Determination of Pu and Am in digested bone and soft tissue samples by SF-ICP-MS: comparison with α-spectrometry

Sergei Tolmachev[1], Michael Ketterer[2], Dorothy Stuit[1] and Anthony James[1]

U.S. Transuranium & Uranium Registries, 1854 Terminal Drive, Richland, WA 99354
Northern Arizona University (NAU), Chemistry & Biochemistry Dept., Box 5698, Flagstaff, AZ 86011

Introduction

The U.S. Transuranium & Uranium Registries (USTUR) study the uptake, translocation and biokinetics of actinides (U, Pu and Am) in humans. Currently α-spectrometry is the primary method for analysis of Pu and Am in human autopsy tissues. However for environmental samples, inductively coupled plasma mass spectrometry (ICP-MS) is now a well established technique for ^{235,238}U and ^{239,240}Pu determination.[1,2] With recent ICP-MS 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 an analytical protocol to measure Pu and Am isotopes in human bone and soft tissue samples from occupationally exposed individuals by the ICP-MS technique, and compare the results with α-spectrometry.

Materials and Methods

Instrumentation

- Sector field ICP-MS @NAU

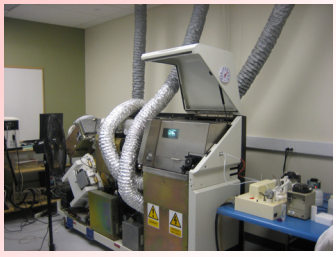

Table 1. SF-ICPMS Operating Conditions

Instrument	VG Axiom MC
Resolving power	R = 410, m/Δm 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
Sample uptake rate	500 μL min^{-1}
$U/^{238}U$	0.00002-0.00003 (measured for ^{238}U)
Mass bias factor	1.005-1.010 (measured using natural $^{238}U/^{235}U$)
Detection method	Electron multiplier, single collector, scanning
Pu mass spectral scans	20 points per m/z in range 236.2-242.8
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 ions monitored	
Plutonium analysis	^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu (spike)
Americium analysis	^{239}Pu, ^{240}Pu, ^{241}Am, ^{243}Am (spike)

- α-spectrometry @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

Fourteen digested samples (6 bones and 8 soft tissues from USTUR Cases 0269, 0425 and 0720) were analyzed for Pu/Am by ICP-MS at NAU. One sample was included as a blind-duplicate.

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.

Results and Discussion

Pu/Am separation procedures for ICP-MS

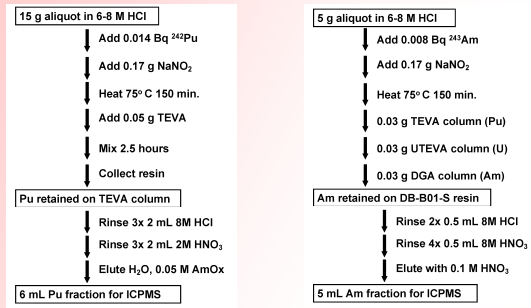

Fig. 1 Developed procedure for Pu/Am determination with SF-ICP-MS

Figures of merit for SF-ICP-MS

- Limit of detection (LOD, 6 σ): $^{239+240}$Pu – 0.1 mBq; ^{241}Pu – 30 mBq; ^{241}Am - 0.35 mBq
- Time per analysis: 10 min (including instrument wash)

Pu and Am analysis in human bones and soft tissues

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	Sacrum[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

Benchmark of SF-ICP-MS *vs* α-spectrometry

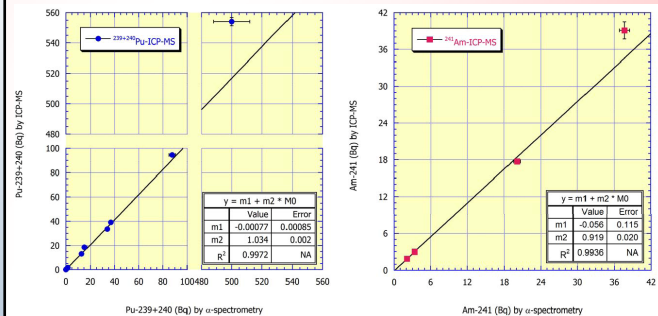

Fig. 2. Comparison of $^{239+240}$Pu measured by ICP-MS *vs* α-spectrometry

Fig. 3. Comparison of ^{241}Am measured by ICP-MS *vs* α-spectrometry

Conclusions

- ✓This study confirmed the suitability of ICP-MS for the analysis of $^{239+240}$Pu ^{240}Pu/^{239}Pu and ^{241}Am in bones and soft tissues of exposed individuals.
- ✓The LODs for SF-ICP-MS 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 ICP-MS over α-spectrometry.
- ✓There is some residual bias in ICP-MS/α-spectrometry measurements for Pu (+3.4%) and Am (-8.1%). This will be investigated.

References

1) Ketterer et al. *Env. Sci. Technol.* 34 (2000) 966 - 972.
2) Ketterer et al. *J. Anal. At. Spectrom.* 19 (2004) 241 - 245.
2) Varga et al. *Radiochim Acta.* 95 (2007) 81 - 87.
4) USTUR Radiochemistry Policies & Procedures Manual. Available at http://www.ustur.wsu.edu/PolicyProcedures/RadChemProcedures.html

Poster available at http://www.ustur.wsu.edu/Conferences/2007_RRMC/index.html