Analysis of 'High-Fired' Plutonium Oxide in Tissues of Occupationally Exposed Workers

Sergei Y. Tolmachev, Elizabeth M. Thomas, George Tabatadze, Maia Avtandilashvili

U.S. Transuranium and Uranium Registries
College of Pharmacy, Washington State University

1845 Terminal Drive, Suite 201, Richland, WA 99354
www.ustur.wsu.edu

"Learning from Plutonium and Uranium Workers"

U.S. Transuranium and Uranium Registries

- Federal grant program funded by U.S. Department of Energy since 1968
- Today's mission is to follow up occupationally exposed individuals, from exposure through full lifespan, by studying the biokinetics (uptake, translocation, retention), and dosimetry of the actinides (Pu, Am, and U)

USTUR Registrants

- Voluntary tissue donors (posthumous):

  whole-(44) and partial-body (305) donations
- Former nuclear workers from DOE sites
- Documented radiation exposure and work history
- Acceptance criteria:
  i. actinide internal deposition of ≥74 Bq (2 nCi)
  ii. external dose to whole body ≥0.1 Sv (10 rem)

USTUR: What Do We Do?

Autopsy → Tissue Collection → Radiochemical Analysis → Biokinetic Modeling

- Drying and Ashing
- Digestion and Dissolution
- Radionuclide Separation
- a-source Preparation
- Actinide Measurements

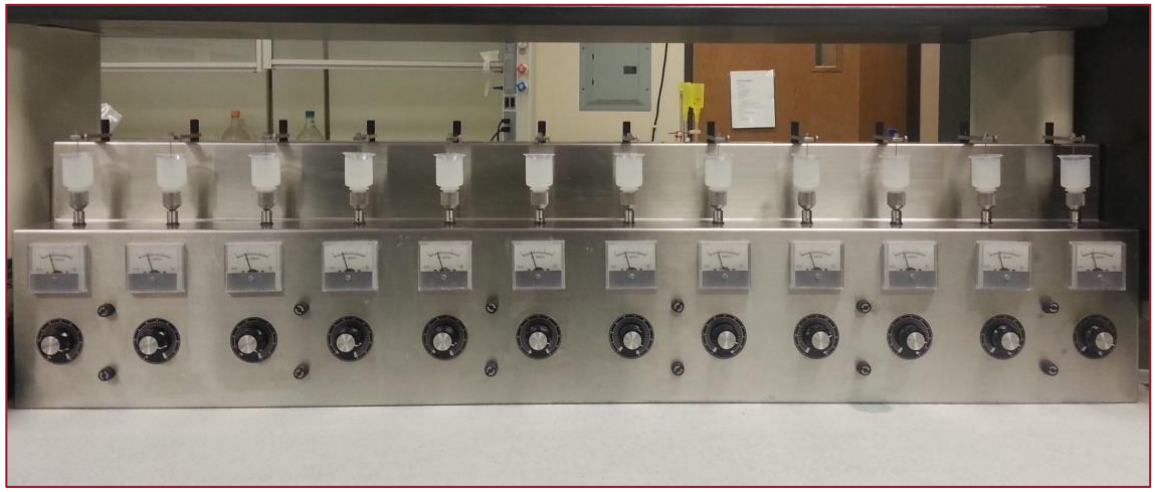
Tissue Sample Digestion

• HNO_3 – HCl – HF, 9:3:4 (ml)	Soft tissues
• HNO_3 – HCl, 10:3 (ml)	Bones
• Microwave unit	CEM MARS 5
• Vessels	EasyPrep®
• Temperature	220 ˚C
• Pressure	40 bar
• Time	30 min

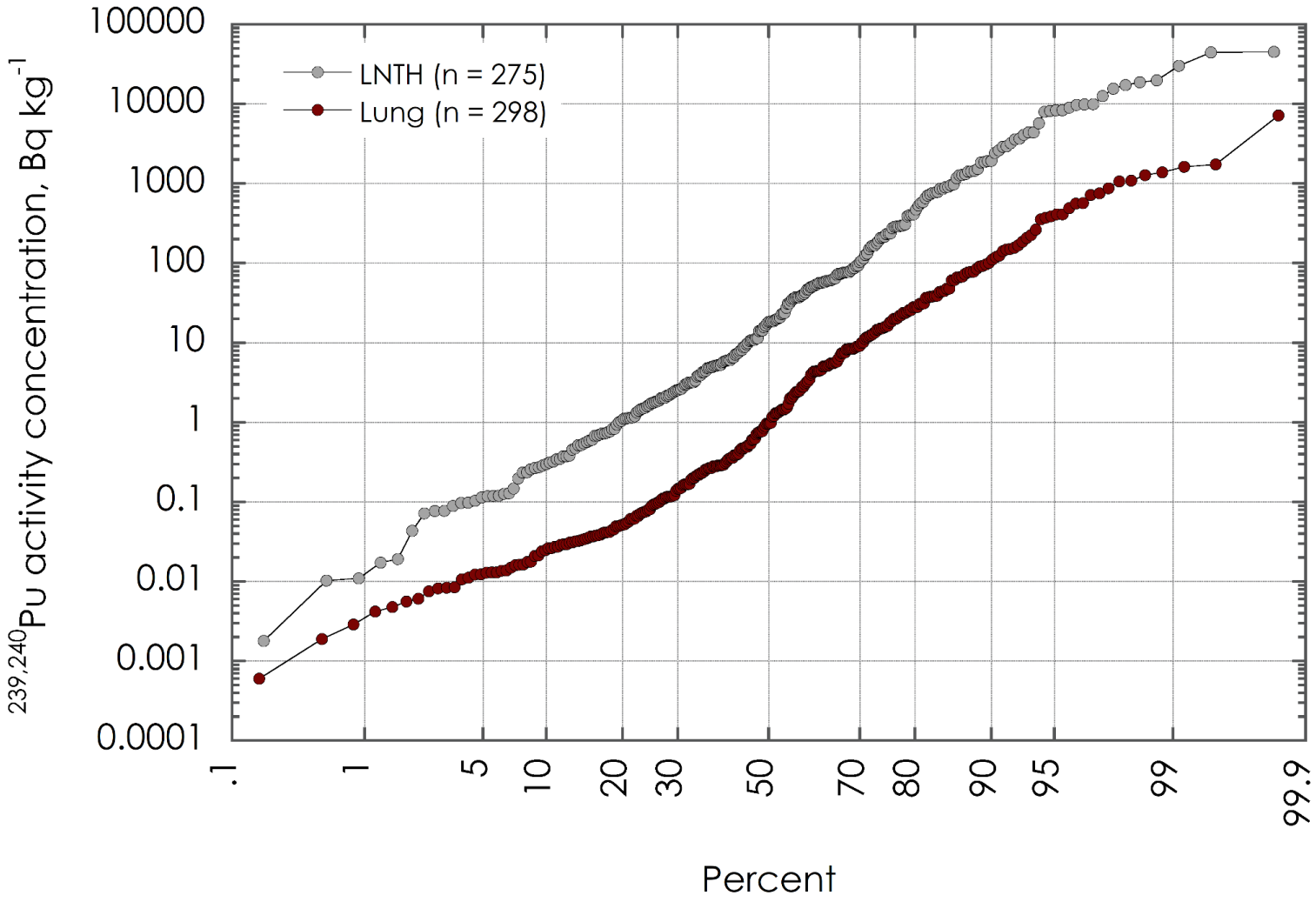
Actinide Radiochemical Separation

Actinide Electrodeposition

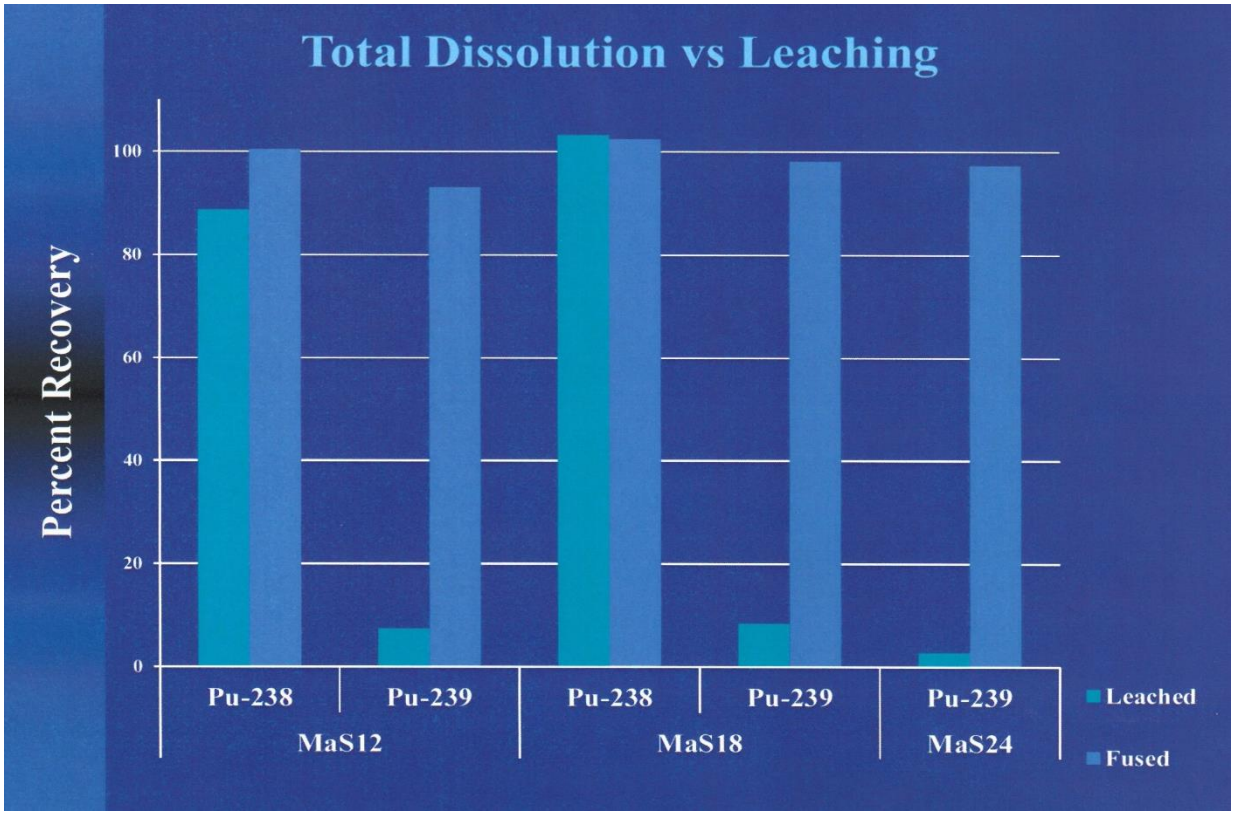
- Phoenix® EP-12 Series electrodeposition unit
- Na_2SO_4 electrolyte solution
- 1-h electrodeposition @ 0.75 A
- a-source: 5/8″ stainless steel disk (planchet)



^{239}Pu in Respiratory Tract Tissues



Wake-up Moment



David S. Sill (Radiological and Environmental Sciences Laboratory, U.S. DOE) In Search of… The Lost Art of Analytical Radiochemistry… The Last Crusade. 60th Radiobioassay and Radiochemistry Measurements Conference (RRMC), Knoxville, TN, October, 2014

http://www.rrmc.info/rrmc-60/rrmc-60-002p.pdf

Method Validation at USTUR

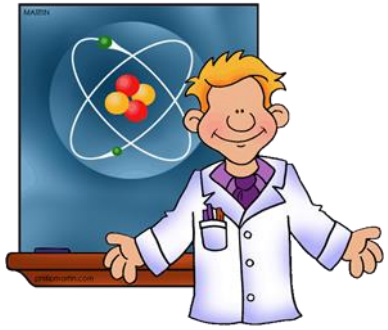
Standard Reference Materials from NIST

- SRM 4351 (Human Lung)
- SRM 4352 (Human Liver)
- SRM 4356 (Human Bone)

Split and spiked samples

No information on actinide material type!

Motivation



- Validation of USTUR tissue analysis protocol for 'high-fired' plutonium oxide ($^{239}PuO_2$)

Why 'High-Fired' Plutonium?

- Primary radionuclide of exposure: ^{239}Pu
- Primary material type: Type S (insoluble)
- Primary route of intake: Inhalation
- Deposition site: Respiratory tract

MAPEP-11-MaS24 Soil

- Prepared: Radiological and Environmental Sciences Laboratory (RESL)
- Reference values (1 pCi = 37 mBq):

^{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

- Plutonium: 'high-fired' $^{239}PuO_2$ @ 900 ˚C

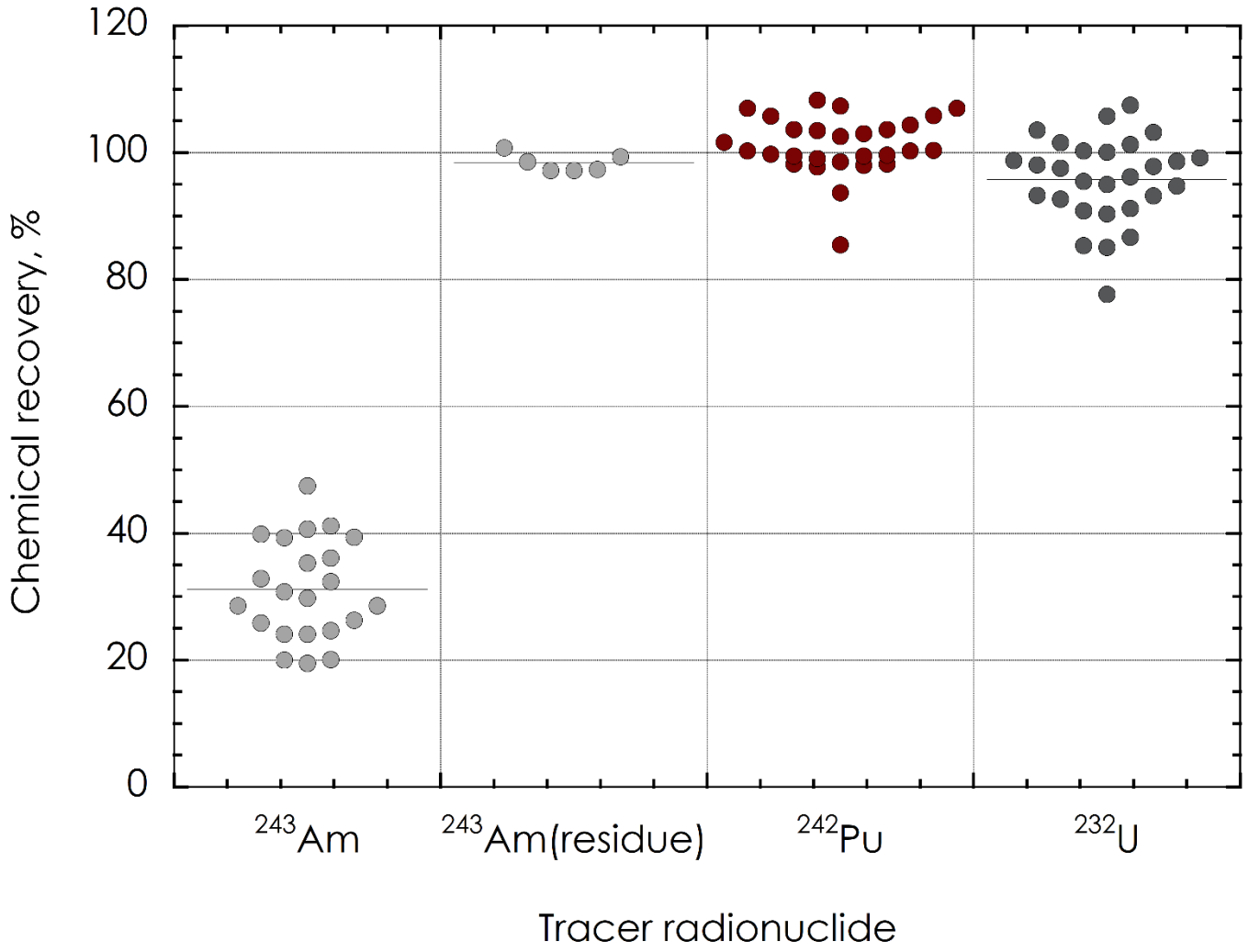
Results: Chemical Recovery of Tracer

Sample		Tracer recovery, %		
Size, g	N	^{243}Am	^{242}Pu	^{232}U
		Digestion with HNO3 – HCl – HF		
0.5 ×2	4	33.4±11.7	101.6±5.9	96.7±6.2
1.0	8	30.8±3.3	99.9±2.7	97.4±5.6
2.0	4	42.3±5.6	101.8±5.7	101.6±6.7
Mean ± 95%CI	16	34.3±3.6	100.8±1.8	98.3±3.0
		Digestion with HNO3 – HCl		
1.0	6	23.0±4.2	101.6±8.8	91.0±7.5
Residue†	6	98.4±1.5	101.7±4.2	93.9±7.4

† - additionally treated with HF

Soil matrix effect on Am separation !

Results: Tracer Recovery

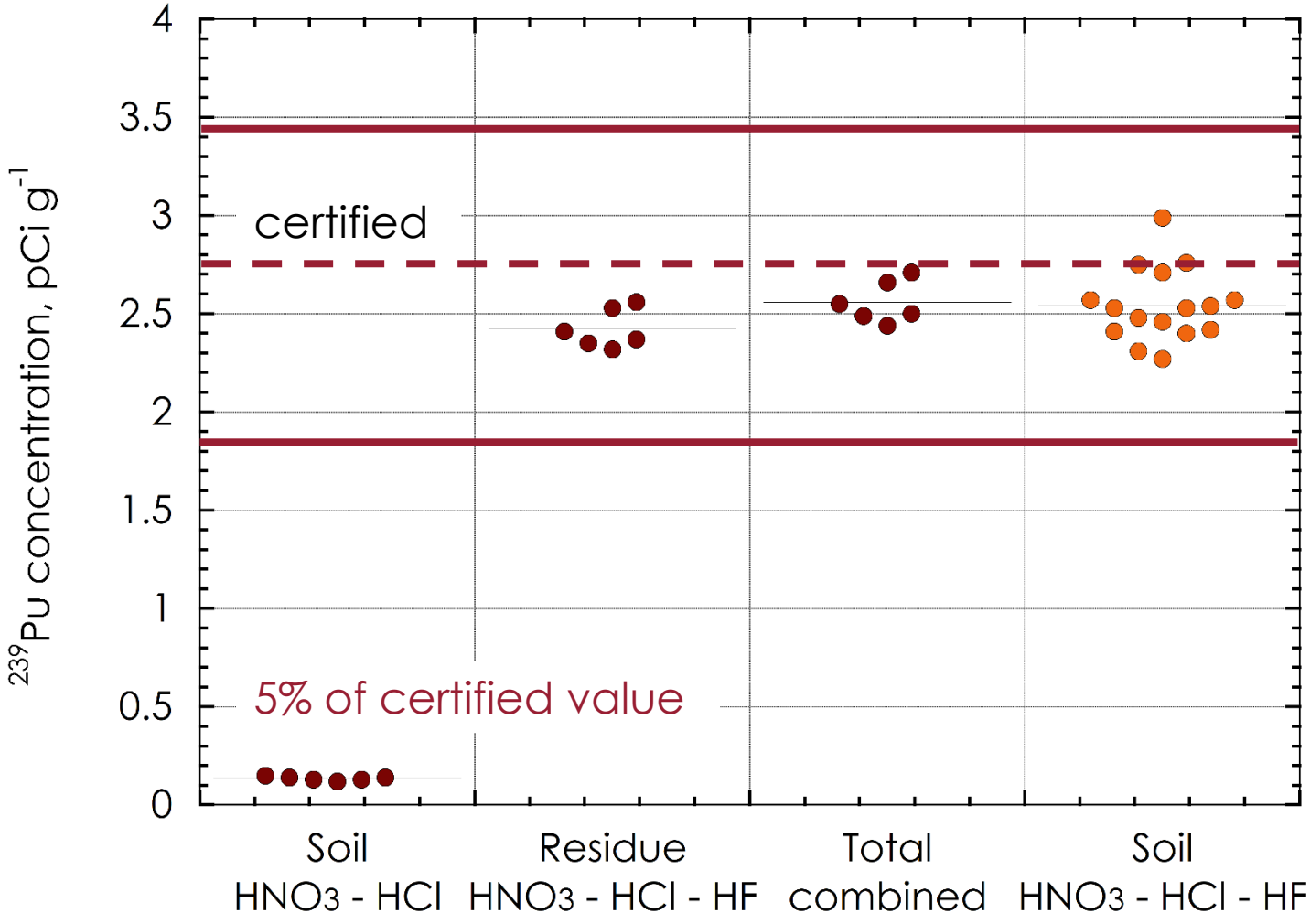


Results: Analyte Activity Concentration

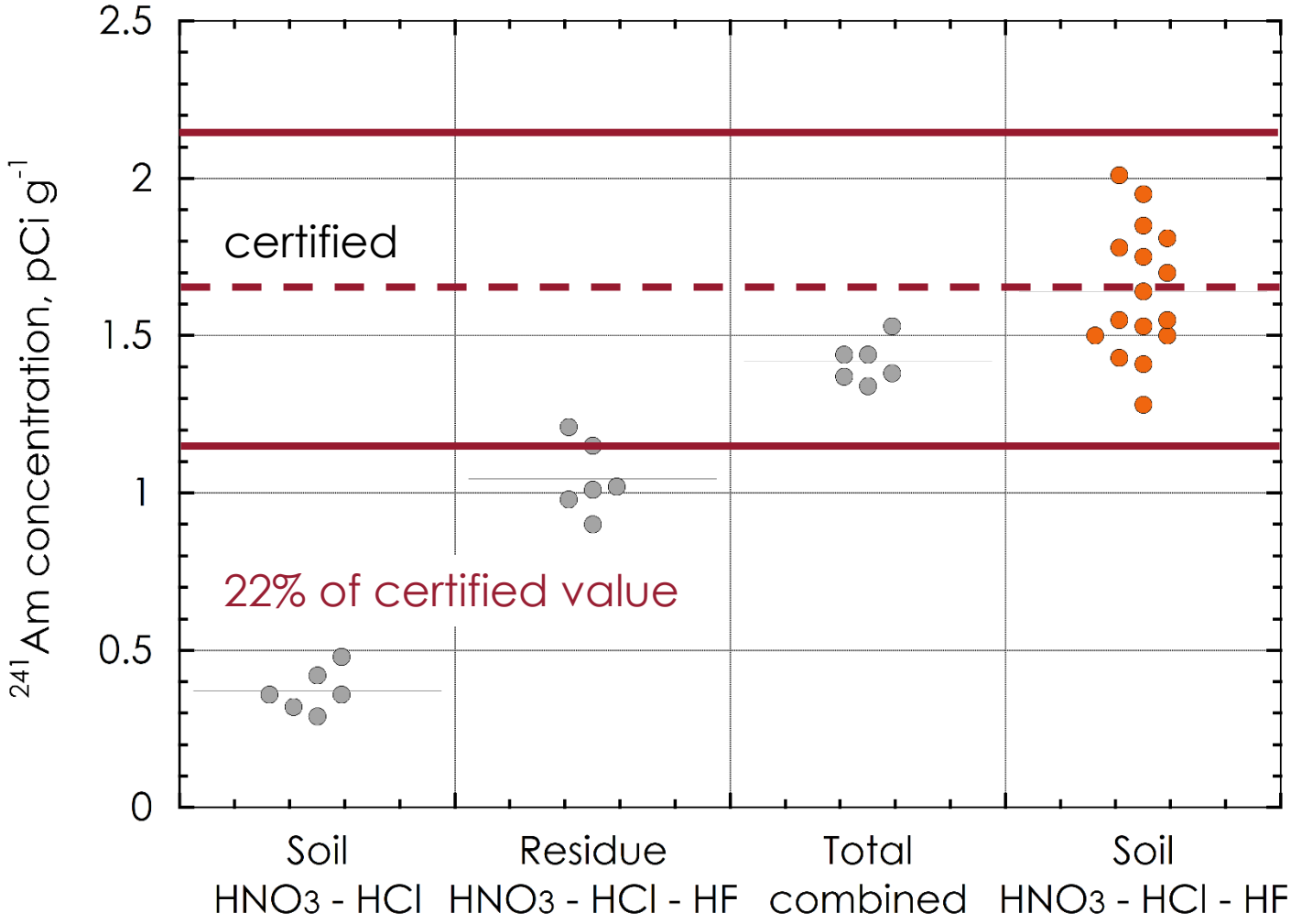
Sample		Analyte concentration, pCi g^{-1}		
Size, g	N	^{241}Am	^{239}Pu	^{238}U
		Digestion with HNO_3 – HCl – HF		
0.5 ×2	4	1.58±0.16	2.38±0.17	4.62±0.45
1.0	8	1.73±0.18	2.66±0.15	4.68±0.40
2.0	4	1.50±0.32	2.48±0.14	4.47±0.27
Mean ± 95%CI	16	1.64±0.11	2.54±0.10	4.61±0.20
		Digestion with HNO_3 – HCl		
1.0	6	0.37±0.07	0.14±0.01	1.39±0.19
Residue†	6	1.05±0.12	2.42±0.10	3.28±0.14
Total combined	6	1.42±0.08	2.56±0.06	4.68±0.14

† - additionally treated with HF

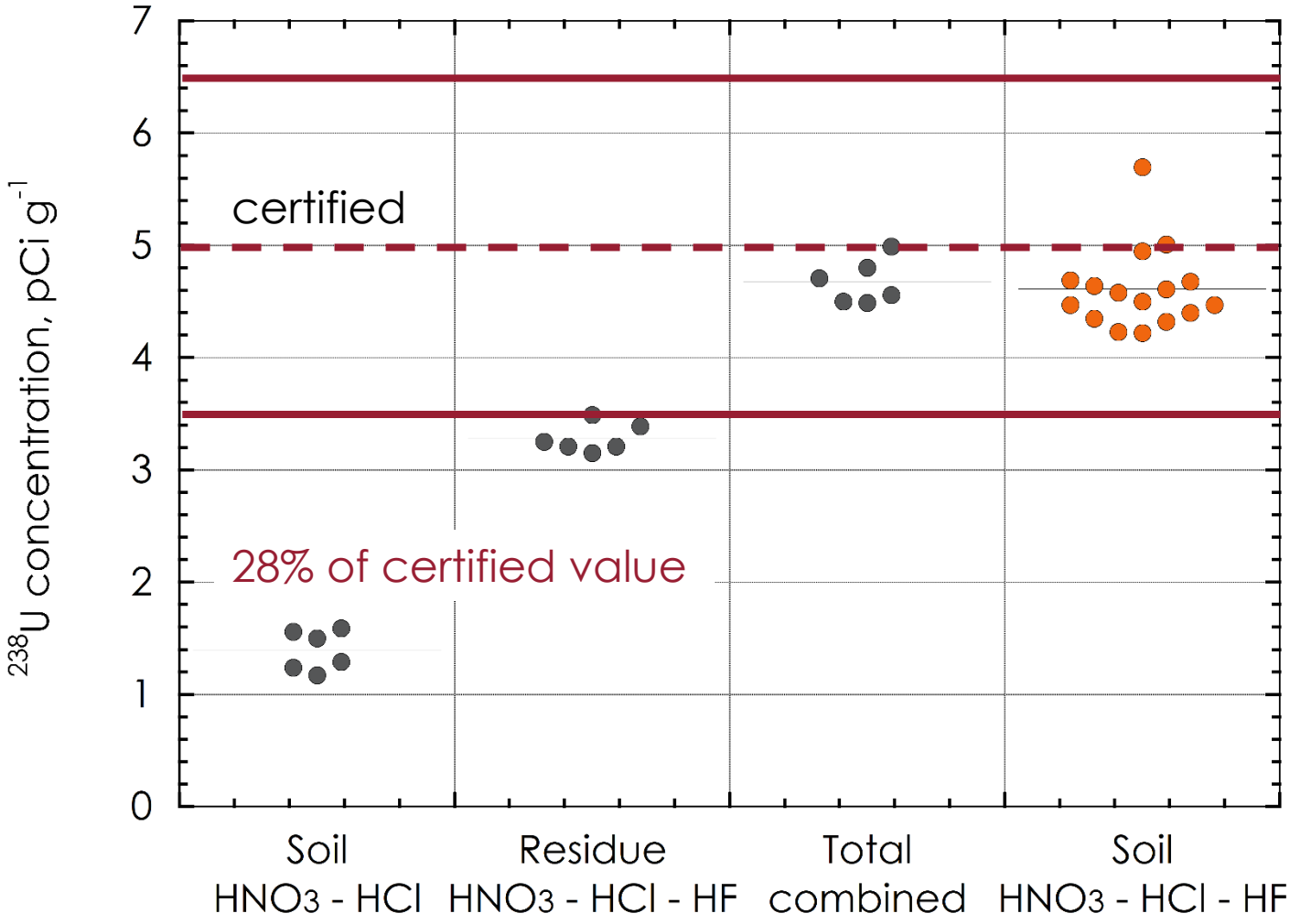
^{239}Pu: Measured vs Certified



^{241}Am: Measured vs Certified



^{238}U: Measured vs Certified



Conclusions

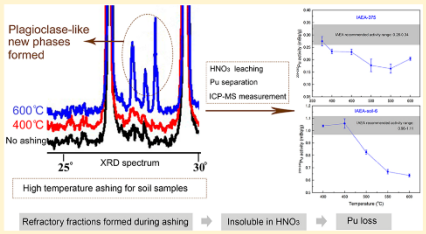
- USTUR tissue analysis protocol was successfully validated for the analysis of 'high-fired' PuO_2

- Microwave-assisted acid digestion with HNO_3 – HCl does not allow for total plutonium dissolution
- Hydrofluoric acid (HF) is critical for analysis of insoluble plutonium material

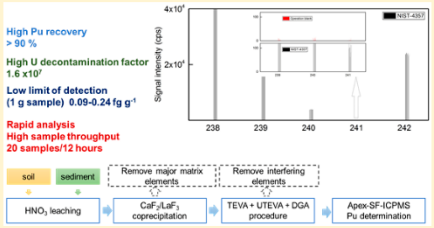
Mystery!

analytical chemistry — Technical Note
pubs.acs.org/ac

ABSTRACT: An acidic leaching method using HNO_3 is widely employed to release the global fallout Pu from soil samples for further chemical separations in radioecology and toxicology studies and in many applications using Pu as a useful tracer. In the method's sample ash treatment step to decompose organic matter in soil, various ashing temperatures (400−900 °C) are used; however, the effect of ashing temperature on the accurate Pu analysis has not been well investigated. In this study, two standard reference soils (IAEA-soil-6 and IAEA-375) were used to determine the ashing temperature effect (from 375 to 600 °C) on the HNO_3 leaching method. The Pu analytical results of both standard reference materials showed that lower $^{239+240}$Pu activity was observed when the ashing temperature exceeded 450 °C, and the $^{239+240}$Pu activity continued to decrease as the ashing temperature was raised. Approximately 40% of the Pu content could not be leached out by concentrated HNO_3 after ashing for 4 h at 600 °C. The Pu loss was attributed to the formation of refractory materials, which are insoluble in HNO_3 solution. This hypothesis was confirmed by the XRD analysis of soil samples, which revealed that plagioclase-like silicate materials were formed after high-temperature ashing. To ensure Pu release efficiency in HNO_3 leaching, we recommend 450 °C as the ideal ashing temperature. This recommendation is also useful for analysis of other important artificial radionuclides (e.g., ^{137}Cs, ^{90}Sr, ^{241}Am) for which an ashing process is needed to decompose the organic content in soil samples.



ABSTRACT: Plutonium is extensively studied in radioecology (e.g., soil to plant transfer and radiological assessment) and geochemistry (e.g., sediment dating). Here, we reported a new chemical separation method for rapid determination of Pu in soil and sediment samples, based on the following investigations: extraction behaviors of interfering elements (IEs, for inductively coupled plasma mass spectrometry (ICPMS) measurement) on TEVA resin; decontamination of U using TEVA, UTEVA, and DGA resins; and the impact of coprecipitation on Pu determination. The developed method consists of four steps: HNO_3 leaching for Pu release; CaF_2/LaF_3 coprecipitation for the removal of major metals and U; the proposed TEVA + UTEVA + DGA procedure for the removal of U, Pb, Bi, Tl, Hg, Hf, Pt, and Dy; and ICPMS measurement. The accuracy of this method in determining $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu isotopic ratios was validated by analyzing five standard reference materials (soil, fresh water sediment, and ocean sediment). This method is characterized by its stable and high Pu recovery (90−97% for soil; 92−98% for sediment) and high decontamination factor of U (1.6×10^7), which is the highest reported for soil and sediment samples. In addition, the short analytical time of 12 h and the method detection limits, which are the lowest yet reported in literature, of 0.56 μBq g^{-1} (0.24 fg g^{-1}) for ^{239}Pu, 1.2 μBq g^{-1} (0.14 fg g^{-1}) for ^{240}Pu, and 0.34 mBq g^{-1} (0.09 fg g^{-1}) for ^{241}Pu (calculated on the basis of a 1 g soil sample) allow the rapid determination of ultratrace level Pu in soil and sediment samples.



"Approximately 40% of the Pu content could not be leached out by concentrated HNO_3 after ashing for 4 h at 600 °C. The Pu loss was attributed to the formation of refractory materials, which are insoluble in HNO_3 solution"

"The developed method consists of four steps: HNO_3 leaching for Pu release; CaF_2/LaF_3 coprecipitation …; the proposed TEVA + UTEVA + DGA procedure ….; and ICPMS measurement.
…This method is characterized by its stable and high Pu recovery (90−97% for soil; 92−98% for sediment)"

Questions?

stolmachev@wsu.edu

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