

Optimization and Application of a Sequential Extraction Procedure for Multiple Actinide Elements

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NSSC Summer Seminar

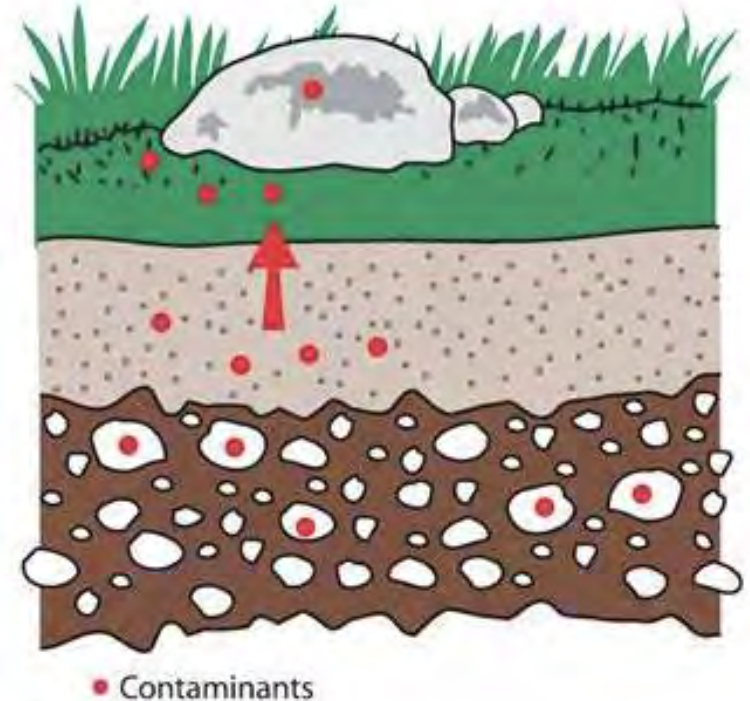
August 15, 2014

Outline

- ▶ Background and Importance
- ▶ Research Goals
 - Procedure modification for analysis of multiple actinide elements
 - Application of sequential extraction procedure to a broad range of soil profiles
 - Addition of a sixth fraction for complete sample dissolution
- ▶ Results
- ▶ Conclusions
- ▶ Future Work

Importance

- ▶ Radionuclide contamination risk is often assessed based on total concentration
- ▶ Potential for contaminant mobility must also be considered due to bioavailability concerns

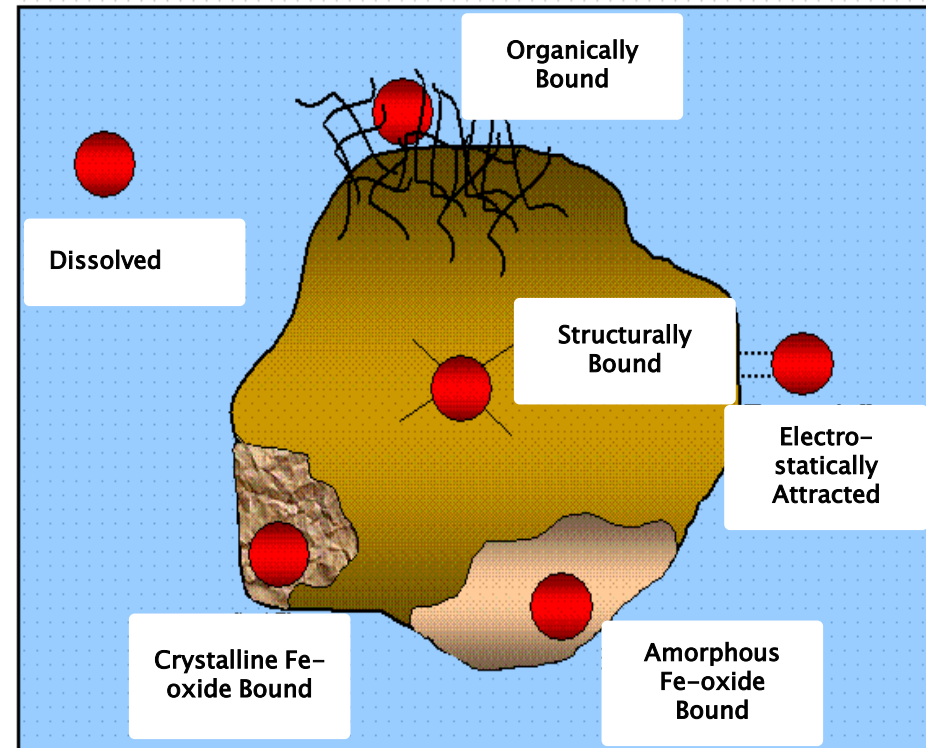


Importance

- ▶ Release conditions are highly dependent on speciation
- ▶ No method currently exists for direct measurement of solid-phase speciation at environmental concentrations
 - Spectroscopic techniques (XANES, EXAFS) will measure speciation in near field aqueous solutions, but does not extend to low concentrations of solid-phase samples
- ▶ Best approach is to indirectly assess contaminant association with primary geochemical host phases

Sequential Extraction

- ▶ Definition:
 - Sequential extraction is the selective dissolution of soil phases with increasingly aggressive chemical treatment
- ▶ Furnishes Information On:
 - Physicochemical and biological availability
 - Mobilization and transport of contaminants
 - Origin



Kaplan, D I. Quantification of thorium and uranium sorption to contaminated sediments. Savannah River Site: U.S. Department of Energy; 2000. WSRC-MS-2000-00184/Rev.1. AC09-96SR18500.

History

- ▶ Tessier (1979)
 - Five operationally defined fractions
 - Most recent work is a slight modification
- ▶ Schultz (1998)
 - Am, Pu, and U extraction from IAEA 135 (marine sediment)
- ▶ Outola (2009)
 - Maximum U and Pu extraction from NIST 4354 lake sediment and NIST 4357 ocean sediment

Promises and Problems

▶ Promises

- Results lead to a better understanding of conditions under which contaminants may be released into the environment

▶ Problems

- Does not fully mimic weathering conditions
 - Strong reagent, short reaction time vs weak reagent, long reaction time
- Method reproducibility varies based on chemical properties of the extracted elements and chemical composition of soils

Research Goals

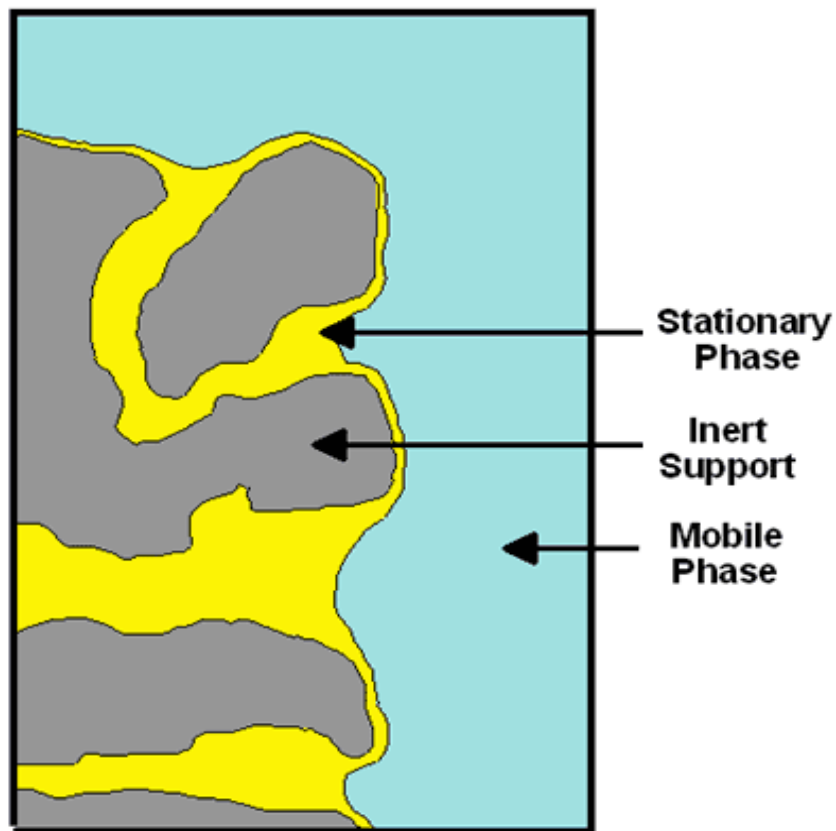
- ▶ Part I – Procedure Modification
 - Single Isotope Study
 - Reagent Interference Study
- ▶ Part II – Procedure Application
 - Use modified procedure to investigate various soil and sediment samples
 - Determine variations in leaching due to different soil fractionation
- ▶ Part III – Evaluation of a Sixth Fraction for Complete Dissolution
 - Evaluate microwave digestion and fusion procedures for complete dissolution
 - Apply chosen procedure to previously leached IAEA 384

Part I – Procedure Modification

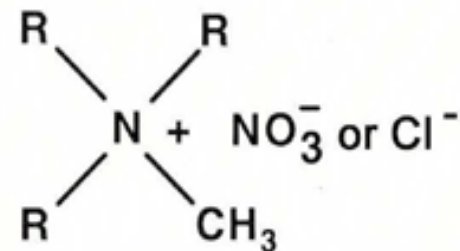
Part I Introduction

- ▶ Outola procedure was optimized for maximum extraction of U and Pu
 - Anion exchange used for separations
- ▶ UNLV would like to add the ability to monitor for more actinides
- ▶ Switch to extraction chromatography based separations
 - Test for breakthrough
 - Verify no interferences created by sequential extraction reagents

Extraction Chromatography



Trialkyl, methylammonium
nitrate (or chloride)



$$k' = D \cdot \frac{v_s}{v_m}$$

k' = free column volume to peak maximum

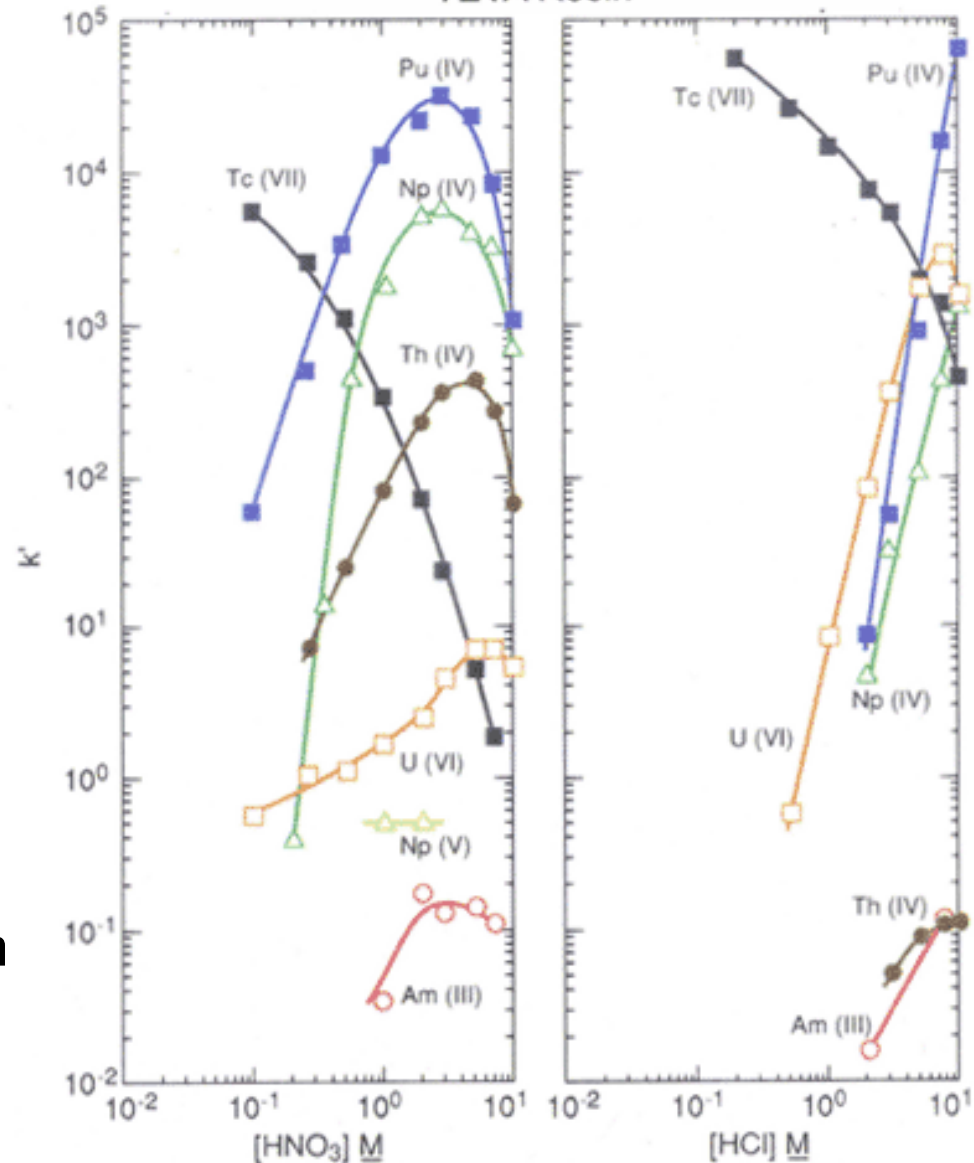
$$D_W = \frac{A_o - A_s}{A_s} \cdot \frac{mg}{L}$$

$A_o - A_s$ = activity sorbed on known resin weight

A_s = activity in known solution volume

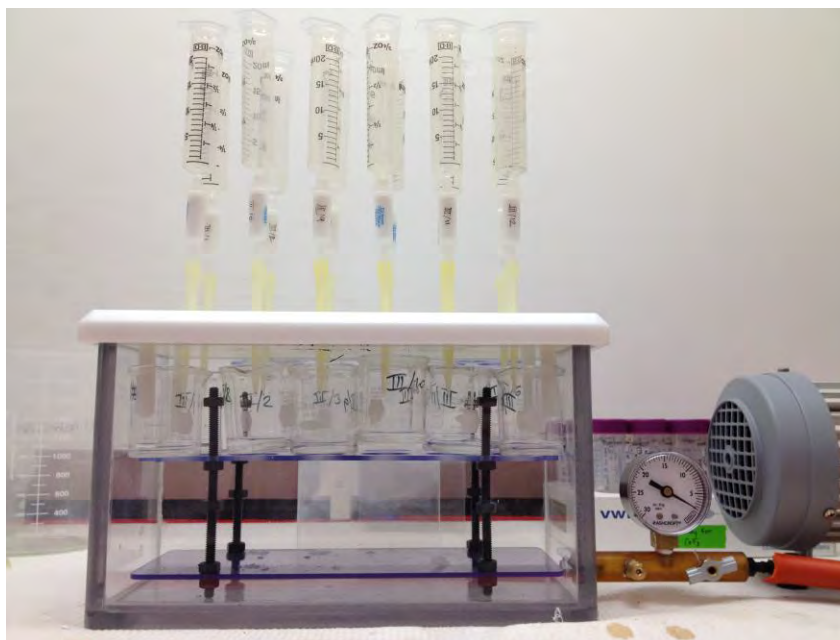
Acid dependency of k' for various ions at 23°C.

TEVA Resin



Separation Procedure

- ▶ Rapid column extraction method for actinides in soil
 - Uses stacked TEVA, TRU and DGA extraction chromatographic resins on a vacuum box.

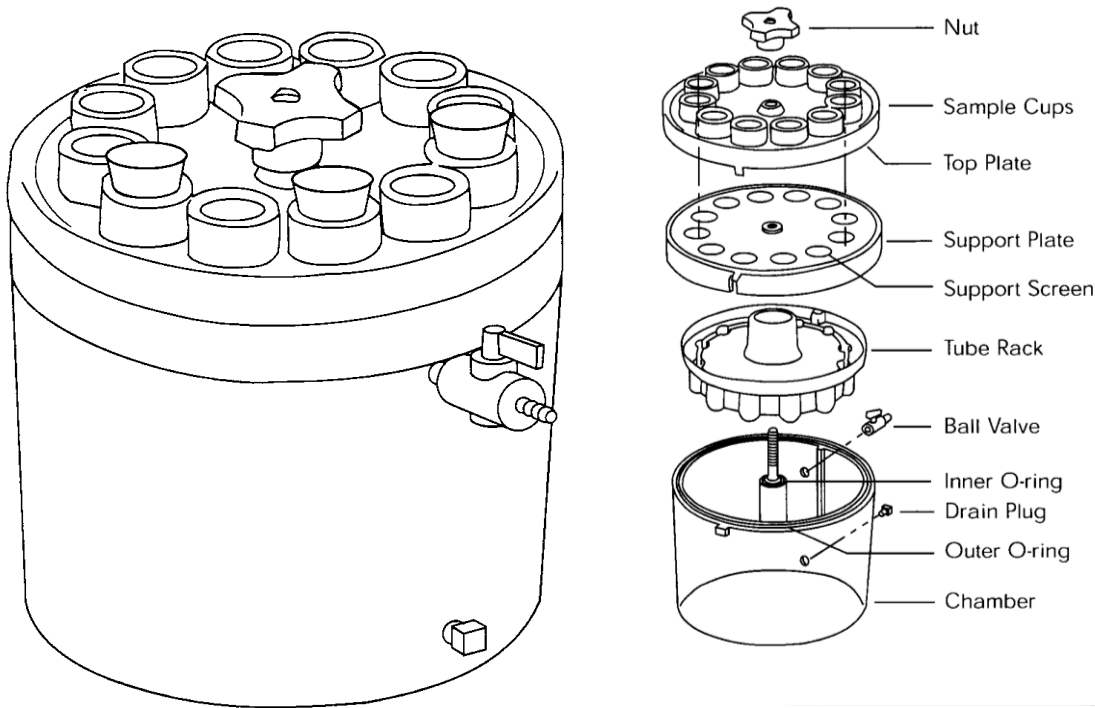


Maxwell III SL, Culligan BK (2006) J. Radioanal. and Nucl. Chem, 270(3):699

Maxwell Procedure

- ▶ Column load solution and valence adjustments
- ▶ Thorium
 - TEVA 9 M HCl
- ▶ Plutonium
 - TEVA 0.1 M HCl – 0.05 M HF – 0.03 M TiCl_3
- ▶ Uranium
 - TRU 0.1 M ammonium bioxalate
- ▶ Am
 - DGA 1 M HCl
 - REE purification on hot plate
 - TEVA 1 M HCl

Source Preparation and Counting



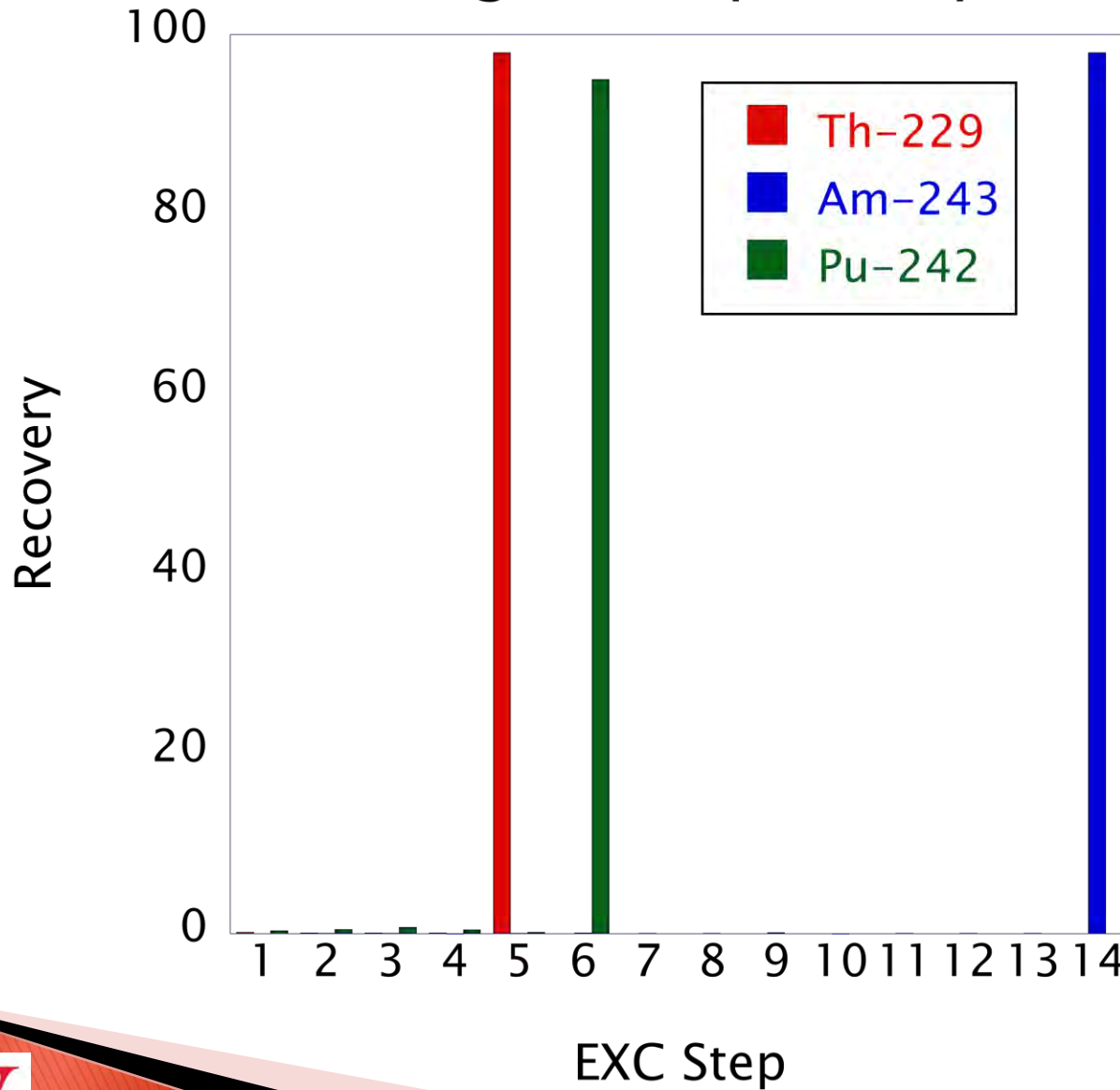
99.4 % procedural recovery for plutonium

Single Isotope Study

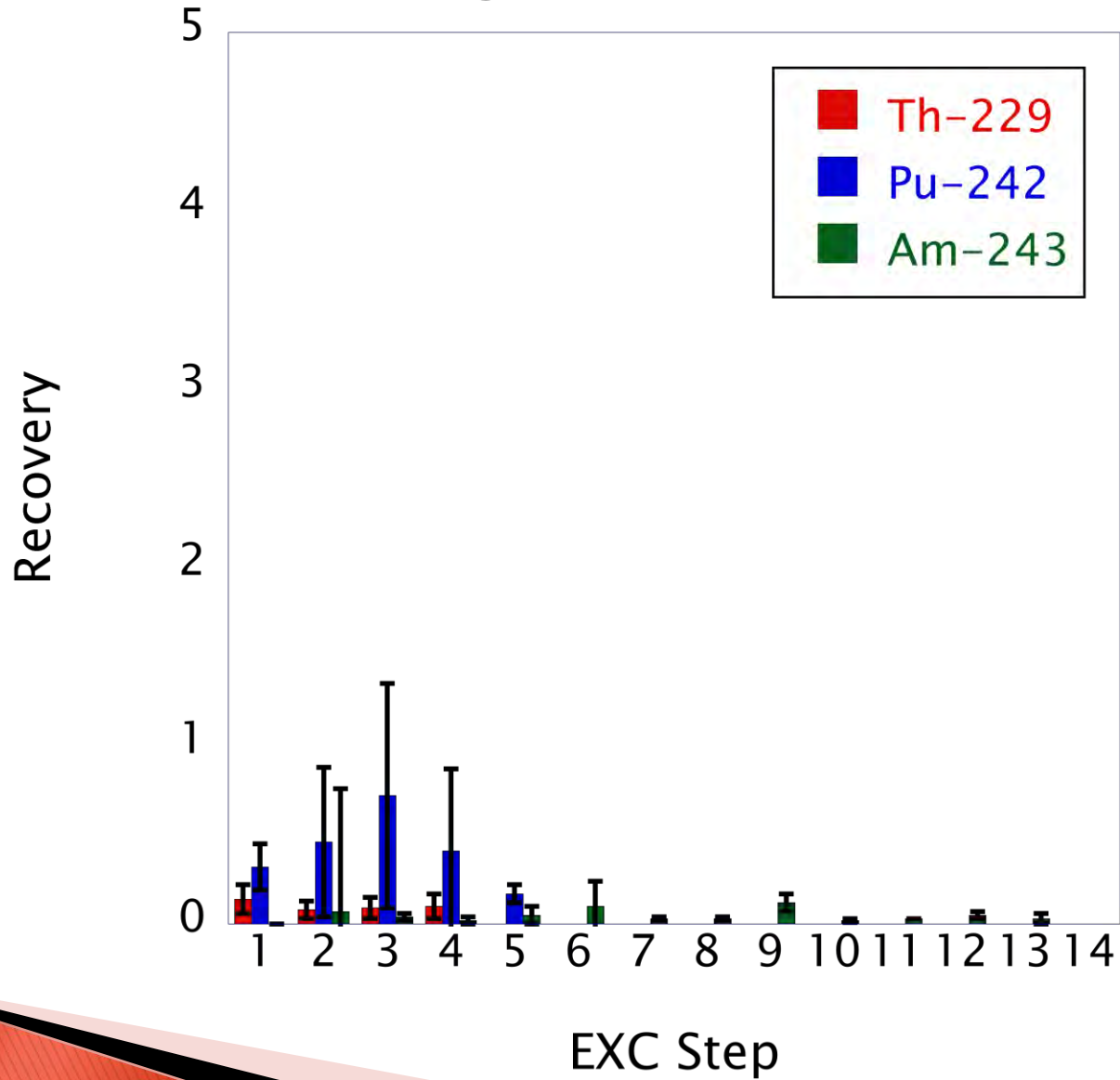
- ▶ To determine breakthrough potential of tracers to be used in application studies
 - Run a single tracer through EXC procedure and analyze all eluates

Tracer	Activity Concentration (Bq mL ⁻¹)
²²⁹ Th	1.70
²³² U	0.101
²⁴² Pu	0.0707
²⁴³ Am	1.76

Single Isotope Study



Single Isotope Study



Reagent Interference Study

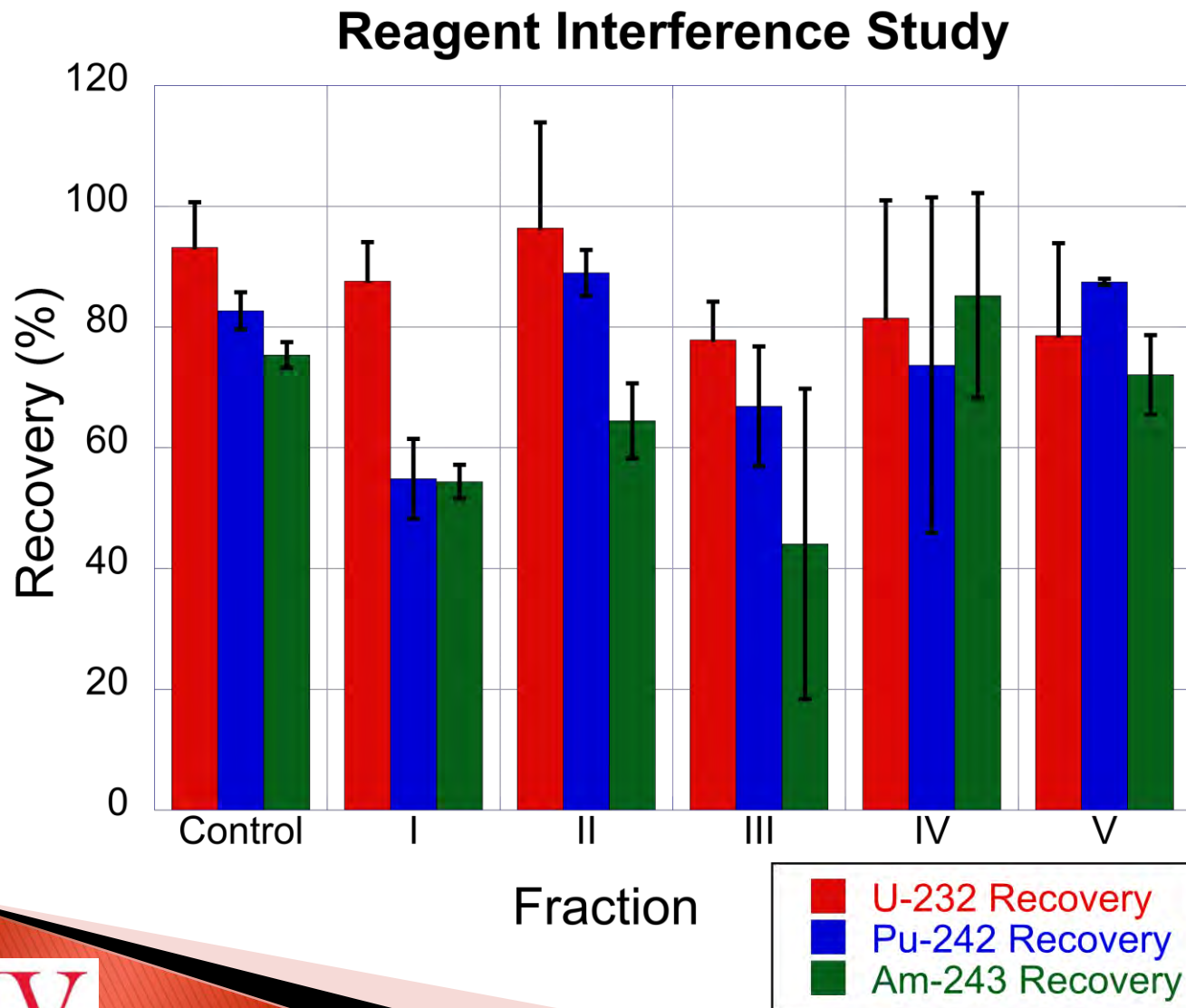
- ▶ Determine if reagents used in sequential extraction procedure will have an effect on recoveries from EXC procedure
 - Prepare maximum concentration of each sequential extraction reagent
 - Add tracers of U, Pu, Am and Th to monitor recoveries
 - Run solutions through EXC procedure
 - Mount with CeF_3 and count by alpha spec

Sequential Extraction Reagents

Reagent	Concentration (M)
MgCl ₂	1
NH ₄ Ac in 25% HAc	2
NH ₂ OH · HCl in 25% HAc	0.1
30% H ₂ O ₂ in 0.05 M HNO ₃	30 wt %
HNO ₃	4

Outola I, Inn K, Ford R, Markham S, Outola P (2009) J. Radioanal. Nucl. Chem.

Reagent Interference Results



Part I Conclusions

- ▶ Single Isotope Study
 - No significant breakthrough was seen for any elements
- ▶ Reagent Interference Study
 - Most recoveries were above 75%
 - Similar recovery to control samples
 - Fractions and elements with lower recoveries will need longer count times

Part II – Procedure Application

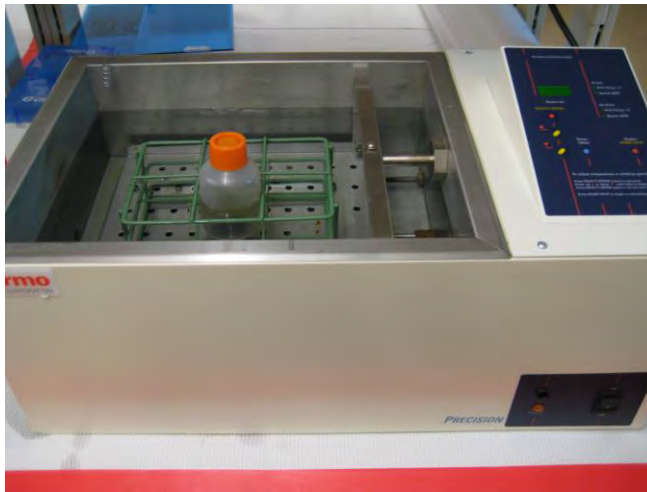
Procedure Application

- ▶ Apply modified sequential extraction procedure to various soil and sediment samples
- ▶ Analyze for multiple actinide elements to determine potential for contaminant mobility under various conditions
- ▶ Monitor trace elements to determine phase selectivity

Reference Materials

Material	Activity Concentration	Soil Profile	Representative of
NIST 4354 Lake Sediment	0.26–28.6 mBq g ⁻¹ Th, U, Pu, Am	Higher organic content	Lake sediment
NIST 4357 Ocean Sediment	0.6–12 mBq g ⁻¹ Th, U, Pu, Am	Higher salt content	Ocean sediment
IAEA 447 Moss Soil	5.3 Bq kg ⁻¹ ²³⁹ + ²⁴⁰ Pu	High organic content	Global fallout record
IAEA 384 Fangataufa Sediment	107 Bq kg ⁻¹ ²³⁹ + ²⁴⁰ Pu	~100 % CaCO ₃	Post-detonation debris

Sequential Extraction Chemistry



Sequential Extraction Procedure

Target Phase	Reagent	Concentration (M)	Temperature (°C)	Time (h)
Exchangeable	MgCl ₂	1	25	1
Carbonates	NH ₄ Ac in 25% HAc	2	50	2
Fe/Mn Oxides	NH ₂ OH · HCl in 25% HAc	0.1	70	6
Organic Material	30% H ₂ O ₂ in 0.05 M HNO ₃	30 wt %	70	3
Persistently Bound	HNO ₃	4	90	4

Outola I, Inn K, Ford R, Markham S, Outola P (2009) J. Radioanal. Nucl. Chem.

Stable Element Analysis

- ▶ Analyze leachates for stable elements by ICP–AES
 - Procedure
 - Al, Ca, Co, Cr, Cs, Fe, K, Mg, Mn, Na, P, Si, Ti, Y, Zn
 - Fission products
 - Sr, Zr
 - Heavy metals
 - Pb



Actinide Analysis

Procedure	Source	Time
Sequential extraction	Outola et al	1 week
Tracer addition/evaporation	N/A	3–4 days
Preconcentration	Fe(III)OH, CeF ₃	1 day
Separations	Maxwell et al	1–2 days
Sample mounting	Sill et al	2 hours
Alpha counting	Canberra Alpha Analyst	1–5 weeks

**Total time: 3-7 weeks
(exclusive of data analysis)**

Preconcentration

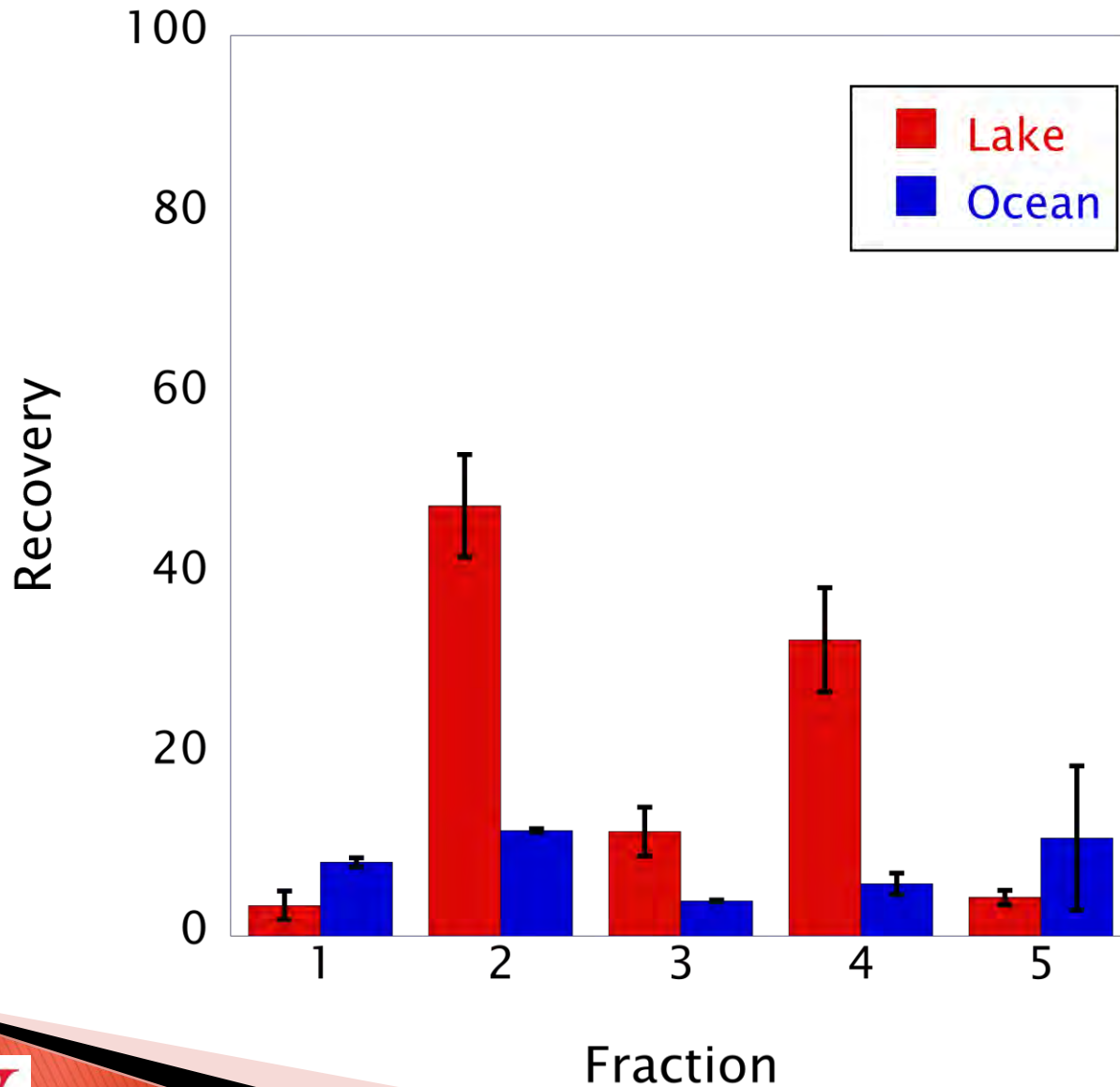
- ▶ Ferric Hydroxide Co-precipitation
 - Concentrate actinides and eliminate major interferences
- ▶ Cerium Fluoride Microprecipitation
 - Reduce sample mass for column loading
 - Precipitate is filtered to separate
 - Filter is washed with 3 M HNO_3 – 0.25 M boric acid to remove precipitate > 90 % removal from filter

Preparation for Alpha Spectroscopy

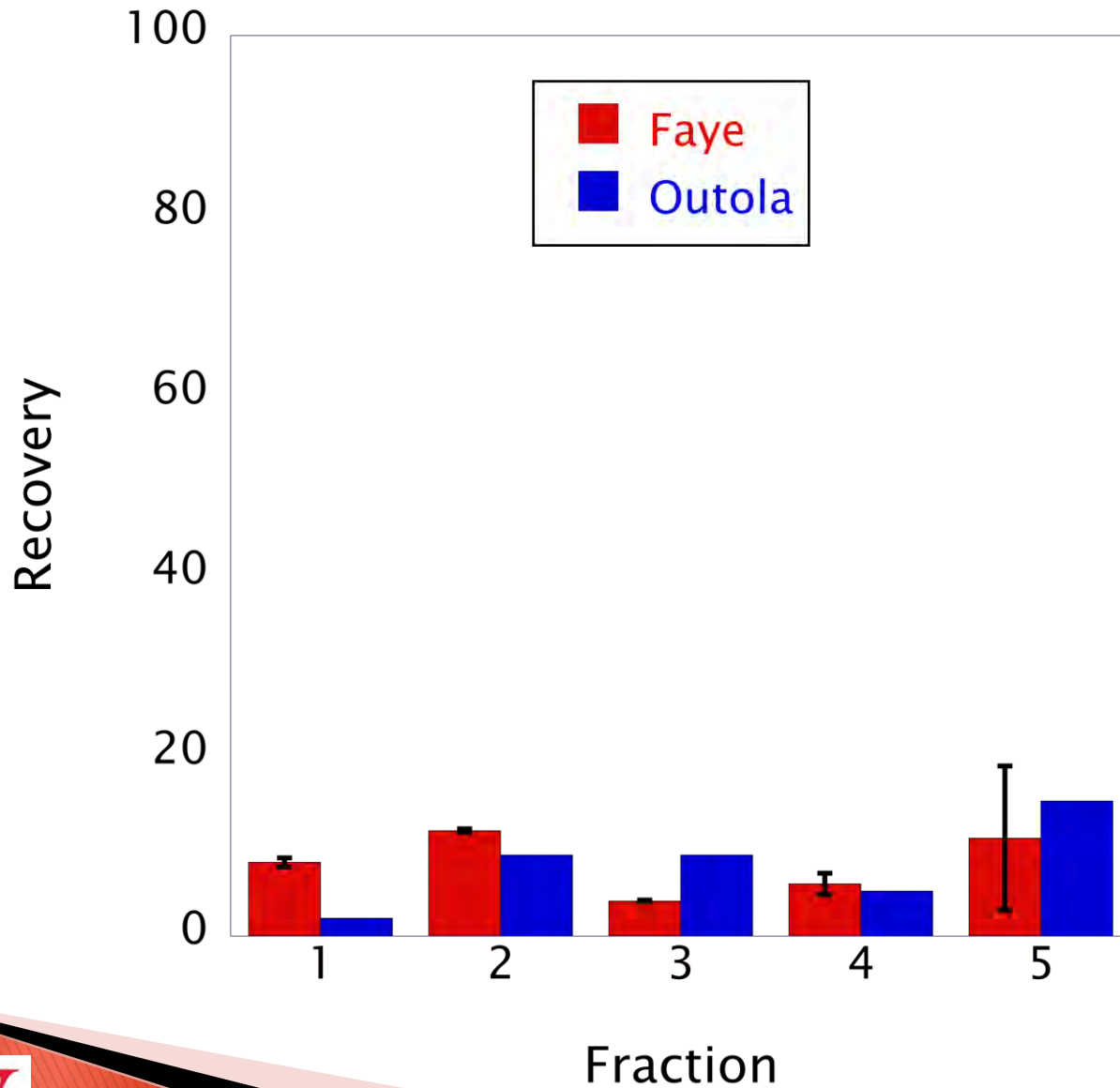
- ▶ Separations
 - Extraction chromatography – Maxwell et al
- ▶ Sample mounting
 - CeF_3 microprecipitation – Sill et al
- ▶ Counting
 - Canberra and Ortec systems using PIPS detectors
 - Counting statistics based on tracer activity

Uranium Results

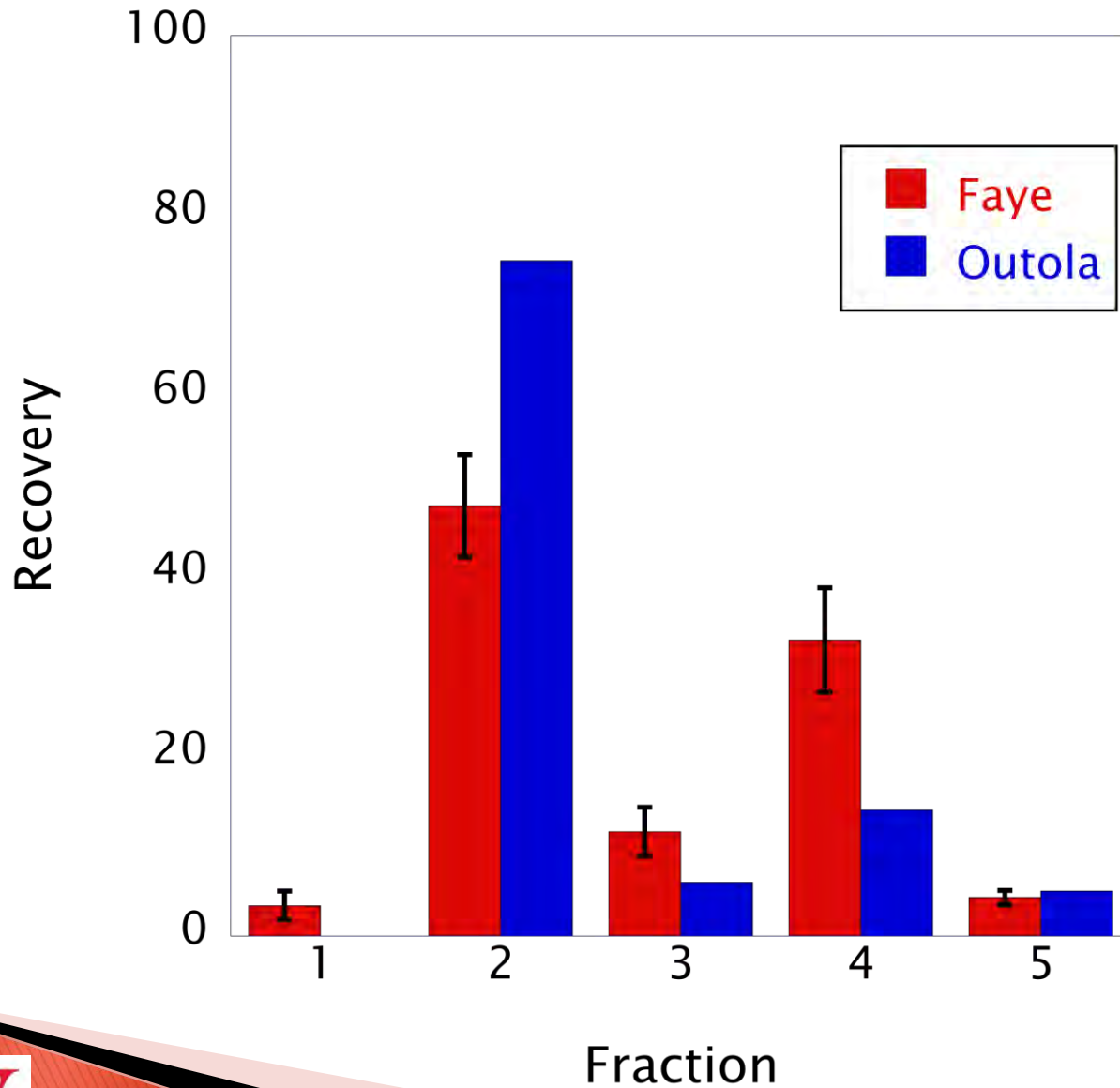
U-238 Lake vs Ocean Sediment



Ocean Sediment U-238

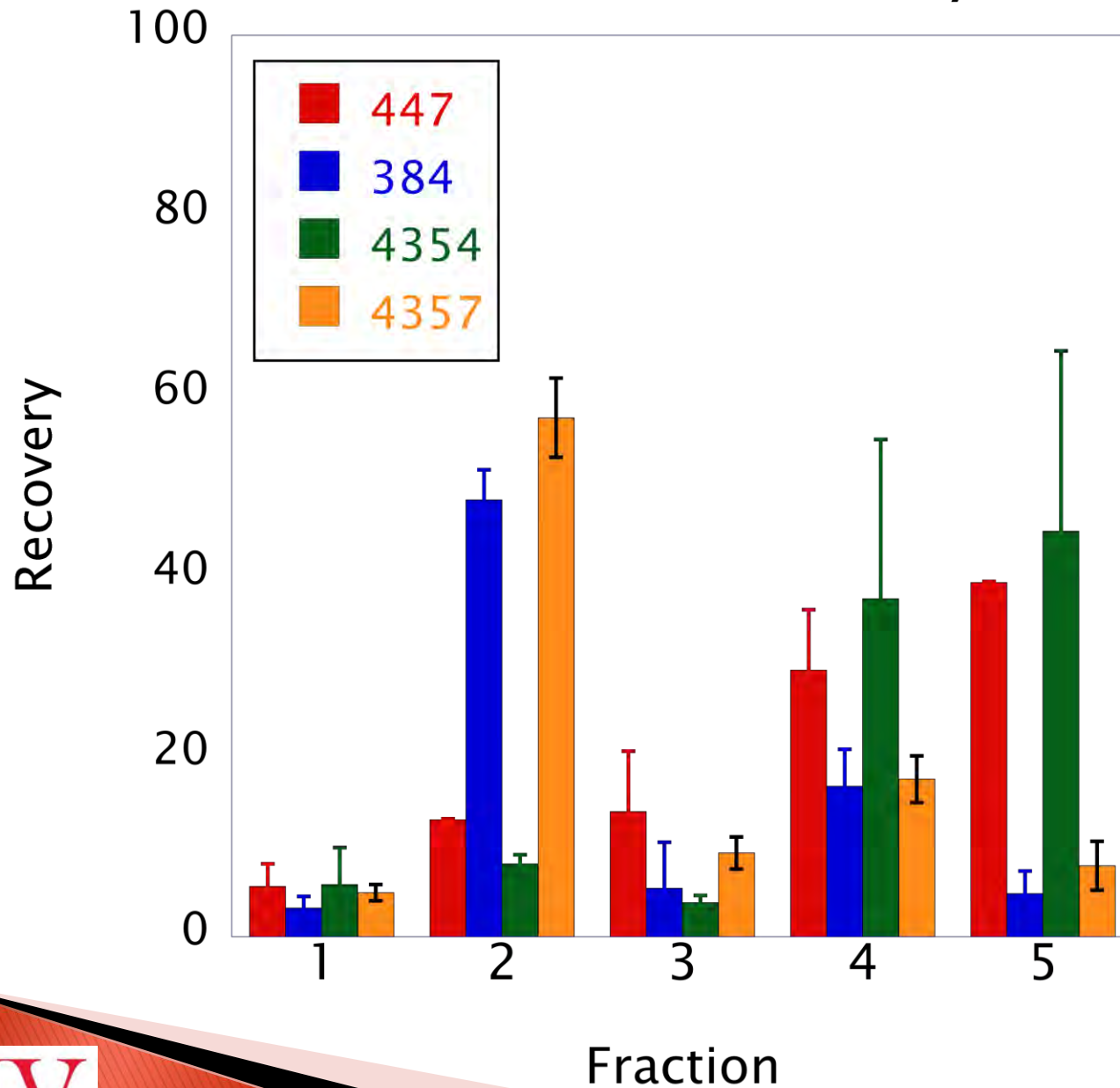


Lake Sediment U-238

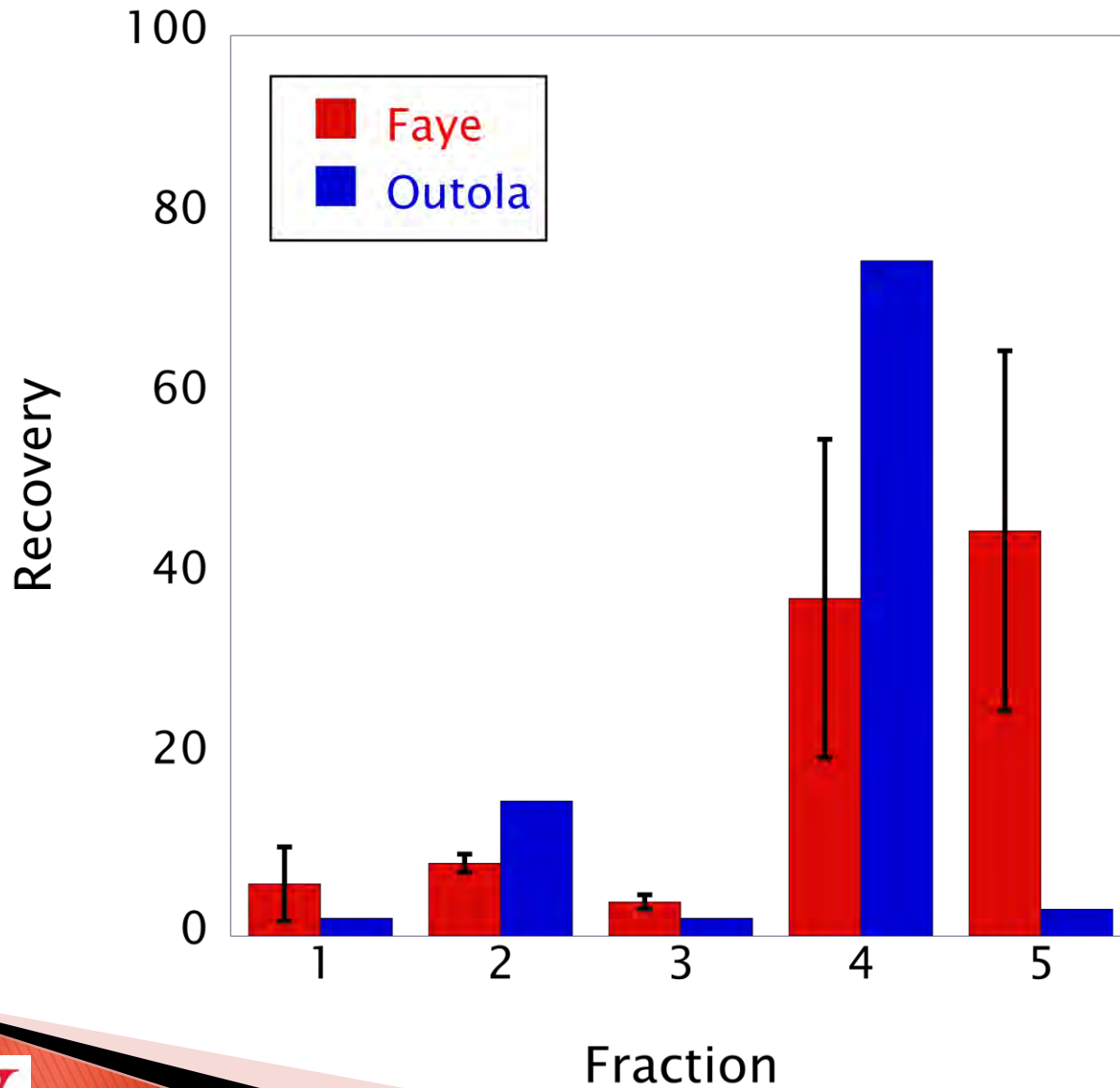


Plutonium Results

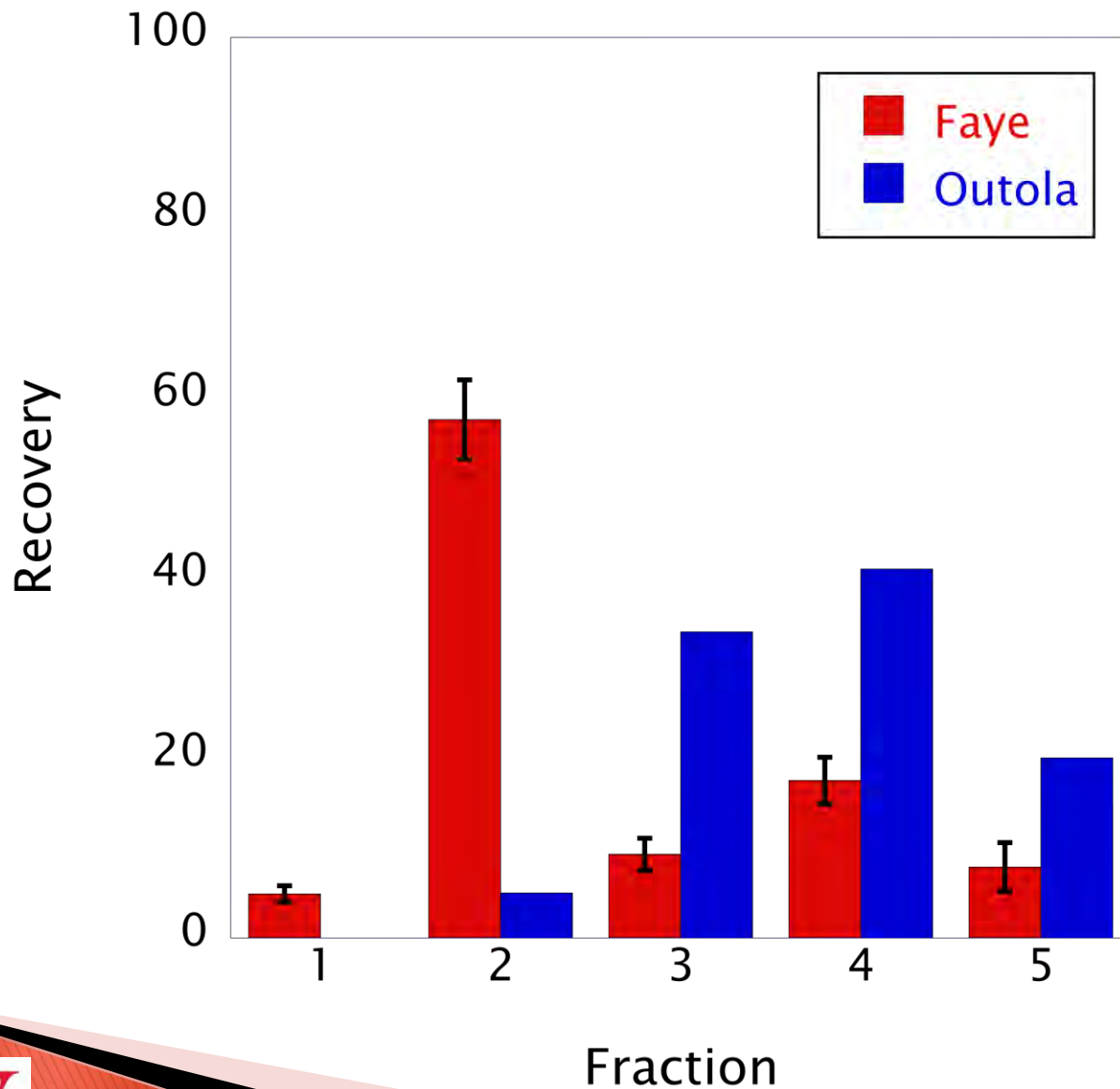
Plutonium Revocery



Lake Sediment Pu-239+240



Ocean Sediment Pu-239+240



Part II Conclusions

- ▶ Obvious differences are seen in contaminant distribution per fraction based on different sediment samples
- ▶ Leaching behavior can be related to soil fractionation of each sediment
- ▶ Differences in leaching based on element being leached

Part III – Evaluation of a Sixth Fraction for Complete Dissolution

Part III Introduction

- ▶ Incomplete dissolution of some elements seen in some soils
- ▶ Attempt to obtain 100 % actinide contaminant recovery with a complete dissolution step at the end of sequential extraction procedure
- ▶ IAEA 384 used based on plutonium activity concentration

Procedure Selection

▶ Microwave Digestion

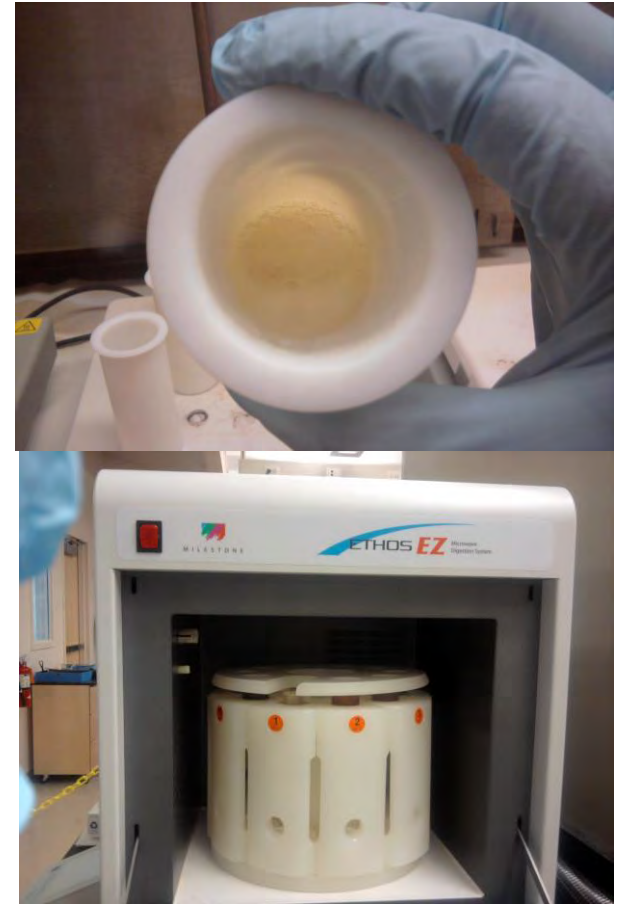
- EPA soil method
 - EPA-600-R-12-636, August 2012
- Carbonate specific method
 - Kemp AJ, Brown CJ (1990) Analyst, 115:1197

▶ Fusion

- Sodium hydroxide fusion for concrete matrices
 - EPA 402-R-14-004, April 2014

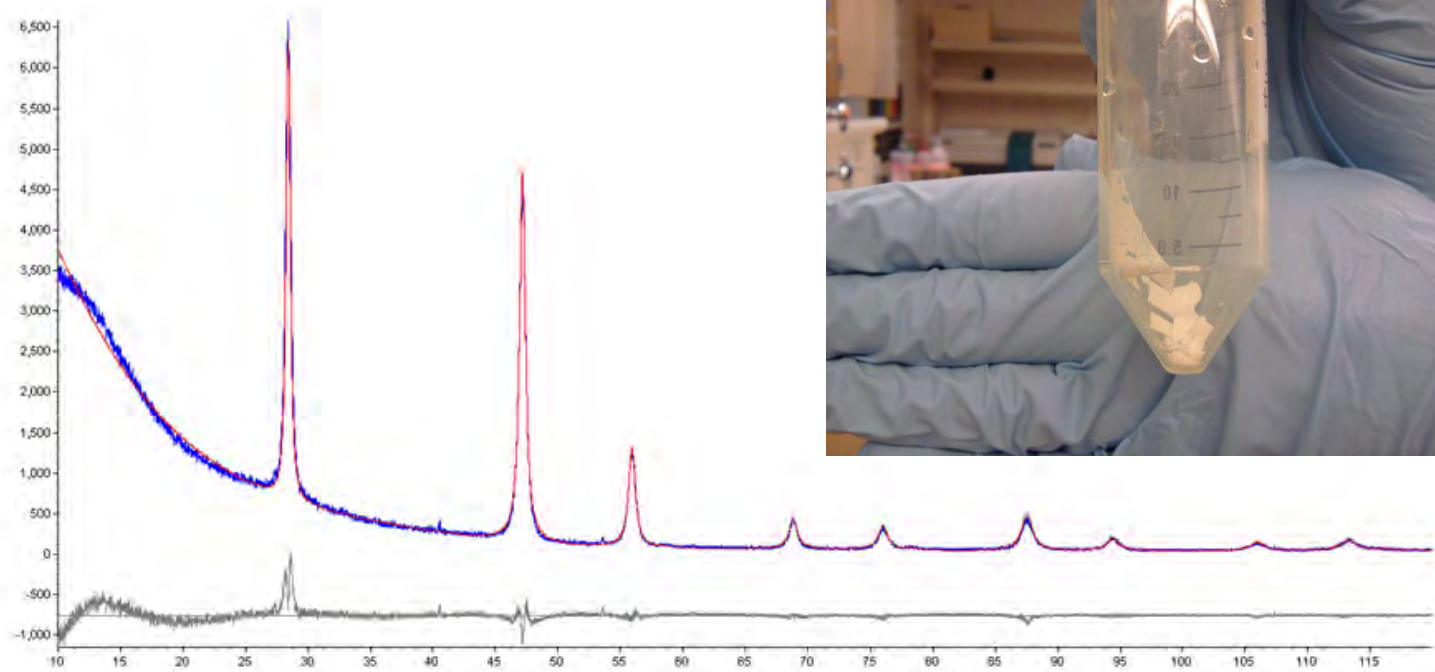
EPA Soil Microwave Digestion

- ▶ 0.25 g IAEA 384
- ▶ 9 mL conc. HNO_3
- ▶ 3 mL conc. HF
- ▶ Microwave conditions:
 - 180 °C, 15 bar, 1000 W



Results

- ▶ White precipitate formed
- ▶ XRD used to verify precipitate was CaF_2



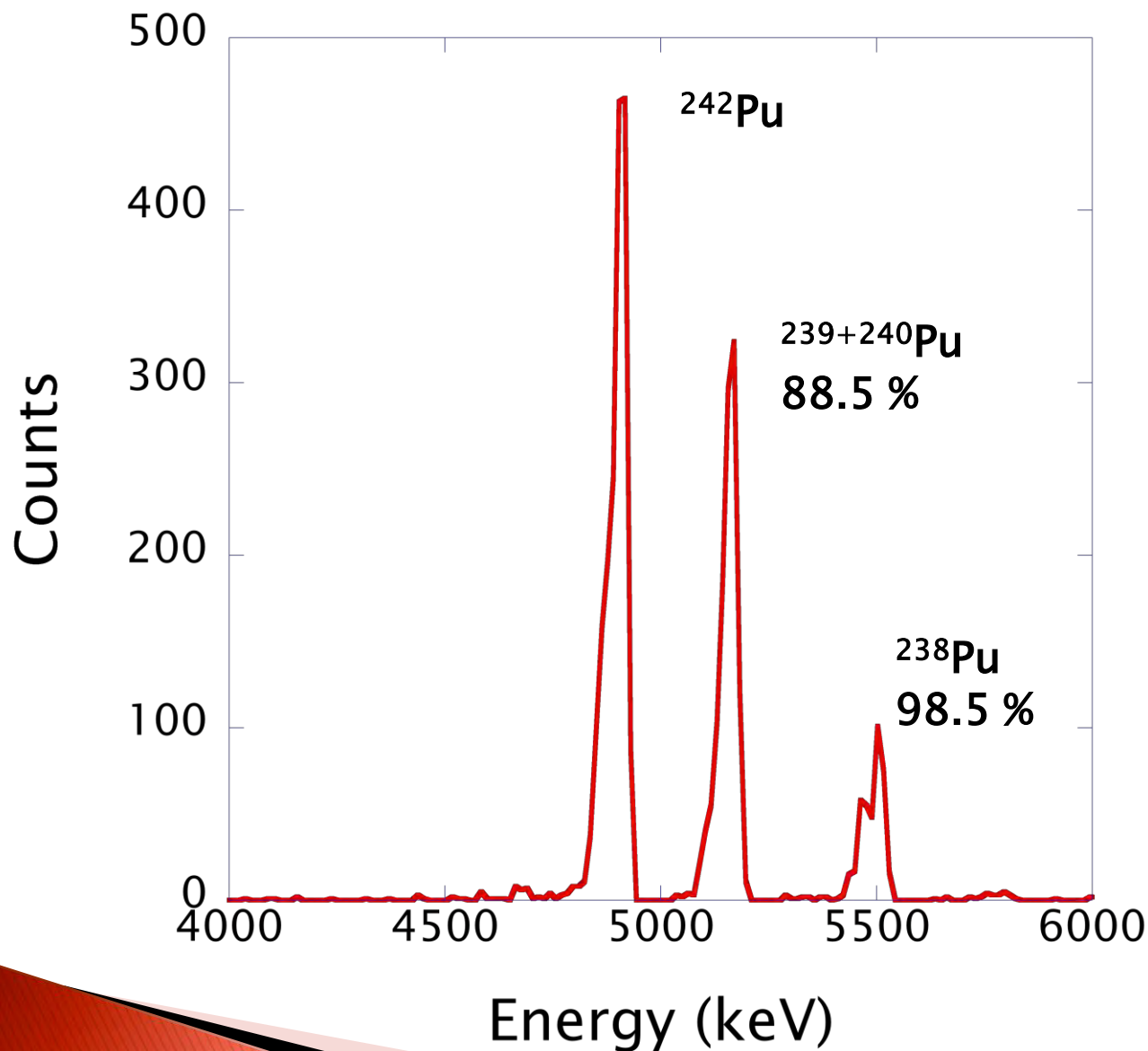
Alpha Results

- ▶ Solution
 - 5 % recovery
- ▶ Dissolved precipitate
 - 95 % recovery

Carbonate Specific Microwave Digestion

- ▶ Add 0.25 g IAEA 384 + 20 mL 0.5 M acetic acid to vessel and place on hot plate to release CO₂ gas
- ▶ Add 0.84 mL conc. HF and 3 mL conc. HNO₃ to vessel
- ▶ Microwave conditions:
 - 180 °C, 15 bar, 630 W, 3 minutes
- ▶ Add 10 mL 4 % boric acid to vessel
- ▶ Microwave conditions:
 - 180 °C, 15 bar, 570 W, 30 minutes

Carbonate Specific Microwave Digestion



Part III Conclusions

- ▶ Problems with EPA soil method
- ▶ Carbonate specific method recommended for IAEA 384
- ▶ Fusion will be completed in near future

Summary

▶ Procedure Modification

- Most recoveries for control samples are above 75 %
- Microprecipitation procedural recovery is near 100 %

▶ Procedure Application

- Obvious differences are seen in contaminant distribution per fraction based on different sediment samples
- Plutonium leaches based on soil fractionation of each sediment

▶ Addition of a Sixth Fraction

- Problems with EPA soil method
- Carbonate specific method recommended for IAEA 384
- Fusion will be completed in near future

Future Work

- ▶ Analyze leachates for stable elements by ICP–AES
 - Al, Ca, Co, Cr, Cs, Fe, K, Mg, Mn, Na, P, Pb, Si, Sr, Ti, Y, Zn, Zr
- ▶ Fusion
- ▶ Apply fraction 6 to IAEA 384

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UNLV Radiochemistry

Thank You!



References

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