Determination of U, Pu and Am in biological samples by SF-ICP-MS for biokinetic studies of actinides

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Introduction

The U.S. Transuranium & Uranium Registries (USTUR) studies the uptake, translocation and biokinetics of actinides (U, Pu and Am) in humans. Currently α-spectrometry is the primary method for analysis of U, Pu and Am in human autopsy tissues. However for environmental samples, inductively coupled plasma mass spectrometry (ICPMS) is now a well established technique for ^{235,238}U and ^{239,240}Pu determination.[1,2] With recent ICPMS instrument developments, it is possible to detect ^{241}Am[3], although application of ICP-MS for the analysis of Pu and Am in biological samples has been limited due to their low concentrations.

The aim of this work was to develop protocols to measure U, Pu and Am isotopes in human bone and soft tissue samples from occupationally exposed individuals by the SF-ICPMS technique, and compare the results with α-spectrometry. ICPMS is expected to offer important advantages for determining isotopic fingerprints of U and Pu.

Materials and Methods

- **Sector field ICPMS at Northern Arizona University**

Table 1. SF-ICPMS Operating Conditions

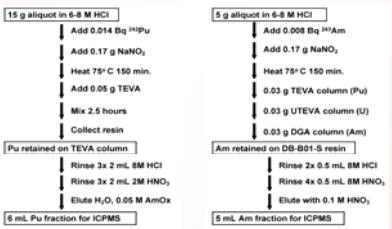
Instrument	VG Axiom MC
Resolving power	R = 410, m/∆m at 10% height
RF power	1280 Watts
Argon gas flows	
Plasma	11.9 L min^{-1}
Auxiliary	1.00 L min^{-1}
Sample gas	0.73-0.85 L min^{-1}
Interface cones	Nickel
Nebulizer type	CETAC U-5000AT ultrasonic
Evaporator temperature	140°C
Condenser temperature	5°C
Sample uptake rate	500 µL min^{-1}
U^{x}/U^{1}	0.00002-0.00003 (measured for ^{236}U)
Mass bias factor	1.005 - 1.01 0 (measured using natural ^{235}U/^{238}U)
Detection method	Electron multiplier, single collector, scanning
Pu mass spectral scans	20 points per m/z in range 236.2-242.8
U mass spectral scans	20 points per m/z in range 233.5-238.6
Am mass spectral scans	20 points per m/z in range 238.5-243.6
Peak jump scan method	Electrostatic sector, 0.2 peak widths, 50 points peak^{-1}
Peak jump dwell time	10 milliseconds
Scans per integration	100 - 200
Integrations per solution	3 - 5
Peak jump isms monitored	
Uranium analysis	^{234}U, ^{235}U, ^{236}U (internal standard), ^{238}U
Plutonium analysis	
Americium analysis	

- **α-spectrometry at USTUR**

Table 2. Alpha Spectrometry Operating Conditions

Instrument	4 units *Octête™ PC* system 4096-channel analyzer
Energy range	3 – 8 MeV in 1024 channels
Detectors	450 mm^2 EG&G ORTEC ULTRA Si(Au)surface barrier
Software	MAESTRO -32 v.6.06 + AlphaVision® -32 v.5.30
Measurement time	
Background	300,000 s
Sample	150,000 s
Plutonium analysis	$^{239+240}$Pu, ^{238}Pu, ^{242}Pu (spike, NIST SRM 4334G)
Americium analysis	^{241}Am, ^{243}Am (spike, NIST SRM 4332D)
Limit of detection	0.0003 Bq sample^{-1}

Samples. Voluntarily donated soft tissue and bone samples are prepared by USTUR following autopsies and are subsequently dry-ashed; the ashed residues are dissolved in 6-8 M HCl (aq). Digested samples from USTUR Cases 0269, 0425, and 0720 (Pu exposure) and 1028 (U exposure) have been analyzed by ICPMS at NAU. All samples were previously analyzed at USTUR using α-spectrometry. The primary methods used were USTUR-100,110 (sample ashing), USTUR-150, 220, 310 (Pu/Am separation) and USTUR 510, 610 (α-counting). All USTUR methods are available on-line.[4] Four samples were analyzed independently by α-spectrometry at a commercial laboratory. All samples are initially ashed and dissolved without U, Pu, and Am yield tracers; these are added to gravimetric aliquots of the sample solutions at the ICPMS or α-spectrometry laboratory. Results are calculated in terms of activity (Bq) present in each original tissue sample.



Separation procedures for ICPMS. Two separation schemes were used for ICPMS (figure above). Resins were obtained from ElChrom (Darien, IL, USA). The procedure at left was used in cases where Pu was the only targeted analyte. The procedure at right was used for the determination of Am. Uranium isotopic compositions were measured after separation on a UTEVA column (chart at right). Samples were analyzed both with and without an added ^{236}U internal standard; some samples contained detectable indigenous ^{236}U. In future work, we plan to use ^{233}U as U yield tracer.

Results and Discussion

Figures of merit for SF-ICPMS. For the "whole sample" (nominally 700 grams of solution) detection limits are: ^{234}U, 0.0001 Bq in the sample using a 5 g aliquot; ^{235}U, 0.006 mBq in the sample using a 5 g aliquot; ^{238}U, 0.00009 Bq in the sample using a 5 g aliquot; $^{239+240}$Pu, 0.005 Bq in the sample using a 15 g aliquot; ^{241}Pu, 1.4 Bq in the sample using a 15 g aliquot; ^{241}Am, 0.05 Bq in the sample using a 5 g aliquot. U, Pu, and Am are all analyzed separately. For each element, the sample throughput is ~ 6 samples per hour. We expect to improve sample throughput in the future with use of an APEX HF sample introduction system with PFA nebulizer.

Activity results. For some samples where high levels of Pu were encountered, it was also possible to detect ^{241}Pu. ^{240}Pu/^{239}Pu atom ratios indicated that the Pu was of weapons-grade isotope composition. The ICPMS results provide several important insights into uranium exposure; the source of the U in USTUR Case 1028 consisted of ^{235}U-enriched material that also contained some ^{236}U. $^{239+240}$Pu, ^{241}Am, and U activities compare favorably for results obtained independently by ICPMS and α-spectrometry.

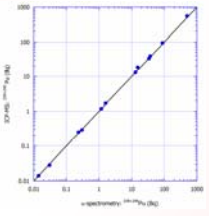
Table 3. Results of analyses of $^{239+240}$Pu, ^{240}Pu/^{239}Pu, ^{241}Pu and ^{241}Am with SF-ICP-MS and α-spectrometry

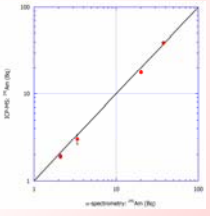
No.	Tissue	$^{239+240}$Pu, Bq				^{240}Pu/^{239}Pu, atom		^{241}Pu, Bq		^{241}Am, Bq			
		α-spectrometry		ICP-MS		ICP-MS		ICP-MS		α-spectrometry		ICP-MS	
		value	± sd[a]	value	± sd[b]	value	± sd	value	± sd	value	± sd	value	± sd
269001	Lung	1.53E+01	2.04E-01	1.86E+01	2.12E-01	6.20E-02	1.80E-03	< 115[c]		2.94E+00	8.9E-02		
269003	Liver	5.00E+02	1.20E+01	5.54E+02	2.69E+00	6.30E-02	1.00E-03	3.12E+02	3.4E+01	3.77E+01	8.4E-01	3.91E+01	1.4E+00
269031	Femur, PE	3.70E+01	6.03E-01	3.91E+01	5.00E-01	6.30E-02	1.00E-03	2.30E+01	7.0E+00	9.65E+00	2.1E-01		
269052	Humerus, PE	1.30E+01	2.10E-01	1.31E+01	1.00E-01	6.30E-02	1.00E-03	8.70E+00	5.0E-01	3.37E+00	6.7E-02	3.00E+00	4.0E-01
425003	Liver	1.59E+00	4.14E-02	1.67E+00	3.00E-02	6.20E-02	1.00E-03			1.66E-01	7.5E-03		
425004	Bladder Gall	1.99E-03	5.64E-04	< 0.005[c]						7.91E-04	4.9E-04		
425007	Spleen	2.34E-01	5.00E-03	2.49E-01	3.00E-03	6.40E-02	2.00E-03			4.78E-02	2.3E-03		
425009	Kidney	1.40E-02	1.55E-03	1.40E-02	1.00E-03	8.00E-02	4.00E-02			8.10E-03	1.2E-03		
425040	Fibula, PE	3.05E-02	2.66E-03	2.80E-02	2.00E-03	8.00E-02	2.00E-02			1.52E-02	1.6E-03		
425057	Scapula Spine	2.99E-01	2.84E-02	2.90E-01	7.00E-03	6.80E-02	1.00E-03			1.43E-01	1.8E-02		
425082	Sacrum	1.17E+00	6.15E-02	1.17E+00	3.00E-02	6.10E-02	1.00E-03			3.55E-01	3.1E-02		
425082	Secrum[d]	1.17E+00	6.15E-02	1.21E+00	1.44E-02	6.30E-02	3.00E-03			3.55E-01	3.1E-02		
720001	Lung	8.78E+01	2.61E+00	9.44E+01	4.00E-01	6.30E-02	1.00E-03	8.30E+01	3.0E+00	2.01E+01	5.6E-01	1.77E+01	4.0E-01
720004	Liver	3.40E+01	1.00E+00	3.36E+01	1.00E-01	5.90E-02	1.00E-03	2.70E+01	4.0E+00	2.10E+00	7.2E-02	1.90E+00	1.0E-01

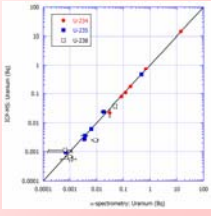
a) - 1σ Poisson counting uncertainty b) - standard deviation of 5 integrations c) - for 0.28 g sample aliquot d) - duplicate

Table 4. Results of analyses of ^{234}U, ^{235}U, ^{238}U, and ^{235}U/^{238}U atom ratio with SF-ICP-MS: comparison to α-spectrometry

Sample #	Tissue	^{234}U, Bq				^{235}U, Bq				^{238}U, Bq				^{235}U/^{238}U, atom	
		α-spectrometry		ICP-MS		α-spectrometry		ICP-MS		α-spectrometry		ICP-MS		ICP-MS	
		value	± sd	value	± sd	value	± sd	value	± sd	value	± sd	value	± sd	value	± sd
269001	Lung			7.33E-03	3.80E-04			3.79E-04	6.8E-05			8.47E-03	5.0E-05		
269003	Liver			2.68E-03	6.40E-04			7.04E-05	6.1E-06			1.36E-03	5.0E-05		
269031	Femur, PE			1.56E-03	3.40E-04			7.11E-05	2.4E-06			1.52E-03	3.0E-05		
269052	Humerus, PE			4.10E-04	1.00E-04			1.41E-05	2.2E-07			3.00E-04	1.0E-05		
425003	Liver	2.63E-03	8.97E-04	4.50E-04	1.10E-04	3.89E-03	1.10E-03	1.92E-05	4.2E-07	1.50E-03	6.9E-04	4.30E-04	1.0E-05		
425004	Bladder Gall	1.10E-02	1.91E-03	2.60E-04	9.00E-05	4.52E-03	1.44E-03	1.15E-05	4.1E-07	1.41E-03	8.5E-04	2.70E-04	1.0E-05		
425007	Spleen	6.69E-03	1.90E-03	2.70E-04	6.00E-05	2.23E-03	1.29E-03	1.48E-05	3.7E-07	1.12E-03	8.3E-04	3.30E-04	1.0E-05		
425009	Kidney	6.44E-03	1.57E-03	1.03E-03	1.20E-04	4.02E-03	1.29E-03	5.06E-05	1.7E-06	1.34E-03	7.1E-04	1.15E-03	2.0E-05		
425040	Fibula, PE	1.73E-02	3.05E-03	8.70E-04	1.00E-04	1.57E-02	2.84E-03	4.54E-05	6.4E-07	6.16E-03	1.7E-03	9.90E-04	1.0E-05		
425057	Scapula Spine	4.50E-02	1.27E-02	5.87E-03	8.20E-04	3.41E-02	1.00E-02	2.83E-04	2.5E-06	6.59E-03	5.4E-03	6.24E-03	1.6E-04		
425082	Secrum	5.71E-02	6.13E-03	4.99E-03	2.30E-04	2.20E-02	4.05E-03	2.51E-04	1.1E-05	1.21E-02	2.8E-03	5.54E-03	1.5E-04		
425082	Sacrum	5.71E-02	6.13E-03	3.46E-03	5.20E-04	2.20E-02	4.05E-03	1.70E-04	1.9E-06	1.21E-02	2.8E-03	3.84E-03	3.0E-05		
720001	Lung			4.63E-02	4.27E-03			3.59E-03	6.5E-05			2.00E-01	5.6E-03		
720004	Liver			1.65E-03	3.90E-04			6.27E-05	4.7E-06			2.67E-03	2.7E-04		
1028001	R. Lung	1.41E+01	3.28E-01	1.42E+01	4.42E-01	4.75E-01	2.19E-02	4.68E-01	8.0E-03	4.88E-02	6.3E-03	3.68E-02	1.6E-03	6.1E-03	1.1E-04
1028007	Spleen	3.07E-02	3.15E-03	2.24E-02	6.30E-03	6.86E-04	5.45E-04	9.63E-04	1.6E-05	1.07E-03	6.2E-04	5.50E-04	1.0E-05	9.1E-04	8.0E-05
1028009	R. Kidney	1.21E-01	6.07E-03	1.09E-01	3.19E-03	3.66E-03	9.69E-04	3.62E-03	7.1E-05	6.60E-04	5.0E-04	1.14E-03	2.0E-05	1.5E-03	2.0E-04
1028027	Femur, MS	6.88E-01	2.66E-02	7.26E-01	1.19E-02	1.82E-02	3.65E-03	2.44E-02	1.8E-04	9.04E-03	2.5E-03	2.45E-03	4.0E-05	6.1E-03	8.0E-05
1028057	Ulna, DS	8.41E-02	4.24E-03	7.85E-02	3.91E-03	3.39E-03	7.81E-04	2.67E-03	9.8E-05	5.95E-05	2.9E-04	3.80E-04	1.0E-05	4.3E-03	8.0E-05
1028061	Humerus, DE	1.85E-01	4.86E-03	1.76E-01	5.44E-03	6.28E-03	7.15E-04	6.18E-03	1.5E-04	9.80E-04	3.0E-04	6.70E-04	1.0E-05	6.0E-03	3.0E-05







Conclusions

✓This study confirmed the suitability of ICPMS for the analysis of $^{239+240}$Pu, ^{240}Pu/^{239}Pu, ^{241}Am, and U isotopes in bones and soft tissues of exposed individuals.

✓The detection limits for SF-ICPMS are comparable with those of α-spectrometry, with time per single analysis significantly shorter.

✓The ability to measure the ^{240}Pu/^{239}Pu isotopic ratio and ^{241}Pu is an substantial advantage of ICPMS over α-spectrometry.

✓There is some residual bias in ICPMS/α-spectrometry measurements for Pu (+3.4%) and Am (-8.1%). This will be investigated.

✓Improvements in the ICPMS-based U measurements are expected using ^{233}U tracer.

References

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3) Varga et al., *Radiochim. Acta* 2007, 95, 81-87.
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