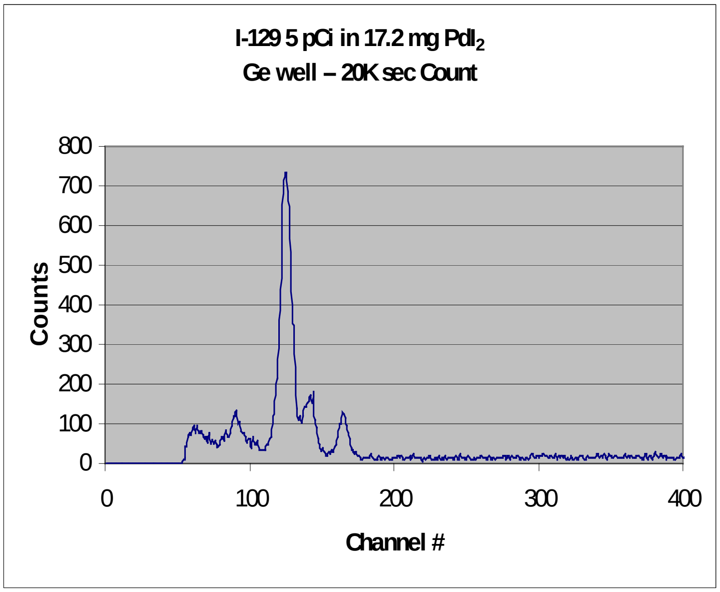


Figure 5. Self-Adsorption of 30 keV X-ray versus Weight of $PdI_2 \cdot H_2O$

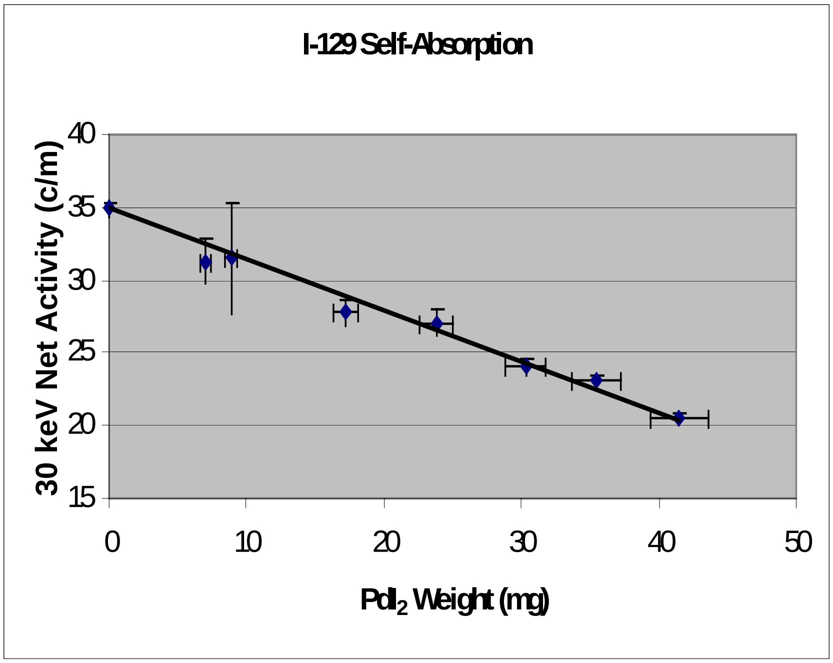
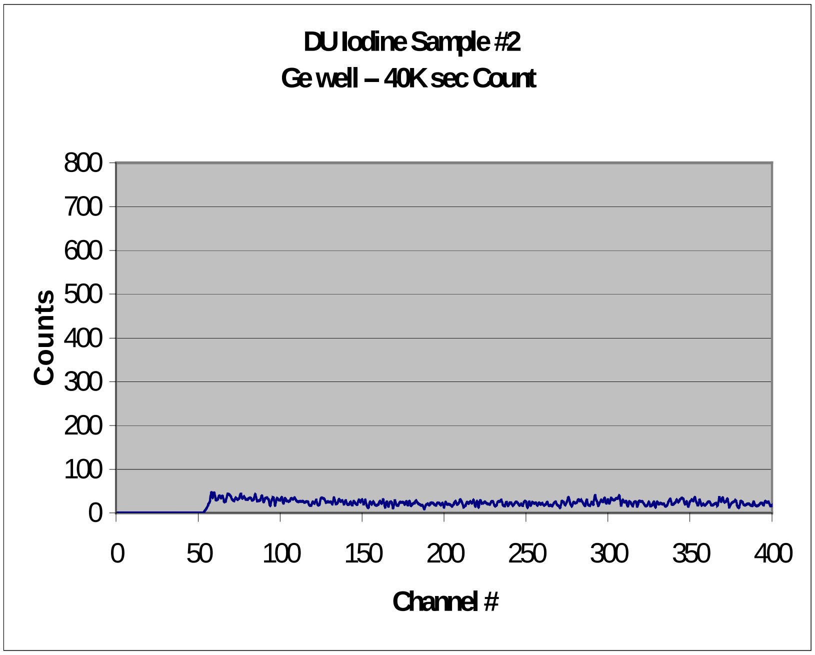


Figure 6. Low-Energy Photon Spectra of DU Sample #2



The measured count rates were corrected for chemical recovery, self-absorption and detector efficiency. No net I-129 activity greater than background was observed in any of the samples. The I-129 MDA's per gram of UO_3 dissolved are listed in Table 10.

Table 10: I-129 Activity in DU Samples, pCi/g

Sample		I-129
1		< 13
2		< 7
3		< 7
4		< 4
5		< 12
6		< 10
7		< 9
8		< 4
9		< 8
10		< 6
11		< 20
12		< 14
13		< 18
14		< 20
15		< 16
16		< 16
17		< 17
18		< 19
19		< 26
20		< 32
21		< 34
22		< 27
23		< 24
24		< 27
25		< 26
26		< 7
27		< 31
28		< 34
29		< 24
30		< 27
31		< 26
32		< 22
33		< 28

Plutonium by Mass Spectrometry

Plutonium-239, Pu-240, Pu-241 and Pu-242 were measured by high sensitivity thermal ionization mass spectrometry (TIMS). Approximately 0.1 gram aliquots were spiked with 5.2 picogram (pg) of Pu-242 tracer. Some replicate samples were analyzed unspiked to determine the Pu-242 content of the samples. Without a tracer in the sample the activity cannot be quantified, however the activity of the spiked sample can be used to quantify the Pu-242 in the unspiked duplicate. A blank was also prepared with each batch and processed through all steps of the procedure.

The samples were dissolved in nitric acid. Sodium nitrate was added to the samples to adjust the plutonium to Pu(IV). The samples were loaded onto a 10-mL anion exchange column conditioned with 8M nitric acid. Under these conditions the resin will retain the plutonium and the uranium will pass through. The column was washed with additional 8M nitric acid to remove the uranium. The column was then washed with 8M hydrochloric acid to remove the Th-234 retained under the nitric acid conditions. Finally the plutonium was eluted using ammonium iodide dissolved in hydrochloric acid. The fraction containing the plutonium was taken to dryness and then the column separation repeated using a smaller 2-mL column. Each column step gives a decontamination factor of uranium from plutonium of 10^3 to 10^4. A total decontamination of 10^9 is required to measure part-per-billion levels of plutonium in uranium.

Final column purification was completed in an environmental lab, under cleaner conditions than can be achieved in the high-level lab. The final column used 2-mL of BioRad MP-1 macroporous resin conditioned with a hydrochloric acid/hydrogen peroxide mixture. The samples were dissolved in the same mixture and loaded to the conditioned columns. The plutonium was eluted with concentrated hydrobromic acid. The acid was taken to dryness and the samples submitted to the NTS mass spectrometric facility.

For analysis by thermal ionization mass spectrometry the sample is loaded onto four resin beads from nitric acid. The beads are physically placed onto a rhenium filament and held in place using collodian. The filaments are placed into a pyrolization chamber at 1400ºC to carborize the sample and then placed into the single-stage mass spectrometer on a sample turret. A current is passed through the selected sample to heat the filament and ionize the plutonium. Ion currents are measured by peak hopping; measured masses include 239, 240, 241, 242, 243 and 243.5. The last two peaks are monitored as a measure of sample background and instrument background, respectively. The ratio of the net 239, 240 or 241 counts to the 242 (added as the tracer) is used to determine the concentration of each isotope in the sample. Samples are typically reported in terms of pg Pu per gram of sample. The half-life of each isotope was then used to convert the concentration (pg/g) to activity (pCi/g); the results are shown in Table 11.

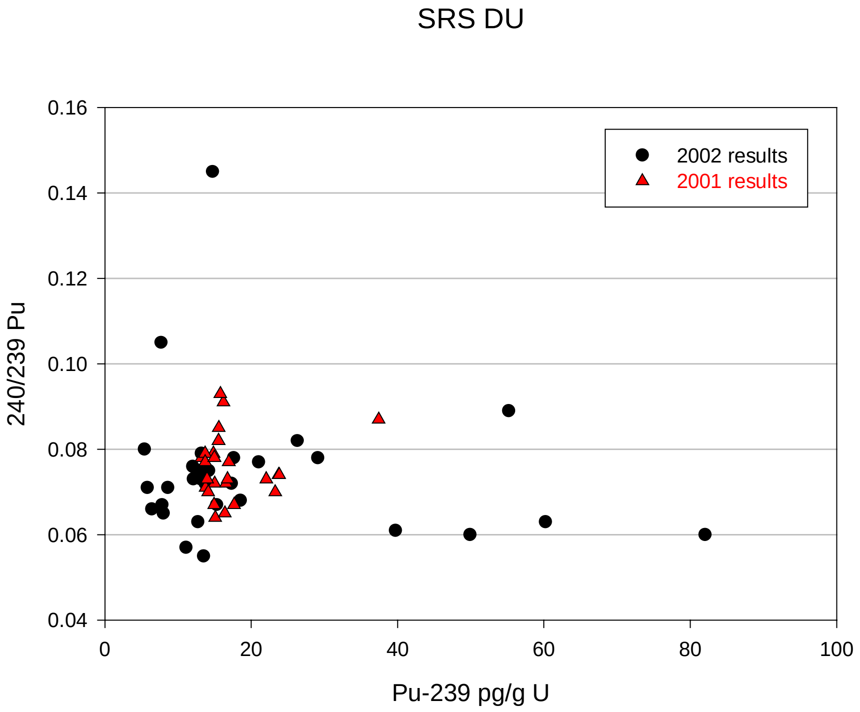
In 2001 the NTS also analyzed a set of SRS DU samples for NMMD. As seen in Figure 7 there is more variation in the 2002 results. Because the origin of the DU may be different this result is not completely unexpected. The figure does show that all SRS DU analyzed to date by the NTS contains less than 100 part-per-trillion plutonium in the uranium.

Table 11. Pu-Isotopic Results by Mass Spectrometry

sample #	239 pg/g	2s error	240 pg/g	2s error	239 pCi/g	240 pCi/g	240/239	2s error	242 pg/g	242 pCi/g	241 pg/g	241 pCi/g
1	8.6	0.2	0.62	0.05	0.53	0.14	0.071	0.007			0.028	2.8
2	11.1	0.8	0.64	0.23	0.69	0.15	0.057	0.021			nd	
3	7.8	0.2	0.53	0.05	0.48	0.12	0.067	0.006			0.009	1.0
4	13.5	0.8	0.74	0.26	0.84	0.17	0.055	0.020			nd	
5	15.3	0.2	1.03	0.07	0.95	0.23	0.067	0.005			0.024	2.5
6	6.4	0.4	0.42	0.10	0.40	0.10	0.066	0.017			nd	
7	5.4	0.3	0.44	0.08	0.34	0.10	0.080	0.016			0.015	1.6
8	14.7	0.4	2.13	0.14	0.91	0.48	0.145	0.011			0.10	10
2 unspk							0.044	0.071	0.087	0.00034	nd	
blank-1	0.31	0.02	0.02	0.01	0.02	0.005	0.065	0.018			nd	
9	55.2	0.3	5.0	0.1	3.43	1.14	0.089	0.002			0.102	11
10	7.7	0.2	0.81	0.06	0.48	0.18	0.105	0.009			0.036	3.8
11	49.9	0.4	3.0	0.1	3.10	0.68	0.060	0.002			0.13	13
12	18.5	0.2	1.26	0.07	1.15	0.29	0.068	0.004			0.026	2.7
13	82	1	5.0	0.3	5.09	1.14	0.060	0.004			0.17	17
14	39.7	0.2	2.43	0.04	2.46	0.55	0.061	0.001			0.073	7.5
15	5.8	0.1	0.41	0.02	0.36	0.09	0.071	0.005			0.009	0.9
16	dnr											
14 unspk							0.099	0.022	3.07	0.012	0.121	12.5
blank-2	0.043	0.003	0.004	0.001	0.003	0.001	0.075	0.003			nd	
17	26.3	0.3	2.2	0.1	1.63	0.50	0.082	0.004			0.039	4.0
18	12.1	0.4	0.9	0.1	0.75	0.20	0.073	0.010			nd	
19	60.2	0.5	3.8	0.1	3.74	0.86	0.063	0.002			0.105	11
20	17.3	0.5	1.2	0.1	1.07	0.27	0.072	0.009			nd	
21	8.0	0.1	0.52	0.02	0.50	0.12	0.065	0.003			0.010	1.1
22	13.1	0.1	0.96	0.04	0.81	0.22	0.073	0.003			0.033	3.4
23	29.1	0.4	2.3	0.1	1.81	0.52	0.078	0.005			0.052	5.3
24	21	1	1.6	0.3	1.3	0.36	0.077	0.017			nd	
21 unspk							0.067	0.014	0.135	0.00053		
blank-3	0.50	0.01	0.047	0.004	0.03	0.01	0.093	0.008			6.4E-05	0.007
25	14.2	0.1	1.07	0.04	0.88	0.24	0.075	0.003			0.025	2.6
26	12.8	0.1	0.96	0.02	0.79	0.22	0.075	0.002			0.026	2.7
27	12.8	0.1	0.96	0.03	0.79	0.22	0.075	0.003			0.028	2.8
28	12.0	0.1	0.92	0.04	0.74	0.21	0.076	0.003			0.033	3.4
29	12.7	0.5	0.8	0.1	0.79	0.18	0.063	0.012			nd	
30	13.7	0.3	0.99	0.08	0.85	0.22	0.072	0.006			0.039	4.0
31	dnr											
32	17.6	0.4	1.4	0.1	1.09	0.32	0.078	0.008			0.024	2.5
33	13.2	0.3	1.05	0.09	0.82	0.24	0.079	0.007			0.017	1.7
28 unspk	dnr											
blank-4	0.27	0.01	0.024	0.002	0.02	0.01	0.089	0.009			nd	

dnr = did not run, nd = not detected

Figure 7. Pu-Isotopic Results on SRS DU from 2001 and 2002



Plutonium-238

The Pu-238 activity was determined by alpha spectrometry. As a result of the analysis the Pu-239+240 activity is also determined. The Pu-239 activity cannot be distinguished from Pu-240 by alpha spectrometry therefore the samples were analyzed by mass spectrometry as described above. For the ^{238}Pu activity determination, approximately 0.1 g aliquots of each sample were dissolved in 8 M HNO_3 and spiked with ^{236}Pu tracer. The tracer was equilibrated with the analyte isotopes by heating the solution followed by the addition of $NaNO_2$ and additional heating. Plutonium was purified using two anion exchange separations, then electrodeposited onto platinum disks and counted by alpha spectrometry. Chemical yields varied between 40 and 60 %, with the exception of sample 29, which had only a 3% recovery. Results for the reagent blanks, samples, and replicates are summarized below.

Four reagent blanks spiked with the ^{236}Pu tracer were run along side the DU samples. None of the Pu reagent blanks had any detectable $^{239+240}$Pu or ^{238}Pu activity. The limit of detection for each isotope was calculated for each blank based on the chemical yield for the blank, the alpha spectrometry detector background and count time. Results for the reagent blanks are shown in Table 12.

Table 12: Detection Limit Calculated for each Reagent Blank

Blank #	Pu-239+240 pCi	Pu-238 pCi
1	<0.007	<0.006
2	<0.007	<0.007
3	<0.002	<0.008
4	<0.009	<0.012

All of the DU samples contained measurable plutonium, with the exception of sample 29, which had a low recovery so only a detection limit is reported. In sample 7, only $^{239+240}$Pu was detected, so the ^{238}Pu was reported as the detection limit. Results for the 33 samples are summarized in Table 13. Most of the $^{239+240}$Pu activities determined by alpha spectrometry agreed well with the mass spectrometry results. The comparisons are shown in Figure 8. A slight positive bias in the mass spectrometry results may be present compared to the alpha spectrometry results for the sum of the Pu-239 and Pu-240 activities. The mass spectrometry results were reported to the customer. DU samples that showed the largest discrepancies between methods were determined to be satisfactory by NMMD because the maximum value was well below the required detection limit.

Four samples were run in duplicate by alpha spectrometry to demonstrate consistency between analyses. The results for the replicate of sample 6 showed that it had both ^{238}Pu and $^{239+240}$Pu activities approximately half of the values determined in sample 6. This was probably the result of the replicate sample accidentally getting a double spike of the ^{236}Pu tracer, which would give a result of half the true value. The value for $^{239+240}$Pu determined in sample 6 also agrees well with the value determined by mass spectrometry, indicating the replicate was double spiked. The other three pairs of replicate samples run were in excellent agreement with each other. The results for the replicate samples are shown in Figure 9.

Figure 8. Comparison of Pu-239+240 Activity as Determined by Alpha Spectrometry and Mass Spectrometry

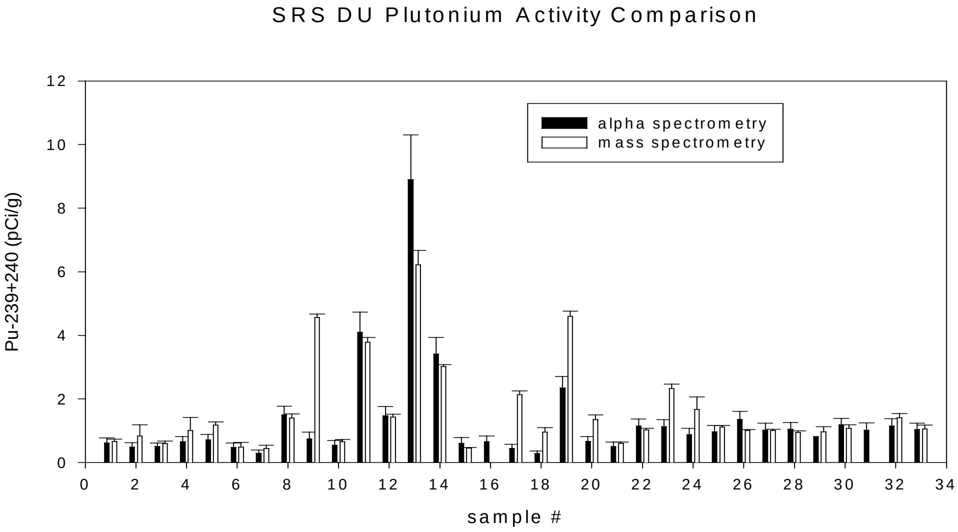
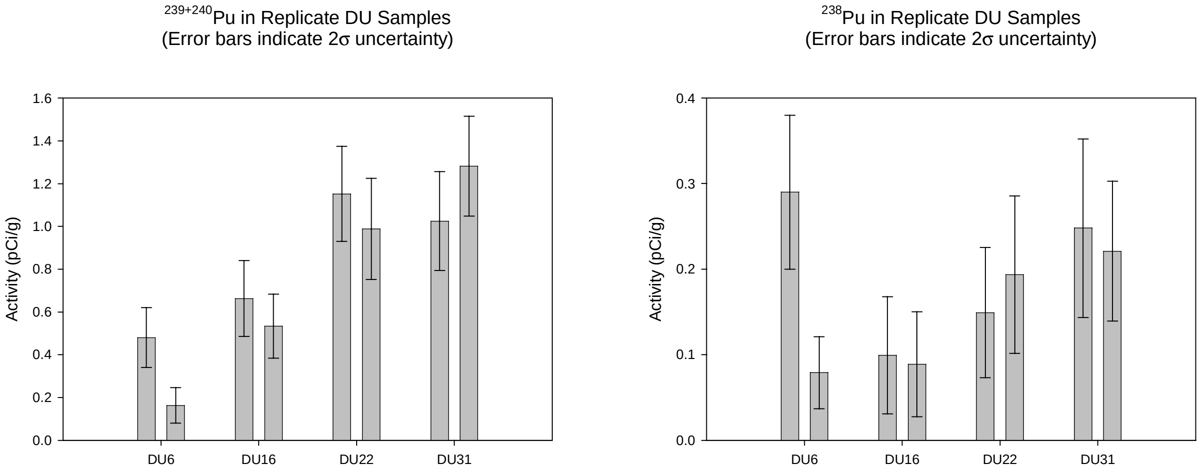


Table 13. Activity of Pu-238 and Pu-239+240 by Alpha Spectrometry

Sample Number	$^{239+240}$Pu (pCi/g)	2 σ	^{238}Pu (pCi/g)	2 σ
DU1P	0.62	0.16	0.114	0.060
DU2P	0.49	0.14	0.099	0.065
DU3P	0.51	0.11	0.065	0.035
DU4P	0.66	0.16	0.129	0.064
DU5P	0.72	0.17	0.086	0.053
DU6P	0.48	0.14	0.163	0.083
DU7P	0.29	0.10	< 0.09	
DU8P	1.50	0.27	1.42	0.26
DU9P	0.75	0.21	0.35	0.14
DU10P	0.54	0.15	0.244	0.098
DU11P	4.10	0.63	0.24	0.10
DU12P	1.47	0.29	0.090	0.058
DU13P	8.9	1.4	0.23	0.11
DU14P	3.41	0.52	0.123	0.065
DU15P	0.61	0.18	0.127	0.083
DU16P	0.66	0.18	0.099	0.069
DU17P	0.44	0.13	0.125	0.066
DU18P	0.278	0.088	0.081	0.047
DU19P	2.35	0.36	0.043	0.033
DU20P	0.67	0.15	0.088	0.047
DU21P	0.51	0.14	0.094	0.067
DU22P	1.15	0.22	0.149	0.076
DU23P	1.13	0.22	0.186	0.075
DU24P	0.88	0.20	0.242	0.098
DU25P	0.97	0.20	0.178	0.077
DU26P	1.36	0.25	0.56	0.14
DU27P	1.02	0.22	0.181	0.079
DU28P	1.05	0.21	0.154	0.067
DU29P	< 0.82		< 0.42	
DU30P	1.19	0.20	0.123	0.052
DU31P	1.02	0.23	0.25	0.10
DU32P	1.15	0.23	0.155	0.070
DU33P	1.04	0.20	0.153	0.065

Figure 9: Comparison between four pairs of replicate DU samples analyzed for $^{239+240}$Pu and ^{238}Pu.



Neptunium-237

The ^{237}Np activities were determined by alpha spectrometry in the same DU aliquots taken for Pu analysis, using ^{236}Pu as a chemical yield tracer. Because Pu and Np are not the same element, the ^{236}Pu tracer cannot be used to determine the exact chemical yield for the Np. However, three QC standards containing known amounts of ^{237}Np were spiked with ^{236}Pu and run through the same chemistry used for the samples to determine the relative recovery of Np compared to Pu.

As shown by the results for these QC samples (Table 14), the chemical recovery for Np relative to Pu was between 29% and 48%. Therefore, to estimate the maximum activity of ^{237}Np in each sample, a worst case relative recovery of 10% was used. The maximum ^{237}Np concentrations were calculated from the sample detection limit if no ^{237}Np was detected in a sample. Calculated maximum ^{237}Np concentrations are shown in Table 15. This approach was conservative and ensured that the real concentration of ^{237}Np in the samples was less than the reported value. The third column in Table 15 indicates whether a peak was noted in the Np-237 region of the alpha spectra in a particular sample, or if the sample detection limit was used to calculate the maximum concentration.

Table 14: Chemical recovery results for ^{237}Np relative to ^{236}Pu for three QC samples

^{237}Np QC Number	pCi Added	pCi Measured	% Recovery Relative to Pu
QC1	1.89	0.54	29%
QC2	1.89	0.91	48%
QC3	1.89	0.76	40%

Table 15: Maximum ^{237}Np concentrations in DU samples

Sample Number	^{237}Np Activity pCi/g	^{237}Np Detected?
DU1	< 0.44	no
DU2	< 2.34	yes
DU3	< 0.33	no
DU4	< 4.61	yes
DU5	< 12.8	yes
DU6	< 8.89	yes
DU7	< 14.3	yes
DU8	< 3.85	yes
DU9	< 6.52	yes
DU10	< 2.43	yes
DU11	< 13.6	yes
DU12	< 11.9	yes
DU13	< 8.55	yes
DU14	< 1.30	yes
DU15	< 6.38	yes
DU16	< 33.5	yes
DU17	< 6.08	yes
DU18	< 2.86	yes
DU19	< 10.2	yes
DU20	< 11.3	yes
DU21	< 1.92	yes
DU22	< 0.77	yes
DU23	< 1.67	yes
DU24	< 0.69	no
DU25	< 1.18	yes
DU26	< 0.65	no
DU27	< 0.94	yes
DU28	< 1.61	yes
DU29	< 11.1	no
DU30	< 0.87	yes
DU31	< 1.04	no
DU32	< 1.32	yes
DU33	< 1.58	yes

Uranium Isotopic Results by Mass Spectrometry

Several samples were analyzed by thermal ionization mass spectrometry to determine the uranium isotopic distribution. Approximately 10 mg of the sample was dissolved in 8M nitric acid. The acid was diluted to 20 mL with DI water, and then 1 mL of this solution was diluted to 100 mL with 0.5 M nitric acid. This resulted in a solution concentration of 500 ng U per mL. Ten μL of this solution (5 ng of U) was submitted to the mass spectrometric facility for the analysis of uranium. Two filaments for each sample were prepared by bead loading the U onto rhenium filaments, similar to the procedure used for

Pu TIMS analyses. The filaments were loaded onto the three-stage thermal ionization mass spectrometer and analyzed using standard protocols. Masses 238, 237, 236, 235, 234, 233, 232 and 229.5 are monitored during the analysis. The 237 and 232 serve to monitor the sample background and 229.5 the instrument background, similarly to that done for the Pu TIMS analyses. The uranium isotopic abundances are reported as atomic percent of each isotope. The results for the analyses completed are shown in Table 16. The results from the two separate analyses were averaged and reported in the Table.

Table 16. Uranium Isotopic Abundances by Mass Spectrometry (as atom percent)

sample #	238	2 sigma	236	2 sigma	235	2 sigma	234	2 sigma	233	2 sigma
3	99.87at%	0.07at%	0.0059at%	0.0001at%	0.124at%	0.0006at%	0.0004at%	0.0000at%	0.0000at%	0.0000at%
8	99.87at%	0.05at%	0.0063at%	0.0001at%	0.124at%	0.0004at%	0.0004at%	0.0000at%	0.0000at%	0.0000at%
9	99.87at%	0.09at%	0.0058at%	0.0001at%	0.123at%	0.0007at%	0.0004at%	0.0000at%	0.0000at%	0.0000at%
17	99.87at%	0.05at%	0.0060at%	0.0001at%	0.124at%	0.0005at%	0.0004at%	0.0000at%	0.0000at%	0.0000at%
20	99.87at%	0.07at%	0.0061at%	0.0001at%	0.126at%	0.0006at%	0.0004at%	0.0000at%	0.0000at%	0.0000at%
25	99.84at%	0.06at%	0.0087at%	0.0001at%	0.148at%	0.0006at%	0.0007at%	0.0000at%	0.0000at%	0.0000at%
30	99.85at%	0.06at%	0.0080at%	0.0001at%	0.138at%	0.0006at%	0.0006at%	0.0000at%	0.0000at%	0.0000at%

Uranium Isotopic Results by Alpha Spectrometry

The relative activities of U-238, U-235+236 and U-234 were determined by alpha spectrometry for all samples submitted. Approximately 0.1 g of the DU was dissolved in 5 mL of 8M nitric acid, then diluted by weight to approximately 20 g. A 0.5 g aliquot of the DU solution was then diluted by weight to 100 g to give a DU concentration of approximately 25 µg DU per gram solution. A one gram sample of this final dilution was electrodeposited onto a stainless steel disk for counting.

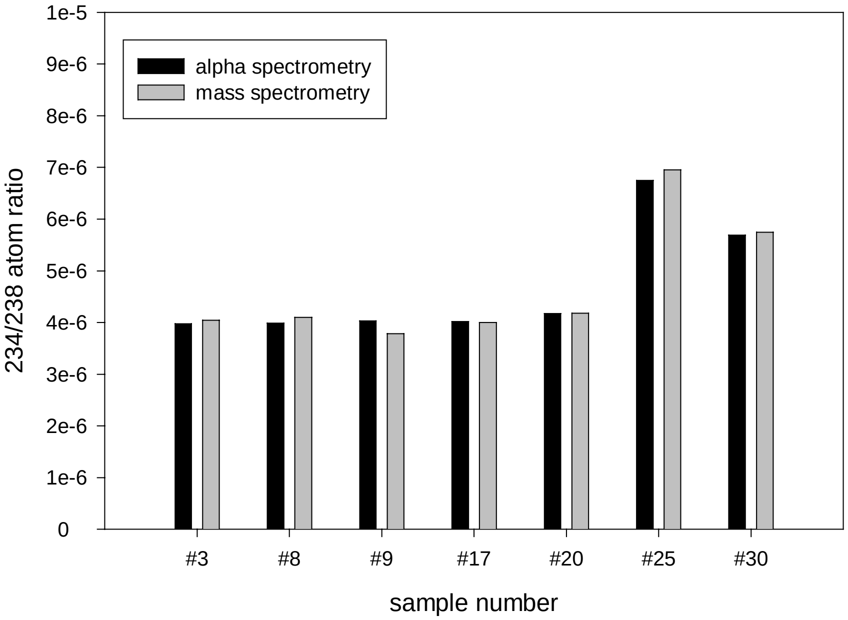
Results of these analyses are shown in Table 17. The relative activities of U-238, U-235+236 and U-234 are expressed in the table as a percent of the total uranium alpha activity. The sum of U-235 plus U-236 is reported because their alpha decay energies are similar and cannot be resolved by alpha spectrometry methods. The alpha decay energies of U-234 and U-233 are similar and cannot be distinguished by alpha spectrometry, either, however no U-233 was noted in the mass spectrometry analysis of the selected samples.

As a quality control check a comparison was made between the U-238/U-234 activity ratio determined by alpha spectrometry and the U-238/U-234 atom ratio determined by mass spectrometry. The alpha spectrometry results were converted to atom ratios and are shown in Figure 10. The two methods are in excellent agreement with each other.

Table 17. Uranium Isotopic Abundances by Alpha Spectrometry
(as percent of total uranium alpha activity)

sample #	U-238	2s error	U-235+236	2s error	U-234	2s error
1	91.7	2.2	1.72	0.22	6.57	0.44
2	91.0	2.0	1.74	0.21	7.28	0.43
3	91.3	2.2	2.04	0.24	6.63	0.44
4	91.3	1.9	1.86	0.20	6.82	0.39
5	91.6	2.2	1.73	0.22	6.67	0.45
6	91.2	2.3	1.76	0.23	7.07	0.48
7	91.2	2.1	1.85	0.22	6.91	0.43
8	91.6	2.2	1.71	0.21	6.67	0.43
9	91.3	2.0	1.98	0.22	6.72	0.41
10	91.8	2.1	1.70	0.21	6.55	0.42
11	91.6	2.2	1.70	0.22	6.75	0.45
12	91.8	1.9	2.04	0.21	6.18	0.37
13	91.3	2.0	1.95	0.22	6.74	0.41
14	91.2	2.2	1.70	0.22	7.09	0.46
15	91.6	2.0	1.74	0.20	6.63	0.41
16	91.4	2.0	1.86	0.20	6.70	0.40
17	91.2	2.0	2.07	0.22	6.70	0.40
18	91.4	2.1	1.86	0.22	6.71	0.42
19	91.7	2.4	1.97	0.26	6.32	0.47
20	90.8	2.3	2.25	0.26	6.92	0.47
21	91.6	2.0	1.73	0.20	6.69	0.41
22	87.5	2.0	2.11	0.23	10.42	0.53
23	88.4	1.8	2.11	0.21	9.46	0.46
24	85.9	1.7	2.51	0.21	11.55	0.47
25	86.9	1.8	2.41	0.22	10.71	0.48
26	86.7	2.0	2.36	0.24	10.90	0.54
27	87.3	2.0	2.27	0.24	10.41	0.53
28	88.0	3.1	2.26	0.36	9.72	0.78
29	87.3	3.4	2.84	0.45	9.91	0.87
30	88.5	3.3	2.27	0.39	9.20	0.82
31	85.9	3.4	2.77	0.46	11.32	0.96
32	88.6	3.2	2.80	0.42	8.61	0.76
33	88.2	4.0	1.83	0.43	9.99	1.03

Figure 10. Comparison of Uranium Alpha and Mass Spectrometry Atom Ratios



Summary

Thirty-three SRS previously irradiated and reprocessed depleted uranium samples were submitted to the NTS for analysis of contaminant radionuclides. Existing methods were validated for use with this matrix. Due to the extremely sensitive nature of the analysis methods used, plutonium was detected in the samples. Of the other analytes measured only Tc-99 was detected above the detection limit of the methods used. All analytes, except Tc-99, were less than 100 pCi per gram of DU oxide, and Ra-226, which was less than 600 pCi/g. The Tc-99 activity varied from about 10-90 nCi/g.