WASHINGTON STATE UNIVERSITY

World Class. Face to Face.

2008 USTUR Scientific Advisory Committee (SAC) Meeting
May 9-10, Red Lion Hotel, Pasco, WA

Radiochemistry Program at USTUR

Sergei Tolmachev, PhD

Lab Manager (Radiochemistry), USTUR

Research Associate Professor, College of Pharmacy, Washington State University

stolmachev@tricity.wsu.edu

"Learning from Plutonium and Uranium Workers"

Outline

USTUR Program from 1-D to 2-D world:

- **Inductively Coupled Plasma Mass Spectrometry (ICP-MS) *vs* α-spectrometry**

QA/QC by USTUR Radiochemistry Group

- **sub-contracted/alternative laboratories**
- **separation method development**

From 2-D to 3-D:

- **Laser Ablation (LA) ICP-MS**

2004 Recommendations

"The Radiochemistry Group should search for funds to purchase or lease an ICP-MS."

2007: ICP-MS Introduction to USTUR

- **Michael E. Ketterer, Professor**
  Northern Arizona University
  Department of Chemistry & Biochemistry
- **The sector field (high-resolution) ICP-MS at NAU was installed in December 2001**
- **It has been used to perform *ca*. 10,000 routine Pu determinations in environmental geological samples**

Touching 2-D: Samples

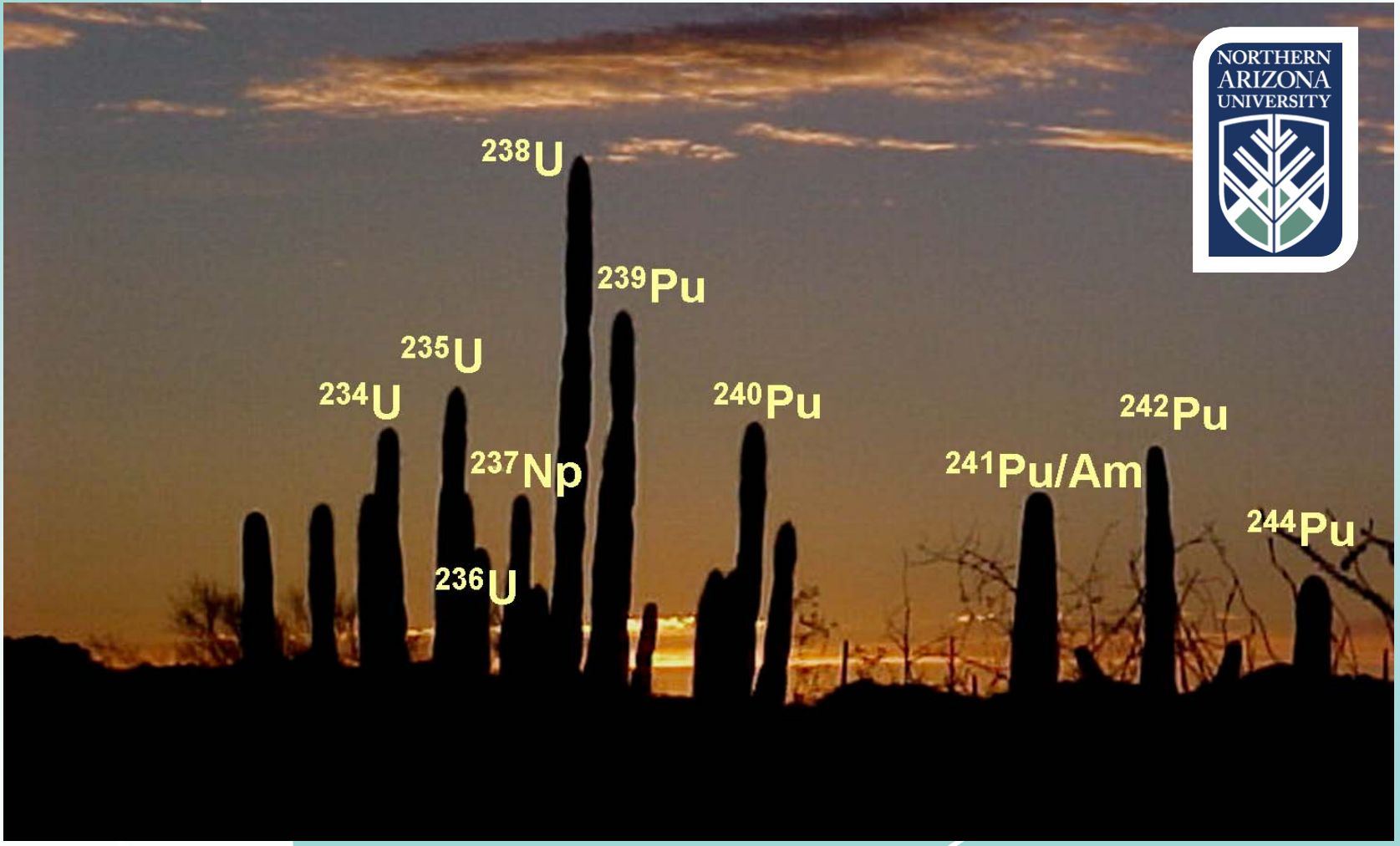
Case #	# of samples	USTUR/NRC		
		U	Pu	Am
0269	4	x	o	o
0425	8	o	o	o
0720	2	x	o	o
1028	6	o	x	x

Case # 0269, 0425, 0720 – Pu cases; #1028 – U case (HEU)

Case # 0425 (Pu) - analyzed for U (natural)

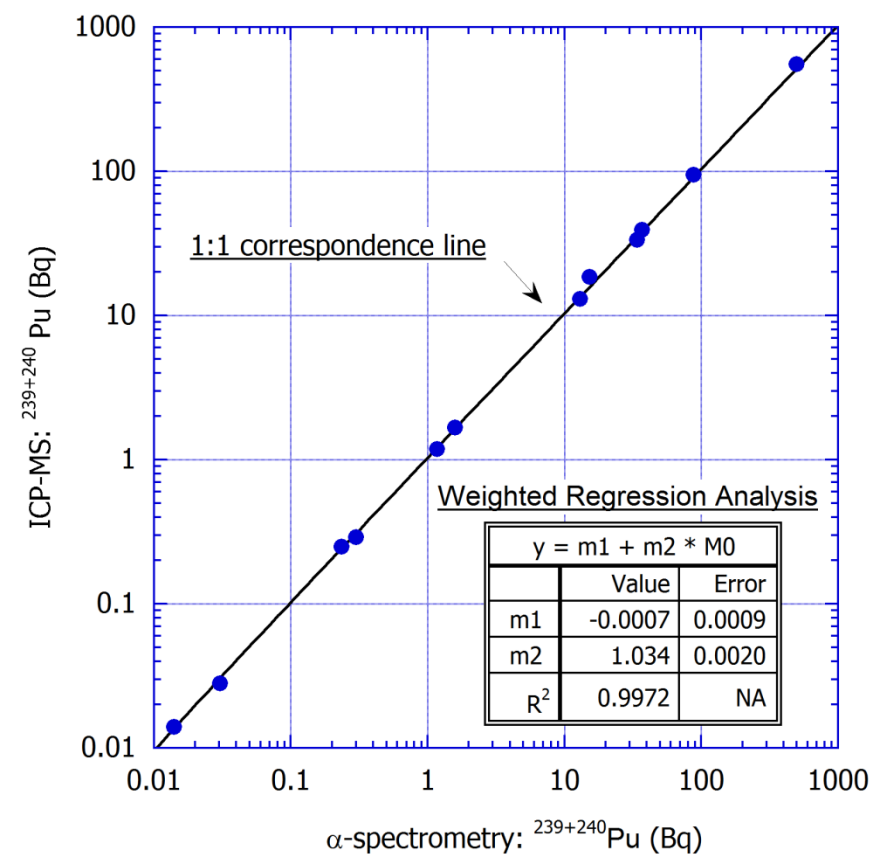
Total: 20 samples (9 bones and 11 soft tissues)

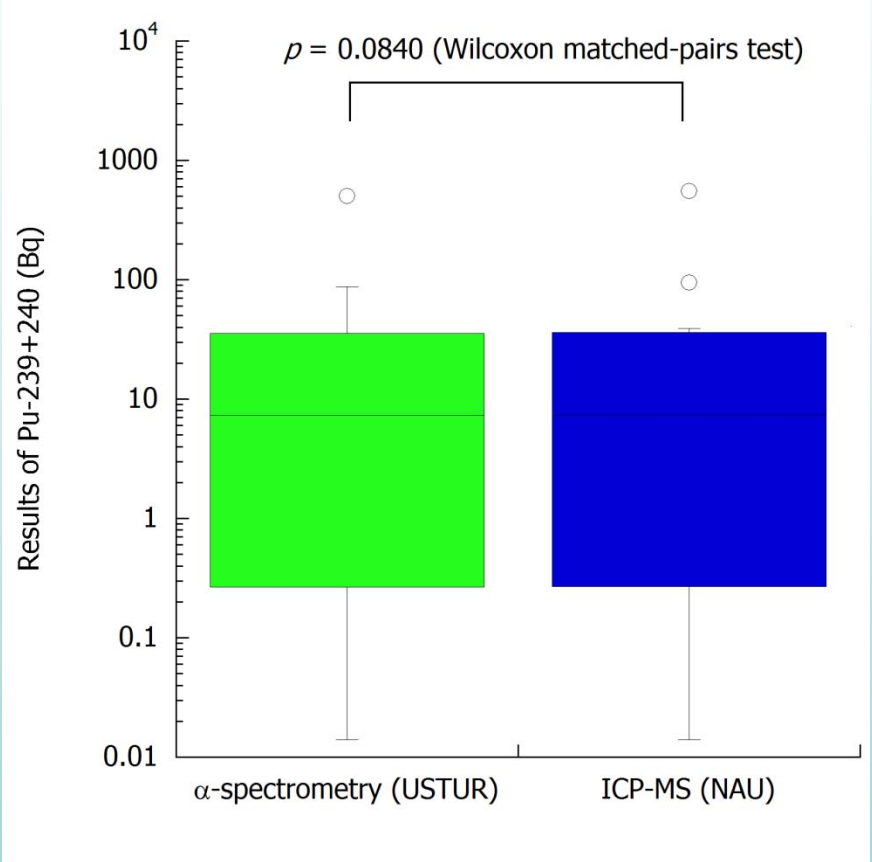
2007 Conclusion: ICP-MS – so far so good



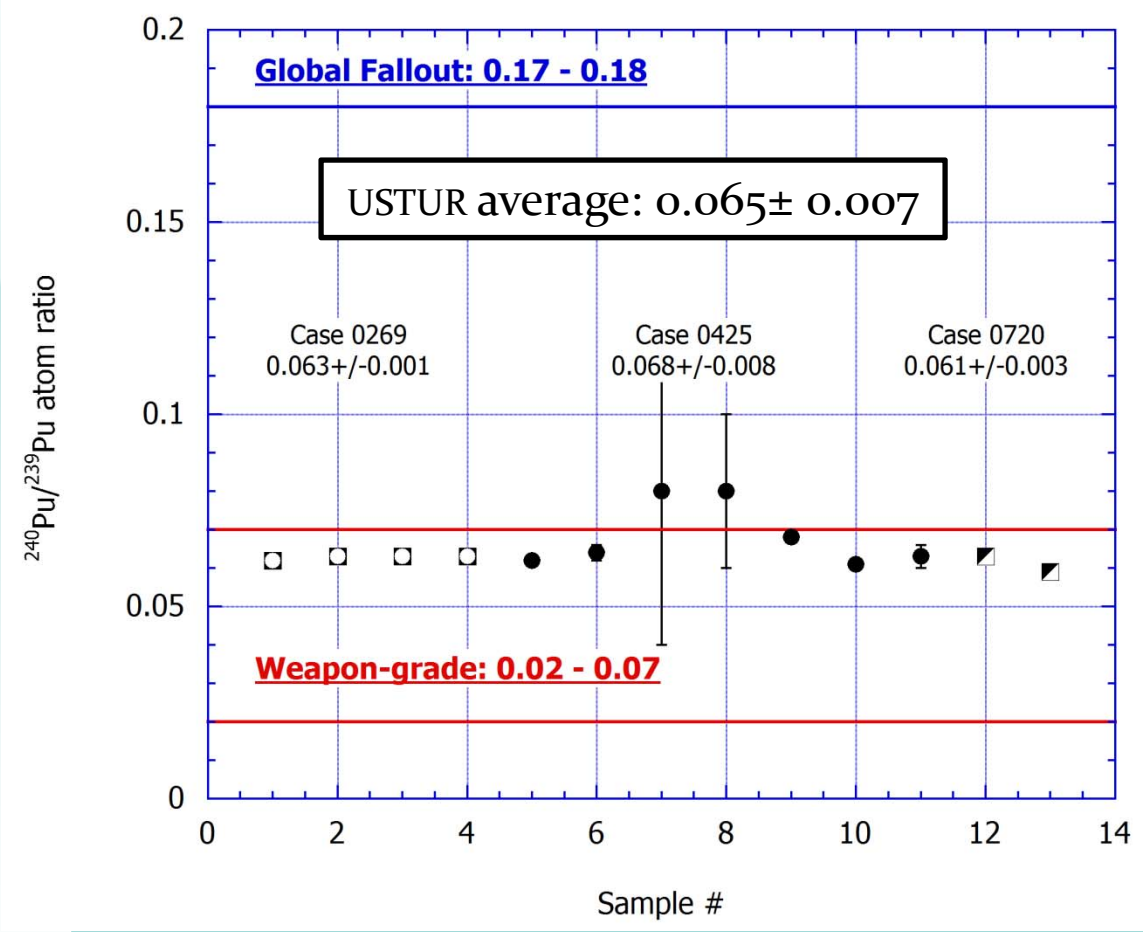
Approaching 2-D: ICP-MS *vs* α-spectrometry

$^{239+240}$Pu: ICP-MS *vs* α-spectrometry





ICP-MS: $^{240}Pu/^{239}Pu$ atom ratio



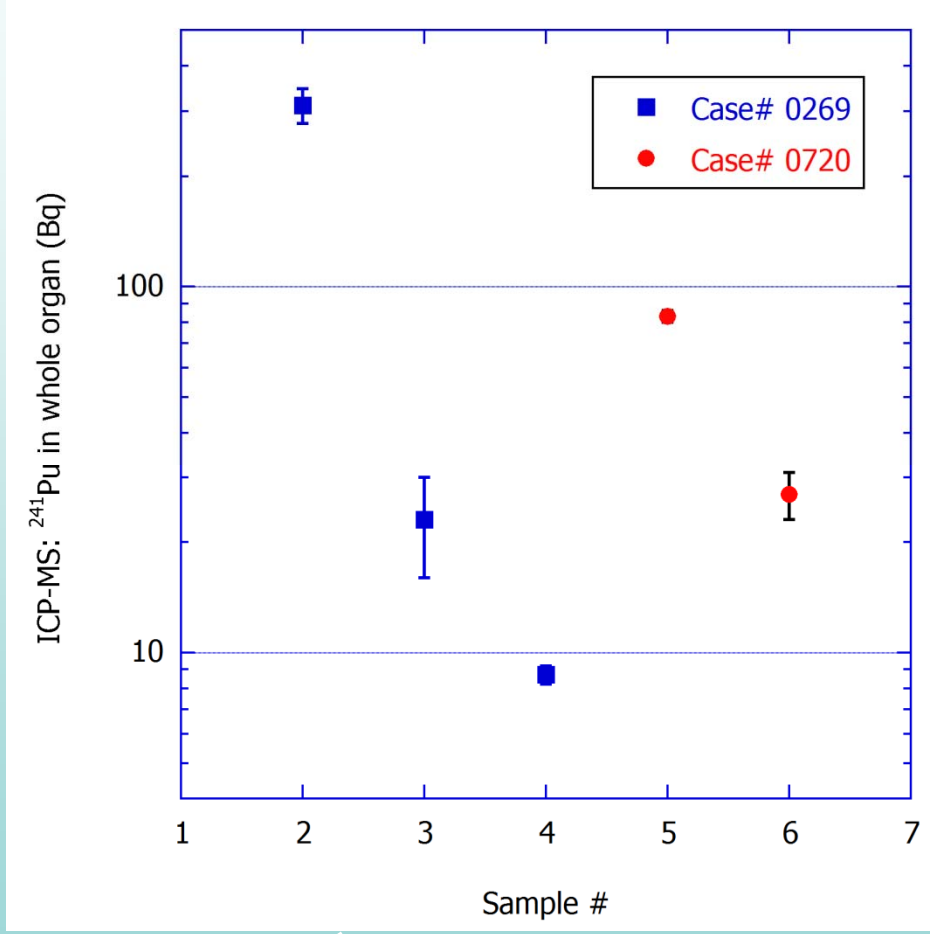
ICP-MS: Determination of ^{241}Pu

^{241}Pu

- $T_{1/2}$ = 14.1 yr, β-emmiter
- not detectable by α-spectrometry

^{241}Pu was detected in:

- 269.003 (liver)
- 269.031 (femur, PE)
- 269.052 (humerus, PE)
- 720.001 (lung)
- 720.004 (liver)



^{241}Am: ICP-MS *vs* α-spectrometry

^{241}Am

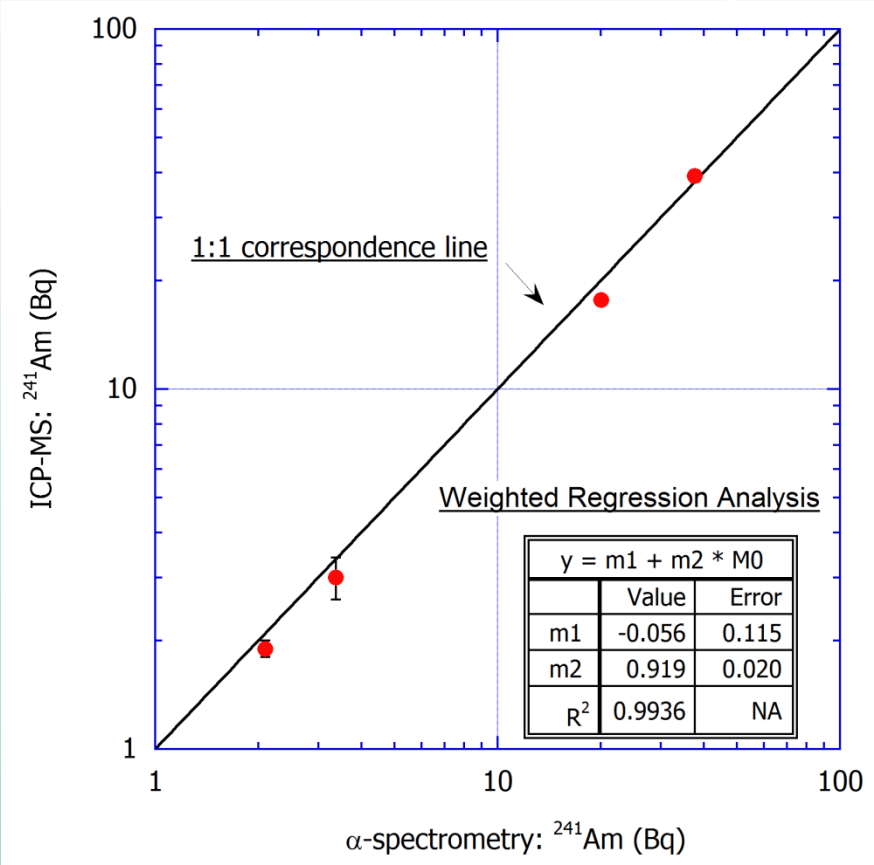
- $T_{1/2}$= 434.4 yr, α-emmiter
- never been measured by ICP-MS in human tissues

^{241}Am was detected in:

- 269.003 (liver)
- 269.052 (humerus, PE)
- 720.001 (lung)
- 720.004 (liver)

Wilcoxon matched-pairs test:

- *p* = 0.9263



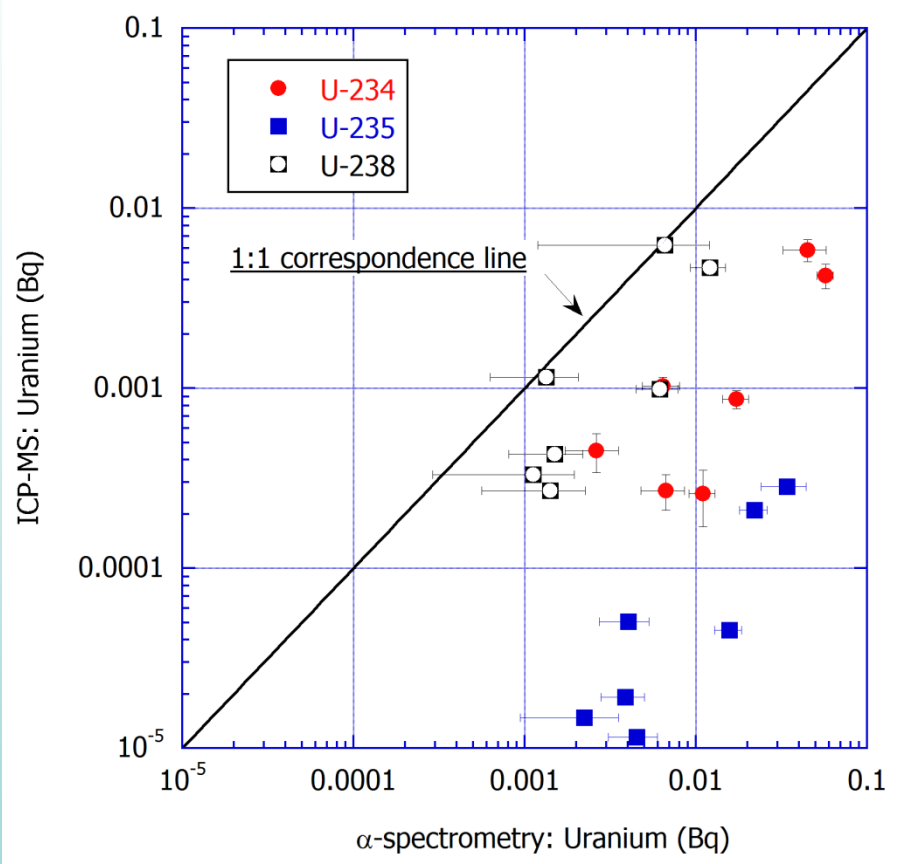
Uranium (nat.): ICP-MS *vs* α-spectrometry

Case #0425:

- **Pu case**
- **none-exposed to U**
- **natural U, low level**

Wilcoxon matched-pairs test:

- ***p* = 0.0078 (^{234}U)**
- ***p* = 0.0078 (^{235}U)**
- ***p* = 0.0078 (^{238}U)**



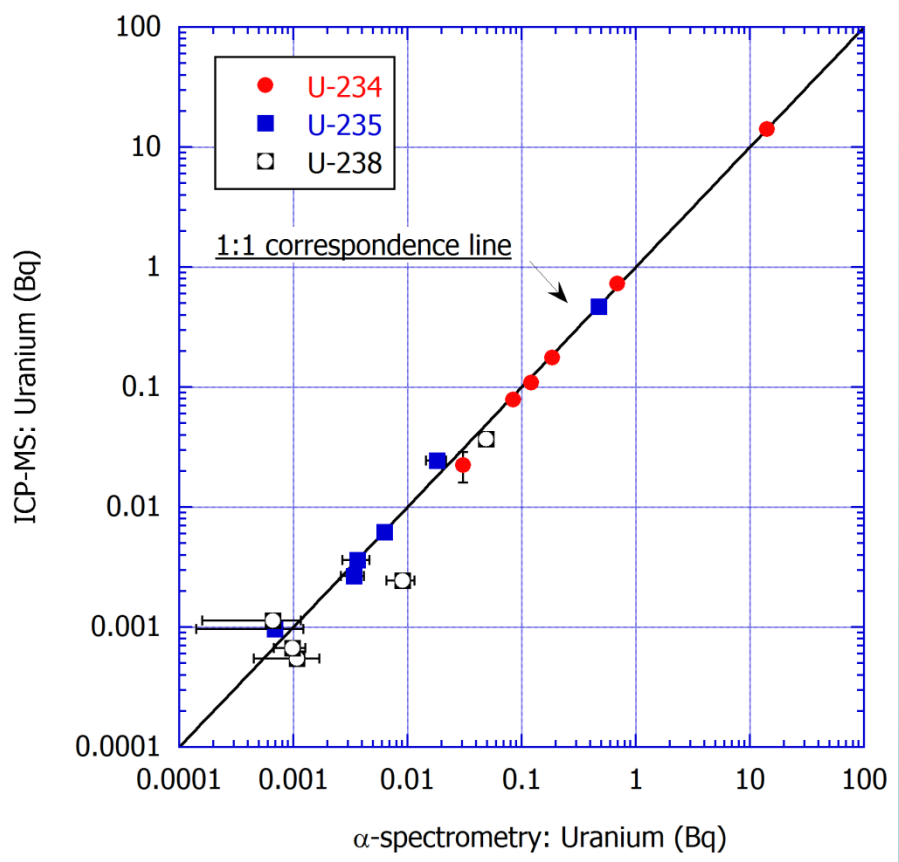
Uranium (ant.): ICP-MS *vs* α-spectrometry

Case #1028:

- **U case**
- **exposed to U**
- **enriched U, high level**

Wilcoxon matched-pairs test:

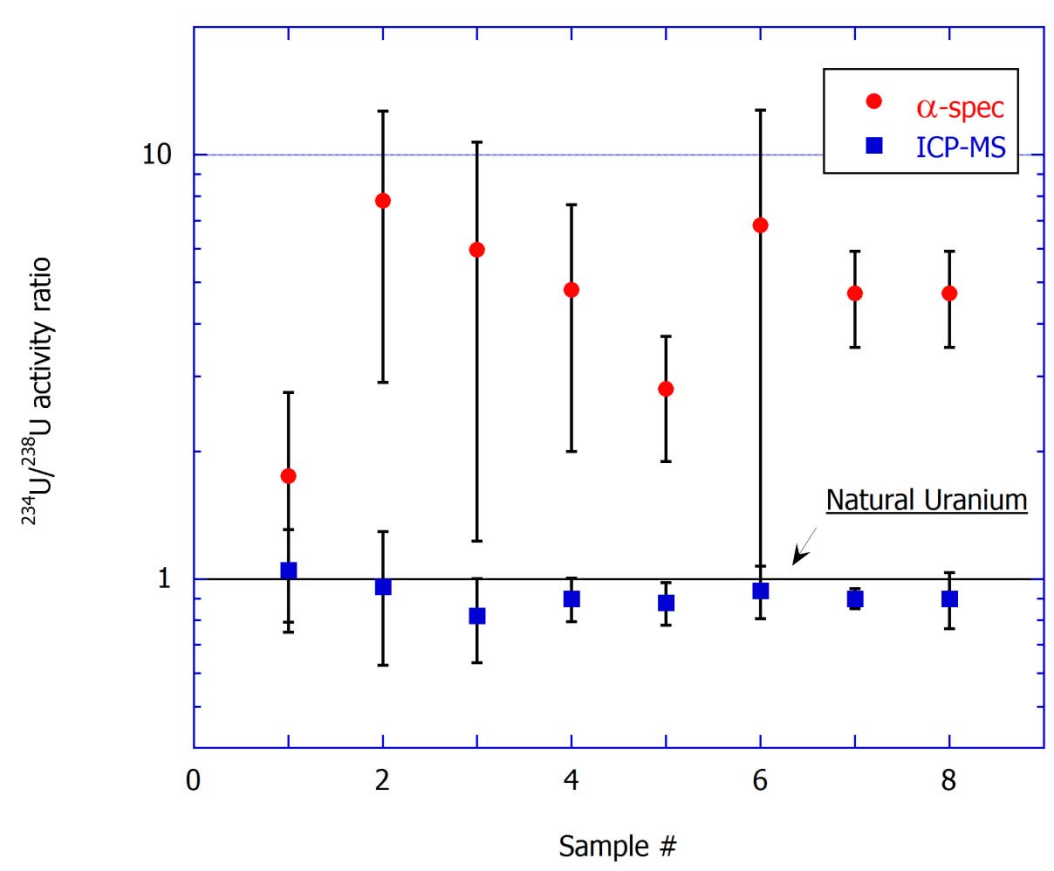
- ***p*** **= 0.9998 (** ^{234}**U)**
- ***p*** **= 0.6875 (** ^{235}**U)**
- ***p*** **= 0.3125 (** ^{238}**U)**



Uranium: Where is the truth?

At secular equilibrium in natural uranium activity ratio $^{234}U/^{238}U = 1.0$

$^{234}U/^{238}U$: ICP-MS *vs* α-spectrometry

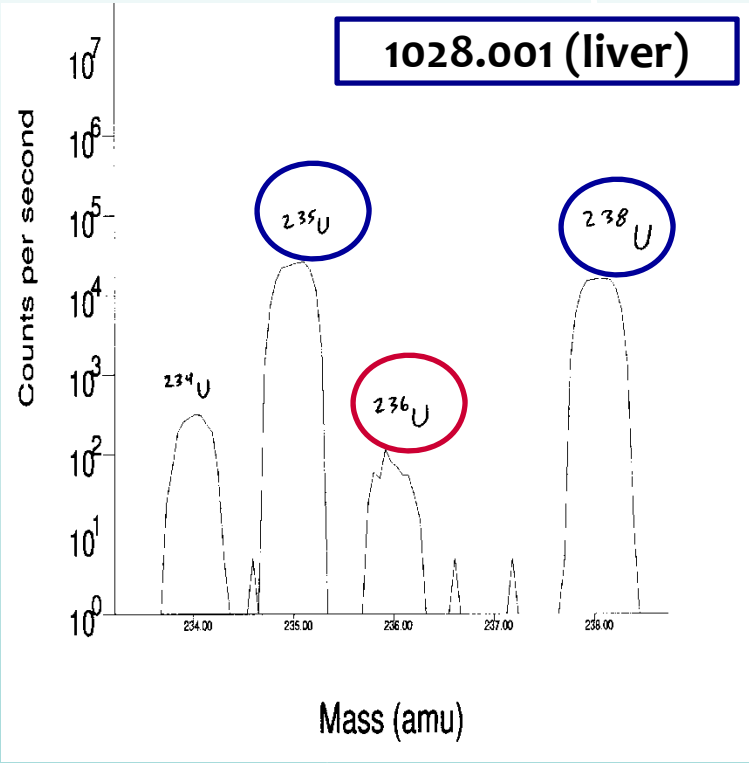


ICP-MS: Anthropogenic ^{236}U

Uranium (nat.) atom ratio:

- $^{235}U/^{238}U = 0.00725$
- $^{234}U/^{235}U = 0.00763$
- $^{236}U/^{238}U = 0.000$

Never been measured at USTUR



Benefits of ICP-MS

- Rapid analysis (10 min *vs* 42 hr for α-spectrometry)
- Low detection limits
- High precision (1-3 %)
- $^{240}Pu/^{239}Pu$ isotopic ratio measurement
- ^{236}U and ^{241}Pu detection

Benefits of α-spectrometry

- ^{238}Pu determination
- ^{241}Am can be measured at lower level
- Easy to operate

Conferences

53rd Annual Radiobioassay and Radiochemical Measurements Conference

Jackson Hole, WY, October 29th – November 2nd 2007

Winter Conference on Plasma Spectrochemistry

Temecula, CA, January 7th – 12th 2008

For abstract and poster download visit:
http://www.ustur.wsu.edu/Conferences/index.html

Conclusion

USTUR Program needs BOTH techniques!

Sub-award agreement G002285 to NAU

Welcome to 2-D!

QA/QC by USTUR
- Radiochemistry Group -

2007: USTUR's Subcontractor Lab

- Severn Trent Laboratories (STL) Richland, WA

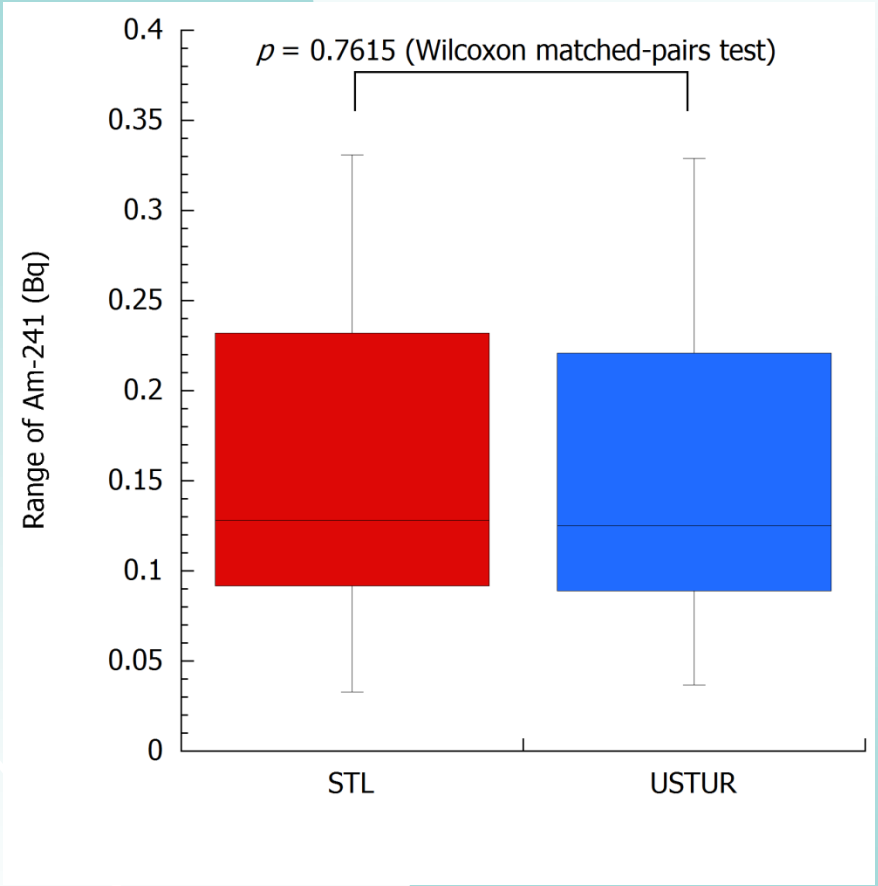
  TestAmerica from January 1, 2008

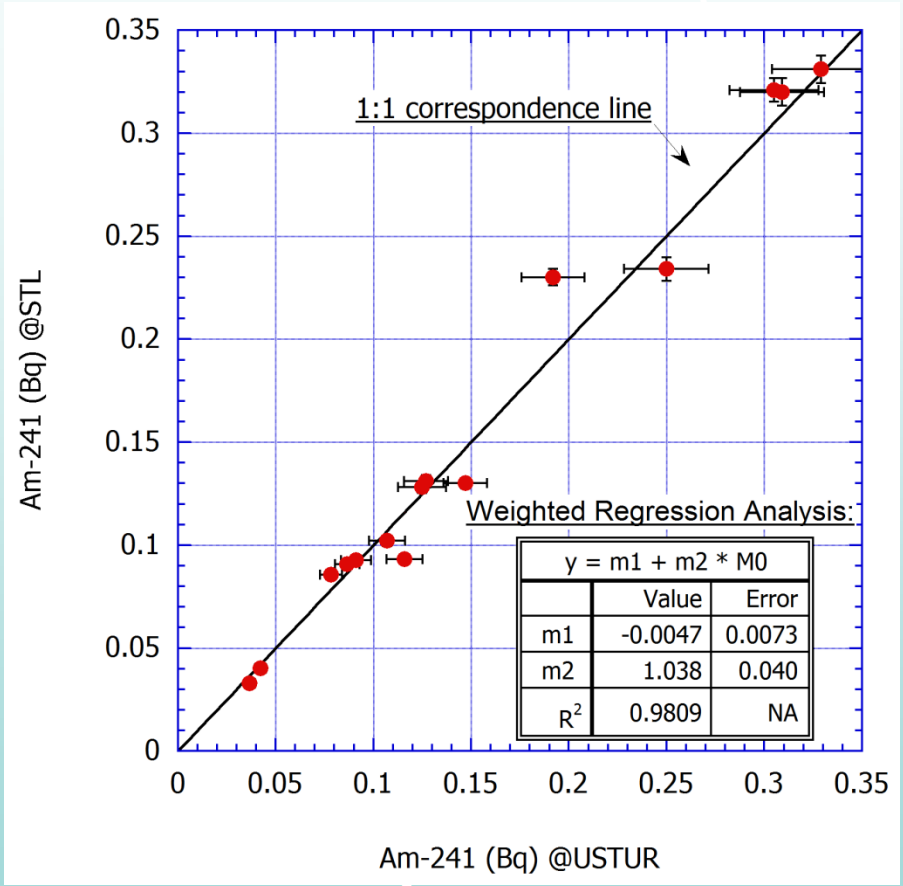
- Sub-contract #G002285 for "external radiochemistry services"

- Project Manager: Sheryl Adams/Erika Jordan

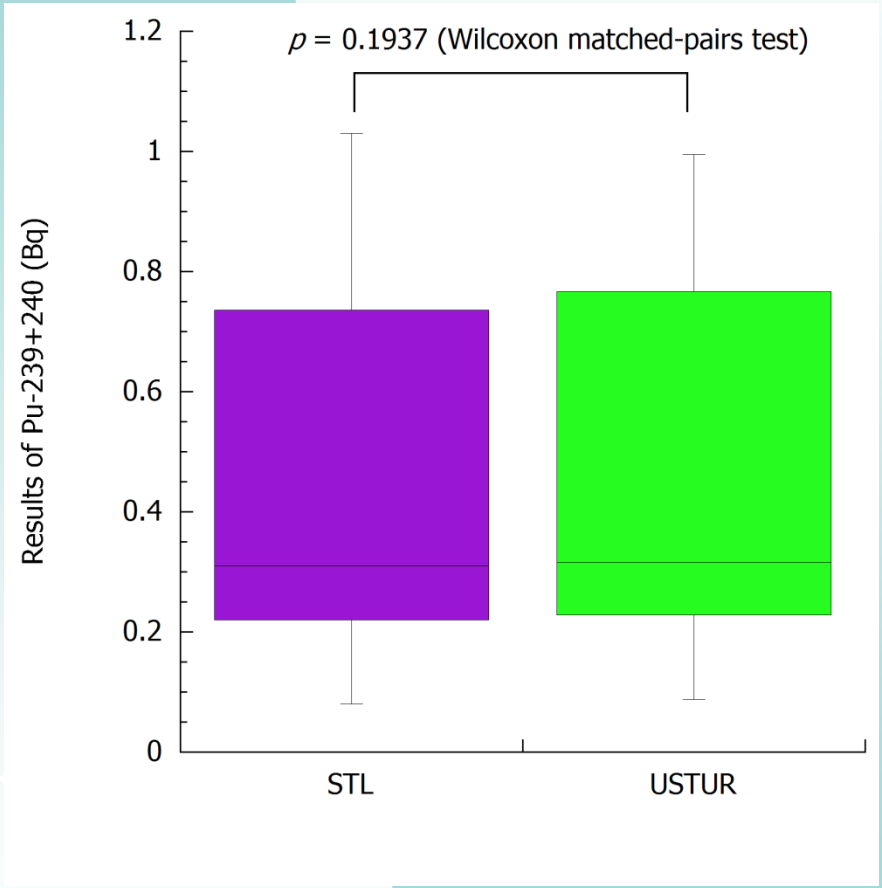
QA/QC : STL Results

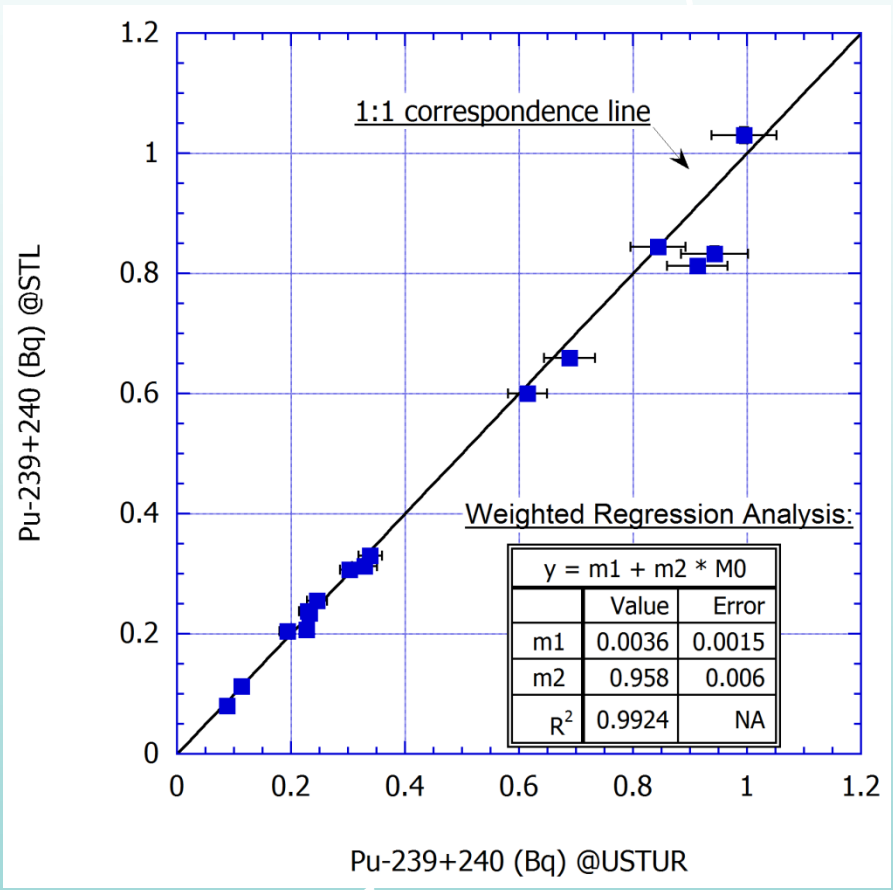
QA/QC Results: ^{241}Am





QA/QC Results: $^{239+240}Pu$





STL QA/QC: Conclusion

Data reported by STL for $^{239+240}$Pu and ^{241}Am are of acceptably high quality

USTUR External Radiochemistry Services: Alternative Laboratories

- GEL Laboratories, Charleston, SC
- Project Manager: Stan Morton/Stacy Calloway
- Samples: Case #0720 (7) and Case #0425 (2): analysis of digested samples for Pu and Am
- 32 planchets from Case #0720 (prepared at USTUR, counted at USTUR and STL)

GEL QA/QC: Conclusion

No statistically (0.05 level) significant differences in $^{239+240}$Pu and ^{241}Am results were observed between 3 labs: STL, GEL and USTUR/NRC/CLS

2007: Task for Radiochemistry Group

"As a part of USTUR QA/QC Program current methods should be revised"

Actinide Separation: Current Method

Journal of Radioanalytical and Nuclear Chemistry, Vol. 234, Nos 1–2 (1998) 183–187

Pre-concentration and separation of thorium, uranium, plutonium and americium in human soft tissues by extraction chromatography

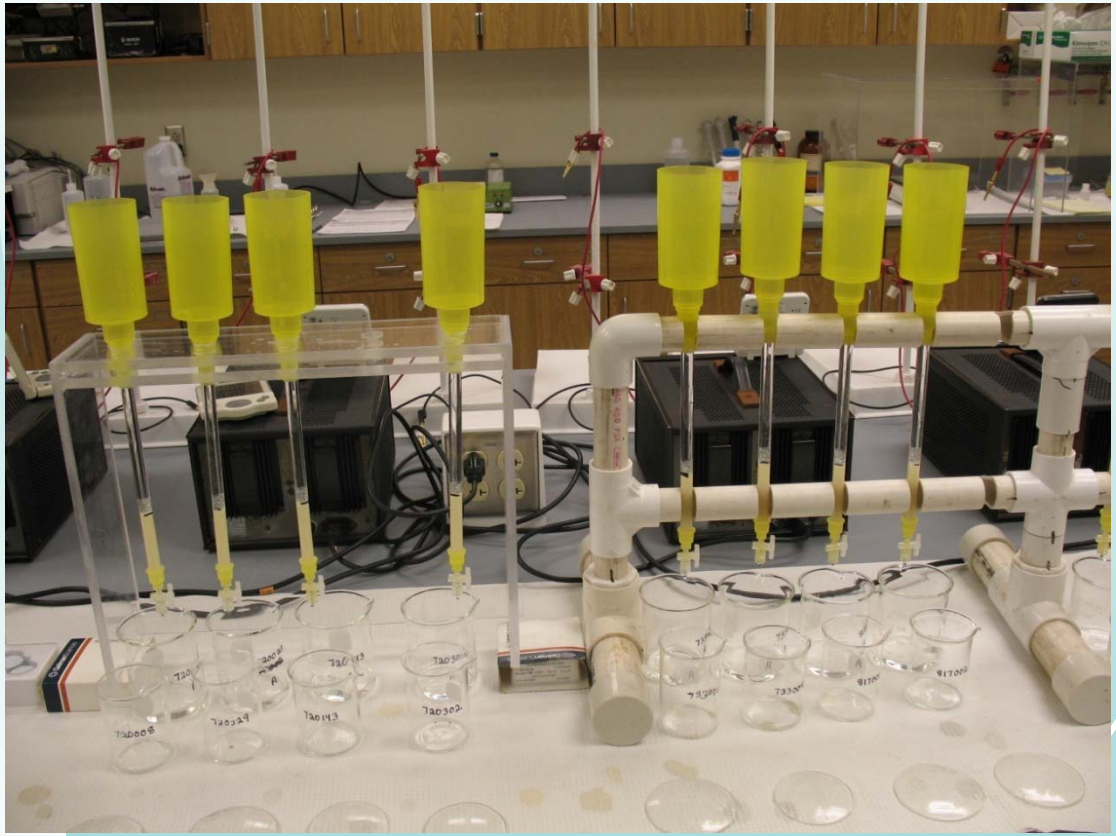
C. A. Moody,[1*+] S. E. Glover,[1,2] D. B. Stuit,[2] R. H. Filby[1,2*]

[1] *Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA*
[2] *Department of Chemistry, Washington State University, Pullman, WA 99163, USA*
[3] *United States Transuranium and Uranium Registries, Washington State University, Pullman, WA 99163, USA*

(Received February 5, 1998)

An extraction chromatographic method is described for the pre-concentration and separation of thorium, uranium, plutonium and americium in human soft tissues. Tissues such as lung and liver are oven dried at 120 °C, ashed at 450 °C and the ashed sample is alternately wet (HNO_3/H_2O_2) and dry ashed, and then dissolved in 8M HCl. Because of the complex matrix and large sample samples (up to 1500 g), the actinides were pre-concentrated from the tissue solution using the TRU™ resin (EIChroM) prior to elemental separation by extraction chromatography and determination of americium, plutonium, uranium and thorium by alpha spectrometry. The actinides were eluted from the preconcentration column and each actinide was individually eluted on TEVA™ and TRU™ resin columns in a tandem configuration. Actinide activities were then determined by alpha spectrometry after electrodeposition from a sulfate medium. The method was validated by analyzing human tissue samples previously analyzed for americium, plutonium, uranium and thorium in the United States Transuranium and Uranium Registries (USTUR). Two National Institute of Standards and Technology (NIST) Standard Reference Materials, SRM 4351-Human Lung and SRM 4352-Human Liver were also analyzed.

Actinide Separation: Current Experimental Setup



"Old-fashioned" ion-exchange column (USTUR-220)

Actinide Separation: Current Performance

- Combination of
  ion-exchange
- Sample loading
- Number of sam
- Acid waste proc
- Time for Am/Pu

USTUR Methods Update: Reasons

- Time/labor consuming
- High acid usage/waste production
- New techniques and products are available

Radiochemistry: New Horizons

(1) Separation technology improvement:

- extraction chromatography *vs* ion-exchange
- vacuum assisted separation *vs* gravity fed
- stack cartridges *vs* single column

(2) Development of new products:

- UTEVA® *vs* TEVA® resin for U
- DGA® *vs* TRU® resin for Am

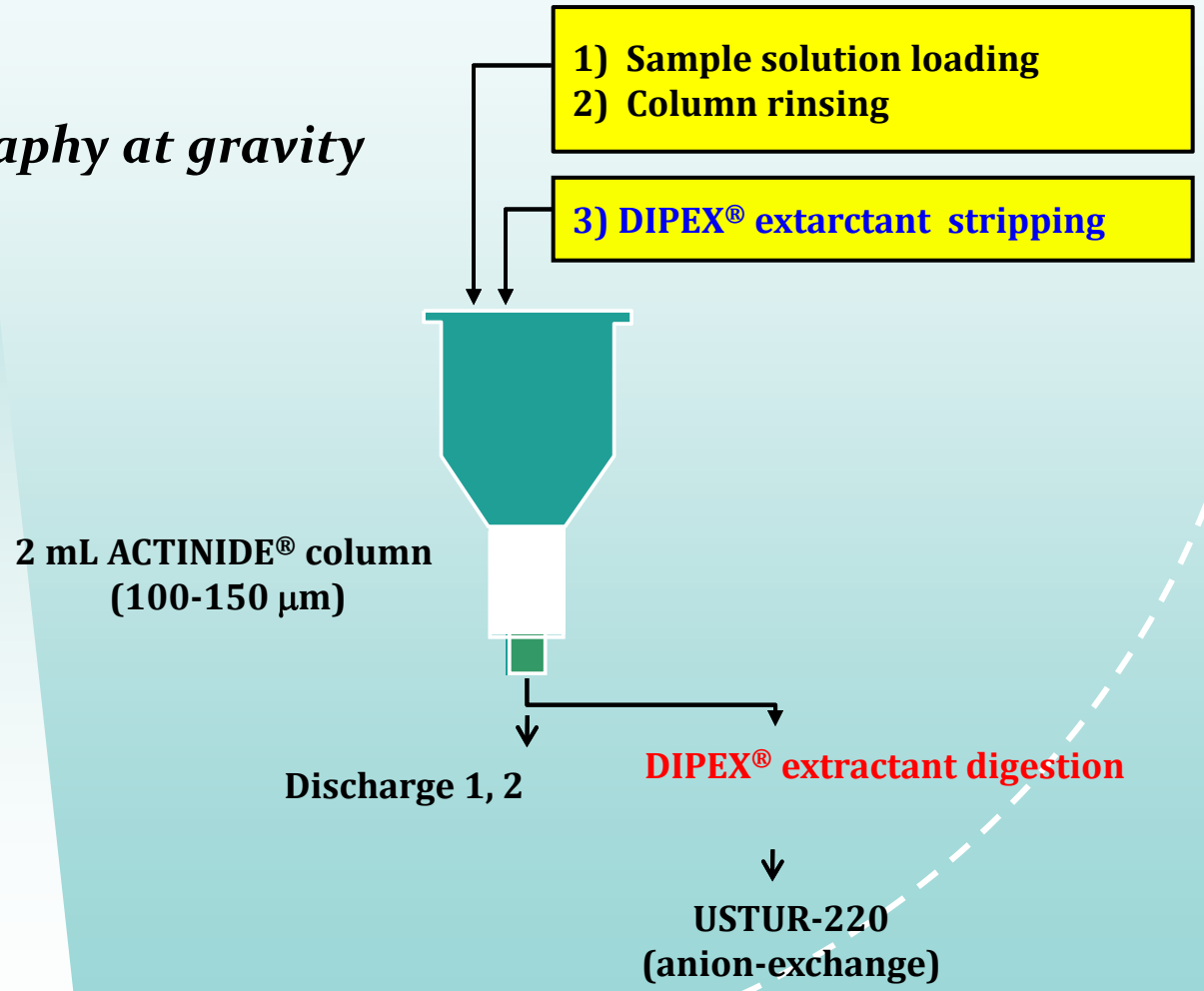
(3) New applications for "old" products:

- ACTINIDE® for Be separation (Be-Resin®) *vs* actinides

Phase I: USTUR Methods Modification

USTUR-150: Actinide Preconcentration

- *Extraction chromatography at gravity flow rate*



USTUR-150 Modification: Vacuum Assisted Separation

- Eichrom's Vacuum Box System (VBS-24)
- Be-Resin® cartridge *vs* ACTINDE® column (DIPEX® extractant)

Phase I: Results

- **Three (3) hr time saving on sample solution loading, column rinsing and DIPEX® striping**

- **DIPEX® digestion: 1+ days**

" We never promoted Qu's method" (USTUR-150)

Lawrence E. Jassin
Director of Sales and Marketing
Eichrom Technologies, Inc.
-2008, Private conversation with SYT-

Phase I: Conclusion

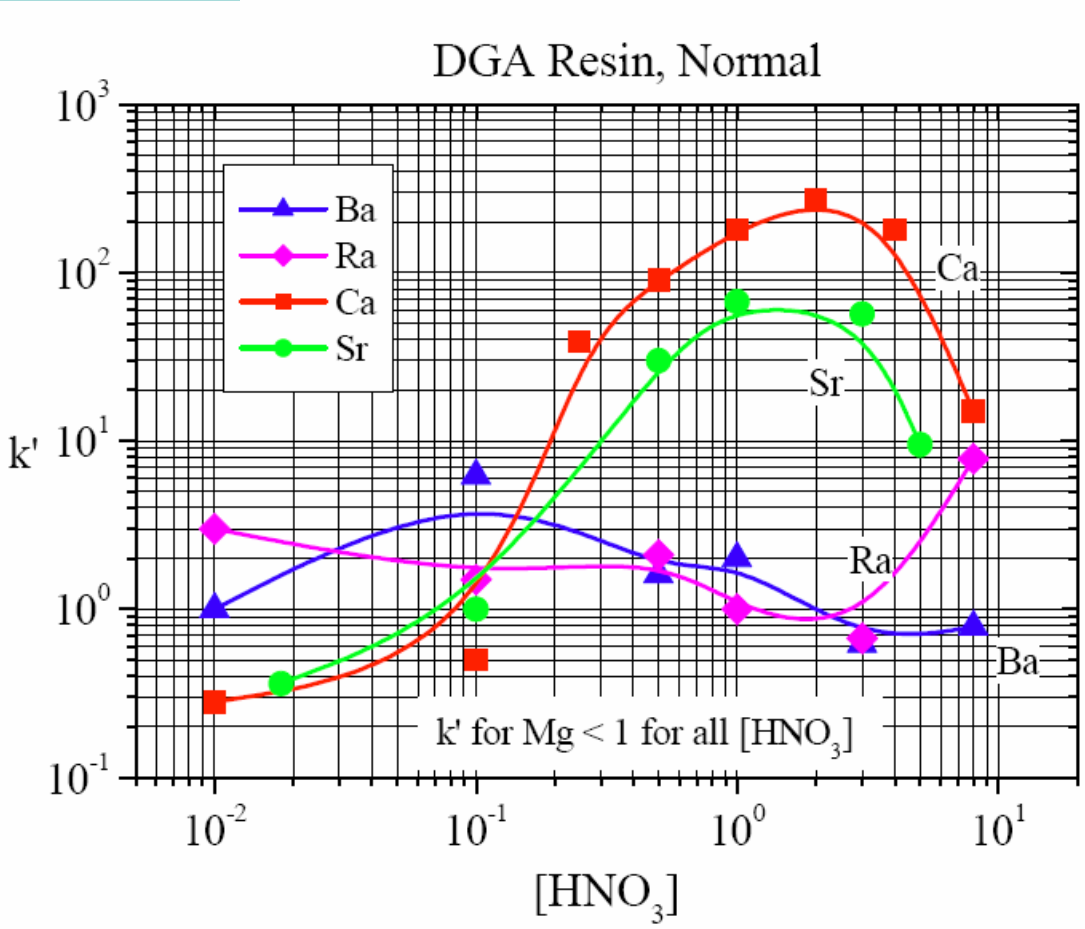
Current USTUR separation methods should be replaced - not modified!

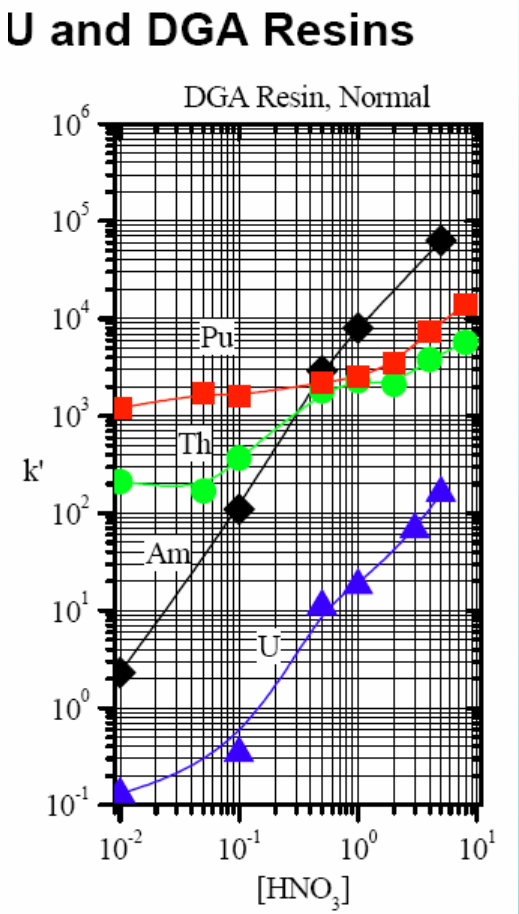
Phase II: New Method Development

Phase II: Information

- Lab experiences (USTUR, STL, GEL, NAU)
- Literature search
- Attending conferences (RRMC 2007)
- Contacts with vendors (Eichrom)

DGA® : New Product for Am Separation





Actinides in Animal Tissues

DOI: 10.1007/s10967-007-7120-4

Journal of Radioanalytical and Nuclear Chemistry, Vol. 275, No.3 (2008) 605–612

Rapid column extraction method for actinides and strontium in fish and other animal tissue samples

S. L. Maxwell III,* D. M. Faison

Washington Savannah River Company, Building 735-B, Aiken, SC 29808, USA

(Received June 12, 2007)

The analysis of actinides and radiostrontium in animal tissue samples is very important for environmental monitoring. There is a need to measure actinide isotopes and strontium with very low detection limits in animal tissue samples, including fish, deer, hogs, beef and shellfish. A new, rapid separation method has been developed that allows the measurement of plutonium, neptunium, uranium, americium, curium and strontium isotopes in large animal tissue samples (100–200 g) with high chemical recoveries and effective removal of matrix interferences. This method uses stacked TEVA Resin®, TRU Resin® and DGA Resin® cartridges from Eichrom Technologies (Darien, IL, USA) that allows the rapid separation of plutonium (Pu), neptunium (Np), uranium (U), americium (Am), and curium (Cm) using a single multi-stage column combined with alpha-spectrometry. Strontium is collected on Sr Resin® from Eichrom Technologies (Darien, IL, USA). After acid digestion and furnace heating of the animal tissue samples, the actinides and $^{89/90}$Sr are separated using column extraction chromatography. This method has been shown to be effective over a wide range of animal tissue matrices. Vacuum box cartridge technology with rapid flow rates is used to minimize sample preparation time.

Who Are You Mr. Maxwell?

- **Sherrod L. Maxwell**

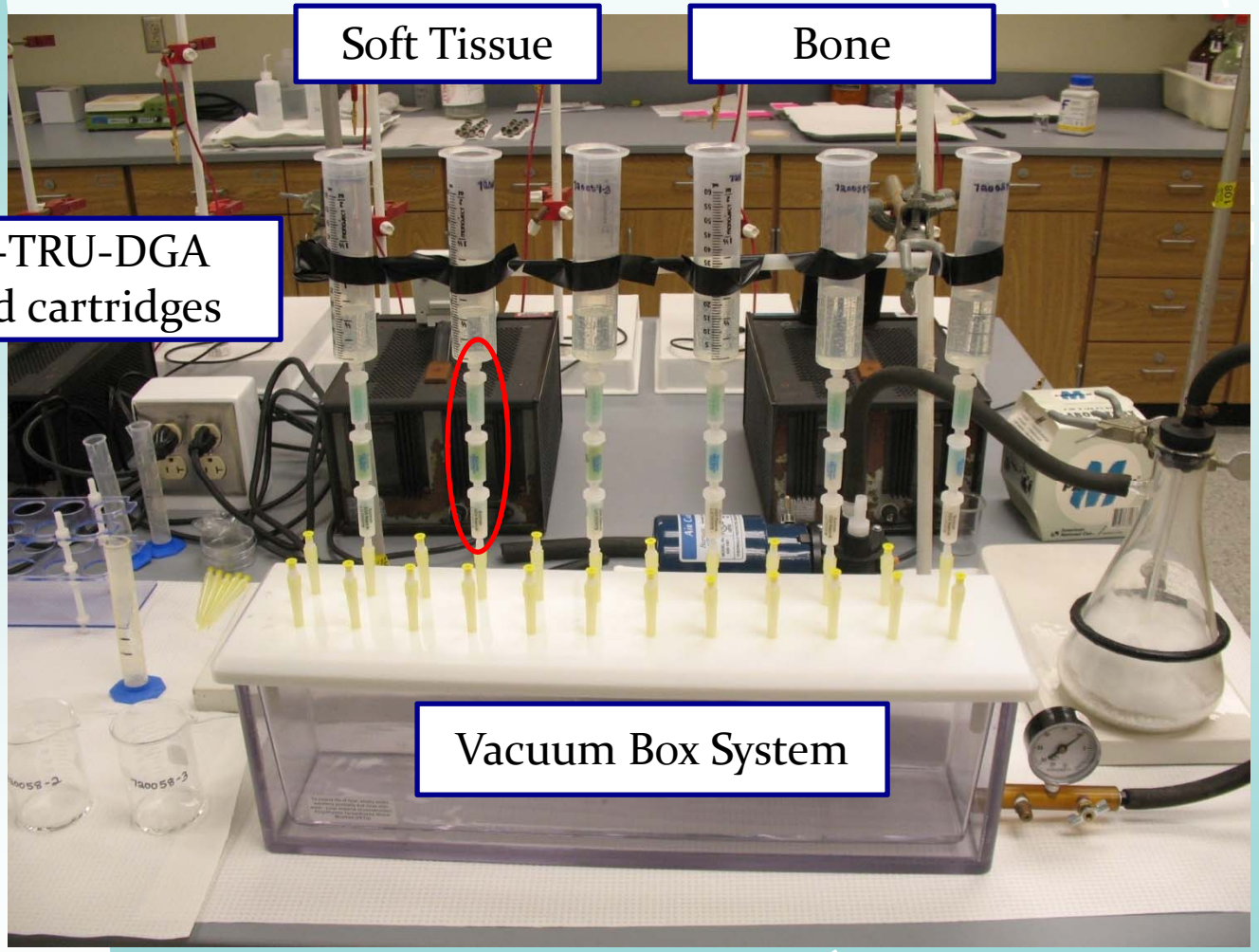
  Senior Fellow Scientist
  DOE Environmental Bioassay Lab
  Savannah River Site (Aiken, SC)

- **He specializes in rapid extraction chromatography techniques and the development of new radiochemistry methods for a wide range of environmental and biological samples**

Phase II: Samples/Method

- "Benchmark" Case #0720:
  STL, GEL and USTUR/NRC/CLS
- Soft Tissue: Liver
- Bone: Humerus (proximal end)
- Vacuum assisted extraction chromatography with TEVA®-TRU®-DGA® resins
- Analysis in triplicate

Actinide Separation: New Experimental Setup



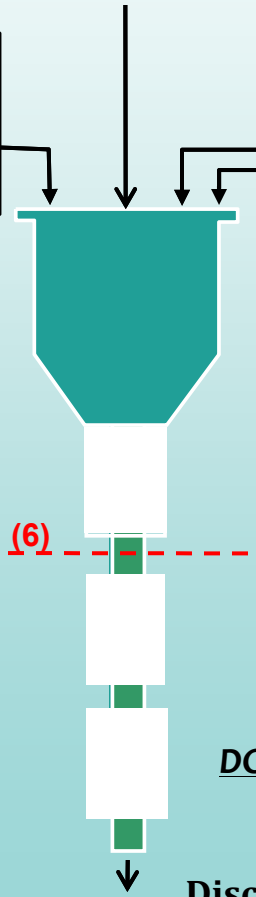
Actinide Column Separation (I)

1) Sample in 12 mL warm 6M $HN0_3$ and 12mL 2M $Al(NO_3)_3$
2) Add 0.75 mL 1.5M Sulfamic Acid + 3 mL 1.5M Ascorbic Acid
3) Add 2.5 mL 3.5 M Sodium Nitrite
4) Sample loading (1 drop sec^{-1})

5) Beaker rinse: 5 mL 6M$HN0_3$
6) Separate cartridges
7) TEVA rinse: 15 mL 3M HNO_3

8) Rinse: 25 mL 9M HCl (Th)

9) Pu Elution: 30 mL
0.1M HCl - 0.05M HF - 0.04M rongalite



DGA resin not affected by Fe^{3+}

Electrodeposition
(USTUR-510)

Alpha spectrometry
(USTUR-600)

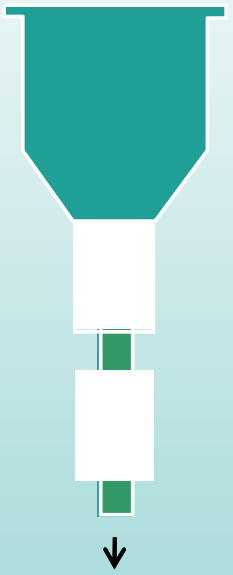
Actinide Column Separation (II)

TRU – DGA cartridges from Step 6

10) Am to DGA: 15 mL 4M HCl
11) Separate cartridges

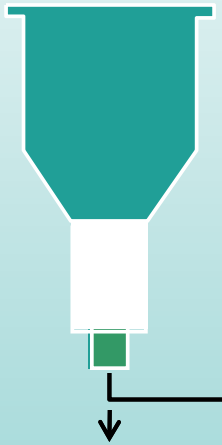
12) Rinse: 3 mL 1M HNO_3
13) Rinse: 10 mL 0.1M HNO_3 (U)

14) Am Elution: 10 mL 0.25M HCl



2 mL TRU-Resin
(50-100 µm)

2 mL DGA-Resin
(50-100 µm)



Discharge 10

Discharge 12,13

Electrodeposition
(USTUR-510)

Alpha spectrometry
(USTUR-600)

New Actinide Separation: Performance

- Sequential vacuum-assisted extraction chromatography
- Sample loading
- Number of sam
- Acid waste pro
- Time for Am/P

Comparison of Analytical Performance: $^{239+240}$Pu Determination in Human Bone Samples

Lab	Tissue	Ash weight, g	$^{239+240}$Pu				Recovery ^{242}Pu, %	Det, %
			Bq	SD	RSD	cnts		
STL/TA	Humerus (PE)	3.03	1.03e00	1.32e-2	1.3%	n/a	79.0	n/a
USTUR/NRC	Humerus (PE)	0.89	9.95e-1	3.36e-2	3.4%	883	54.2*	24.4
USTUR/CLS	Humerus (PE)	2.91	1.01e00	1.81e-2	1.8%	3094	63.4	24.8
USTUR/CLS	Humerus (PE)	2.91	1.01e00	1.95e-2	1.9%	2674	57.2	23.7
USTUR/CLS	Humerus (PE)	2.91	1.02e00	1.72e-2	1.7%	3501	71.6	24.6

Average (Bq, n=3, ±SD)	1.01 e-01±5.51e-3
Accuracy (%)	1.3
Precision (RSD, %)	0.5
Recovery (AVE±SD, %)	64.1±7.2

* - USTUR/NRC average ^{242}Pu recovery is 80%

Comparison of Analytical Performance: ^{241}Am Determination in Human Bone Samples

Lab	Tissue	Ash weight, g	^{241}Am				Recovery ^{243}Am, %	Det eff, %
			Bq	SD	RSD	cnts		
STL	Humerus (PE)	3.03	3.20E-01	6.62E-03	2.1%	2356	104.0%	32.3%
USTUR/NRC	Humerus (PE)	0.89	3.11E-01	1.78E-02	5.7%	311	60.5%*	25.2%
USTUR/CLS	Humerus (PE)	2.91	3.10E-01	8.64E-03	2.8%	1295	87.1%	24.7%
USTUR/CLS	Humerus (PE)	2.91	3.12E-01	8.43E-03	2.7%	1374	91.4%	25.0%
USTUR/CLS	Humerus (PE)	2.91	3.14E-01	8.56E-03	2.7%	1345	89.9%	24.7%

Average (Bq, n=3, ±SD)	3.12 e-01±1.56e-3
Accuracy (%)	0.4
Precision (RSD, %)	0.5
Recovery (AVE±SD, %)	89.5±2.4

* - USTUR/NRC average ^{243}Am recovery is 80%

Comparison of Analytical Performance: Soft Tissue *vs* Bone Matrices

Lab	Tissue	Aliquot, g	$^{239+240}$Pu		^{241}Am		Recovery, %	
			Bq	SD	Bq	SD	^{242}Pu	^{243}Am
STL	Humerus	68	1.03E+00	1.32E-02	3.20E-01	6.62E-03	79.0%	104.0%
USTUR/NRC	Humerus	20	9.95E-01	3.36E-02	3.11E-01	1.78E-02	54.2%	60.5%
USTUR/CLS	Humerus	65	1.01E+00	1.81E-02	3.10E-01	8.64E-03	63.4%	87.1%
USTUR/CLS	Humerus	65	1.01E+00	1.95E-02	3.12E-01	8.43E-03	57.2%	91.4%
USTUR/CLS	Humerus	65	1.02E+00	1.72E-02	3.14E-01	8.56E-03	71.6%	89.9%
GEL	Liver (R)	12	2.94E+01	4.25E-01	2.00E+00	3.50E-02	105.0%	90.0%
USTUR/NRC	Liver (R)	10	3.40E+01	1.00E-01	2.09E+00	5.11E-02	89.2%	88.5%
USTUR/CLS	Liver (R)	10	3.40E+01	2.40E-01	2.22E+00	6.39E-02	74.3%	65.9%
USTUR/CLS	Liver (R)	10	3.31E+01	2.92E-01	2.15E+00	5.82E-02	48.3%	78.7%
USTUR/CLS	Liver (R)	10	3.35E+01	3.10E-01	2.12E+00	6.50E-02	43.0%	60.8%

Results

- Excellent precision and accuracy (<3%)
- High (90%) recovery of ^{243}Am for bone samples
- Moderate (70%) recovery of ^{243}Am for soft tissue samples
- Low (60%) recovery of ^{242}Pu

Further Method Development

Separate batches for soft tissue and bone samples:

- **Soft tissues: liver, kidney, spleen**
- **Bones: humerus (proximal end)**
  humerus (distal shaft)
  humerus (distal end)

Samples (digested tissues) were from Case #0720

Sample analyses were performed in triplicate

Soft Tissue *vs* Bone Matrices: Results

Sample	Mixed batch		Soft tissues batch		Bones batch	
	^{242}Pu,%	^{243}Am,%	^{242}Pu,%	^{243}Am,%	^{242}Pu,%	^{243}Am,%
Liver	55.2±16.7	68.5±9.2	64.4±13.1	95.7±0.6		
Kidney			55.7±3.70	90.5±3.2		
Spleen			61.8±11.4	91.8±1.7		
Humerus (PE)	64.1±7.2	89.5±2.2			63.2±1.2	93.1±1.9
Humerus (DS)					54.6±8.6	86.2±5.2
Humerus (DE)					61.3±8.9	84.1±5.5
Blank			62.5	91.6	52.3	95.4
LCS			66.5	93.8	58.9	99.2

Uncertainty is given as SD (n=3)

Soft Tissue *vs* Bone Matrices: Conclusions

- High (90%) recovery of ^{243}Am was achieved for soft tissue and bone samples:
  - for future analyses - bones and soft tissues should be separated as individual sample batches
- Low (60%) recovery of ^{242}Pu was independent on sample matrix:
  - should be investigated

Low Plutonium: Possible Reasons

- "Chemistry":
  - incomplete Pu uptake during sample loading
  - incomplete Pu elution from TRU® resin
- Electrodeposition (USTUR-510)

Low Plutonium: Investigation

- **"Chemistry":**
  - **Pu (IV) valence adjustment**
  - **sample loading flow rate adjustment**
  - **0.1M HCl-0.05M HF-0.04M rongalite (SRS)**

    vs

    0.1M HCl-0.05M HF -0.1M NH_4I (USTUR, SRS, STL)
- **Electrodeposition: post-chemistry *vs* direct spike**

Experiment: Chemistry *vs* Direct Spike

- **Chemistry**
  - 25 ml *3M HNO_3 – 1M $Al(NO_3)_3$* + 5 dpm ^{242}Pu [Pu(IV) adj]
  - Sample loading on TRU® resin
  - Elution with 20 or 30 mL of *0.1M HCl-0.05M HF-0.04M rongalite* and 30 mL of *0.1M HCl-0.05M HF -0.1M NH_4I*
  - Electrodeposition (USTUR-510) → ^{242}Pu α-counting
- **Direct Spike**
  - 20 or 30 mL of *0.1M HCl-0.05M HF-0.04M rongalite* and 30 mL of *0.1M HCl-0.05M HF -0.1M NH_4I* + 5 dpm ^{242}Pu
  - Electrodeposition (USTUR-510) → ^{242}Pu α-counting

^{242}Pu Recovery: Results

0.1M HCl-0.05M HF-0.04M rongalite				0.1M HCl-0.05M HF - 0.1M NH_4I	
20 ml		30 ml		30 ml	
DIRECT	CHEM	DIRECT	CHEM	DIRECT	CHEM
58.2	59.4	68.0	66.7	65.3	64.1
63.8	70.6	67.1	*47.45**	71.9	71.7
72.8	54.3	68.2	60.8	64.4	65.6
64.9±7.4	61.5±8.3	67.8±0.6	63.7±4.2	67.2±4.1	67.1±4.0
	94.6%		94.0%		99.9%

(*) - excluded value

Average (%) value ±SD is given in blue

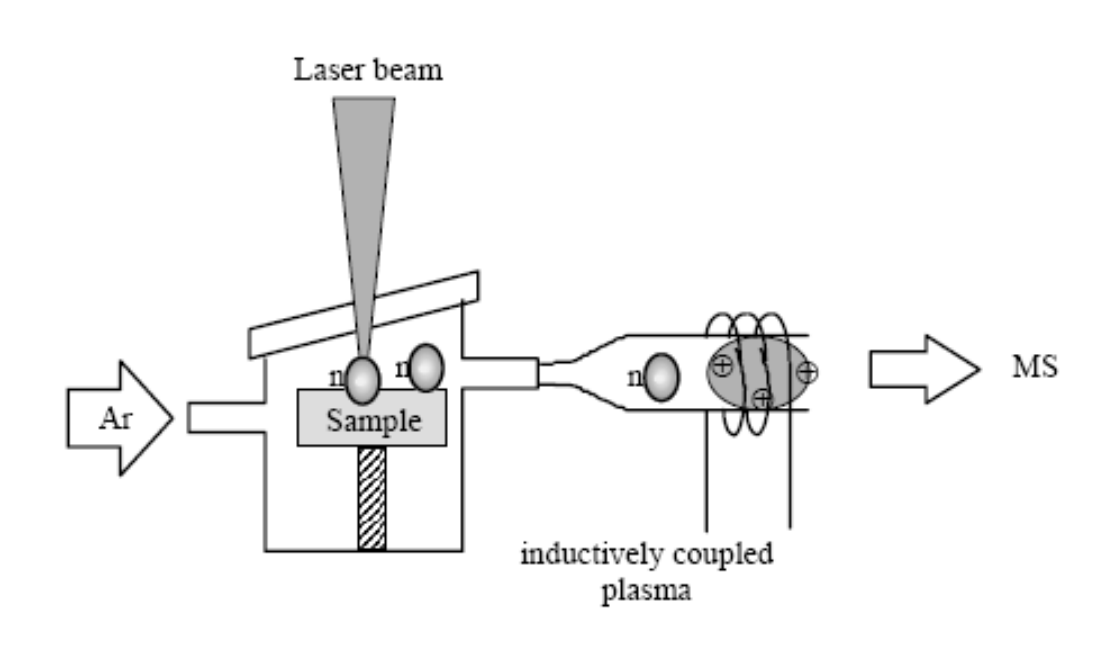
Chemical recovery (CHEM/DIRECT) is given in red

^{242}Pu Recovery: Conclusions

- Plutonium, as Pu(IV) was qualitatively stabilized and quantitatively extracted by TRU® resin from sample loading solution under current experimental conditions
- Either *0.1M HCl-0.05M HF-0.04M rongalite* or *0.1M HCl-0.05M HF -0.1M NH_4I* can be used for Pu quantitatively elution (>95%) from TRU® resin
- Currently used at USTUR electrodeposition procedure (USTUR-510) should be optimized

From 2-D to 3-D:
Laser Ablation (LA) ICP-MS

LA-ICP-MS: What Is It?



PRO:

- **simple sample prep**
- **speed & easy to use**
- **high sample throughput**
- **high sensitivity**
- **good precision & accuracy**
- **multi-element analysis**

CON:

- **need for well-characterized homogeneous standards**

"Laser Ablation ICP-MS - technique for lazy chemist"

LA-ICP-MS: Applications to USTUR

- Spatial distribution of actinides, ^{226}Ra and major matrix elements (Ca, Mg, Sr, P) in bones
- Actinides and ^{226}Ra concentrations measurements /comparison with other techniques
- Others?

LA-ICP-MS at ETH Zürich

ETH: Swiss Federal Institute of Technology

- **Detlef Günther, Associate Professor**
  Head of Laboratory of Inorganic Chemistry

The Günther Group

Trace Element and Micro Analysis

The research and development of <u>new analytical techniques</u> and methods is the driving force allowing <u>new insights</u> and improved understanding of <u>micro-, nano- and femto-scale processes.</u>

http://www.analytica.ethz.ch/research.htm

USTUR/ETH Start

From: Günther Detlef [guenther@inorg.chem.ethz.ch]
Sent: Sunday, February 25, 2007 7:29 AM
To: Sergei Tolmachev
Subject: RE: from Sergei

Dear Ser

thanks f
for a st
group -
further!

beste gr

Detlef

From: Detlef Günther [guenther@inorg.chem.ethz.ch]
Sent: Wednesday, June 20, 2007 1:21 AM
To: 'Sergei Tolmachev'
Subject: RE: USTUR/ETH

Dear Sergei,

Now, concerning the LA-ICP-MS analysis, We have one publication (it is one of my co-workers) on bone samples. However, most of the work has not been published - depends on the museum where the samples belong to!

However, you could integrate into your proposal The new capabilities of a femtosecond laser ablation-ICP-MS (Q, SF and MC) offers unique strategies to access trace element concentrations in bone samples. High resolution analysis will be carried out to investigate the detection and quantification capabilities. These data will be compared to total digests. Furthermore, the matrix element distribution will be mapped using a micro XRF, which will provide the element distribution of the major elements necessary for internal standardization.

Best greetings
Detlef

USTUR/ETH Experiments

- **Selected (trial) samples will be sent to ETH (*Summer*):**
  - **Radium Dial Painters**
  - **Plutonium Case**
  - **Uranium Case**
  - **Thorotrast Study**
- **Visit to ETH for LA-ICP-MS measurement (*Autumn*)**