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Rapid Determination of Actinides in Urine by Inductively-Coupled Plasma Mass Spectrometry and Alpha Spectrometry: A Hybrid Approach

Sherrod L. Maxwell, III, and Vernon D. Jones

Sherrod L. Maxwell

Savannah River Nuclear Solutions, LLC

Building 735-B

Aiken, SC 29808, USA

phone #: 803-952-7473

Fax#: 803-952-7881

Email: sherrod.maxwell@srs.gov

Vernon D. Jones

Savannah River Nuclear Solutions, LLC

Building 772-F

Aiken, SC 29808, USA

Abstract

A new rapid separation method that allows separation and preconcentration of actinides in urine samples was developed for the measurement of longer-lived actinides by inductively-coupled plasma mass spectrometry (ICP-MS) and short-lived actinides by alpha spectrometry; a hybrid approach. This method uses stacked extraction chromatography cartridges and vacuum box technology to facilitate rapid separations. Preconcentration, if

required, is performed using a streamlined calcium phosphate precipitation. Similar technology has been applied to separate actinides prior to measurement by alpha spectrometry, but this new method has been developed with elution reagents now compatible with ICP-MS as well. Purified solutions are split between ICP-MS and alpha spectrometry so that long and short-lived actinide isotopes can be measured successfully. The method allows for simultaneous extraction of 24 samples in less than 3 hours (<7.5 minutes per sample). The simplicity and speed of this new method makes it attractive for radiological emergency response. If preconcentration is applied, the method is applicable to larger sample aliquots for occupational exposures as well. The chemical recoveries are typically greater than 90%, in contrast to other reported methods using flow injection separation techniques where plutonium yields were 70-80%. This method allows measurement of both long-lived and short-lived actinide isotopes. ^{239}Pu, ^{242}Pu, ^{237}Np, ^{243}Am, ^{234}U, ^{235}U and ^{238}U were measured by ICP-MS, while ^{236}Pu, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{243}Am and ^{244}Cm were measured by alpha spectrometry. The method can also be adapted so that the separation of uranium isotopes for assay is not required, if uranium assay by direct dilution of the urine sample is preferred instead. Multiple vacuum box locations may be set-up to supply several ICP-MS units with purified sample fractions such that a high sample throughput may be achieved, while still allowing for rapid measurement of short-lived actinides by alpha spectrometry.

Introduction

The use of nuclear power and the ongoing development of nuclear weapons have led to growing public concern about potential contamination of radioactive materials on the environment and on the health of individuals. Actinides are considered extremely hazardous radionuclides due to their chemical toxicity, alpha activity and very long half-lives for many

of the isotopes. Even small quantities of actinides can cause can cause serious health hazards. The measurement of actinides in urine is not only important for occupational health monitoring but also in response to a radiological emergency event, such as the nuclear accident at Chernobyl or detonation of a radiological dispersal device (RDD) by terrorists. There is an increasing need to develop faster analytical methods with high sample throughput for emergency response, including emergency urine samples [1]. Rapid methods using extraction chromatography and alpha spectrometry have been reported by this laboratory for both emergency water and urine samples [2, 3, 4]. Inductively-coupled plasma mass spectrometry (ICP-MS) is a versatile technique for elemental and isotopic analysis. The measurement time for sequential assay by ICP-MS is typically shorter than alpha spectrometry, although the alpha spectrometry measurements may be performed simultaneously with large numbers of detectors. ICP-MS is particularly effective for longer-lived actinide isotopes, where alpha spectrometry works well for short-lived actinide isotopes. Alpha spectrometry cannot differentiate between the alpha isotopes with overlapping alpha energies, such as ^{239}Pu and ^{240}Pu, which are easily differentiated by ICP-MS. Actinide determination by ICP-MS can be hampered by isobaric, polyatomic interferences and signal suppression [5]. Both measurement techniques may require separation of interferences to determine actinide isotopes accurately, depending on the sample matrix and the detection limit required.

A large number of flow injection techniques coupled with ICP-MS instrumentation have been reported. Hang *et al* using TRU Resin to separate actinides, but this work lacked the selectivity needed to measure actinides at ultra trace levels in urine, due to overlapping of actinide peaks [6]. Epov *at al* reported an automated preconcentration system using TRU Resin, but indicated that the separation of uranium

from plutonium was not complete [7]. Lariviere *et al* reported an automated flow injection system using TEVA Resin with chemical yields averaging 83% for 10 ml urine sample aliquots, but when a co-precipitation step was added for larger sample aliquots, the chemical yield for Pu dropped to approximately 70% [5]. This system was effective, but this work was limited to plutonium separation only. Zoriy also reported chemical yields of about 70% for plutonium in urine using TEVA Resin [8].

TEVA Resin has been used in the Savannah River Site (SRS) Environmental Bioassay Laboratory for many years, with excellent recovery of Pu. The key to achieving quantitative elution for trace level Pu from TEVA Resin is the use of a reductant during the elution step to reduce Pu (IV) to unretained Pu (III) [1, 9].

Recently, the SRS lab participated in the NIST NRIP emergency response exercise and reported actinide results for emergency urine samples in 3-4 hours. This rapid method employed calcium phosphate precipitation, stacked TEVA Resin and TRU Resin cartridges and alpha spectrometry with very rapid flow rates [3].

A new method has been developed in the Savannah River Site (SRS) Environmental Bioassay Laboratory to allow a flexible, hybrid approach: the separation of longer-lived actinide isotopes for measurement by ICP-MS and short-lived actinide isotopes by alpha spectrometry. The rapid separation method uses stacked TEVA and TRU Resin cartridges, followed by DGA Resin to allow additional purification of Am/Cm isotopes and the use of a more desirable eluant for ICP-MS applications. If uranium separation is not required for measurement (direct dilution for U isotopes is used instead), TRU Resin is not required, and a stacked TEVA Resin plus DGA Resin column may be used. ^{239}Pu, ^{242}Pu, ^{237}Np, ^{243}Am, ^{234}U, ^{235}U and ^{238}U were measured by ICP-MS, while ^{236}Pu, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{243}Am, and ^{244}Cm were measured by alpha spectrometry.

The same column chemistry may be used with small or large urine aliquots. Direct urine aliquots (20 ml or less) may be analyzed with acidification, while large volume sample aliquots may be analyzed when a calcium phosphate preconcentration step is applied. The calcium phosphate precipitation has been streamlined such that it only adds about an hour to the sample preparation time. The goal of this work was to provide a rapid separation chemistry compatible with both alpha spectrometry and ICP-MS to offer maximum flexibility so that both short-lived and long-lived actinide isotopes can be measured using a complementary, hybrid approach.

Experimental

Reagents

The resins employed in this work are TEVA Resin® (Aliquat ™336), TRU-Resin ® (tri-n-butylphosphate (TBP) and N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)), and DGA Resin ® (N,N,N',N' tetraoctyldiglycolamide), available from Eichrom Technologies, Inc., (Lisle, Illinois, USA). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc., Pittsburg, PA, USA). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS reagent grade and were used as received. Radiochemical isotopes ^{239}Pu, ^{242}Pu, ^{237}Np, ^{243}Am, ^{234}U, ^{235}U , ^{238}U ^{236}Pu, ^{238}Pu, ^{241}Am and ^{244}Cm were obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to the appropriate levels.

Procedures

Column preparation. TEVA, TRU, and DGA-Resin columns were obtained as cartridges containing 2 ml of each resin from Eichrom Technologies, Inc. (Lisle, IL,

USA). Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies). Flow rates of 1-2 ml min^{-1} were typically used for this work.

Sample Preparation-Two different approaches were used. A small volume urine aliquot (5 ml) was acidified with ~3M HNO_3 and processed through the column chemistry. For large urine aliquots (100 ml), calcium phosphate co-precipitation was applied .

Sample Preparation-No Co-precipitation. A 5 ml urine sample was aliquoted into a 50 ml plastic tube. Tracers were added and 1.5 ml 15.7M HNO_3 was added to adjust the acidity of each sample to ~3M HNO_3. The samples were swirled to mix each solution. Valence adjustment of the samples was performed by adding 0.25 ml 1.5M sulfamic acid and 0.5 ml 1.5M ascorbic acid with a three minute wait step to reduce plutonium to Pu^{3+}.When ^{237}Np separation was desired, 0.05 ml 5 mg/ml Fe as ferric nitrate was also added to facilitate ^{237}Np reduction to Np^{4+}. The ferric ions are reduced to ferrous ions by the ascorbic acid, which reduces Np effectively to Np^{4+}. After the reduction step, 1 ml 3.5M sodium nitrite was added to oxidize plutonium to Pu^{4+}. This column load solution was now ready for column separation as described below.

Sample Co-precipitation. After the 100 ml urine sample aliquots were dispensed, 1 ml 1.25M calcium nitrate (50 mg Ca) and 3 ml 3.2M ammonium hydrogen phosphate were added to each sample. For samples, the sample dispensing and the above reagent additions were performed in 225 ml (urine) centrifuge tubes to save time. The pH was adjusted to ~pH 9.5 with concentrated ammonium hydroxide using a dark pink phenolphthalein endpoint. For darker urine samples, pH paper or a pH meter may be

used. The samples were centrifuged at 3500 rpm for ~7 minutes. After discarding the supernatant, the precipitate was rinsed once with ~ 15-20 ml of water and centrifuged again at 3500 rpm for ~5 minutes. The precipitate was dissolved in 8 ml 6M HNO_3 and 8 ml 2M $Al(NO_3)_3$ directly in the centrifuge tubes. The final load solution contained 16 ml 3M HNO_3 and 1M $Al(NO_3)_3$. The aluminum nitrate was previously scrubbed to remove trace uranium by passing approximately 250 ml 2M aluminum nitrate through a large column (Environmental Express, Mount Pleasant, SC, USA) containing ~7 ml of UTEVA Resin ® (Eichrom Technologies) at ~10 ml per minute. The column was prepared from a water slurry of the UTEVA resin. For the 100 ml samples, valence adjustment was performed by adding 0.5 ml 1.5M sulfamic acid and 1.25 ml 1.5M ascorbic acid with a three minute wait step to reduce plutonium to Pu^{3+}.When Np-237 separation was desired, 0.4 ml of 5 mg/ml Fe as ferric nitrate was also added to facilitate Np-237 reduction to Np^{4+}. To oxidize plutonium to Pu^{4+}, 2 ml 3.5M sodium nitrite was added to each sample solution. This column load solution was now ready for column separation.

Column separation. The following column separation was performed on small volume or large volume urine sample aliquots. TEVA and TRU Resin cartridges were stacked on the vacuum box from top to bottom, in that order. Fifty milliliter centrifuge tubes were used to collect rinse or final purified fractions.

After the valence adjustment, the sample solution was loaded onto the stacked column at approximately ~1 drop per second. After the sample was loaded, a tube rinse of ~3 ml 3M HNO_3 was transferred to the stacked column and allowed to pass through the resin at ~1-2 drops per second. Years of experience in this laboratory has shown there

are no channeling or performance issues with small particle resin cartridges going dry. A rinse of 5 ml 3M HNO_3 was added directly to the stacked column at ~2 drops per second. The TRU Resin cartridges were removed and the TEVA cartridges were kept on the vacuum box. The TEVA cartridge was rinsed with 15 ml 3M nitric acid at ~2 drops per second to remove sample matrix components. To elute thorium from TEVA Resin, 15 ml 9M hydrochloric acid was added at ~1-2 drops per second and discarded.

The plutonium was stripped from TEVA Resin with 14 ml 0.25M hydrochloric acid-0.005M hydrofluoric acid –0.0001M titanium (III) chloride. The volume was adjusted after elution to exactly 15 ml with the same solution**.** Typically in this laboratory, when a tracer is used, no volume adjustment is made and 15 ml would be added directly to the column. Since no tracer was used to perform chemical yield adjustment for the ICP-MS measurements, the eluant volume was added in this way with a final volume adjustment after elution. The purified solutions were analyzed by alpha spectrometry and ICP-MS. Five milliliters of each plutonium/neptunium solution was transferred to a separate 50 ml tube and 50 ug of cerium as cerium nitrate were added to the tubes, along with 1 ml concentrated hydrofluoric acid (49%). A 0.5 ml volume of 30 wt% hydrogen peroxide was added after the plutonium was eluted to oxidize any residual uranium to U^{6+} as a precaution. After waiting 15 minutes, the solutions were filtered onto 0.1 micron 25 mm polypropylene filters (Resolve® filter-Eichrom Technologies) and counted by alpha spectrometry. The remaining solution was transferred to the ICP-MS for Pu/Np measurement.

The TRU cartridges were placed on a separate vacuum box and processed at the same time as the TEVA Resin cartridges to save time. DGA Resin cartridges were placed

below each TRU Resin cartridge. Americium/curium was eluted from TRU Resin onto DGA Resin with 15 ml 4M HCl at ~1-2 drops per second. The TRU Resin cartridges were removed and the DGA Resin was rinsed with 3 ml 1M HNO_3, then 5 ml of 0.1M HNO_3 at ~1 drop per second. Am and Cm were eluted using 9.5 ml of 0.25 M HCl at ~1 drop per second. The volume was adjusted after elution to exactly 10 ml with the same solution for reasons described previously. Two milliliters of each solution was transferred to a separate 50 ml tube containing ~10 ml of 0.25M HCL and 50 ug of cerium as cerium nitrate were added to the tubes, along with 1 ml of concentrated hydrofluoric acid (49%), and filtered after about 15 minutes to prepare alpha spectrometry mounts. The remaining solution was transferred to the ICP-MS for Am measurement.

Uranium was stripped from TRU Resin using 14 ml 0.01M ammonium bioxalate at ~1-2 drops per second. The volume was adjusted after elution to exactly 15 ml with the same solution. If uranium separation and measurement is not required, TRU Resin is not needed, and TEVA and DGA Resins can be stacked in tandem without TRU Resin. An increased rinse volume of DGA Resin (15 ml 0.1M HNO_3 vs 5 ml HNO_3) can be used to remove uranium if TRU Resin is not in place to collect U. It would be possible to strip Am/Cm directly from TRU Resin without DGA Resin but this would require a strong acid such as 4M HCl, which would typically have to be diluted prior to analysis using ICP-MS. DGA allows Am/Cm elution with 0.25M HCl, which is more compatible with ICP-MS, and can provide additional uranium removal if needed.

Actinide filters were counted by alpha spectrometry for approximately 16 hours, but shorter count times (<1 hour) can also be performed for emergency response samples using higher level tracers [2], depending on the detection limit needed.

Apparatus

Plutonium, americium, and uranium measurements were performed by alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors. Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 ml plastic tubes were used. Two boxes were connected to a single vacuum source by using a T-connector and individual valves on the tubing to each box.

An Agilent Quadrupole ICP-MS was used to perform the ICP-MS measurements. The instrument operating conditions are shown in Table 1.

The ICP-MS methodology is described in American Society for Testing and Materials (ASTM) Vol. 12.01, C1590-04 "Standard Practice for Alternate Actinide Calibration for Inductively Coupled Plasma-Mass Spectrometry" [10]. The calibration is mass bias adjusted using thorium-232 (^{232}Th) and uranium-238 (^{238}U) standards. At each standard concentration, the slope of the line defined by ^{232}Th and ^{238}U is used to derive linear calibration curves for each mass of interest (amu 232-244) using interference equations. The mass bias corrected calibration curves, although generated from interference equations, are specific to the instrument operating parameters and tuning in effect at the time of data acquisition. One of the benefits of this standard practice is the ability to calibrate for the analysis of highly radioactive actinides using calibration standards at much lower specific activities.

Results and Discussion

The rapid separation of actinides was performed on ten 100 ml urine samples. Samples 1-5 were blank human urine, while samples 6-10 were synthetic urine samples. Known amounts of actinide isotopes were added to each sample. Calcium phosphate precipitation, as described above, was applied to all ten samples. Samples were analyzed for short-lived isotopes by alpha spectrometry and longer-lived actinide isotopes were analyzed by ICP-MS. ^{239}Pu and ^{243}Am isotopes were measured by both ICP-MS and alpha spectrometry techniques. The results for the determination of Am-Cm isotopes by alpha spectrometry are shown in Table 2. The average tracer recovery for ^{243}Am was 105% (±2.5% RSD), with an average measured value for ^{243}Am of 1.947 pCi (-2.65% bias) and an average measured value for ^{244}Cm of 1.767 pCi (+2.14% bias). The ^{241}Am and ^{244}Cm results were corrected for the ^{243}Am tracer recoveries in each sample. The Am/Cm recoveries were excellent, with high chemical yield and very little bias for ^{241}Am and ^{244}Cm. The results for the Pu isotopes by alpha spectrometry are shown in Table 3. The average tracer recovery for ^{236}Pu was 99.0% (±10% RSD). The average result for ^{238}Pu was 1.992 pCi (1.63% bias) and the average result for ^{239}Pu was 23.08 pCi (2.58% bias). The MDA using alpha spectrometry, which is dependent on sample volume used and count time, can be adjusted as needed for emergency or routine samples [3]

The Pu/Np isotope results by ICP-MS are shown in Table 4. The average ^{239}Pu result at the ICP-MS was 0.0252 ng/ml (4.02% bias) and the average ^{242}Pu result was 0.1366 ng/ml (-0.01% bias). The Pu results by ICP-MS were not corrected for ^{242}Pu tracer, but instead were corrected for a negative bias at the ICP-MS observed on a Pu

standard in the same matrix that did not undergo column separation. This bias was only seen on this particular analysis run and does not seem to be caused by the eluant matrix, which has been used previously with no negative bias. The average result for ^{237}Np was 0.1829 ng/ml (0.24% bias), indicating excellent recovery of ^{237}Np as well. Six additional 100 ml urine samples were analyzed for Pu isotopes by ICP to verify that the Pu eluant matrix does not cause a negative bias at the ICP-MS. Table 5 shows the Pu results by ICP-MS from this test. The average ^{239}Pu result was 0.0447 ng/ml (-7.71% bias) and the average ^{242}Pu result was 0.1278 ng/ml (-6.42%), indicating the Pu eluant matrix does not cause any significant bias at the ICP-MS and confirming that the method provides a high chemical yield for plutonium. Figure 1 shows the ^{209} Bi internal standard measurements for the same set of six urine samples analyzed for Pu isotopes by ICP-MS. There is a slight reduction in ^{209} Bi internal standard signal for the urine samples in the Pu sample eluant matrix (avg. = 1.24E6 cps) compared to the 1% nitric acid blanks (avg. = 134E6 cps) analyzed along with the samples. This is only a 7.5% reduction in internal standard signal, well within the normal range of instrument drift, demonstrating minimal potential impact on signal reduction using the Pu eluant matrix (0.25M HCL-0.005M HF-0.0001M $TiCl_3$) without dilution.

The results for ^{238}U by ICP-MS are shown in Table 6. The first five results from human urine sample show an average result for ^{238}U of 3.556 ng/ml at the ICP-MS (6.79% bias), while the synthetic urine sample showed a significant positive bias. It was found that the synthetic urine had ^{238}U content in the blank solution of 1.79 ng ^{238}U /ml. After the sample results were corrected for this uranium content in the unspiked synthetic urine the result was reduced from 5.54 to 3.74, only a 12.5% positive bias.

Table 7 show uranium isotope results from the analysis of an emergency urine sample received from the National Institute of Standards and Technology (NIST). Five ml replicate sample aliquots were analyzed without calcium phosphate preconcentration. The average result for ^{234}U was 0.0036 ng/ml (13.28% bias). This result is very good, considering the shorter half life of ^{234}U and the low level of ^{234}U present. The average result for ^{235}U was 0.4296 ng/ml (-0.44%) and the average ^{238}U measured value was 60.99 (2.71% bias). The other actinides in the NIST emergency exercise samples were too low to measure with the five milliliter aliquots analyzed. This illustrates the value of rapid calcium phosphate precipitation preconcentration step to improve detection limits.

Table 8 shows method LLD and LLQ values for the different isotopes by ICP-MS using a 100 ml sample aliquot. The LLD and LLQ results were calculated using the equations as prescribed by Taylor [12]. These method LLD and LLQ results include a preconcentration factor of 6.67 for all the isotopes except the ^{243}Am results, which include a preconcentration factor of 10. The LLD and LLQ results can be lowered by increasing the sample aliquots as needed. Table 9 shows method LLD and LLQ values for the uranium isotopes by ICP-MS using a 5 ml direct sample aliquot. These method LLD and LLQ results include a dilution factor of 1/3 when a 5 ml aliquot is taken, increasing the LLD and LLQ. The LLD and LLQ results can be lowered by increasing the sample aliquots as needed. The ^{238}U LLD and LLQ values are likely higher due to slight ^{238}U contamination, which may have added variability to the ^{238}U measurements.

The rapid column separation is compatible with ICP-MS or alpha spectrometry and can be used with or without calcium phosphate preconcentration. The chemical yields were very good and the accuracy and precision of the measurements on the

actinide isotopes spiked into the urine samples standards were excellent. The trace level titanium chloride (0.0001M) used in the plutonium stripping solution effectively reduces Pu to Pu^{3+} for effective elution of Pu from TEVA Resin without adversely affecting the ICP-MS assay. The 0.25M HCl and 0.01M ammonium bioxalate eluting reagents are also very compatible with ICP-MS.

The vacuum box column separation system is a low budget alternative to flow injection separation techniques. This stacked cartridge approach provides rapid flow rates and effective removal of spectral and other sample matrix interferences for a large number of samples prepared simultaneously. The separation method is flexible and can be adapted to fit specific analytical needs. For example, if uranium separation is not required, TRU Resin is not required in the separation method . Direct urine aliquots up to ~20 ml may be analyzed with acidification, while calcium phosphate coprecipitation may be applied to very large urine aliquots as needed. Multiple vacuum box locations can be used to prepare a large number of samples in an emergency that can be analyzed by alpha spectrometry and/or ICP-MS.

Conclusions

A new rapid separation method that allows separation and preconcentration of actinides in emergency or routine urine samples was developed for the determination of longer-lived actinides by inductively-coupled plasma mass spectrometry (ICP-MS) and short-lived actinides by alpha spectrometry, a hybrid approach. This method uses stacked extraction chromatography cartridges and vacuum box technology to facilitate rapid separations. The method can be used with small acidified urine aliquots or using a streamlined calcium

phosphate co-precipitation to preconcentrate actinides in larger sample aliquots. Similar technology has been applied to separate actinides prior to measurement by alpha spectrometry, but this new method has been developed with elution reagents now compatible with ICP-MS as well. The ASTM standard practice for alternate actinide ICP-MS calibration is a good analytical fit with the separation methods described. A single mass bias corrected calibration based on ^{232}Th and ^{238}U enables rapid ICP-MS determination of a suite of actinide isotopes. Purified solutions are split between ICP-MS and alpha spectrometry so that long and short-lived actinide isotopes can be measured successfully. The method is rapid, flexible, offers high chemical recoveries, excellent removal of interferences and can be used to provide high sample throughput in a radiological emergency.

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Table Captions

Table 1 Operating Conditions for Agilent 7500 ICP-MS

Table 2 Am/Cm Isotope Results by Alpha Spectrometry

Table 3 Pu Isotope Results by Alpha Spectrometry

Table 4 Pu/Np Isotope Results by ICP-MS

Table 5 Pu Isotope Results by ICP-MS

Table 6 ^{238}U Results on Urine Samples by ICP-MS

Table 7 U Isotopes Results on NIST Emergency Urine Samples by ICP-MS

Table 8 LLD and LLQ ICP-MS Results Using 100 ml Sample Aliquots

Table 9 LLD and LLQ ICP-MS Results Using 5 ml Sample Aliquots

Table 1 Operating Conditions for Agilent 7500 ICP-MS

Plasma Conditions		
	RF Power	1300 W
	RF Matching	1.7 V
	Torch Depth	6 mm
	Plasma Gas	15 L/min
	Carrier Gas	1 L/min
	Sample Pump	0.1 rps
Ion Lenses		
	Extract 1	-195 V
	Extract 2	-100 V
	Einzel 1, 3	-100 V
	Einzel 2	18 V
	Omega Bias	-33 V
	Omega (+)	11 V
	Omega (-)	8 V
	QP Focus	12 V
	Plate Bias	-36 V
Q-Pole		
	AMU Gain	122
	AMU Offset	124
	Axis Gain	0.999
	Axis Offset	0.04
	QP Bias	0 V
Detector		
	Discriminator	8.7 V
	Analog HV	1820 V
	Pulse HV	1230 V
Typical Tune		
	Counts	>100,000 cps Tl-205 at 10 ug/L
	RSD%	< 5%
	Oxide 156/140	< 1%
	Background	< 10 cps at Tl-205
	Resolution	0.65 - 0.80 amu at 10% peak height
Data Acquisition		
	Integration	0.33 sec/pt., 3 pt/amu, 0.99 sec/amu
	Replicates	6

Table 2 Am/Cm Isotope Results by Alpha Spectrometry

	^{241}Am	^{241}Am	^{244}Cm
	% recovery	pCi	pCi
1	104.1	1.98	1.69
2	102.9	1.77	1.92
3	108.2	1.95	1.67
4	102.2	1.96	1.95
5	105.6	1.96	1.79
6	108.6	1.85	1.61
7	108.3	2.16	1.73
8	103.3	2.08	1.77
9	101.9	1.90	1.60
10	105.2	1.86	1.94
Avg.	105.03	1.947	1.767
% RSD	2.5	5.8	7.5
	Reference	2.00	1.73
	% Difference	-2.65	2.14

Table 3 Pu Isotope Results by Alpha Spectrometry

	^{236}Pu	^{238}Pu	^{239}Pu
	% Recovery	pCi	pCi
1	96.7	1.90	25.4
2	110.5	1.66	20.8
3	91.0	2.09	24.8
4	115.3	1.81	20.6
5	99.1	2.14	23.8
6	98.0	2.02	24.2
7	81.7	2.46	25.7
8	98.9	1.96	22.1
9	108.9	1.74	19.4
10	89.8	2.14	24.0
Avg.	99.0	1.992	23.08
% RSD	10.4	11.7	9.5
	Reference	1.96	22.5
	% Difference	1.63	2.58

Table 4 Pu/Np Isotope Results by ICP-MS

	^{237}Np	^{239}Pu	^{242}Pu
	ng/ml	ng/ml	ng/ml
1	0.1790	0.0233	0.1511
2	0.1649	0.0211	0.1357
3	0.1666	0.0226	0.1319
4	0.1684	0.0189	0.1434
5	0.1821	0.0253	0.1431
6	0.1915	0.0241	0.1325
7	0.1910	0.0246	0.1268
8	0.1990	0.0294	0.1376
9	0.1903	0.0374	0.1293
10	0.1968	0.0251	0.1344
Avg.	0.1829	0.0252	0.1366
% RSD	6.62	19.31	5.15
Reference	0.1825	0.0242	0.1366
% Difference	0.24	4.02	-0.01

Pu results corrected by result of direct Pu standard vs. calibration
Concentration (ng/ml) in final solution at ICP-MS

Table 5 Pu Isotope Results by ICP-MS

	^{239}Pu	^{242}Pu
	ng/ml	ng/ml
1	0.0440	0.1260
2	0.0440	0.1270
3	0.0450	0.1260
4	0.0450	0.1280
5	0.0440	0.1280
6	0.0460	0.1320
Avg.	0.0447	0.1278
% RSD	1.67	1.59
Reference	0.0484	0.1366
% Difference	-7.71	-6.42

No correction made for direct Pu standard vs. calibration
Concentration (ng/ml) in final solution at ICP-MS

Table 6 ^{238}U Results on Urine Samples by ICP-MS

Human Urine

	^{238}U ng/ml
1	3.671
2	3.554
3	3.605
4	3.546
5	3.406
Average	3.556
% RSD	2.75
Reference	3.33
% Difference	6.79

Concentration (ng/ml) in final solution at ICP-MS

Synthetic Urine

	^{238}U ng/ml	Blank ng/ml	* Net ^{238}U ng/ml
6	5.355	1.79	3.565
7	5.475	1.79	3.685
8	5.511	1.79	3.721
9	5.782	1.79	3.992
10	5.554	1.79	3.764
Average	5.535		3.745
% RSD	2.83		4.18
Reference	3.33		3.33
% Difference	66.22		12.46

Concentration (ng/ml) in final solution at ICP-MS
*U-238 corrected for U-238 content in blank synthetic urine

Table 7 U Isotopes Results on NIST Emergency Urine Samples by ICP-MS

	^{234}U	^{235}U	^{238}U
	ng/ml	ng/ml	ng/ml
1	0.0036	0.4593	63.32
2	0.0040	0.4576	63.45
3	0.0033	0.4440	61.76
4	0.0036	0.4191	58.02
5	0.0038	0.4460	60.82
6	0.0035	0.4093	56.73
7	0.0029	0.3877	54.38
8	0.0043	0.4136	56.22
Avg.	0.0036	0.4296	59.34
% RSD	11.77	6.02	5.83
Reference	0.0032	0.4315	60.99
% Difference	13.28	-0.44	-2.71

Concentration (ng/ml) in final solution at ICP-MS

Table 8 LLD and LLQ ICP-MS Results Using 100 ml Sample Aliquots

	^{237}Np	^{238}U	^{239}Pu	^{242}Pu	^{243}Am
	ng/ml	ng/ml	ng/ml	ng/ml	ng/ml
Overall Method LLD	5.4E-03	6.7E-02	1.3E-03	2.4E-03	2.6E-04
Overall Method LLQ	1.8E-02	2.2E-01	4.3E-03	7.9E-03	8.6E-04

Table 9 LLD and LLQ ICP-MS Results Using 5 ml Sample Aliquots

	^{234}U	^{235}U	^{238}U
	ng/ml	ng/ml	ng/ml
Overall Method LLD	3.8E-03	2.3E-01	3.1E+01
Overall Method LLQ	1.3E-02	7.8E-01	1.0E+02

Figure 1 ^{209} Bi Internal Standard Response for Pu Samples by ICP-MS