



# Rapid determination of actinides in urine by inductively coupled plasma mass spectrometry and alpha spectrometry: A hybrid approach

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## 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 (including QC samples) in less than 3 h. Simultaneous sample preparation can offer significant time savings over sequential sample preparation. For example, sequential sample preparation of 24 samples taking just 15 min each requires 6 h to complete. 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 for urine samples where plutonium yields were 70–80%. This method allows measurement of both long-lived and short-lived actinide isotopes.  $^{239}\text{Pu}$ ,  $^{242}\text{Pu}$ ,  $^{237}\text{Np}$ ,  $^{243}\text{Am}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  were measured by ICP-MS, while  $^{236}\text{Pu}$ ,  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{243}\text{Am}$  and  $^{244}\text{Cm}$  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.

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## 1. Introduction

The use of nuclear power and the risks associated with nuclear proliferation 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 and high dose contribution for many of the isotopes. Even small quantities of actinides 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 [2–4]. 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 very well for short-lived actinide isotopes. Alpha spectrometry cannot differentiate well between alpha isotopes with overlapping alpha energies. Although alpha spectrometry can measure total  $^{239}\text{Pu} + ^{240}\text{Pu}$ , for example, it cannot differentiate between  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  isotopes. In contrast,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  are easily differentiated by ICP-MS. Actinide determination by ICP-MS, however, can be hampered by isobaric, polyatomic interferences and signal suppression [5]. Both mea-

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surement techniques may require separation of interferences to determine actinide isotopes accurately, depending on the sample matrix and the detection limit required. A variety of online and offline separation techniques have been reported in recent reviews for ICP-MS applications, covering a wide range of matrices (soil, sediment, water, biological and urine samples) [6]. This paper will focus more specifically on recent developments and progress with regard to assay of actinides in urine samples, but progress in rapid actinide separation techniques for urine have application to environmental and biological matrices as well.

A large number of flow injection techniques coupled with ICP-MS instrumentation have been reported for urine. 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 [7]. Pappas et al. reported a rapid method for emergency response for Pu in 1 ml urine samples without digestion or coprecipitation before chemical separation. TEVA resin was used along with a desolvating introduction system to minimize the impact of  $^{238}\text{U}^1\text{H}^+$  and other interferences at  $m/z = 239$ . The plutonium was eluted from TEVA Resin with 1 ml 1.4 M HF, after rinsing TEVA Resin with 0.8 M  $\text{HNO}_3$ . The reduction in uranium interference was significant, and the accuracy of Pu-239 in spiked urine samples was very good, but Pu-242 yield results were not reported. [8]. Epov et al. reported an automated preconcentration system using TRU Resin, but indicated that the separation of uranium from plutonium was not complete. In addition, the Pu yields using TRU Resin were variable and at times less than 50%, without yield correction using  $^{175}\text{Lu}$  tracer. After correction using  $^{175}\text{Lu}$  tracer, which was also retained on TRU Resin, the Pu recoveries were typically greater than 90%. Urine sample matrix effects were reduced with sample digestion, but this increased sample analysis time from 1 to 4 h for 5 samples [9]. 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 very rapid and effective, but this work was limited to plutonium separation only. Zoriy, who used a similar calcium phosphate protocol for occupational health samples, also reported chemical yields of about 70% for plutonium in urine using TEVA Resin [10].

Varga et al. used alpha spectrometry to determine the relatively short-lived isotopes  $^{241}\text{Am}$  and  $^{238}\text{Pu}$  and inductively coupled plasma sector field mass spectrometry (ICP-SFMS) for  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  and  $^{241}\text{Am}$  in small soil samples [11]. UTEVA and TRU Resins were used to separate Am and Pu fractions. The Pu strip solution (0.1 M ammonium bioxalate) and the Am strip solution (9 M  $\text{HCl}$  + 4 M  $\text{HCl}$ ) from TRU Resin were evaporated to dryness multiple times and wet-ashed with concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  to prior to analysis by ICP-SFMS and alpha spectrometry, increasing the sample preparation time.

Ayranov et al. reported a method which employed TOPO (tri-*n*-octylphosphine oxide) in cyclohexane liquid–liquid extraction combined with subsequent TRU Resin and TEVA Resin separations [12]. The initial separation using TOPO extraction was reported to be somewhat time-consuming, but more effective for removal of U and Th interferences than using the TRU Resin/TEVA Resin alone. The chemical yields for Pu and Am using this method were good. The Pu recoveries were greater than 90% by high resolution inductively coupled mass spectrometry (HR-ICP-MS), but 79.7% by alpha spectrometry. The Am recoveries were 87% by HR-ICP-MS, but 79% by alpha spectrometry. Pu was stripped from TEVA Resin using 0.02 M  $\text{HNO}_3$ –0.02 M HF, referencing a 1997 paper from this SRS laboratory [13].

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) [1,14]. Our experience has been that TEVA Resin eluant strip solutions such as 0.02 M  $\text{HNO}_3$ –0.02 M HF work well for higher level Pu samples (nuclear process level samples), but not very well for low level Pu (environmental and bioassay samples). Low level Pu is not stripped effectively from TEVA Resin without the presence of a reductant in the eluant solution. With a reductant present, the stripping of Pu from TEVA Resin is quantitative.

Recently, the SRS lab participated in the NIST NRIP emergency response exercise and reported actinide results for emergency urine samples in 3–4 h. This rapid method employed calcium phosphate precipitation, stacked TEVA Resin and TRU Resin cartridges and alpha spectrometry with very rapid flow rates [3]. This work has shown that alpha spectrometry methods, using vacuum boxes and stacked cartridge technology, can be performed very rapidly. The goal of this work was to adapt this rapid separation technology for ICP-MS measurements of actinides in urine samples.

A new method has been developed in the Savannah River Site (SRS) Environmental Bioassay Laboratory to allow a flexible, hybrid approach for urine samples: 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.  $^{239}\text{Pu}$ ,  $^{242}\text{Pu}$ ,  $^{237}\text{Np}$ ,  $^{243}\text{Am}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  were measured by ICP-MS, while  $^{236}\text{Pu}$ ,  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{243}\text{Am}$ , and  $^{244}\text{Cm}$  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.

## 2. Experimental

### 2.1. 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, IL, USA). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc., Pittsburgh, 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  $^{239}\text{Pu}$ ,  $^{242}\text{Pu}$ ,  $^{237}\text{Np}$ ,  $^{243}\text{Am}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{238}\text{U}$ ,  $^{236}\text{Pu}$ ,  $^{238}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  were obtained from Analytix, Inc. (Atlanta, GA, USA) and diluted to the appropriate levels. The synthetic urine composition is shown in Table 1.

### 2.2. Procedures

#### 2.2.1. Column preparation

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

**Table 1**  
Composition of the synthetic urine material.

	Reagent	CAS #	% Weight
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	Oxalic acid	6153-56-6	0.002
Pepsin	Pepsin	9001-75-6	0.003
CH <sub>3</sub> CHOHCO <sub>2</sub> H	Lactic acid (liquid)	50-21-5	0.009
MgSO <sub>4</sub> ·7H <sub>2</sub> O	Magnesium sulfate	10034-99-8	0.044
C <sub>5</sub> H <sub>11</sub> O <sub>5</sub> CHO	Glucose(dextrose)	50-99-7	0.046
Citric acid	Citric acid	77-92-9	0.051
CaCl <sub>2</sub> ·2H <sub>2</sub> O	Calcium chloride	10035-04-8	0.060
C <sub>9</sub> H <sub>9</sub> NO <sub>3</sub> , 98%	Hippuric acid	495-69-2	0.060
Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	Sodium silicate	13517-24-3	0.007
NH <sub>4</sub> Cl, 99%	Ammonium chloride	12125-02-9	0.101
C <sub>4</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub> ·H <sub>2</sub> O	Creatine	6020-87-7	0.104
NaCl	Sodium chloride	7647-14-5	0.220
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	Sodium dihydrogen phosphate	10049-21-5	0.259
KCl	Potassium chloride	7447-40-7	0.325
Na <sub>2</sub> SO <sub>4</sub>	Sodium sulfate	7757-82-6	0.409
CH <sub>4</sub> N <sub>2</sub> O, 98%	Urea	57-13-6	1.517
HNO <sub>3</sub>	Conc. nitric acid (50 ml)	7697-37-2	6.701
H <sub>2</sub> O	Water		90.084

IL, USA). Small particle size (50–100  $\mu$ m) resin was employed, along with a vacuum extraction system (Eichrom Technologies). Flow rates of 1–2 ml min<sup>-1</sup> were typically used for this work.

### 2.2.2. Sample preparation

Two different approaches were used. A small volume urine aliquot (5 ml) was acidified to ~3 M HNO<sub>3</sub> and processed through the column chemistry. For large urine aliquots (100 ml), calcium phosphate co-precipitation was applied.

### 2.2.3. 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 15.7 M HNO<sub>3</sub> was added to adjust the acidity of each sample to ~3 M HNO<sub>3</sub>. The samples were swirled to mix each solution. Valence adjustment of the samples was performed by adding 0.25 ml 1.5 M sulfamic acid and 0.5 ml 1.5 M ascorbic acid with a 3-min wait step to reduce plutonium to Pu<sup>3+</sup>. When <sup>237</sup>Np separation was desired, 0.05 ml 5 mg/ml Fe as ferric nitrate was also added to facilitate <sup>237</sup>Np reduction to Np<sup>4+</sup>. The ferric ions are reduced to ferrous ions by the ascorbic acid, which reduces Np effectively to Np<sup>4+</sup>. After the reduction step, 1 ml 3.5 M sodium nitrite was added to oxidize plutonium to Pu<sup>4+</sup>. This column load solution was now ready for column separation as described below.

### 2.2.4. Sample co-precipitation

After the 100 ml urine sample aliquots were dispensed, 1 ml 1.25 M calcium nitrate (50 mg Ca) and 3 ml 3.2 M 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 min. After discarding the supernatant, the precipitate was rinsed once with ~15–20 ml of water and centrifuged again at 3500 rpm for ~5 min. The precipitate was dissolved in 8 ml 6 M HNO<sub>3</sub> and 8 ml 2 M Al(NO<sub>3</sub>)<sub>3</sub> directly in the centrifuge tubes. The final load solution contained 16 ml 3 M HNO<sub>3</sub> and 1 M Al(NO<sub>3</sub>)<sub>3</sub>. The aluminum nitrate was previously scrubbed to remove trace uranium by passing approximately 250 ml 2 M aluminum nitrate through a large column (Environmental Express, Mount Pleasant, SC, USA) containing ~7 ml of UTEVA Resin® (Eichrom Technologies) at ~10 ml/min. 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 1.5 M sulfamic acid and 1.25 ml 1.5 M ascorbic acid with a 3-min wait step to reduce plutonium to Pu<sup>3+</sup>.

When <sup>237</sup>Np separation was desired, 0.4 ml of 5 mg/ml Fe as ferric nitrate was also added to facilitate <sup>237</sup>Np reduction to Np<sup>4+</sup>. To oxidize plutonium to Pu<sup>4+</sup>, 2 ml 3.5 M sodium nitrite was added to each sample solution. This column load solution was now ready for column separation.

### 2.2.5. Column separation

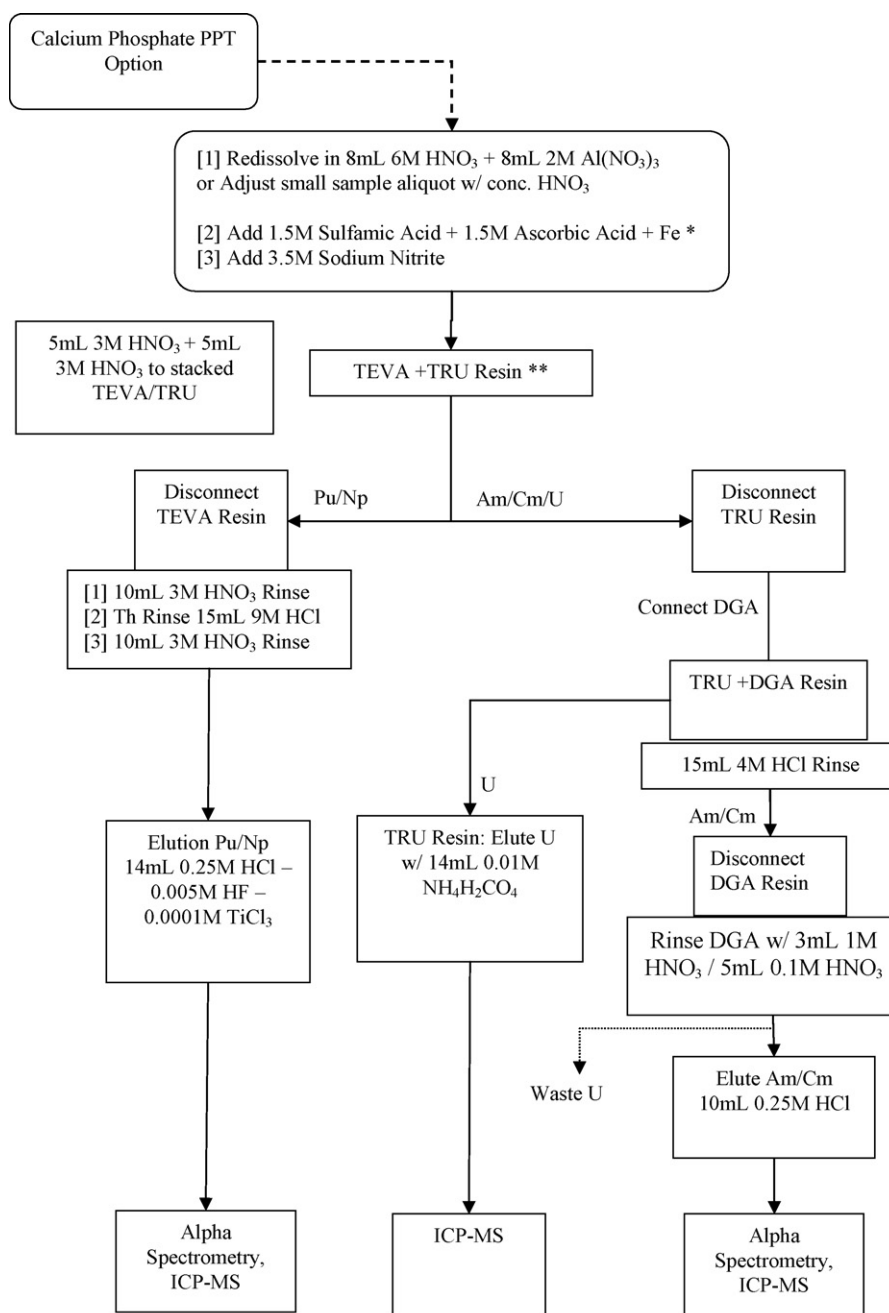
The following column separation was performed on small volume or large volume urine sample aliquots (Fig. 1). TEVA and TRU Resin cartridges were stacked on the vacuum box from top to bottom, in that order. Fifty-milliliter centrifuge tubes were used to collect rinse or final purified fractions.

After the valence adjustment, the sample solution was loaded onto the stacked column at approximately ~1 drop/s. After the sample was loaded, a tube rinse of ~5 ml 3 M HNO<sub>3</sub> was transferred to the stacked column and allowed to pass through the resin at ~1–2 drop/s. 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 3 M HNO<sub>3</sub> was added directly to the stacked column at ~2 drop/s. The TRU Resin cartridges were removed and the TEVA cartridges were kept on the vacuum box. The TEVA cartridge was rinsed with 10 ml 3 M HNO<sub>3</sub> at ~2 drop/s to remove sample matrix components. To elute thorium from TEVA Resin, 15 ml 9 M hydrochloric acid was added at ~1–2 drop/s and discarded. An additional 10 ml 3 M HNO<sub>3</sub> rinse was added after the 9 M HCl rinse to minimize extractant bleedoff during the plutonium elution step and to reduce ICP-MS signal suppression, which may occur with a change in solution viscosity.

The plutonium was stripped from TEVA Resin with 14 ml 0.25 M hydrochloric acid–0.005 M hydrofluoric acid–0.0001 M 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 to 15 ml after elution. The purified solutions were analyzed by alpha spectrometry and ICP-MS. Five milliliters of each plutonium/neptunium eluant solution was transferred to a separate 50 ml tube and 50  $\mu$ g 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<sup>6+</sup> as a precaution. After waiting 15 min, the solutions were filtered onto 0.1  $\mu$ m 25 mm polypropylene filters (Resolve® filter-Eichrom Technologies) and counted by alpha spectrometry. The remaining solution was transferred to the ICP-MS for Pu and 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 4 M HCl at ~1–2 drop/s. The TRU Resin cartridges were removed and the DGA Resin was rinsed with 3 ml 1 M HNO<sub>3</sub>, then 5 ml of 0.1 M HNO<sub>3</sub> at ~1 drop/s to remove any residual uranium. Am and Cm were eluted using 9.5 ml of 0.25 M HCl at ~1 drop/s. 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 0.25 M HCl and 50  $\mu$ g of cerium as cerium nitrate were added to the tubes, along with 1 ml of concentrated hydrofluoric acid (49%), and filtered after about 15 min 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 0.01 M ammonium bioxalate at ~1–2 drop/s. The volume was adjusted after elution to exactly 15 ml with the same solution. If uranium sep-



\* Fe added only if Neptunium is required.

\*\* If Uranium analysis is not required, TEVA + DGA Resin may be used instead (no TRU Resin)

Fig. 1. Flow chart of rapid column extraction method for urine.

aration 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 0.1 M HNO<sub>3</sub> vs 5 ml HNO<sub>3</sub>) 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 4 M HCl, which would typically have to be diluted or evaporated and wet-ashed prior to analysis using ICP-MS. DGA allows Am/Cm elution with 0.25 M 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 h, but shorter count times (<1 h) can also be performed for emergency response samples using higher level tracers [2], depending on the detection limit needed.

### 2.3. 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 2.

The ICP-MS methodology is described in "Standard Practice for Alternate Actinide Calibration for Inductively Coupled Plasma-Mass



**Table 2**  
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 µg/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 s/pt., 3 pt/amu, 0.99 s/amu
Replicates	6

Spectrometry" [15]. The calibration is mass bias adjusted using thorium-232 ( $^{232}\text{Th}$ ) and uranium-238 ( $^{238}\text{U}$ ) standards. At each standard concentration, the slope of the line defined by  $^{232}\text{Th}$  and  $^{238}\text{U}$  is used to derive linear calibration curves for each mass of interest (232–244 amu) 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.

### 3. 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 10 samples. Samples were analyzed for short-lived isotopes by alpha spectrometry and longer lived actinide isotopes were analyzed by ICP-MS.  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  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 3. The average tracer recovery for  $^{243}\text{Am}$  was 105% ( $\pm 2.5\%$  RSD), with an average measured value for  $^{243}\text{Am}$  of 72.0 mBq ( $-2.65\%$  bias) and an average measured value for  $^{244}\text{Cm}$  of 65.4 mBq ( $+2.14\%$  bias). The  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  results were corrected for the  $^{243}\text{Am}$  tracer recoveries in each sample. The Am/Cm recoveries were excellent, with high chemical yield and very little bias for  $^{241}\text{Am}$  and  $^{244}\text{Cm}$ .

**Table 3**  
Am and Cm isotope results by alpha spectrometry.

	$^{243}\text{Am}$ % Recovery	$^{241}\text{Am}$ mBq	$^{244}\text{Cm}$ mBq
1	104.1	73.3	62.5
2	102.9	65.5	71.0
3	108.2	72.2	61.8
4	102.2	72.5	72.2
5	105.6	72.5	66.2
6	108.6	68.5	59.6
7	108.3	79.9	64.0
8	103.3	77.0	65.5
9	101.9	70.3	59.2
10	105.2	68.8	71.8
Avg.	105.03	72.0	65.4
% RSD	2.5	5.8	7.5
	Reference	74.0	64.0
	% Difference	−2.65	2.14

**Table 4**  
Pu isotope results by alpha spectrometry.

	$^{236}\text{Pu}$ % Recovery	$^{238}\text{Pu}$ mBq	$^{239}\text{Pu}$ mBq
1	96.7	70.3	939.8
2	110.5	61.4	769.6
3	91.0	77.3	917.6
4	115.3	67.0	762.2
5	99.1	79.2	880.6
6	98.0	74.7	895.4
7	81.7	91.0	950.9
8	98.9	72.5	817.7
9	108.9	64.4	717.8
10	89.8	79.2	888.0
Avg.	99.0	73.7	854.0
% RSD	10.4	11.7	9.5
	Reference	72.9	832.5
	% Difference	1.12	2.58

The results for the Pu isotopes by alpha spectrometry are shown in Table 4. The average tracer recovery for  $^{236}\text{Pu}$  was 99.0% ( $\pm 10\%$  RSD). The average result for  $^{238}\text{Pu}$  was 73.7 mBq (1.12% bias) and the average result for  $^{239}\text{Pu}$  was 854 mBq (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 and Np isotope results by ICP-MS are shown in Table 5. The average  $^{239}\text{Pu}$  result at the ICP-MS was 0.0252 ng/ml (4.02% bias) and the average  $^{242}\text{Pu}$  result was 0.1366 ng/ml ( $-0.01\%$  bias). The Pu results by ICP-MS were not corrected for 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. Tracer correction using  $^{242}\text{Pu}$  would have also corrected for the bias observed for this analysis run. The average result for  $^{237}\text{Np}$  was 0.1829 ng/ml (0.24% bias), indicating excellent recovery of  $^{237}\text{Np}$  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 significant negative bias at the ICP-MS. Table 6 shows the Pu results by ICP-MS from this test. The average  $^{239}\text{Pu}$  result was 0.0447 ng/ml ( $-7.71\%$  bias) and the average  $^{242}\text{Pu}$  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. Tracer correction using  $^{242}\text{Pu}$  could have been applied, if desired, and an even smaller negative bias would have resulted.

**Table 5**  
Pu and Np isotope results by ICP-MS.

	<sup>237</sup> Np ng/ml	<sup>239</sup> Pu ng/ml	<sup>242</sup> Pu 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 6**  
Pu isotope results by ICP-MS.

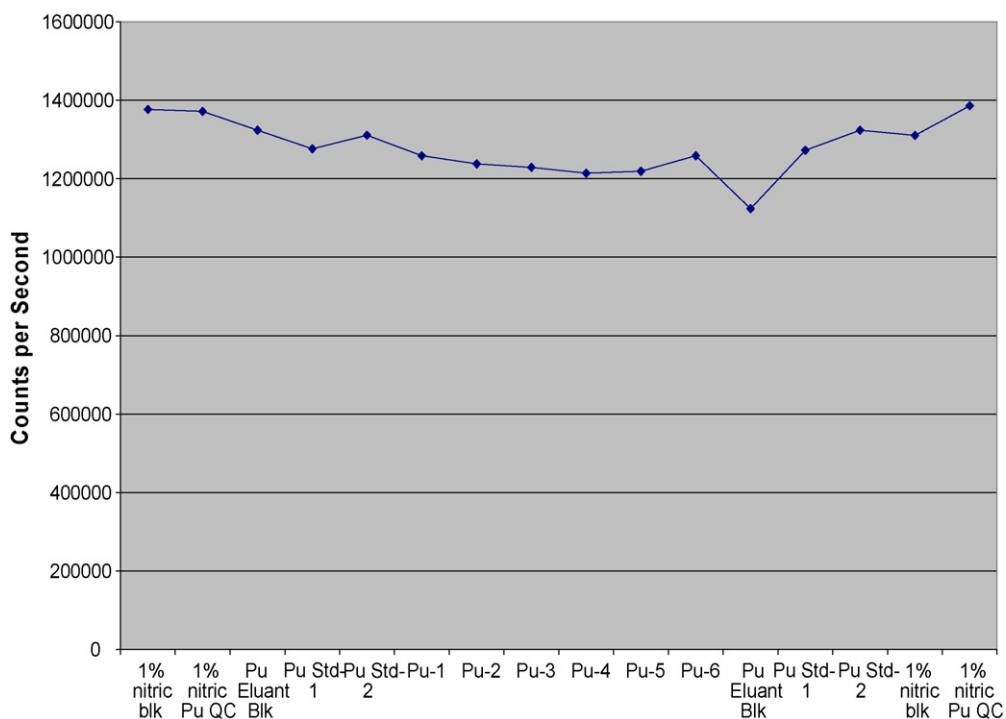
	<sup>239</sup> Pu ng/ml	<sup>242</sup> Pu ng/ml
1	0.0440	0.1260
2	0.0440	0.1270
3	0.0450	0.1260
4	0.0450	0.1280
5	0.0440	0.1280
6	0.0460	0.1320
Avg.	0.0447	0.1278
% RSD	1.67	1.59
Reference	0.0484	0.1366
% Difference	−7.71	−6.42

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

Fig. 2 shows the <sup>209</sup>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 <sup>209</sup>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. = 1.34E6 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 (0.25 M HCl–0.005 M HF–0.0001 M TiCl<sub>3</sub>) without dilution. The decontamination factor (DF) from uranium is very good using TEVA Resin, with sufficient rinsing with 3 M HNO<sub>3</sub> to remove U. The amount of U-238 found in most of the Pu fractions was not detectable by ICP-MS. The DF for uranium was estimated at >1000, which is typical for a single column extraction chromatography separation.

Table 7 shows Am-243 isotope results by ICP-MS. The Am-241 and Cm-244 levels were too low to determine, but the Am-243 measurements were very good. The average <sup>243</sup>Am result at the ICP-MS was 0.0244 ng/ml (−2.44% bias). No chemical yield correction was applied. This test demonstrates that Am can be measured by ICP-MS using this method, including <sup>241</sup>Am if the ICP-MS used had sufficient sensitivity. The decontamination factor from uranium is excellent because the Am and Cm is moved from TRU Resin to DGA Resin, with a additional rinsing prior to elution of Am and Cm. The average amount of U-238 found in the Am fraction was 0.0013% (DF = ~75,000). The Am/Cm eluant strip solution for DGA, 0.25 M HCl, was analyzed directly by ICP-MS without evaporation or wet-ashing. As noted earlier, if U measurement is not required, a stacked column using TEVA Resin + DGA Resin may be used instead. The only change in protocol is increased rinsing of DGA with 0.1 M HNO<sub>3</sub> to ensure adequate uranium removal from DGA.

The results for <sup>238</sup>U by ICP-MS are shown in Table 8. The first five results from human urine sample show an average result for <sup>238</sup>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 <sup>238</sup>U content in the blank solution of



**Fig. 2.** <sup>209</sup>Bi internal standard response for Pu samples by ICP-MS.

**Table 7**  
Am isotope results by ICP-MS.

	<sup>243</sup> Am ng/ml
1	0.0238
2	0.0240
3	0.0253
4	0.0249
5	0.0252
6	0.0239
7	0.0245
8	0.0250
9	0.0223
10	0.0250
Avg.	0.0244
% RSD	3.58
Reference	0.025
% Difference	−2.44

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

**Table 8**  
<sup>238</sup>U results on urine samples by ICP-MS.

Human urine			
	<sup>238</sup> 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		
Synthetic urine			
	<sup>238</sup> U ng/ml	Blank ng/ml	<sup>a</sup> Net <sup>238</sup> 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.

<sup>a</sup> U-238 corrected for U-238 content in blank synthetic urine.

1.79 ng <sup>238</sup>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 9 shows 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 <sup>234</sup>U was 0.0036 ng/ml (13.28% bias). This result is very good, considering the shorter half life of <sup>234</sup>U and the low level of <sup>234</sup>U present. The average result for <sup>235</sup>U was 0.4296 ng/ml (−0.44%) and the average <sup>238</sup>U measured value was 60.99 (2.71% bias). The other shorter lived actinide isotopes (<sup>238</sup>Pu, <sup>241</sup>Am) in the NIST emergency exercise samples were too low to measure by ICP-MS with the 5 ml aliquots analyzed. This illustrates the value of rapid calcium phosphate precipitation preconcentration step to improve detection limits. Other shorter lived actinide isotopes

**Table 9**  
U isotopes results on NIST emergency urine samples by ICP-MS.

	<sup>234</sup> U ng/ml	<sup>235</sup> U ng/ml	<sup>238</sup> U 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 10**  
LLD and LLQ ICP-MS results using 100 ml sample aliquots.

	<sup>237</sup> Np ng/ml	<sup>238</sup> U ng/ml	<sup>239</sup> Pu ng/ml	<sup>242</sup> Pu ng/ml	<sup>243</sup> Am 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 11**  
LLD and LLQ ICP-MS results using 5 ml sample aliquots.

	<sup>234</sup> U ng/ml	<sup>235</sup> U ng/ml	<sup>238</sup> U 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

(<sup>238</sup>Pu, <sup>241</sup>Am) present in the NRIP urine samples were too low to determine using ICP-MS using a 5 ml sample aliquot.

Table 10 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 [17]. These method LLD and LLQ results include a preconcentration factor of 6.67 for all the isotopes except the <sup>243</sup>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 11 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 <sup>238</sup>U LLD and LLQ values are likely higher due to slight <sup>238</sup>U contamination, which may have added variability to the <sup>238</sup>U measurements.

The MDA (Minimum Detectable Activity) for the actinide isotopes by alpha spectrometry were calculated according to equations prescribed by Currie [16]:

$$MDA = \frac{3 + 4.65\sqrt{B}}{CT \times R \times V \times EFF \times 0.060}$$

where  $B$  = total background counts, = BKG (rate)  $\times$  BKG count time;  $CT$  = sample count time (min);  $R$  = chemical recovery;  $V$  = sample volume (l);  $EFF$  = detector efficiency; 0.060 = conversion from dpm to mBq

In low-level counting, where a zero background count is quite common, the constant 3 is used to prevent an excessively high false positive rate.

The MDA for the alpha spectrometry results can be adjusted as needed, depending on the sample aliquot and count time. Pappas has established the <sup>239</sup>Pu action level as 4.8 mBq l<sup>−1</sup> based on a single dose exposure of 500 mSv [5]. For a 100 ml sample aliquot,

the MDA for a 2 h count time is  $16.3 \text{ mBq l}^{-1}$ . For a 400 ml sample aliquot and 2 h count time the MDA is  $4.07 \text{ mBq l}^{-1}$ . For a 100 ml sample aliquot, the MDA for a 22 h count time is  $1.5 \text{ mBq l}^{-1}$ . For a 400 ml sample aliquot and 22 h count time the MDA is  $0.37 \text{ mBq l}^{-1}$ . Depending on the MDA required, the sample aliquot and count time may be adjusted accordingly.

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 ( $0.0001 \text{ M}$ ) used in the plutonium stripping solution effectively reduces Pu to  $\text{Pu}^{3+}$  for effective elution of Pu from TEVA Resin without adversely affecting the ICP-MS assay. The  $0.25 \text{ M}$  HCl and  $0.01 \text{ M}$  ammonium bixalate 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  $\sim 20 \text{ ml}$  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. Tracer corrections were not applied to the ICP-MS results to highlight the high chemical yields and minimal sample matrix impacts observed, but tracer corrections may be easily applied as needed.

#### 4. 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  $^{232}\text{Th}$  and  $^{238}\text{U}$  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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