JAAS

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

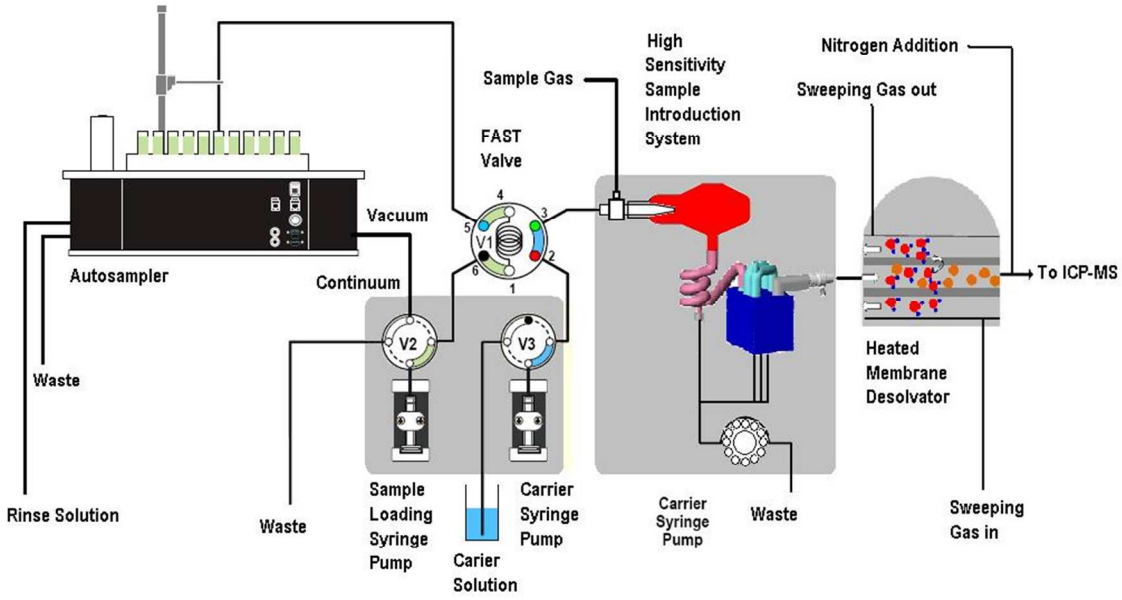
Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas

Table of Contents

Colour graphic



A micro-flow injection ICP-MS method was applied to radiological emergency monitoring of Plutonium and Neptunium

Journal of Analytical Atomic Spectrometry

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Technical Note

ICP-MS method for Pu and Np isotopes in population monitoring by a micro-flow injection sample introduction system

Youqing Shi [a]*, Xiongxin Dai [a], Chunsheng Li [b], Roxanne Collins [a], Sheila Kramer-Tremblay [a], Remi Riopel [a] and Carrie Broome [a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

An ICP-MS method using a micro-flow injection (μ-FI) sample introduction system was developed for measuring ^{237}Np and $^{239, 240, 241}$Pu in urine samples for sensitive and rapid population monitoring following a radiological or nuclear accident. Good selectivity from the chemical separation method allowed the determination of ^{237}Np together with Pu isotopes using ^{242}Pu as a tracer. Significant improvements in ICP-MS sensitivity and detection limit were achieved using the μ-FI sample introduction and the desolvation techniques. The method developed has been successfully applied to a set of human urine samples spiked with Pu isotopes and a set of rat urine samples with metabolized Pu isotopes from research experiments.

Journal of Analytical Atomic Spectrometry

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Technical Note

Introduction

Following a radiological or nuclear accident, a large group of workers/responders or the public may be internally contaminated with the radionuclides involved, through inhaling contaminated air or ingesting contaminated food and water.[1] They need to be assessed for internal contamination and the associated health risk, usually through *in vivo* counting the radionuclides in the whole body or specific organs, such as the lungs, or through *in vitro* measuring the radionuclides in bioassay samples, such as urine.[2]

For *in vitro* bioassay, radiometric methods and techniques have been used for decades.[3-6] However, for long-lived radionuclides, counting the number of atoms in a sample is more advantageous than counting the radiation it emits. Over the years, atom counting techniques including thermal ionization mass spectrometry (TIMS),[7-9] accelerator mass spectrometry (AMS),[10-12] and inductively coupled plasma mass spectrometry (ICP-MS)[13-15] have been developed as alternatives to the radiometric methods and techniques that are usually used in radiochemistry laboratories.

ICP-MS, a versatile analytical technique for trace measurements, is becoming increasingly popular for analysing long-lived actinide isotopes, such as Pu isotopes.[16] It has been used for the measurement of alpha-emitting radionuclides in bioassay samples in many laboratories.[17-21] Since the concentrations of actinides (e.g., $^{239,\ 240,\ 241}$Pu and ^{237}Np) in typical bioassay samples are usually very low, a separation procedure is necessary to remove the complex sample matrix and to pre-concentrate the analytes of interest prior to their measurement. Using the conventional sample introduction method at a sample up-take rate of 100 to 500 µL min^{-1}, 5 to 10 mL of the final processed sample solution may be required by ICP-MS analysis with detection limits close to 2 to 5 fg.[22-23] In order to increase the sensitivity and to reduce the interference to ^{239}Pu by ^{238}UH^{+} ions, a desolvation sample introduction system has been applied to lower the limit of detection (LOD) for ^{239}Pu and ^{240}Pu with a processed final sample volume of 2 to 3 mL.[24-25] Using a direct injection high-efficiency nebulizer (DIHEN) to introduce samples at a up-take rate of 60 µL min^{-1}, an ICP-MS measurement was performed on a sample volume of 0.5 mL to achieve a LOD of around 1 fg for the determination of ^{239}Pu in 1 litre of urine samples[18].

Since the technique is based on liquid sample introduction, the ICP-MS detection limit can be lowered through pre-concentrating the analytes in the available sample into a very small volume. To implement this strategy, a method involving a high-efficiency sample introduction system and a membrane desolvator, has been reported[26]. This method analysed Pu isotopes in marine settling particles after pre-concentrating the analyte into 0.7 mL of liquid and reported a LOD of 0.07 fg for Pu isotopes. Although the method was not applied to real urine samples, a nano-volume flow injection (nFI) sample introduction ICP-MS method[27] was reported for analysis of a sample volume as small as 180 µL with the LOD of 0.091 and 0.015 fg for ^{238}U and ^{242}Pu in the tested standards.

^{242}Pu has been an ideal tracer in monitoring the recovery of other Pu isotopes in almost all the sample preparation procedures. However, there is no suitable isotopic tracer available for the determination of ^{237}Np, a radionuclide having similar radiological toxicity to Pu isotopes. Considering the similarities of the chemical properties of these two elements[28], we tested the suitability of ^{242}Pu as a tracer for the determination of ^{237}Np along with the Pu isotopes.

In this paper, an ICP-MS method with a micro-flow injection sample introduction system coupled with a high sensitivity nebulizer and a membrane desolvator was developed for the determination of four radionuclides, namely ^{237}Np, ^{239}Pu, ^{240}Pu, and ^{241}Pu in urine samples.

Experimental

Reagent and materials

All the chemicals and resins used in this study were analytical grade or above. The anion exchange resin AGMP-1M (Cl^{-} form, 100-200 mesh) was purchased from Bio-Rad Laboratories Canada Ltd. (Mississauga, Ontario, Canada). The ultra-pure water (UPW) was obtained from a Millipore Direct-Q5 ultra-pure water system. Nitric acid, hydrochloric acid, hydrofluoric acid, titanium oxychloride, ammonium hydroxide, hydrogen peroxide and sodium nitride were obtained from Sigma-Aldrich Canada (Oakville, Ontario, Canada).

Certified standard solutions of radioisotopes ^{239}Pu, ^{241}Pu, and ^{242}Pu were supplied by the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), and the standard solution of ^{237}Np was purchased from the Eckert & Ziegler Isotope Products Laboratories (Valencia, California, USA).

The ultra-trace impurities of the radioisotope standards used in this study were examined by TIMS and AMS analysis. The ^{239}Pu, ^{242}Pu and ^{237}Np standards were found to be sufficiently pure with negligible amounts of other Pu/Np isotopes. However, significant impurities of ^{239}Pu and ^{240}Pu were found in the ^{241}Pu standard. Since the NIST standard certificate did not provide certified $^{239/240}$Pu concentrations in the ^{241}Pu standard, an in-house calibration was performed using TIMS after anion exchange purification to accurately determine the ^{239}Pu and ^{240}Pu impurities

in this standard.

To verify the method performance, two sets of intercomparison test urine samples were prepared in Health Canada. The 1st set consisted of 3 replicates of pooled human urine spiked with a known amount of ^{239}Pu along with 3 human urine blanks. The 2nd set of the samples were 3 replicates of rat urine samples with metabolized ^{239}Pu and 3 rat urine blanks. All the intercomparison samples were acidified to 1% HCl before shipping to the Chalk River Laboratories for analysis.

Rapid urine bioassay procedure for plutonium

An emergency bioassay procedure for actinides in urine samples, based on hydrous titanium oxide (HTiO) co-precipitation followed by anion exchange/extraction chromatography separation, was developed previously for the preparation of the counting source for alpha spectrometry.[29] This procedure was modified for the separation of Pu and Np from urine matrix for the ICP-MS analysis. Approximately 50 pg of ^{242}Pu, used as yield tracer, was added to 50 mL of urine sample. The sample was further acidified by adding 2.5 mL of concentrated nitric acid. After mixing, 2 mL of 7% $TiOCl_2$ solution was added to facilitate HTiO co-precipitation. The sample was then neutralized with ammonium hydroxide to pH ~7, and HTiO precipitate formed. The sample was centrifuged and the supernatant solution discarded. The precipitate was then rinsed and centrifuged twice with 30 mL of UPW (ultra pure water) each time to remove residual salt, and the rinses were discarded. The precipitate was subsequently dissolved in 3 mL of concentrated HNO_3 with the addition of 0.5 mL of H_2O_2, and made up to a total volume of 20 mL with 8 M HNO_3 for anion exchange purification.

The anion exchange column was prepared by loading a slurry of AGMP-1M resin in UPW into a 2-mL cartridge and pre-conditioned with 10 mL of UPW followed by 10 mL of 8 M HNO_3. Prior to the column separation, 0.2 mL of 3 M $NaNO_2$ was added to the sample solution and was allowed to sit for 10 minutes for valence adjustment. The sample was then passed through the column at ~1 mL min^{-1} to extract Pu and Np, whereas the sample matrix and other elements including U would not be absorbed by the resin. The column was further rinsed with 10 mL of 8 M HNO_3, and any thorium extracted onto the resin was removed with 5 mL of concentrated HCl. Plutonium and neptunium were eluted off the column with 12 mL of 0.2 M HNO_3 + 0.05 M HF.

For each sample, two aliquots of the final eluate were taken for ICP-MS measurements: one aliquot of 3 mL eluate was used for ICP-MS analysis using the Apex Q sample introduction system; and the other aliquot of 3 mL eluate was evaporated to near dryness and re-dissolved into 0.3 mL of 0.2 M HNO_3 + 0.05 M HF for the analysis by μ-FI-ICP-MS.

Instrumentation

The ICP-MS instrument used in this work was a sector field (SF) model Element XR, manufactured by Thermal Scientific, Hanna-Kunath-Str 11, d-28199 Bremen, Germany. A fumehood adaptation was attached to the instrument to enclose the sample introduction system and the ICP ionization source for safe analysis of radioactive samples.

Two sample introduction methods were used in the analysis for comparison. The first was a high-efficiency sample introduction method consisting of an Apex Q desolvation system and a PFA-ST nebulizer through a SC-2 DX auto-sampler, all manufactured by Elemental Scientific Inc. (ESI. Omaha NE, USA). The typical sample volume for this method was 2 mL. The second was a μ-FI sample introduction method including a microFAST system, an Apex-Q, and a heated membrane desolvation unit (Spiro TMD, ESI). The microFAST system was composed of a SC-2 DX auto-sampler with two FAST valve controllers and dual flowing rinse, a 4-channel standalone micro peristaltic pump, as well as a continuum of two micro-flow dual reciprocating syringe pumps. The Apex Q was integrated with a CTFE fluoro-polymer high-flow FAST valve. A sample loop of 100 μL volume and a PFA μ-flow ST nebulizer were used for sample analysis at an uptake rate of 50 μL min^{-1}. Approximately 200 μL of the sample was needed for each injection. The whole sample introduction system was software controlled and fully automated.

To achieve the highest sensitivity on the ICP-MS, the low resolution mode (R=300) was used throughout the experiments. All parameters of the mass spectrometer system were optimized before use. For convenience, most of the parameters were optimized through the Tune page using only the Apex Q sample introduction system. The parameters related to the microFAST and Spiro TMD, including the flow rates of sample gas, nitrogen addition gas, and sweeping gas, were optimized after switching to the μ-FI system by running sequences under different combinations of these gas flow rates. Typical instrument working conditions are listed in Table 1.

Table 1 Instrumental parameters of the μ-FI-ICP-MS system

SF-ICP-MS	
Plasma power	1250 W
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.1 L min^{-1}
Sample gas flow rate	0.95 L min^{-1}
Resolution	m/Δm = 300
Acquisition mode	E-Scan (peak jumping)
Mass Monitored	$^{238}U^+$, $^{239}Pu^+$, $^{240}Pu^+$, $^{241}Pu^+$, and $^{242}Pu^+$
Dwell time	0.005 s for $^{238}U^+$, 0.02 s for rest
No of Scans (runs × passes)	5 × 6
Mass Window	5%
Sample per Peak	100
Search Window	0
Integration Window	5%
Integration Type	Average
Time per Analysis	120 s
microFAST System	
Sample loop	100 μL
Sample uptake rate	50 μL min^{-1}
Carrier solution	0.2 M HNO_3 + 0.05 M HF
Apex Q Desolvation Unit	
Spray Chamber Temperature	140 °C
Condenser Temperature	2 °C
Spiro Teflon Membrane Desolvator (TMD)	
Sweeping Gas pressure	50 psi
N_2 flow	8 mL min^{-1}

Results and Discussions

Optimization of the microFAST-Apex Q-TMD sample introduction system

To analyze actinide isotopes at the femtogram level, optimization of the instrument system is very important for a high sensitivity, stable response, and reasonably low and stable background signal in the mass range of interest. Various parameters in the ESI microFAST software were carefully tuned so that about 200 µL of sample was withdrawn from the sample tube of the auto-sampler and filled into the sample loop (100 µL). By switching the valve, the sample solution inside of the loop was pushed into the nebulizer for analysis, while the sample line and sample probe were rinsed for the injection of the next sample. The uptake time and measure time in the Sequence files of the Element XR software were carefully in synchronized with the parameters from the FAST software. Figure 1 shows an analyte signal (^{238}U) of multiple injections from the µ-FI-ICP-MS system.

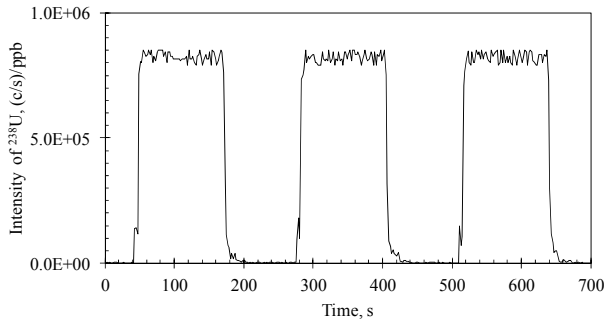


Figure 1 ^{238}U Signal of multiple injections from the µ-FI-ICP-MS system

Effects of uranium hydride ions and mass spectrometer abundance sensitivity

Owing to the ubiquity of uranium in the samples, the accurate determination of ^{239,240,241}Pu and ^{237}Np is hampered by the interferences from uranium hydride ions and the abundance sensitivity of the mass spectrometer. This is particularly true for the determination of ^{239}Pu which suffers from overlapping by $^{238}U^{1}H^{+}$ and the highest ^{238}U peak tail at 1 mass distance. In this work, four different sample introduction techniques, namely pneumatic nebulisation (PFA nebulizer/cyclonic chamber), pneumatic nebulisation with Peltier cooling desolvation, pneumatic nebulisation with heating/Peltier cooling desolvation (Apex-Q), and pneumatic nebulisation with heating and Peltier cooling in combination with membrane desolvation (Apex-Q and Spiro TMD), were tested for the effectiveness in reduction of the uranium hydride ion formation rate. It can be seen from Figure 2 that utilization of Peltier cooling, heating/Peltier cooling, and the combination of heating/Peltier cooling and membrane desolation can reduce the hydride formation rate to about 50%, 20%, and 7% of that from only pneumatic nebulisation. The lowest uranium hydride rate of 7.2×10^{-6} achieved from using a combination of Apex Q and Spiro TMD sample introduction method was found to be similar to the abundance sensitivity at ±1 mass of about 8.7×10^{-6}.

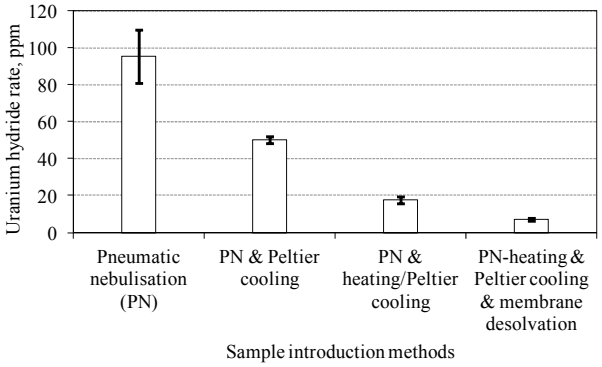


Figure 2 Uranium hydride formation rates using different sample introduction methods

Sensitivity and limit of detection

The flow injection (FI) sample introduction method increases the sensitivity through efficient utilization of the sample available for measurements. The µ-FI method further increases the sensitivity through increasing the nebulisation efficiency on a low flow nebulizer. To show the improvement of the ICP-MS method sensitivity, two solutions spiked with the same amount of ^{242}Pu (6.84 pg) in total volumes of 2 mL and 0.3 mL were analysed using the Apex Q and the µ-FI-Apex Q sample introduction methods under their optimized conditions, respectively. The absolute sensitivities of the two sample introduction methods, expressed as counts per second per pg of Pu, are listed in Table 2. It can be seen that the absolute sensitivity increased from 1,900 c/s for the Apex Q method to 7,600 c/s per pg of Pu isotopes for the µ-FI-Apex Q method.

Table 2 ICP-MS sensitivity from the different sample introduction methods

Sample intro method	Volume per analysis, mL	Concentration of ^{242}Pu, pg mL^{-1}	Amount of ^{242}Pu per analysis, pg	Sensitivity of ^{242}Pu, (c/s) pg^{-1}
Apex Q	2	3.42	6.84	1,900
µ-FI-Apex Q	0.3	22.8	6.84	7,600

The LOD, defined as 3 times of the standard deviation of the procedural blank, depends on the final volume of the processed sample and the sample introduction system used. As expected, the lowest LOD was achieved from the measurement of a small volume of 300 µL by the µ-FI-ICP-MS using both Apex Q and Spiro TMD as the sample introduction method. This LOD was estimated for the Pu and Np isotopes experimentally. The effect of the amount of co-existing ^{238}U on the LOD of the Pu and Np isotopes was also tested by running replicate blanks with different amounts of U added. The estimated LOD are listed in Table 3. A few conclusions can be drawn from the numbers listed in the table. Without a significant amount of uranium present, a LOD of about 0.3 fg was achieved for ^{237}Np, ^{240}Pu and ^{241}Pu, whereas a LOD of slightly above 1 fg was found for ^{239}Pu. The higher LOD for ^{239}Pu was likely caused by the contamination of "real" ^{239}Pu blank in the instrument system, considering the fact that the abundance sensitivity effect is expected to be the same for ^{239}Pu

and ^{237}Np in the absence of uranium.

For all the Pu and Np isotopes tested, the LOD was not affected if the ^{238}U was less than 30 pg. Obviously, the detection limits deteriorated at a higher amount of uranium. As a result, the LOD was significantly higher for all the Pu and Np isotopes when the uranium amount was as high as 2500 pg. As expected, from Table 3, it can be seen that the interference from uranium to the LOD of the three Pu isotopes decreased with increasing mass number (i.e., decreasing abundance sensitivity of the mass spectrometer). Through measurement, the amount of uranium in the final prepared solution was found to be 6±4 pg and 160±60 pg for human urine samples and rat samples, respectively. The effect to the LOD was minimal.

Table 3 LODs of the analytes with the presence of different amount of ^{238}U

Co-existing ^{238}U, pg	LOD, fg			
	^{237}Np	^{239}Pu	^{240}Pu	^{241}Pu
0	0.32	1.0	0.33	0.26
3	0.29	1.4	0.22	0.23
30	0.37	1.3	0.23	0.27
280	1.6	1.5	0.54	0.35
2500	10	8.6	7.3	2.6

Spike recovery test

To evaluate the performance of the μ-FI-ICP-MS method, a series of test solutions spiked with ^{237}Np and ^{239,240,241}Pu in the fg range were analyzed following the separation procedure. As illustrated in Figure 3, good agreement between the expected and measured values was achieved. The uncertainties, expressed as one standard deviations (the same below), are relatively small when the spike is above 10 fg. At a spiking level below 10 fg, higher relative uncertainties are observed for all measured isotopes. The uncertainties for ^{237}Np and ^{239}Pu are generally greater than those for ^{240,241}Pu, indicating more serious interferences from the uranium hydride ions and ^{238}U peak tailing on the measurement of ^{237}Np and ^{239}Pu. In addition, the overall chemical recovery for processing 50 mL of urine samples by the separation procedure was measured to be 80%±10%.

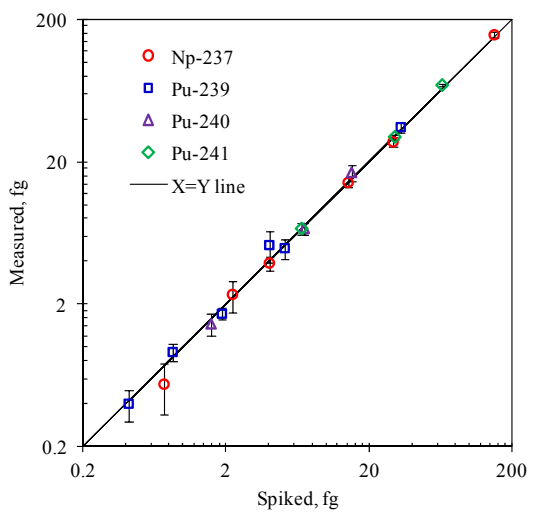


Figure 3 Spiked and measured values from the procedure tested with standards

Analysis of urine samples

Two sets of inter-comparison urine samples (totally twelve), as described in the experimental section above, were analyzed following the separation procedure. The ICP-MS measurements were performed with and without μ-FI sample introduction. With no μ-FI, 3 mL of the 12 mL eluate was used directly with the Apex Q; while, with the μ-FI, 300 μL of liquid concentrated from 3 mL of the eluate was injected using both Apex Q and Spiro TMD as the sample introduction method. For the purpose of intercomparison, the measured ^{239}Pu concentration in the urine samples together with the expected value, instead of the total amount of ^{239}Pu in a sample, are listed in Table 4. Although the statistical means of the metabolized rat urine samples were not yet available as the inter-laboratory comparison was still in progress, a good agreement between the measurements and the expected value of ^{239}Pu for the human urine spike samples is evident. Overall, lower LODs, better accuracy and precision were achieved using the μ-FI-ICP-MS method.

Table 4 Results of intercomparison urine samples

Sample ID	Sample Description	^{239}Pu, fg		
		Expected	Apex Q	μ-FI-Apex Q
HC-13-Pu-3	Human urine blank		<0.14	<0.06
HC-13-Pu-4			<0.11	<0.05
HC-13-Pu-5			<0.12	<0.04
HC-13-Pu-6	Human urine spike	6.66	6.4±0.3	6.6±0.3
HC-13-Pu-7			5.7±0.3	6.7±0.4
HC-13-Pu-8			6.3±0.5	6.3±0.3
HC-13-Pu-9	Rat urine blank		<0.14	<0.04
HC-13-Pu-10			<0.14	<0.04
HC-13-Pu-11			<0.13	<0.04
HC-13-Pu-12	Rat urine metabolized		1.8±0.5	2.0±0.3
HC-13-Pu-13			1.5±0.4	2.1±0.3
HC-13-Pu-14			2.0±0.5	1.7±0.3

Conclusions

A μ-FI-ICP-MS method using a microFAST sample introduction system coupled with a high sensitivity nebulizer and a membrane desolvator was developed for the determination of ^{237}Np, ^{239}Pu, ^{240}Pu, and ^{241}Pu in urine samples. Experiments proved that ^{242}Pu can serve as the recovery monitor for ^{237}Np in the separation and pre-concentration procedure developed. Reduction of the uranium hydride ion formation in ICP-MS using three different sample introduction techniques was evaluated, and the best reduction was achieved using pneumatic nebulisation with heating and Peltier cooling in combination with membrane desolvation. The results showed that the presence of up to 30 pg of U would not affect the method detection limit, although the LOD for Pu and Np isotopes started to rise with further increases of the U content. The μ-FI sample introduction system can increase the sensitivity through concentrating the analytes into a small volume and using the micro-flow injection technique. Spike tests showed excellent recoveries of all four nuclides tested and good analytical results were obtained for real urine samples spiked with ^{239}Pu.

Notes and references

[a] *Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River ON K0J 1J0, Canada, E-mail: shiy@aecl.ca*

[b] *Radiation Protection Bureau, Health Canada, Ottawa, ON Canada E-mail: Li.Chunsheng@hc-sc.gc.ca.*

1 N. Matsuda, A. Kumagai, A. Ohtsuru, N. Morita, M. Miura, M. Yoshida, T. Kudo, N. Takamura and S. Yamashita, *Radiat. Res.*, 2013, **179**, 663-669.

2 C. Li, K. Inn, R. Jones, J.-R. Jourdain, N. Priest, D. Wilkinson, B. Sadi, R. Ko, K. Capello and G. H. Kramer, *Health Phys.*, 2011, **101**, 107-111.

3 D. W. Efurd, R. E. Steiner, S. P. LaMont, and D. Lewis, *J. Radioanal. Nucl. Chem*., 2008, **276**: 499-504.

4 N. E. Bores, M. K. Schultz, J. M. Rankin, A. J. Denton, G. F. Payne, R. E. Steiner, S. P. LaMont, and S. B. Ortiz, *J. Radioanal. Nucl. Chem*., 2008, **276**: 513-518.

5 X. Dai, *J. Radioanal. Nucl. Chem*., 2011, **289**: 595-600.

6 A. Gagné, J. Surette, S. Kramer-Tremblay, X. Dai, C. Didychuk and D. Larivière, *J. Radioanal. Nucl. Chem*., 2013, **295**: 477-482.

7 S. P. LaMont, C. R. Shick, P. Cable-Dunlap, D. J. Fauth, T. R. LaBone, *J. Radioanal. Nucl. Chem.*, 2005, **263**, 477-481.

8 N. L. Elliot, G. A. Bickel, S. H. Linauskas and L. M. Paterson, *J. Radioanal. Nucl. Chem.*, 2006, **267**, 637-650.

9 C. Li, N. L. Elliot, S. Tolmachev, S. McCord, T. Shultz, Y. Shi and G. H. Kramer, *J. Anal. At. Spec.*, 2011, **26**:2524-2527.

10 N. D. Priest, G. M. Pich, L. K. Fifield and R. G. Cresswell, *Radiat. Res.*, 1999, **152**, S16-S18.

11 H. Hernández-Mendoza, E. Chamizo, A. Yllera, M. García-León and A. Delgado, *J. Anal. At. Spectrom.*, 2010, **25**, 1410-1415.

12 X. Dai, M. Christl, S. Kramer-Tremblay and H.-A. Synal, *J. Anal. At. Spectrom.*, 2012, **27**, 126-130.

13 D. Lariviere, T. Cumming, S. Kiser, C. Li and J. Cornett, *J. Anal. At. Spectrom.*, 2008, **23**, 352-360.

14 Y. Shi, X. Dai, R. Collins and S. Kramer-Tremblay, *Health Phys*, 2011, **101**, 148-153.

15 J. Qiao, X. Hou, P. Roos and M. Miro, *Anal. Chem.*, 2013, **85**, 2853-2859.

16 C-S. Kim, C-K. Kim, P. Martin, and U. Sansone, *J. Anal. At. Spectrom.*, 2007, **22**, 827-841.

17 E. J. Wyse and D. R. Fisher, *Radiat. Prot. Dosim.*, 1994, **55**, 199-206.

18 M. V. Zoriy, C. Pickhardt, P. Ostapczuk, R. Hille, J. S. Becker, *Int. J. Mass Spectrom.*, 2004, **232**, 217-224.

19 C. Li, K. Benkhedda, Z. Varve, V. Kochermin, B. Sadi, E. Lai, G. H. Kramer and J. Cornett, *J. Anal. At. Spectrom*., 2009, **24**, 1429-1433.

20 C. Li, B. Sadi, K. Benkhedda, N. St-Amant, G. Moodie, R. Ko, A. DiNardo and G. H. Kramer, *Radiat. Prot. Dosimet.*, 2010, **141**, 228-232.

21 S. L. Maxwell, B. K. Culligan, V. D. Jones, S. T. Nichols, G. W. Noyes, and M. A. Bernard, *Health Phys*, 2011, **101**, 180-186

22 H. Hernández-Mendoza, E. Chamizo, A. Delgado, M. García-León and A. Yllera, *J. Anal. At. Spec.*, 2011, **26**:1509-1513.

23 F. Pointurier, P. Hémet and A. Hubert, *J. Anal. At. Spec.*, 2008, **23**:94-102.

24 R. S. Pappas, B. G. Ting, and D. Paschal, *J. Anal. At. Spec.*, 2004, **19**:762-766.

25 V. N. Epov, R. D. Evans, J. Zheng, O. F. X. Donard, and M. Yamada, *J. Anal. At. Spec.*, 2007, **22**:1131-1137.

26 J. Zheng and M. Yamada, *Talanta,* 2006, **69**:1246-1253.

27 D. Schaumlöffel, P. Giusti, M. V. Zoriy, C. Pickhardt, J. Szpunar, R. Lobiński and J. S. Becker, *J. Anal. At. Spec.*, 2005, **20**:17-21.

28 M. S. Milyukova, N. I. Gusev, I. G. Sentyurin, and I. S. Sklyarenko, *Analytical Chemistry of Plutonium*, 1967, Israel Program for Scientific Translation, Jerusalem, 5-6

29 X. Dai and S. Kramer-Tremblay, *Health Phys*, 2011, **101**, 144-147