INL/EXT-13-29351

Multi-Collector Inductively Coupled Plasma Mass Spectrometer – Operational Performance Report

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The INL is a U.S. Department of Energy National Laboratory
operated by Battelle Energy Alliance

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Prepared for the
U.S. Department of Defense
and for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

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Abstract

The INL made an assessment of the commercially available inductively coupled plasma mass spectrometers (ICPMS) for actinide analysis; emphasizing low detection limits for plutonium. INL scientists subsequently determined if plutonium was present on a swipe, at a 10 million atom decision level. This report describes the evaluation of ICPMS instruments and the operational testing of a new process for the dissolution, separation and analysis via ICPMS of swipes for plutonium and uranium. The swipe dissolution, plutonium and uranium isolation, separation and purification are wet chemistry methods following established procedures. The ICPMS is a commercially available multi-collector magnetic sector mass spectrometer that utilizes five ion counting detectors operating simultaneously. The instrument includes a sample introduction system allowing for sample volumes of < 1 mL to be reproducibly injected into the instrument with minimal waste of the sample solution, while maximizing the useable signal. The performance of the instrument was measured using SRM 996 (^{244}Pu spike) at concentrations of 12 parts per quadrillion (ppq, fg/mL) and with SRM 4350B Columbia River Sediment samples spiked onto swipes at the 10 million atom level. The measured limit of detection (LOD, defined as 3σ) for ^{239}Pu is 310,000 atoms based upon the instrument blank data. The limit of quantification (LOQ defined as 10 σ) for ^{239}Pu is 105,000 atoms. The measured limit of detection for ^{239}Pu from the SRM 4350B spiked onto a swipe was 2.7 million atoms with the limit of quantification being 9.0 million atoms.

Introduction

The measurement of ultratrace levels of plutonium in the presence of uranium in swipes taken from laboratories or sampling equipment presents a significant challenge to mass spectrometry. Historically, such determinations were made via thermal ionization mass spectrometric (TIMS) measurement of a sample that required extensive laboratory effort to isolate plutonium free from uranium isobaric interference. The TIMS measurement, however, was very time consuming and ICPMS makes a much quicker measurement step. While not as sensitive as TIMS, significant progress has been made for ICPMS sensitivity over the past decade. Newer coupling of multi-collector technology with ICPMS has resulted in the most sensitive ICPMS instruments to date.

Chemistry development by Eichrom has provided a separation scheme that will isolate uranium and plutonium. The UTEVA TRU scheme was chosen as it attempts to remove the uranium and allows the plutonium to pass on to the second cartridge. This is the correct order, so that as little uranium as possible comes in contact with the trapping medium used for plutonium. The separation factor provided as k' is 600 for UTEVA and 100 for the TRU column[1]. The traps are separated and individual fractions of uranium and plutonium are produced for the ICPMS analysis.

Two vendors provide commercial MC-ICPMS instruments: Nu and Thermo. An evaluation of the specifications for these instruments showed that either could produce the desired results when coupled with the Elemental Scientific Inc. (ESI) small volume sample introduction system.

Wieser and Schwieters[2] provide a comprehensive description of the development of multiple-collector isotope ratio mass spectrometry. In the commercial multi-collector instruments available today, various types of electron multipliers coupled to pulse counters are used to detect extremely low-level signals. However, space constraints at the focal plane of the instruments limit the number or type of electron multipliers that can be used. Nu Instruments[3] employs discrete dynode multipliers; Thermo-Scientific[4] utilizes miniaturized discrete dynode multipliers and full-sized detectors on selected channels.

Instrumental Evaluation and Selection

The only instrument physically evaluated for this measurement was the Thermo Neptune Plus. Nu Instruments was not able to meet the production needs for the period of performance. INL scientists tested samples that were prepared at INL on the Neptune Plus at the Thermo factory.

At the Thermo facilities, the Neptune Plus instrument was set up with the micro injection system from ESI which maximizes sensitivity via small injections and desolvation of the sample prior to introduction into the ICPMS plasma. This was the configuration determined by Thermo to be best suited to maximize sensitivity when sample size was limited. The instrument was in working order using the ESI front end when we started on our sample injections.

First, a uranium standard was injected at 10 parts per trillion (ppt). This was followed by a mixed standard of 10 ppt U and 6 ppt Pu. The response was 140k counts per second (cps) for U and 100k cps for Pu. The ratio of the concentrations of uranium / plutonium was 1.7 in the mixed standard. The ratio of the response of uranium/plutonium was 1.4. Plutonium produces ions more efficiently than uranium. This validated our assumption that the plutonium would respond in the instrument at least as well as uranium.

Introduction of this mixed standard was followed by blank samples. The blanks showed an elevated background at mass 244. Initially the mass 244 signal was ~1 cps. After the 6 parts per trillion (ppt, pg/mL) plutonium standard, the 244 blank was ~300 cps. The washing solutions and rinse times and steps in the ESI auto-sampler were adjusted to remove the background. Washing for longer times with 10% nitric acid and 1% hydrochloric acid and manipulating the valves used in the system reduced the background to 5 cps at mass 244 in two hours.

On day two, injection of a plutonium standard containing 480 fg ^{244}Pu that had been processed through the chemical separation and purification method, produced a 200 cps signal from an injection of 20 micro-liters per minute over 4 minutes at mass 244 resulting in 200 seconds of useable data. The 480 fg had been diluted to 1.2 mL, resulting in a 400 ppq concentration of ^{244}Pu, assuming 100% of the plutonium came through the chemical separation. The blank was ~3 cps at 244. All unprocessed standards, processed standards and processed blank swipe materials were run, some with replicate injections and some duplicate samples. This allowed us to evaluate the reproducibility of both the injections and the overall process.

From the data gathered, the following was determined. The chemistry processing of samples for plutonium was only delivering 10% of the initial sample to the instrument. A calibration curve was prepared from samples at three different levels taken through the chemistry. At 10% recovery, there is still a reasonable linear response. Additionally, at the 10% yield, the goal of measuring 4 fg was successfully demonstrated.

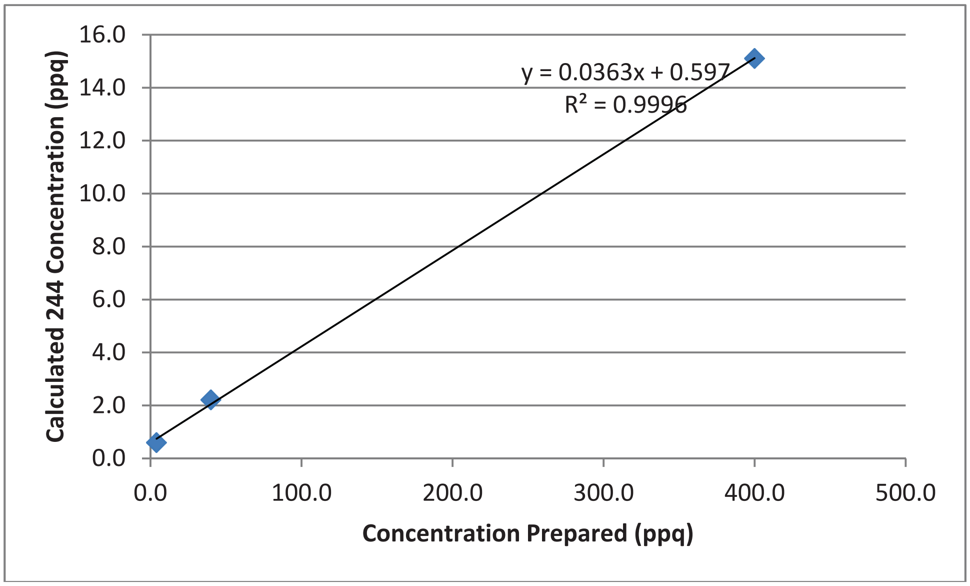


Figure 1. Prepared concentration of ^{244}Pu from SRM 996 vs. measured content of ^{244}Pu after chemistry at Thermo factory demonstration.

Uranium was monitored throughout the plutonium evaluation. The uranium blanks were 1-4000 cps immediately following samples with signals in the millions of counts. It was determined that the chemistry was introducing uranium and INL scientists needed to investigate and make improvements. Uranium signals of this magnitude will tail into mass 239 and produce uranium hydride at 239 as well. Hydride production was determined to be ~1.2E-5 times the 238 mass signal.

Uranium fractions of the corresponding plutonium samples were also analyzed at Thermo. The 235 and 238 mass signals were measured on Faraday cups and the other masses measured with ion counters. The uranium data is shown below. It appears that the samples fall between naturally occurring ratios and Columbia River Sediment for the 235/238 ratio, and high for the 234/238 ratio. The reality is that the errors on all the measurements overlap. There is a contribution of natural uranium, likely from the reagents and chemicals used. The acid used for this work was checked on the Neptune Plus and is not a significant source of uranium compared to the samples.

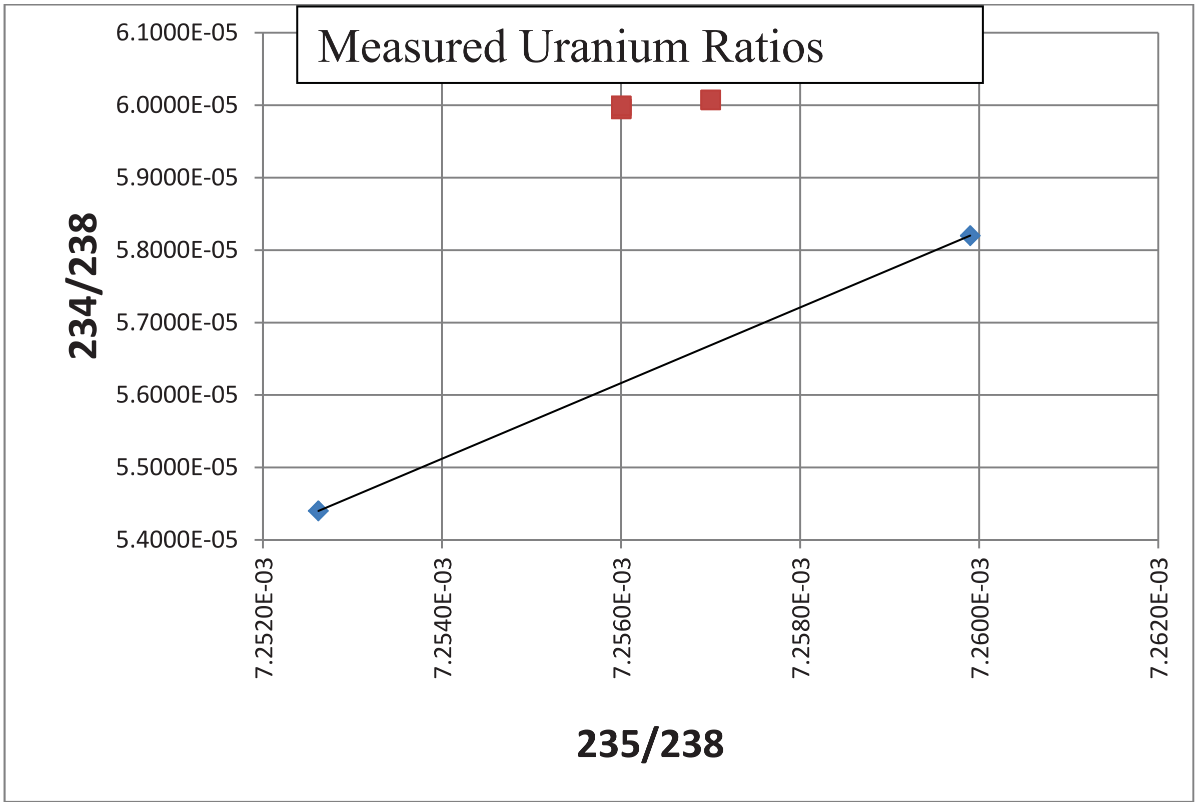
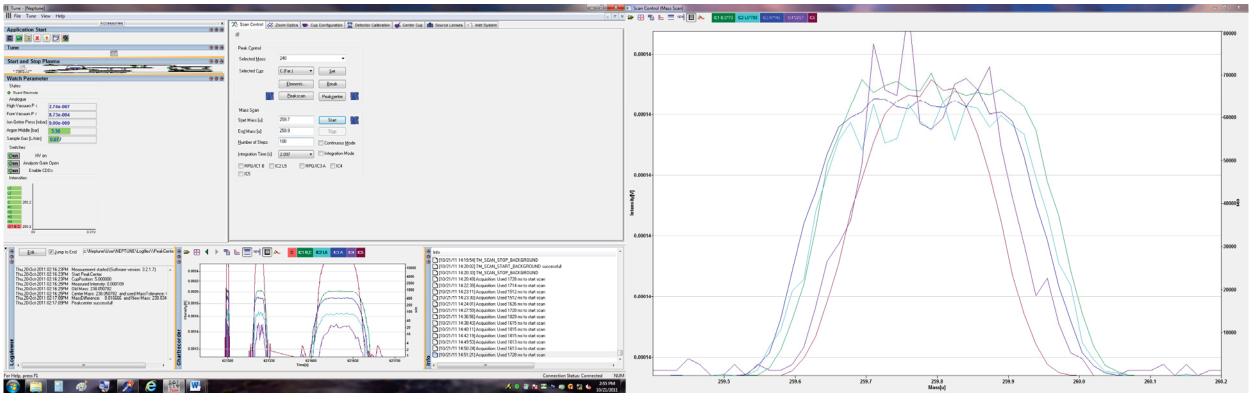


Figure 2. Uranium data plotted for SRM 4350 B analysis (red) with a mixing line between natural and SRM 4350B (blue) uranium isotopic content.

Instrument Design and Installation

The instrument design was prepared by the vendor as the Neptune Plus is a relatively mature product. INL provided input on the end use to assure the best detector array would be installed. The array was optimized for plutonium isotopic measurements. It is possible to simultaneously measure masses 239, 240, 241, 242 and 244 all on ion counting detectors. The detector array was requested to be viable for uranium measurements.

In order to be used as a multi-collector, the detector array and electronic lenses of the system had to be aligned and optimized. This was initially performed by the vendor at the factory and tested in the installation at INL. The service engineer wasn't able to stay at INL through a solid block of time to complete the installation. He came to the INL for a week and then returned a couple of weeks later to complete the installation. The engineer suggested we become familiar with the instrument in his absence. During this time we were able to align signals on the detector array and were ready to run when the vendor returned. The figure below shows the output on all five ion counting detectors. The signals are low for some masses due to minor isotope abundance, and therefore noisy. The important thing to note is that the center of all the peaks is in nearly the same spot. Therefore, when we tune the beam into the center of the detectors, we are on the flat top of all five masses and making the best measurements.



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Fore Vacuum P < 8.73e-004
Ion Getter Press [mbar] 9.00e-009
Argon Middle [bar] 3.30
Sample Gas [L/min] 0.977

HV on: on
Analyzer Gate Open: on
Enable CDDs: on

Selected Mass: 240
Selected Cup: C (Far.)
Start Mass [u]: 259.7
End Mass [u]: 259.9
Number of Steps: 100
Integration Time [s]: 2.097
☐ Continuous Mode
☐ Integration Mode
☐ RPQ/IC1 B ☐ IC2 L5 ☐ RPQ/IC3 A ☐ IC4
☐ IC5

☑ Jump to End c:\Neptune\User\NEPTUNE\Logfiles\\PeakCente

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Thu,20-Oct-2011 02:16:23PM  Measurement started (Software version: 3.2.1.7)
Thu,20-Oct-2011 02:16:23PM  Start PeakCenter
Thu,20-Oct-2011 02:16:23PM  CupPosition: 5.000000
Thu,20-Oct-2011 02:16:25PM  Measured Intensity: 0.000109
Thu,20-Oct-2011 02:16:25PM  Old Mass: 238.050782
Thu,20-Oct-2011 02:16:25PM  Center Mass: 238.050782  and used MassTolerance: (
Thu,20-Oct-2011 02:17:08PM  MassDifference:    0.016666  and New Mass: 238.034
Thu,20-Oct-2011 02:17:09PM  Peakcenter successfull
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[10/21/11 14:19:54] TM_SCAN_STOP_BACKGROUND
[10/21/11 14:20:02] TM_SCAN_START_BACKGROUND successfull
[10/21/11 14:20:33] TM_SCAN_STOP_BACKGROUND
[10/21/11 14:20:49] Acquisition: Used 1728 ms to start scan
[10/21/11 14:22:39] Acquisition: Used 1714 ms to start scan
[10/21/11 14:23:11] Acquisition: Used 1512 ms to start scan
[10/21/11 14:23:30] Acquisition: Used 1512 ms to start scan
[10/21/11 14:24:01] Acquisition: Used 1626 ms to start scan
[10/21/11 14:27:59] Acquisition: Used 1728 ms to start scan
[10/21/11 14:36:56] Acquisition: Used 1829 ms to start scan
[10/21/11 14:38:43] Acquisition: Used 1615 ms to start scan
[10/21/11 14:40:11] Acquisition: Used 1815 ms to start scan
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[10/21/11 14:49:53] Acquisition: Used 1613 ms to start scan
[10/21/11 14:50:24] Acquisition: Used 1613 ms to start scan
[10/21/11 14:51:21] Acquisition: Used 1728 ms to start scan
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Figure 3. Neptune Plus alignment for plutonium at INL using SRM 996. Purple = mass 239, dark blue = mass 240, light blue = mass 241, green = mass 242, maroon = mass 244.

Performance Testing Results

Plutonium

The Neptune Plus has not required further instrument optimization, and is performing as well as when it was set up by Thermo and ESI. Injection of a 12 ppq standard regularly produces 400-500 cps. Injections are 200 uL at a rate of 50 uL / min. The Neptune is very stable and routinely delivers the same signal levels from the same injections day after day.

To assess the performance of the instrument a series of samples prepared at INL using SRM 996 (^{244}Pu spike) alone as well as combined with SRM 4350B (Columbia River Sediment) was analyzed. The quantitative results reflect both the performance of the instrument alone and of the combined instrument and sample processing. This combination of standards demonstrates the Neptune capability and the current INL analysis capability applied to the detection of 10,000,000 atoms of ^{239}Pu.

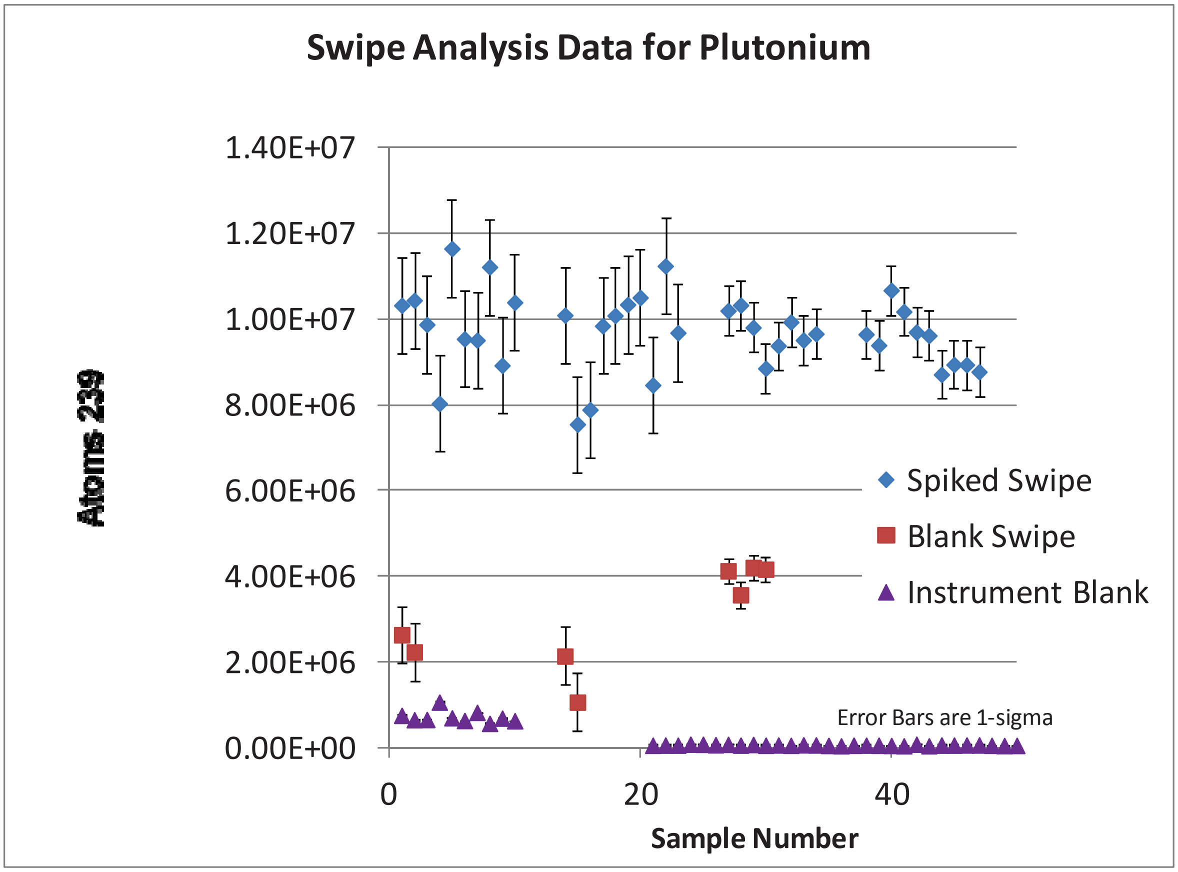

Figure 4. Spiked Swipe and Blank data from INL.

The data labeled atoms of 239 (blue diamonds) is data from 38 swipe samples that were spiked with 10 million atoms of ^{239}Pu and with a known amount of ^{244}Pu for quantification of the ^{239}Pu. The data shows a clear separation from the 10 million atom level of the 38 spiked swipes and the instrument blank data (purple triangles) and the blank swipe data (red squares). The standard deviation of the 10 swipes shows that the detection limit for ^{239}Pu calculated at 3-sigma is 2.7 million atoms of ^{239}Pu and the quantification limit is 9.0 million atoms of ^{239}Pu.

The graph in Figure 4 positively shows an improvement in the uncertainty of the data set. The 4 sets of sample data shown can be divided into two groups with the latter data being the most recent in time and having the lowest uncertainty. This shows an improving process for the complete analysis scheme of laboratory preparation and instrumental analysis. A large difference can be seen in the first half of the data compared to the second half. This is the point where the Neptune Plus received preventative maintenance by the Thermo service engineer. Additionally, the data represent the work of two chemists and shows that the process is being established at the INL with the capability of multiple analysts.

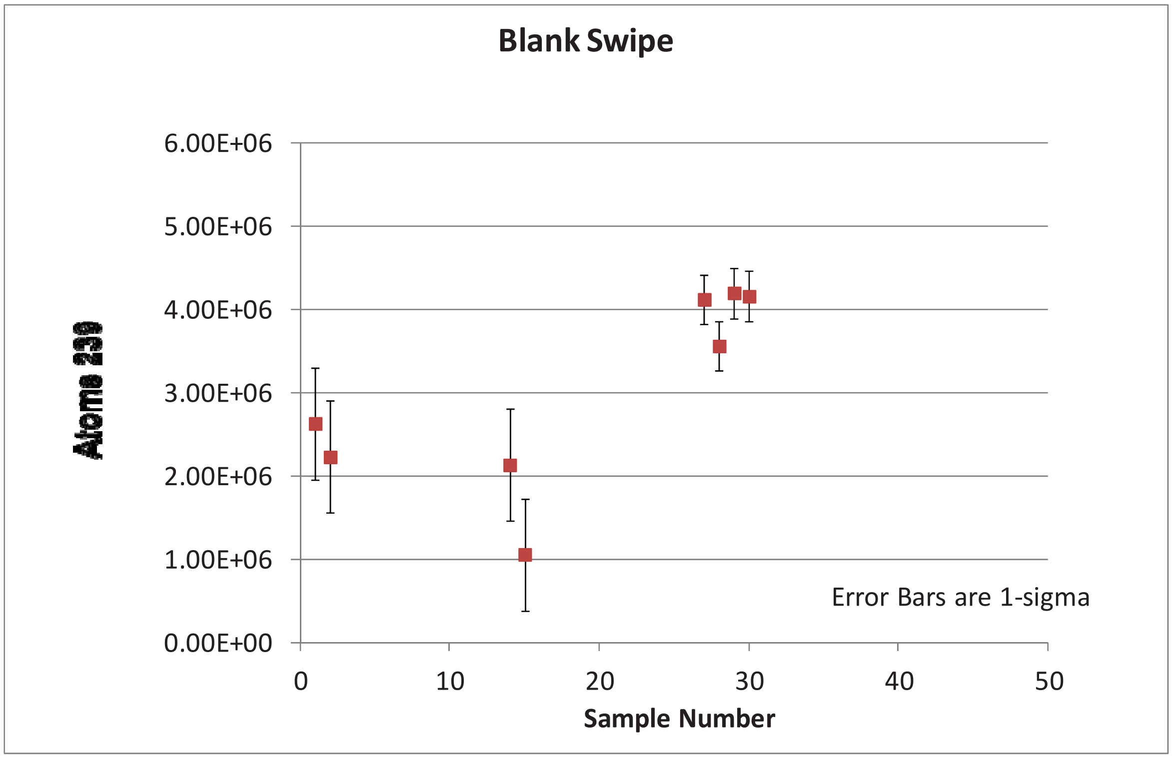

Figure 5. Blow up of figure 4 to show the blank swipe data.

The blank swipe data shows the 239 signal measured when a blank swipe is processed through the chemistry. The level was initially about 2 million atoms. This blank value is subtracted from the sample results to determine how much ^{239}Pu is contained on a swipe sample. The step function up in the blank data shows some very important points. The background as measured in the plutonium fraction is not constant. A blank swipe is a necessary part of each sample batch for subtraction from production samples. The signal observed is not plutonium, but a combination of the tailing of a ^{238}U signal and ^{238}U^{1}H signal produced in the plasma. It is possible to work on the chemistry and improve separation of the plutonium and uranium. This would minimize the impact of this factor on the analysis. The data presented above show that this background can be effectively taken into account and the decision limit of 10 million atoms can be met.

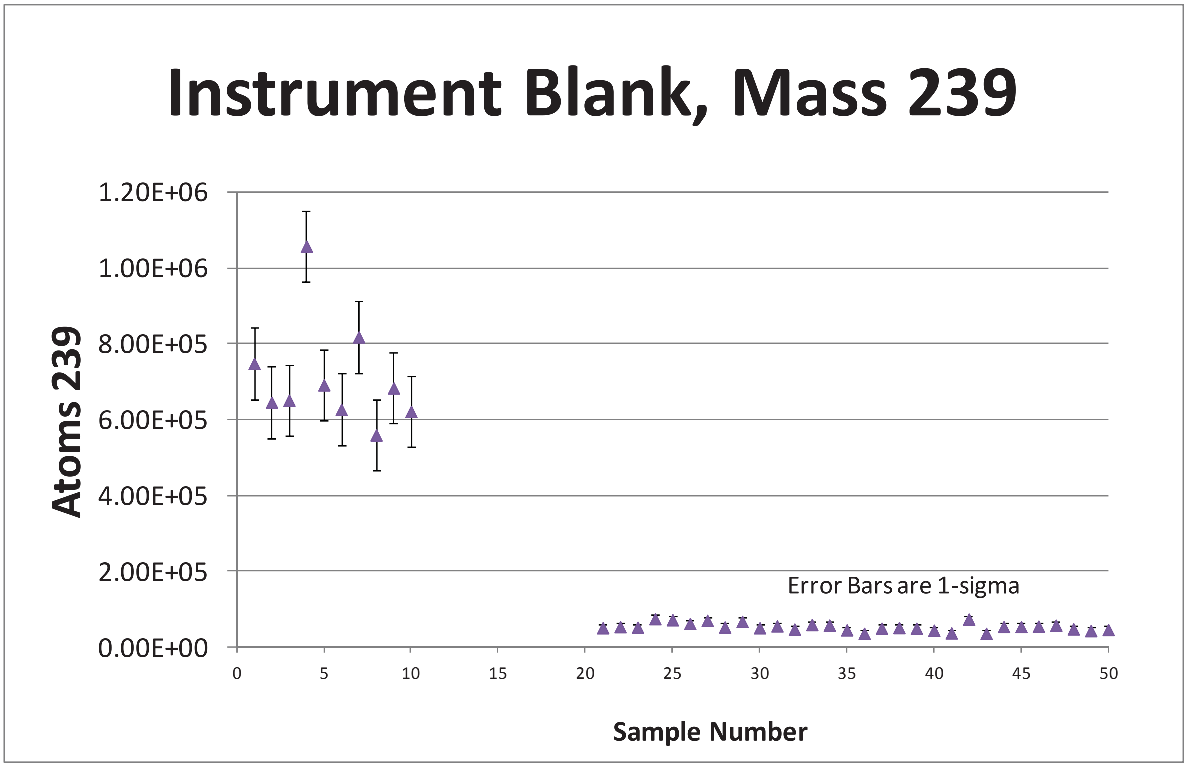

Figure 6. Instrument blank data for mass 239. Blank signal is converted to atoms of ^{239}Pu assuming similar dilution of the blank as the dilution for samples and similar signal levels for spiked ^{244}Pu.

The instrument blank is shown in the above graph and illustrates the capability of the instrument. When typical sample dilutions for a processed sample are included, a detection limit can be determined. The blank response for ^{239}Pu in counts per second is divided by the lowest response for the ^{244}Pu spike. This is then multiplied by the number of atoms of the ^{244}Pu spiked. This calculation produces the atom equivalent of 239 atoms that are injected in the blank matrix. This shows the contribution of the reagents and instrument to the response at mass 239. Taking the nearly 40 values presented in the graph and calculating the standard deviation allows calculation of the limit of detection (3σ) and limit of quantification (10σ). The instrument detection limit is then 31,000 atoms and the quantification limit is 105,000 atoms.

Calculating atoms of ^{239}Pu:

$$^{239}\text{Pu atoms} = \frac{^{239}\text{Pu(counts/sec)}}{^{244}\text{Pu(counts/sec)} \;/\; 10{,}000{,}000 \text{ atoms } ^{244}\text{Pu}}$$

Standard Deviation is calculated with:

$$\sigma = \sqrt{\frac{\sum (x-\bar{x})^2}{(n-1)}}$$

Limit of Detection:

$$3\sigma$$

Limit of Quantification:

$$10\sigma$$

Sample Preparation

The ^{244}Pu spike solution is a dilution of SRM 996. Two solutions were received from Pacific Northwest National Laboratory, a stock solution and a working solution. Serial dilution was used as required by PNNL scientists to produce the desired concentrations.

As a source of ^{239}Pu, Columbia River Sediment was used (SRM 4350B). A working solution of the Columbia River Sediment was prepared by dissolving 10 g of the reference material to assure a representative sample. Aliquots of the solution equivalent to the desired number of ^{239}Pu atoms were then spiked onto swipes before ashing the swipes in the muffle furnace. 10 million atoms of ^{244}Pu (6.1 fg) spike was added to the samples at the start of the chemical processing which provided a measure of the overall yield of the chemistry and analysis plus quantification of the ^{239}Pu atoms present on the swipe from the SRM 4350B.

After the furnace ashing step, a wet ash was performed in a Teflon beaker using nitric, hydrofluoric and perchloric acids. Following complete dissolution, the separation of uranium and plutonium was accomplished using a TRU cartridge with a UTEVA cartridge stacked above it. The cartridges are commercial products from the vendor Eichrom. Eichrom is also the source of the analytical separation scheme. The Eichrom scheme was followed to obtain the Pu and U fractions. The resulting fractions for uranium and plutoniumwere then analyzed on the Neptune Plus ICPMS.

The major lessons learned in this work for the chemistry preparation deal with reagents and the final sample preparation for the ICPMS. Certain reagents must be prepared fresh, as indicated by PNNL. The sodium nitrite oxidation of the Pu^{3+} to Pu^{4+} must be done with nitrite that is fresh and the solution is mixed just before use. As a visual indication that the solution is fresh it should have a bluish tint. When the tint is not present, it indicates that the nitrite has reacted within the bottle and is not adequate to oxidize the plutonium as needed for the separation. The final eluent from the TRU cartridge contains plutonium complexed by bioxalate. This is difficult to destroy, but must be done if the analysis on the ICPMS is to perform well. Hydrogen peroxide is added to the sample when it is dissolved in hot nitric acid. This is followed by multiple oxidation steps with concentrated nitric acid. When these critical steps are folloed, the method performs well.

Uranium

The removal of uranium from the plutonium fraction is necessary. This is achieved by passing the sample through a UTEVA column which has an affinity for uranium at the conditions used to load the plutonium onto the TRU column. When these two columns are separated as required by the procedure to produce the plutonium fraction with the least amount of uranium interference, an opportunity is present for a uranium analysis. The UTEVA cartridge is simply rinsed and then the uranium is eluted from the column.

The resulting uranium fraction is too concentrated for direct injection into the INL configured Neptune Plus ICPMS. The uranium is diluted to a level where the ^{238}U is detected on a faraday cup and the 233, 234, 235 and 236 masses are detected with ion counting detectors. The uranium samples are spiked with ^{233}U for quantification. Additionally, the isotopic composition is measured using the multi-collector capability of the Neptune.

To produce the best data, the ion counters' yield is determined daily. The mass alignment is also checked daily. The ion counters' yield is determined by comparison to the Faraday cup where the ^{238}U signal is detected. Two corrections are needed to determine the proportion of the signal at mass 236 that is attributable to ^{236}U. A hydride contribution from the $^{235}U^{1}H$ is determined and subtracted from the gross ^{236}U mass counts. The hydride ratio is determined by taking a ratio of the 239 mass signal to the 238 mass signal. It is assumed that the 239 mass signal is $^{238}U^{1}H$ and will provide the hydride production ratio when divided by the ^{238}U signal. Also a baseline correction due to tailing from the 238 signal or the 235 signal into the mass 236 signal is performed. This is done with measurements of the signal at mass 235.5 and 236.5 and the average subtracted from the ^{236}U mass counts. Mass 233, 234, 235 and 238 are used as measured with no correction.

CRM 145 is used to determine if a sample isotopic content is perturbed from the natural uranium isotopic distribution. This standard is injected throughout the ICPMS sample queue. The average isotopic response is used to determine if the $^{235}U/^{238}U$ and $^{234}U/^{238}U$ ratios for the samples are perturbed. Two sets of data for 10 samples each are included in the two tables below. Corrections are not being made to this standard. It is being used as a comparison standard, with CRM 145 representing natural. The samples are a blank swipe that has the equivalent of 0.026g of SRM4350B (Columbia River Sediment) added as a source of uranium.

	Description	234/238	235/238	236/238 Corr
1	SRM 4350b + Swipe	5.85E-05	7.11E-03	8.01E-09
2	SRM 4350b + Swipe	5.86E-05	7.10E-03	-2.09E-08
3	SRM 4350b + Swipe	5.90E-05	7.11E-03	-1.91E-08
4	SRM 4350b + Swipe	5.86E-05	7.10E-03	9.27E-09
5	SRM 4350b + Swipe	5.86E-05	7.10E-03	-1.27E-08
6	SRM 4350b + Swipe	5.83E-05	7.10E-03	4.25E-09
7	SRM 4350b + Swipe	5.72E-05	7.13E-03	3.02E-08
8	SRM 4350b + Swipe	5.78E-05	7.13E-03	-4.20E-08
9	SRM 4350b + Swipe	5.85E-05	7.13E-03	-1.25E-08
10	SRM 4350b + Swipe	5.90E-05	7.13E-03	-6.19E-08
11	Blank Swipe	6.82E-05	7.12E-03	-2.53E-07
12	Blank Swipe	6.18E-05	7.13E-03	-1.10E-07
	Measured CRM 145 Avg	5.15E-05	7.11E-03	-9.63E-08
	CRM 145 Std Dev	2.85E-07	1.73E-05	4.08E-08
	-2s	5.09E-05	7.08E-03	
	+2s	5.20E-05	7.15E-03	
	CRM 145 Certificate	5.28E-05	7.254E-03	
	-2s	5.27E-05	7.246E-03	
	+2s	5.30E-05	7.262E-03	
	SRM 4350b (lit value)	5.82E-05	7.260E-03	n.d.
	-2s	5.06E-05	7.255E-03	
	+2s	6.58E-05	7.264E-03	

Table 1. Set of 10 swipes spiked with SRM 4350b and analyzed for isotopic content compared to CRM 145.

The data in Table 1 does show a difference in the ^{234}U/^{238}U ratio for the samples 1-10 compared to the measured CRM 145 ^{234}U/^{238}U ratio. The SRM 4350B has a literature value that shows a possible elevation in the ^{234}U/^{238}U ratio, the uncertainty shows it isn't statistically different from the certificate value of the CRM 145. The values measured at INL have an average of 5.84E-5 for the ^{234}U/^{238}U ratio and a standard deviation of 0.05E-5. This indicates the ratio ^{234}U/^{238}U is elevated compared to the measured value for CRM 145. Some work remains on the uranium mass fractionation correction of the ICPMS to report a more precise ratio, but the data does show a difference from natural.

For the ^{235}U/^{238}U ratios, the certificate value for the CRM 145 and the literature value for the 4350B agree with each other. The measured ^{235}U/^{238}U ratios for the samples 1-10 that have SRM 4350B are bounded by the average of the measured ^{235}U/^{238}U ratio for the CRM 145. This all indicates that the ^{235}U/^{238}U ratio needs mass fractionation correction to be more precise for reporting, but it is not perturbed from natural.

The two blanks run with this sample set show that the ^{235}U/^{238}U ratio of the swipe material is in agreement with the measured CRM 145 ratio. The ^{234}U/^{238}U ratio does seem to be elevated, but the ratio is calculated from lower signals than for the samples that have the SRM 4350B added. The elevation in the ratio is a representation of increased uncertainty, not a perturbed isotopic.

The ^{236}U/^{238}U ratio using the corrected ^{236}U signal varies above and below zero, demonstrating the ^{236}U signal is a non-detect as is reported for the CRM 145 and the SRM 4350B certificates and literature values.

	Description	233/238	234/238	235/238	236/238 Corr	238 (g)
1	SRM 4350b + Swipe	8.68E-05	5.88E-05	7.17E-03	-2.75E-09	3.77E-08
2	SRM 4350b + Swipe	8.62E-05	5.83E-05	7.16E-03	3.37E-08	3.79E-08
3	SRM 4350b + Swipe	8.67E-05	5.87E-05	7.17E-03	3.43E-08	3.77E-08
4	SRM 4350b + Swipe	8.50E-05	5.80E-05	7.17E-03	2.62E-08	3.85E-08
5	SRM 4350b + Swipe	8.71E-05	5.78E-05	7.17E-03	-3.20E-08	3.75E-08
6	SRM 4350b + Swipe	8.39E-05	5.83E-05	7.17E-03	1.47E-08	3.90E-08
7	SRM 4350b + Swipe	8.55E-05	5.77E-05	7.17E-03	4.63E-08	3.83E-08
8	SRM 4350b + Swipe	8.44E-05	5.85E-05	7.17E-03	2.02E-08	3.88E-08
9	SRM 4350b + Swipe	8.27E-05	5.75E-05	7.17E-03	1.34E-08	3.96E-08
10	SRM 4350b + Swipe	8.43E-05	5.89E-05	7.17E-03	3.81E-08	3.88E-08
11	Blank Swipe	8.22E-04	6.22E-05	7.16E-03	-1.15E-07	3.98E-09
12	Reagent Blank	1.11E-02	7.31E-05	7.18E-03	8.16E-07	2.94E-10
	CRM 145 Avg		5.19E-05	7.17E-03	-6.91E-08	
	CRM 145 Std Dev		2.78E-07	4.30E-06	2.69E-08	
	-2s		5.14E-05	7.16E-03	-1.23E-07	
	+2s		5.25E-05	7.17E-03	-1.53E-08	
	SRM 4350b (lit value)		5.82E-05	7.260E-03	n.d.	
	-2s		5.06E-05	7.255E-03		
	+2s		6.58E-05	7.264E-03		

Table 2. Set of 10 swipes with SRM 4350B added as known sample. Samples spiked with SRM 111A for quantification of uranium. Samples were analyzed for isotopic content compared to CRM 145. A blank swipe and a reagent blank were processed with the sample set.

The data in Table 2 does show that there is a difference in the ^{234}U/^{238}U ratio for samples 1-10 compared to the measured CRM 145 ^{234}U/^{238}U ratio. This is similar to the data in table 1 and validates a perturbed ^{234}U/^{238}U ratio for the samples. For the ^{235}U/^{238}U ratios, the certificate value for the CRM 145 and the literature value for the 4350B agree with each other. The measured ^{235}U/^{238}U ratios for samples 1-10 containing SRM 4350B are bounded by the average of the measured ^{235}U/^{238}U ratio for the CRM 145. The ^{235}U/^{238}U ratio is not perturbed from natural. The two blanks run with this sample set show that the ^{235}U/^{238}U ratio of the swipe material is in agreement with the measured CRM 145 ratio. The ^{236}U/^{238}U ratio using the corrected ^{236}U signal are above and below zero, demonstrating that the ^{236}U signal is a non-detect as is also reported for the CRM 145 and the SRM 4350B.

The samples in Table 2 were spiked with ^{233}U for quantification. The ratio of ^{233}U/^{238}U is used in conjunction with the known amount of ^{233}U spike. The column labeled 238 (g) is calculated to show the amount of uranium in the samples. The samples have an average of 39 ng of uranium in them. The swipe blank is roughly an order of magnitude less at 4 ng and the reagent blank is 0.3 ng of uranium.

Using the corrected $^{236}U/^{238}U$ ratio and the amount of ^{238}U present, a standard deviation for the amount of ^{236}U detected can be calculated. The limit of detection estimate based upon 3σ would be 3 fg of ^{236}U present in the sample, and a limit of quantification estimate based upon 10σ would be 9 fg of ^{236} U in the presence of 38 ng of ^{238}U.

Conclusion

The performance of the instrument was evaluated using SRM 996 (^{244}Pu spike) alone and combined with the SRM 4350B Columbia River Sediment standard. The measured limit of detection (3σ) for ^{239}Pu is 31,000 atoms for SRM 996. The limit of quantitation (LOQ), defined as 10 σ, is 105,000 atoms. The measured limit of detection (3σ) for ^{239}Pu is 2.7 million atoms from a swipe matrix. The limit of quantitation (LOQ), defined as 10 σ, is 9.0 million atoms. The INL capability for swipe analysis to determine the presence or absence of 10,000,000 atoms of ^{239}Pu stands ready to receive and process samples and report results.

The uranium analysis is shown to be operating and it is desired to use the initial production plutonium analysis as an opportunity to analyze for uranium as well. The laboratory scheme is working for uranium and the work to finalize the stand up of the uranium capability needs data to evaluate the processing and handling of the data properly. This will allow for the determination of the minimum amount of perturbed material that must be present to detect a perturbed isotopic content for the $^{234}U/^{238}U$ or $^{235}U/^{238}U$ ratios. The minimum detectable amount of ^{236}U is estimated at 3 fg of ^{236}U (7,000,000 atoms of ^{236}U), but will become a better determined detection limit with more data analyzed.

INL would like to receive no more than 500 swipes per year in FY13 while we build up our capability to analyze 1000 swipes per year in the out years.

[1] Eichrom product information.

[2] M. E. Wieser and Johannes B. Schwieters, Int. J. Mass Spectrom. 242 (2005) 97-115.

[3] Nu Instruments Ltd, Wrexham LL13 9XS North Wales, UK; www.nu-ins.com

[4] Thermo-Scientific, Waltham, MA 02454, USA