



Radiobioassay and Radiochemical Measurements Conference
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**Analysis of High Fired Plutonium Oxide and Other Actinides in
MAPEP Soil Samples**



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Outline

- Background
- Motivation
- Methods
- Results and Discussion
- Conclusions





Mission

- Evaluate health outcomes, causes of death, and life expectancy of former nuclear workers (volunteer Registrants) who had documented accidental intakes of uranium and the transuranium elements

<http://www.ustur.wsu.edu/Mission/index.html>

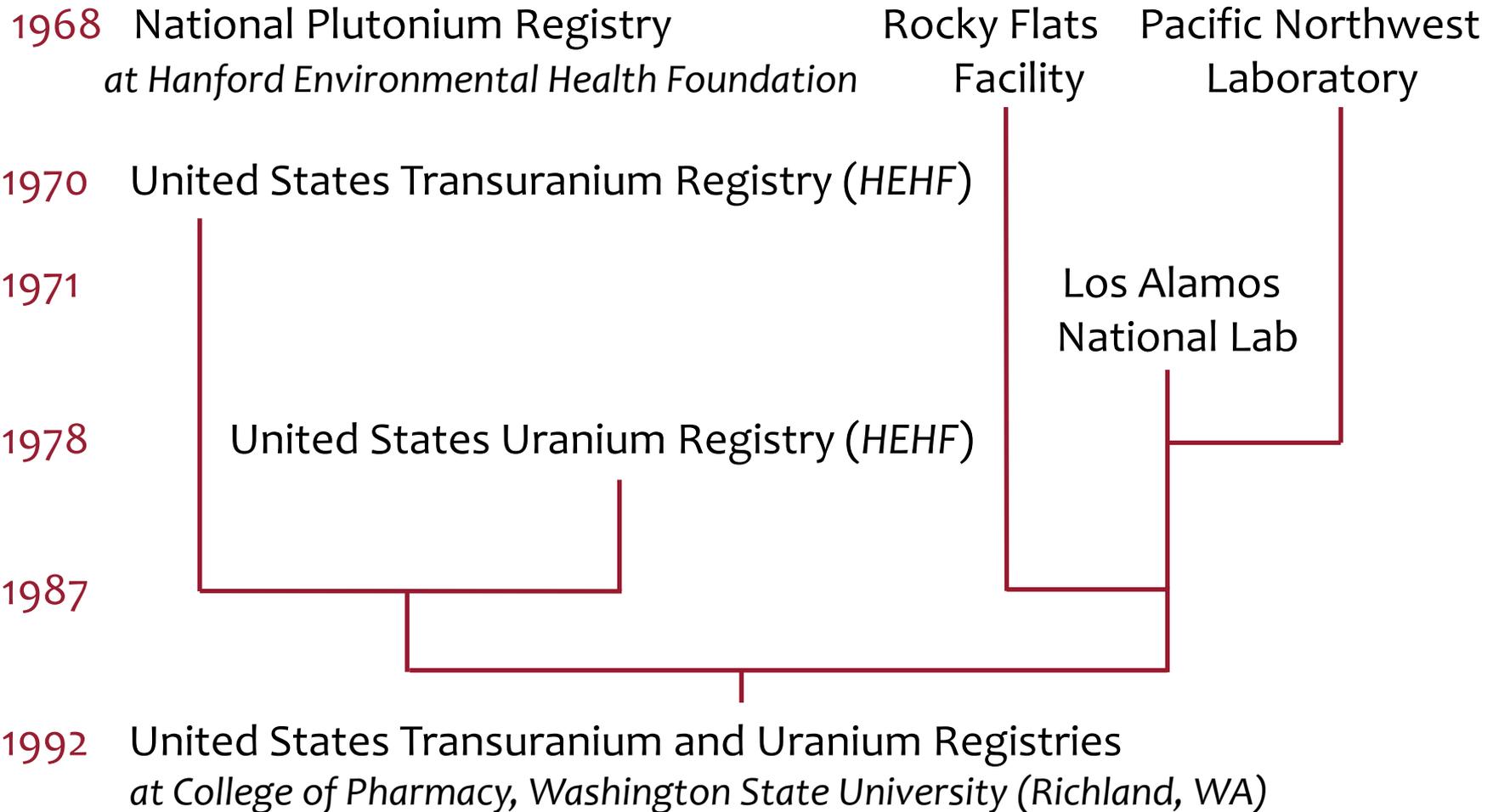




Genealogy of the USTUR

REGISTRIES MANAGEMENT

ANALYTICAL SUPPORT





Background: USTUR Tissue Analysis

- Radiochemical analysis: human bones and soft tissues
- Sample analysis: ^{241}Am , $^{238,239}\text{Pu}$, $^{234,235,236,236}\text{U}$, and ^{232}Th
- USTUR SOPs validation: SRM 4351 (Human Lung); SRM 4352 (Human Liver); SRM 4356 (Human Bone)

No information on material type!

- Inhalation of PuO_2 aerosols (Type S material)
 - ✓ Lung and thoracic LN – insoluble
 - ✓ Other tissues – soluble



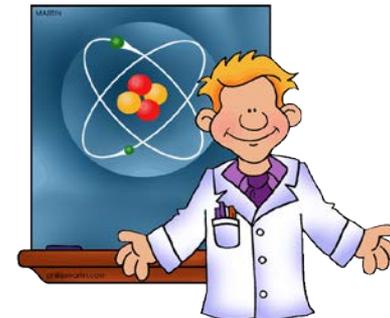
Background: Case 0407 – Exposure to High-Fired $^{239}\text{PuO}_2$

- Whole-body donation
- Pu fire accident at the Rocky Flats Plant in 1965
- Inhalation of high-fired PuO_2 generated at $\sim 1,800^\circ\text{C}$





Motivation



- Validation of United States Transuranium and Uranium Registries' (USTUR) tissue analysis protocol for high-fired plutonium oxide (PuO_2)



MAPEP Soil Analysis

Analysis: $^{238,239}\text{Pu}$, ^{241}Am , and $^{234,235,238}\text{U}$

- MAPEP-11-MaS24: Radiological and Environmental Sciences Laboratory (RESL)
- Certified: ^{239}Pu , ^{241}Am , ^{234}U , and ^{238}U
- Pu form: high-fired $^{239}\text{PuO}_2$ @ 900°C





Methods: Sample Analysis Protocol

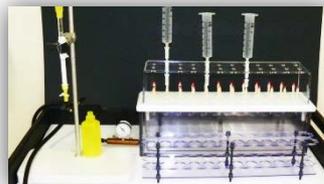
Drying/Ashing



Digestion/Dissolution



Radionuclide Separation



α -source Preparation



Actinide Measurements
(Alpha-Spec)





USTUR 106: Sample Drying and Ashing

- Drying: @ 100 °C for 4 days, max. 48 samples
- Ashing: @450 °C for 4 days (×2), max. 32 samples



VWR® 1685 HAFO Series Forced-Air Oven, Fisher Scientific® Isotemp® Muffle Furnace 550 Series, LINDBERG® Muffle Furnace Model 52641





USTUR 110: Sample Digestion

- Microwave Digestion
 - ✓ Soft tissue: HNO_3 – HCl – HF , 9:3:4 (mL)
 - ✓ Bone: HNO_3 – HCl , 10:3 (reverse *aqua regia*)
 - ✓ Controlled temperature: 220 °C
 - ✓ Monitored pressure: 40 bar



MARS-5 Microwave



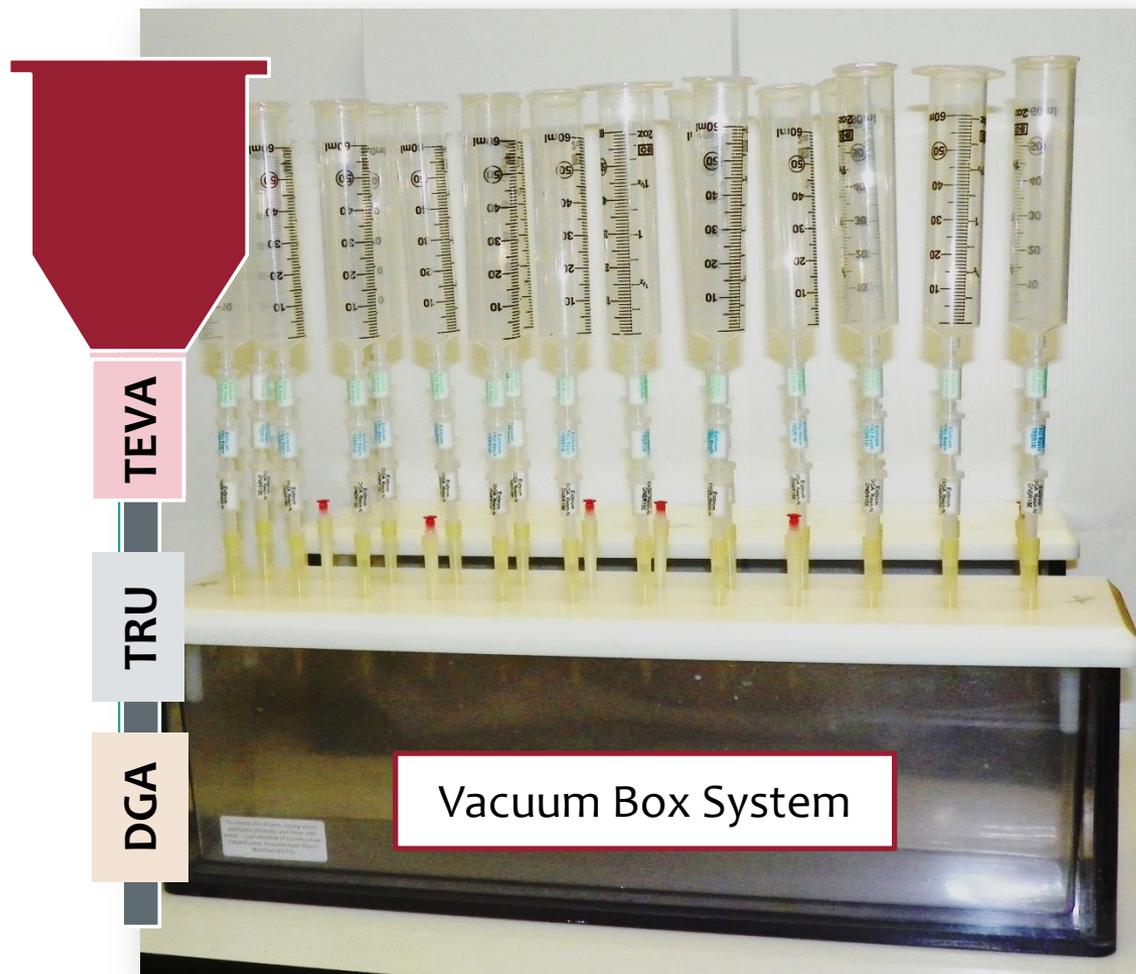
EasyPrep® Vessel





USTUR 350: Actinide Separation

Vacuum-Assisted Extraction Chromatography





USTUR 350: Actinide Column Separation (I)

- 1) Sample in 40 mL 3M HNO₃ – 1M Al(NO₃)₃
- 2) Add 0.75 mL 1.5M Sulfamic Acid + 6 mL 0.75M Ascorbic Acid
- 3) Add 2.5 mL 3.5 M Sodium Nitrite
- 4) Sample loading (1 drop sec⁻¹)

- 5) Beaker rinse: 2 × 5 mL 3M HNO₃
- 6) Separate cartridges
- 7) TEVA rinse: 30 mL 3M HNO₃

- 8) Rinse: 20 mL 9M HCl (Th)

- 9) Pu Elution: 20 mL
0.1M HCl - 0.05M HF – 0.04M Rongalite

1 mL TEVA Resin
(50-100 μm)

(6)

1 mL TRU-Resin
(50-100 μm)

1 mL DGA-Resin
(50-100 μm)

↓
Discard (4 – 8)

Electrodeposition

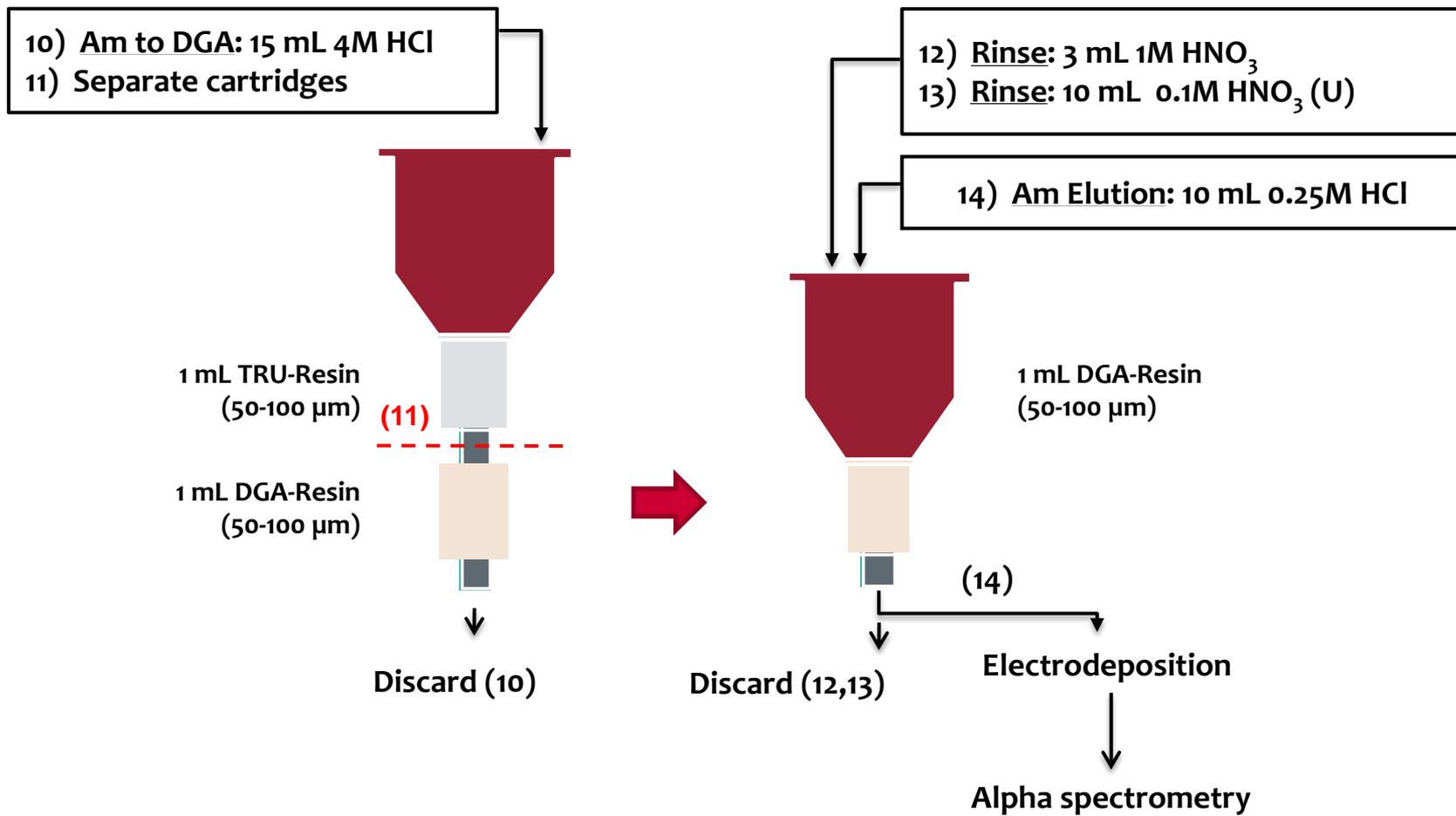
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Alpha spectrometry





USTUR 350: Actinide Column Separation (II)

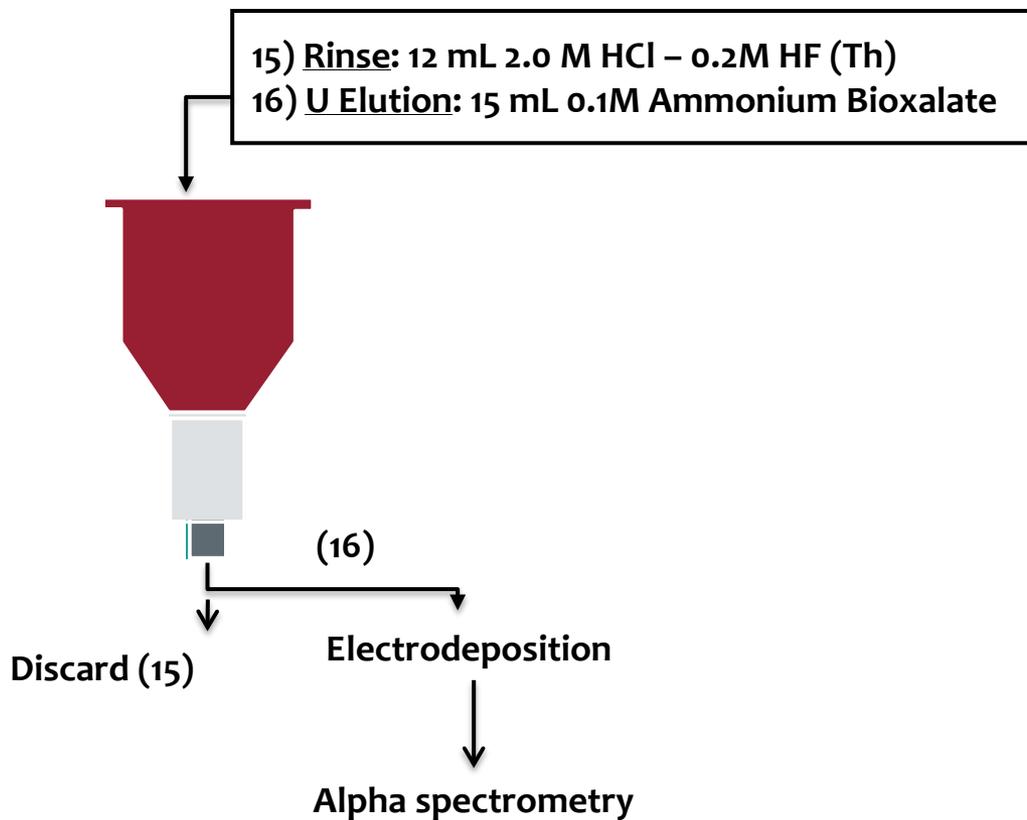
TRU – DGA cartridges from Step 6





USTUR 350: Actinide Column Separation (III)

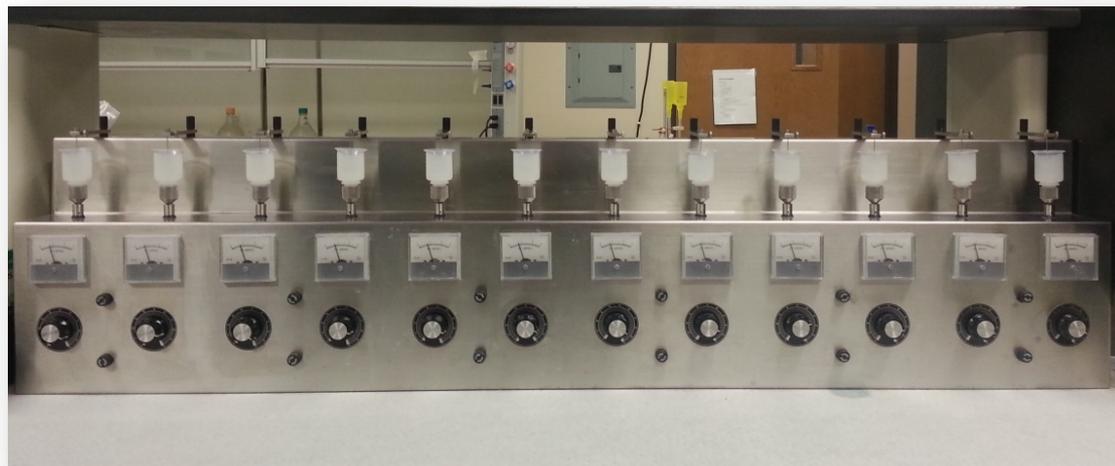
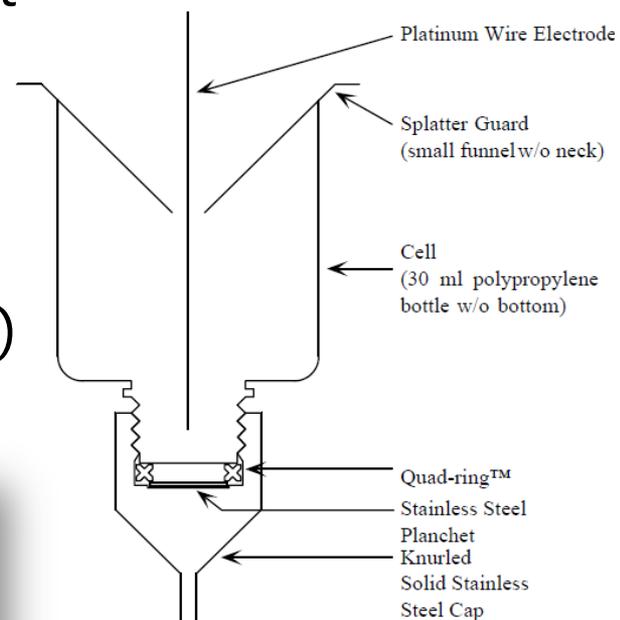
TRU cartridge from Step 11





USTUR 520: Electrodeposition

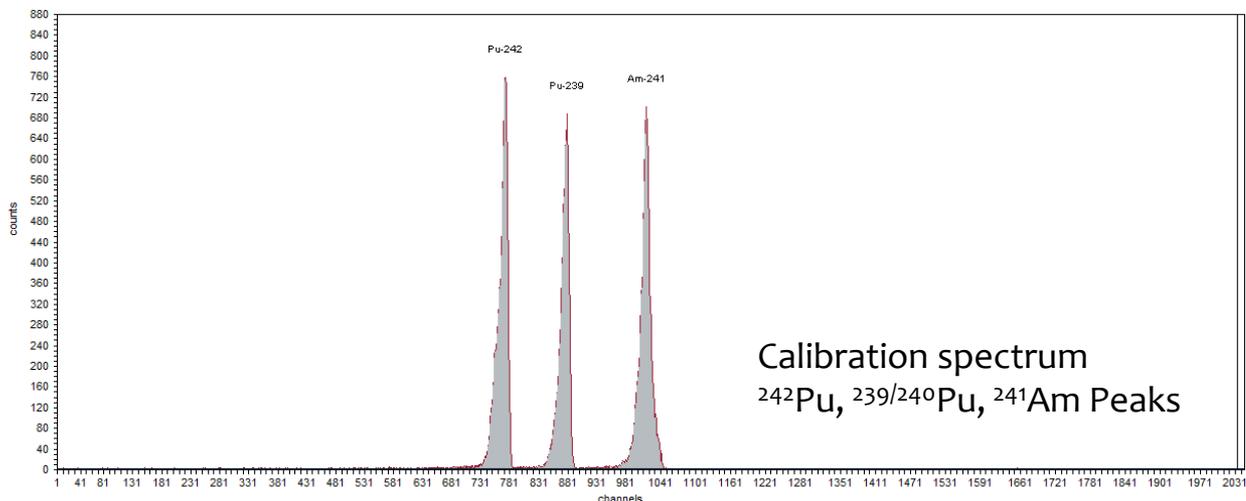
- Phoenix[®] EP-12 Series electrodeposition unit
- Custom Electrolytic Cell
- Na₂SO₄ electrolyte solution
- 1 hr electrodeposition @ 0.75 A
- α -source: 5/8" stainless steel disk (planchet)





USTUR 600: Alpha-Spectrometry

- ORTEC: Ensemble (2) and Octête PC (3) systems
- Detector: ENS-U450 (36)
- Software: AlphaVision 6.0.4
- Calibration: E&Z Analytics (1); USTUR (8)



- Sample count time: 150,000 s





MAPEP Study

- Sample size, g: 0.5x2, 1.0, 2.0
- MW digestion reagent mixture:
 - ✓ USUTR SOP for soft tissue: HNO₃ – HCl – HF, 9:3:4 (mL)
 - ✓ USUTR SOP for bone: HNO₃ – HCl, 10:3 (reverse *aqua regia*)
- Radiochemical tracers (NIST): ²⁴²Pu, ²⁴³Am, ²³²U
- MAPEP-11-MaS24 reference values (RESL):

²⁴¹ Am	²³⁹ Pu	²³⁴ U	²³⁸ U
Concentration Acceptance Range, pCi g⁻¹			
1.16 - 2.15	1.85 - 3.44	3.32 - 6.19	3.49 - 6.46
Mean ± 95%CI, pCi g⁻¹			
1.66±0.02	2.65±0.04	4.76±0.14	4.96±0.15





MAPEP Results: Chemical Recovery

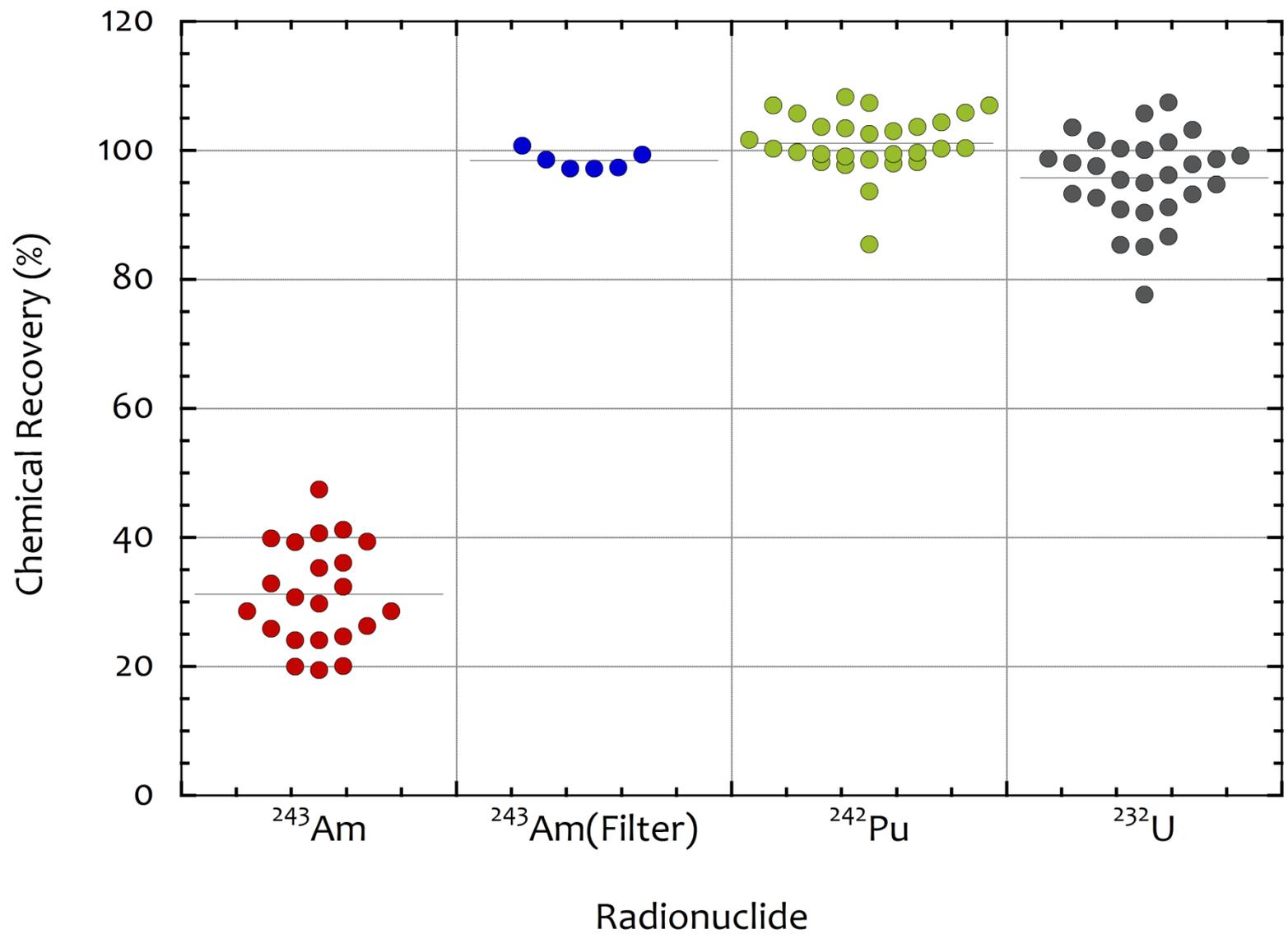
Sample		Chemical Recovery, %		
Size, g	N	^{243}Am	^{242}Pu	^{232}U
<i>Reagent Mixture HNO₃ – HCl – HF</i>				
1.0	8	30.8±3.3	99.9±2.7	97.4±5.6
0.5×2	4	33.4±11.7	101.6±5.9	96.7±6.2
2.0	4	42.3±5.6	101.8±5.7	101.6±6.7
Mean ± 95% CI		34.3±3.6	100.8±1.8	98.3±3.0
<i>Reagent Mixture HNO₃ – HCl</i>				
1.0	6	23.0±4.2	101.6±8.8	91.0±7.5
Residue (Filter)	6	98.4±1.5	101.7±4.2	93.9±7.4

- Soil matrix effect: low $^{243}\text{Am}^{3+}$ tracer recovery





MAPEP Results: Chemical Recovery





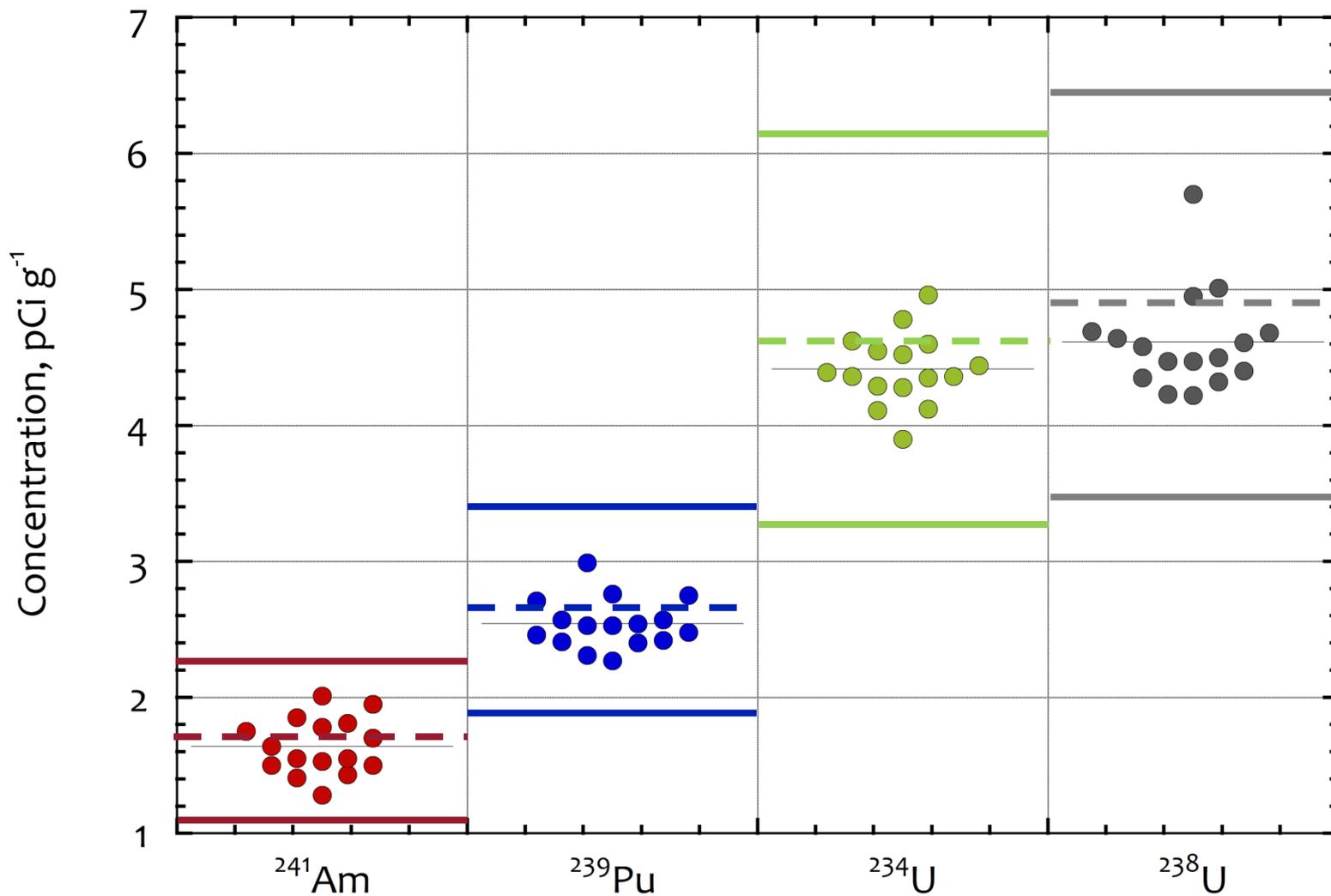
MAPEP Results: Actinide Concentrations

Sample		Concentration, pCi g ⁻¹				Bias, %			
Size, g	N	²⁴¹ Am	²³⁹ Pu	²³⁴ U	²³⁸ U	²⁴¹ Am	²³⁹ Pu	²³⁴ U	²³⁸ U
<i>Reagent Mixture HNO₃ – HCl – HF</i>									
1.0	8	1.73±0.18	2.66±0.15	4.46±0.29	4.68±0.40	4.5	0.3	-6.2	-5.6
0.5×2	4	1.58±0.16	2.38±0.17	4.41±0.23	4.62±0.45	-4.7	-10.1	-7.3	-6.9
2.0	4	1.50±0.32	2.48±0.14	4.32±0.27	4.47±0.27	-9.5	-6.4	-9.2	-9.8
Mean ± 95% CI		1.64±0.11	2.54±0.10	4.41±0.14	4.61±0.20	-1.3	-4.0	-7.2	-7.0
<i>Reagent Mixture HNO₃ – HCl</i>									
1.0	6	0.37±0.07	0.14±0.01	1.33±0.14	1.39±0.19	-77.6	-94.9	-72.1	-71.9
Residue (Filter)	6	1.05±0.12	2.42±0.10	3.09±0.19	3.28±0.14	-36.9	-8.6	-35.1	-33.8
Total:		1.42±0.08	2.56±0.06	4.42±0.14	4.68±0.14	-14.5	-3.5	-7.1	-5.7



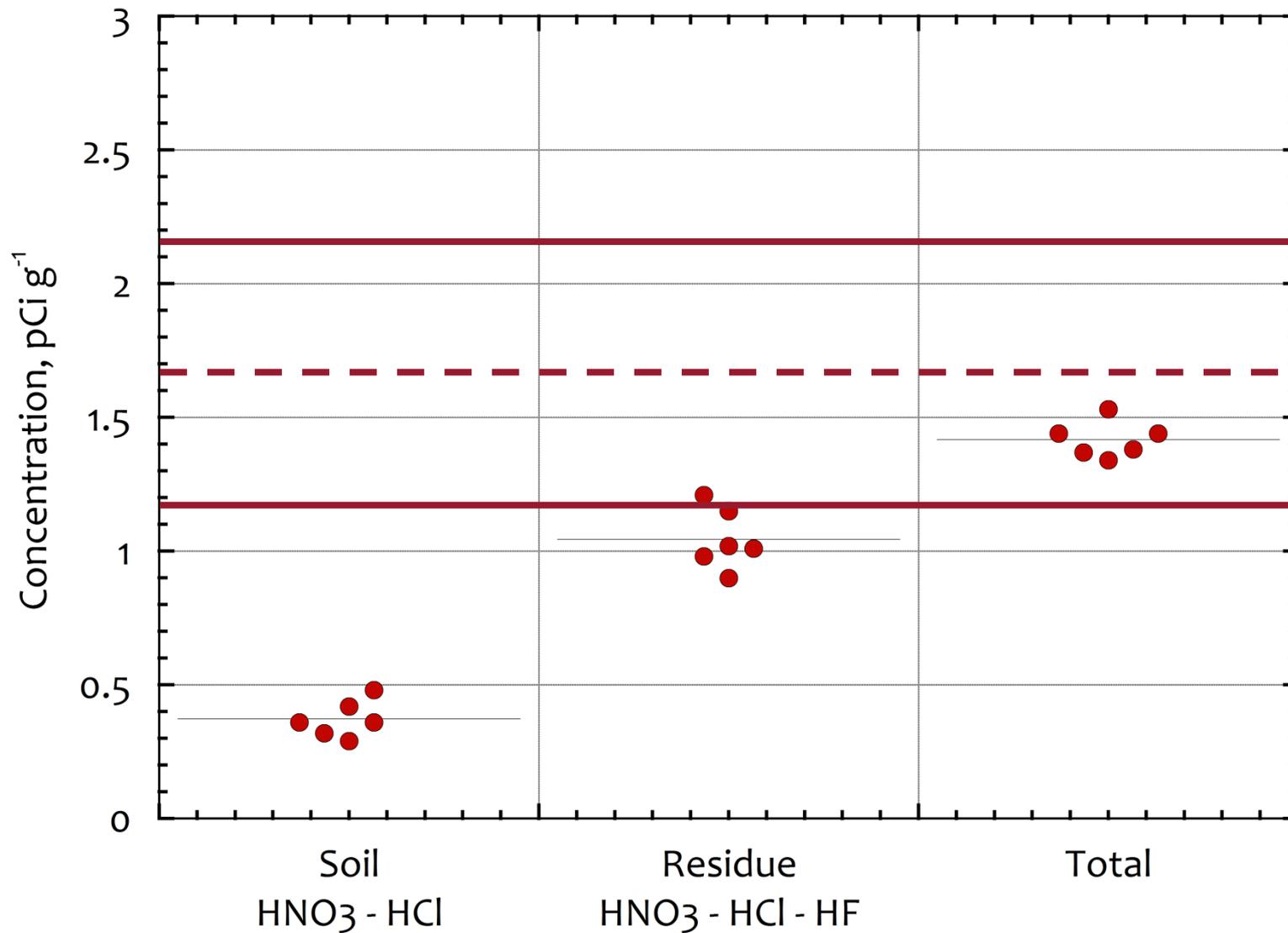


MAPEP Results: Measured vs Certified ($\text{HNO}_3\text{-HCl-HF}$)



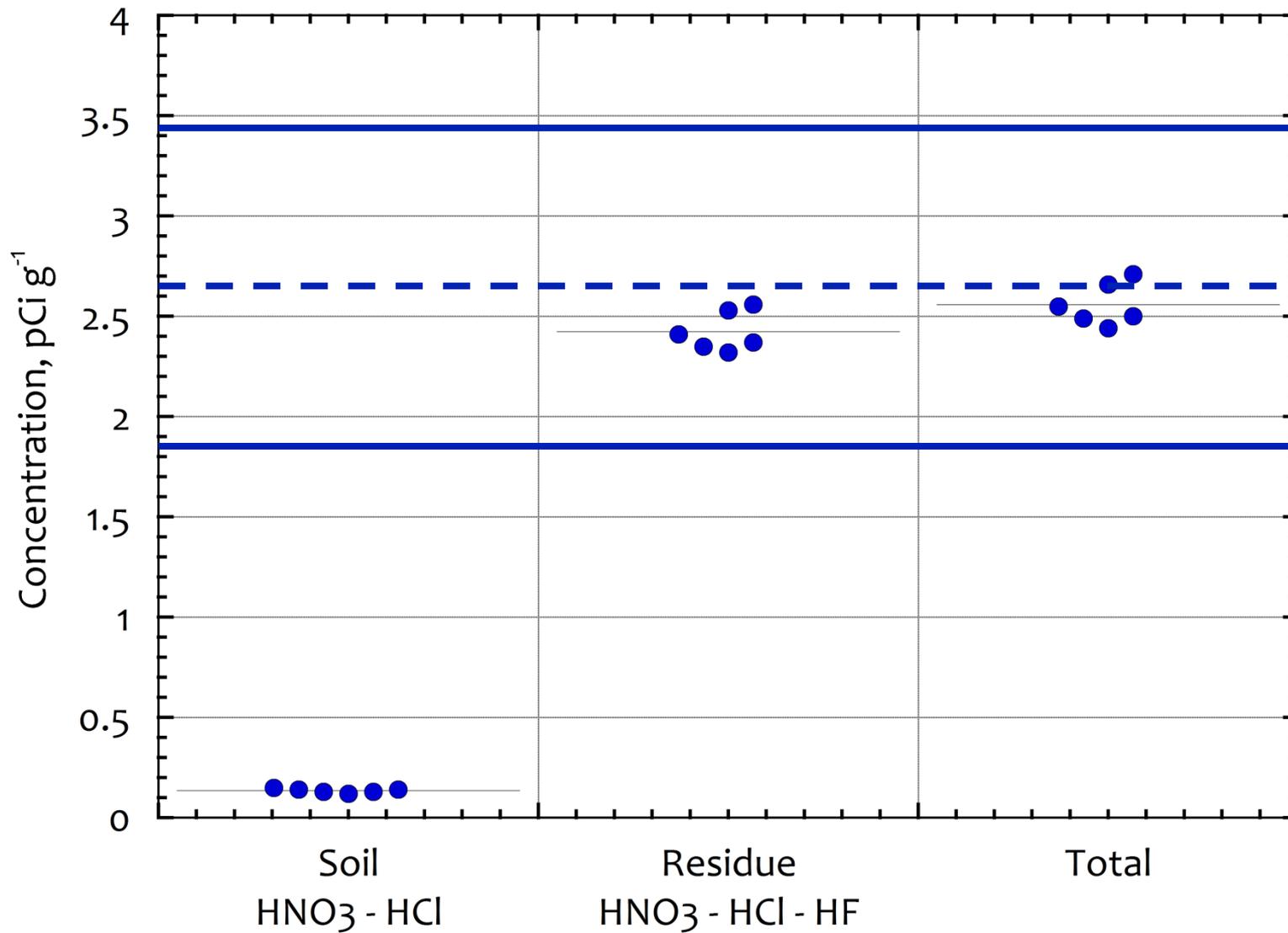


^{241}Am Results: Measured vs Certified



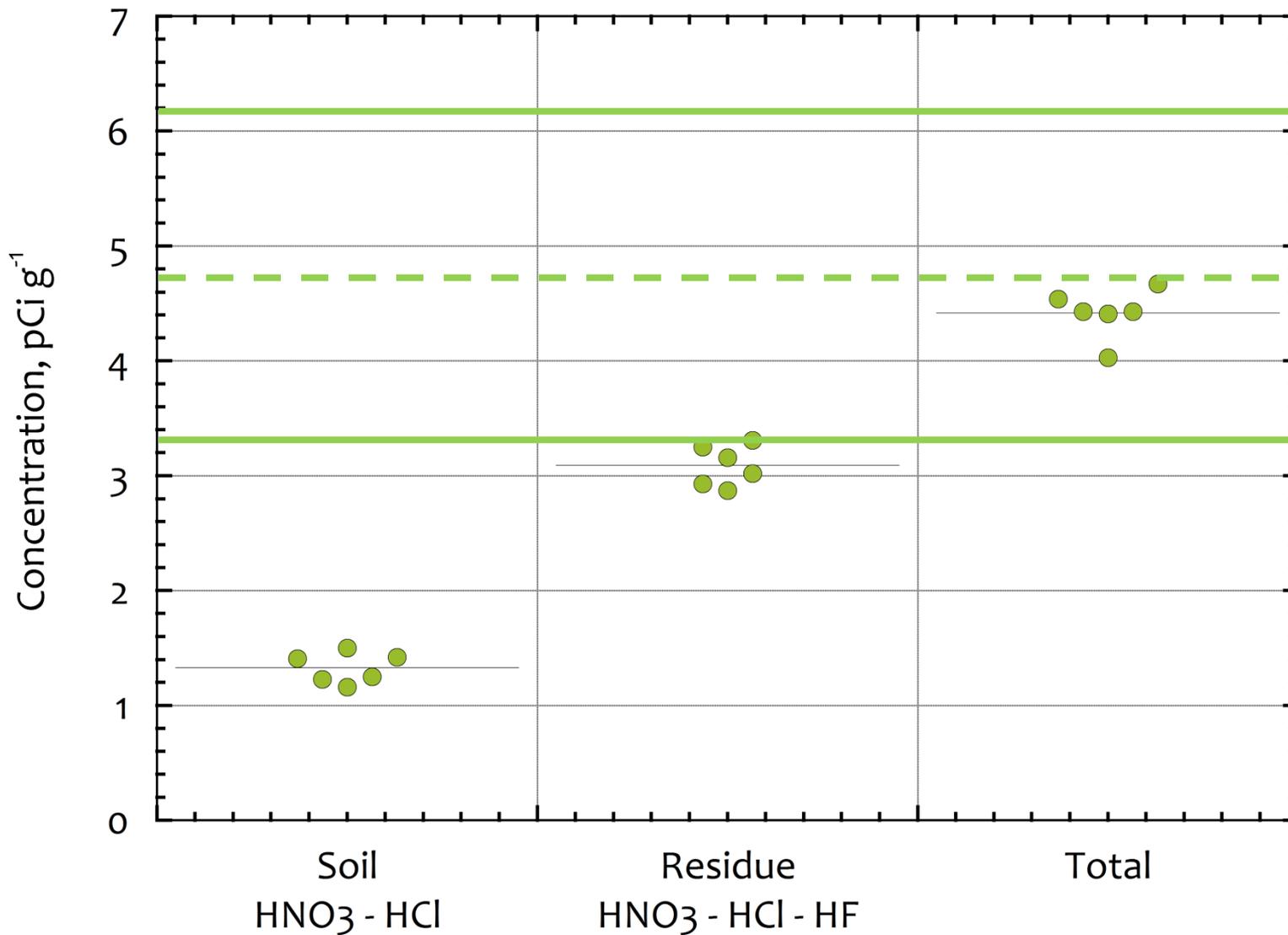


^{239}Pu Results: Measured vs Certified





^{234}U Results: Measured vs Certified

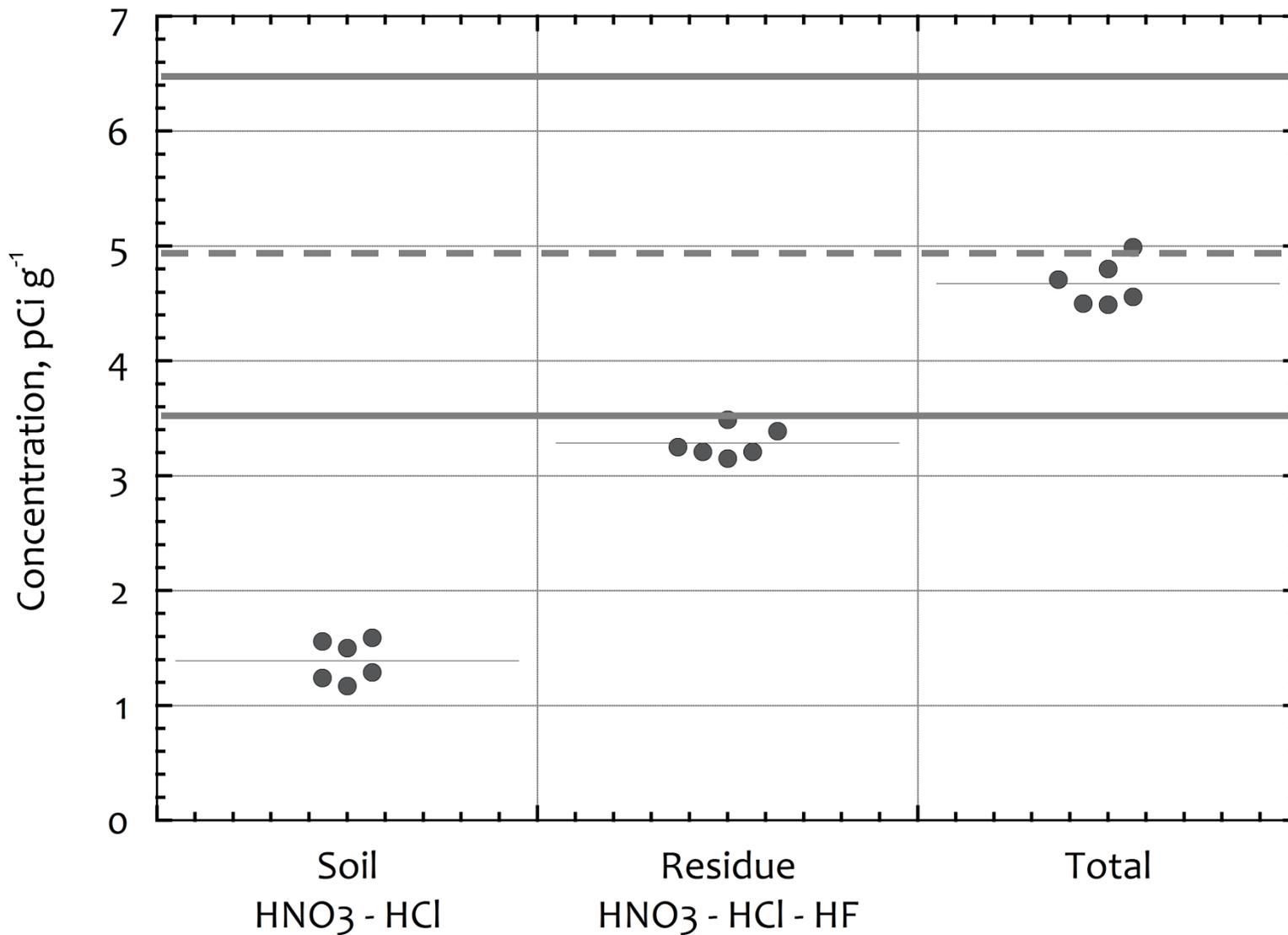


RRMC 2015: Iowa City, Iowa





^{238}U Results: Measured vs Certified





Conclusions

Complete high-fired PuO_2 digestion with $\text{HNO}_3 - \text{HCl} - \text{HF}$

- ✓ Complete soil matrix digestion
- ✓ Actinide digestion efficiency: ^{239}Pu (96%), ^{241}Am (99%) $^{234,238}\text{U}$ (93%)

Incomplete digestion of PuO_2 with $\text{HNO}_3 - \text{HCl}$

- ✓ Incomplete soil matrix digestion
- ✓ Actinide digestion efficiency: ^{239}Pu (5%), ^{241}Am (22%) $^{234,238}\text{U}$ (28%)

Observations

- ✓ No matrix effect on Pu and U chemistry: 92 – 102% tracer recovery
- ✓ Soil matrix effect on Am chemistry: <35% tracer recovery





Thank you for your attention!

