Welcome to the Eichrom Workshop on Emergency Response Methods- Actinides, Sr and Ra-226

Who can name where Larry Is?

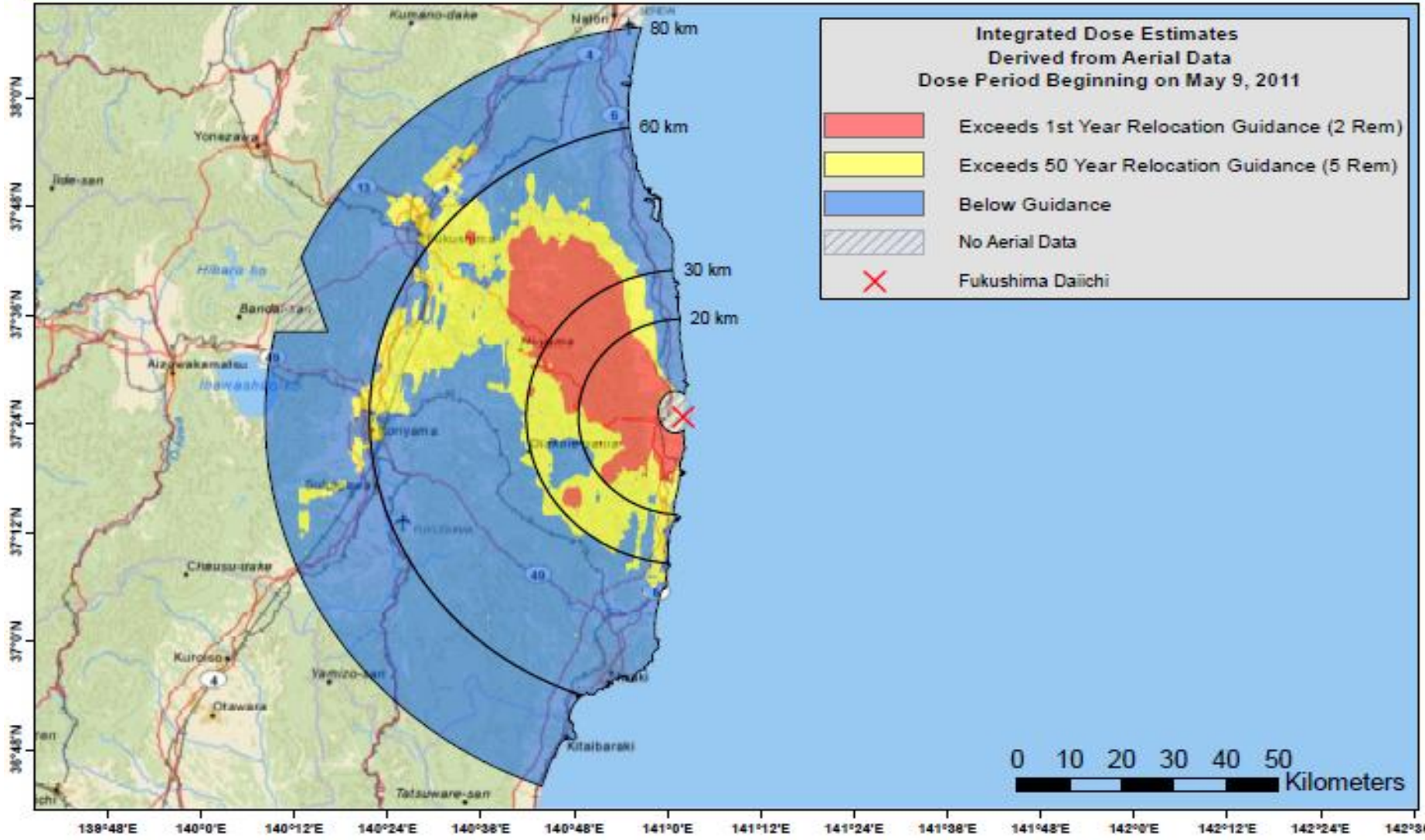

A lot happens between MARC Conferences
Summer 2010, Olkiluoto-3, Finland

National Nuclear Security Administration

Aerial Measuring Results

Joint US/Japan Survey Data

FUKUSHIMA DAIICHI
JAPAN



Map created on 5/07/11 07:21:00 JST

UNCLASSIFIED

Preparedness and Emergency Response

- Eichrom and the Basics of Extraction Chromatography
- First Wave Response
- Approaches to alpha and beta Emergency Response Measurements
  - FDA
  - CDC
  - EPA

Outline Continued

- S. L. Maxwell Publications- Actinides/Sr
  - Air Filters
  - Soil
  - Concrete/Brick
  - Food/ Vegetation

1930

1940

1950

1960

1970

1980

1990

2000

2010

Federal lab consortium awards

Researchers honored for tech transfer efforts

Four Argonne researchers have been honored for their accomplishments in commercializing discoveries made through federally funded research.

E. Philip Horwitz (CHM), Mark Dietz (CHM), Richard W. Siegel (MSD) and Kevin Myles (CMT) received awards from the Federal Laboratory Consortium. The consortium is made up of representatives from federal laboratories, industry, academia, and state and local governments.

Horwitz and Dietz were honored for their development

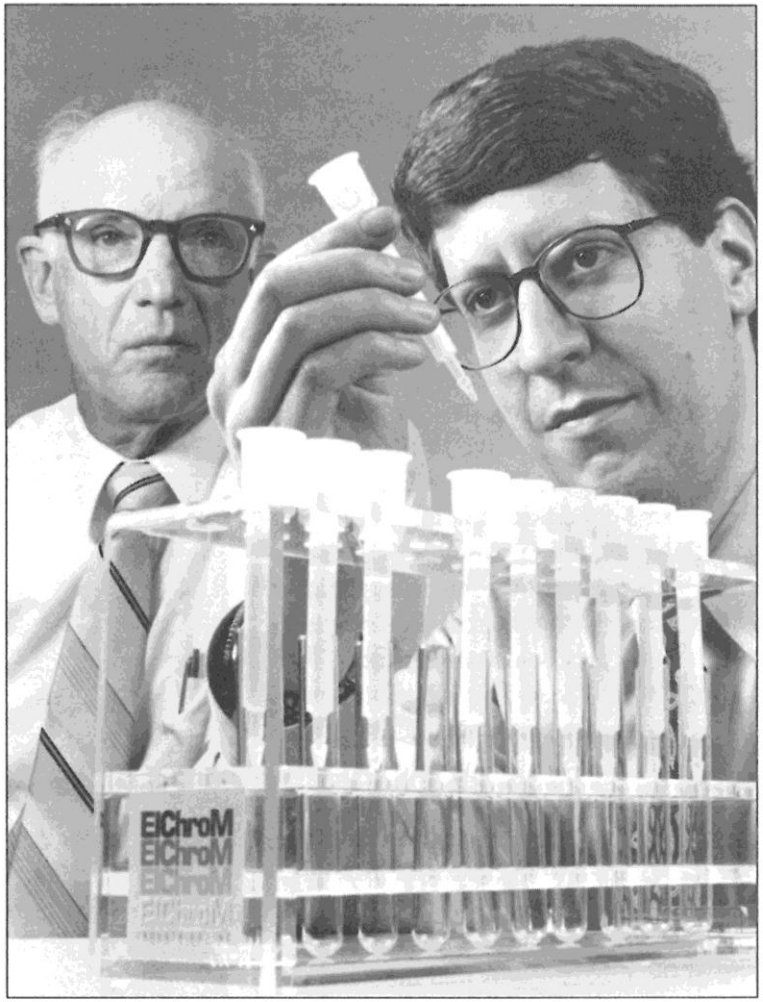
E. Philip Horwitz (CHM), Mark Dietz (CHM), Richard W. Siegel (MSD) and Kevin Myles (CMT) received awards commercializing discoveries made through federally funded research.

of a series of new chemical resins capable of selectively removing certain radioactive materials from radioactive waste, and biological and environmental samples.

The process developed by Horwitz and Dietz is less complex than previous methods, leading to an estimated cost savings of $300-$400 per sample, and results in much smaller volumes of waste.

A senior chemist at Argonne, Horwitz received the the U.S. Department of Energy's Distinguished Associate Award in 1990 for developing the TRUEX (transuranium extraction) process, a scientific and technical breakthrough which greatly reduces the volume of radioactive wastes requiring deep burial.

Horwitz is chief scientific consultant for EIChroM



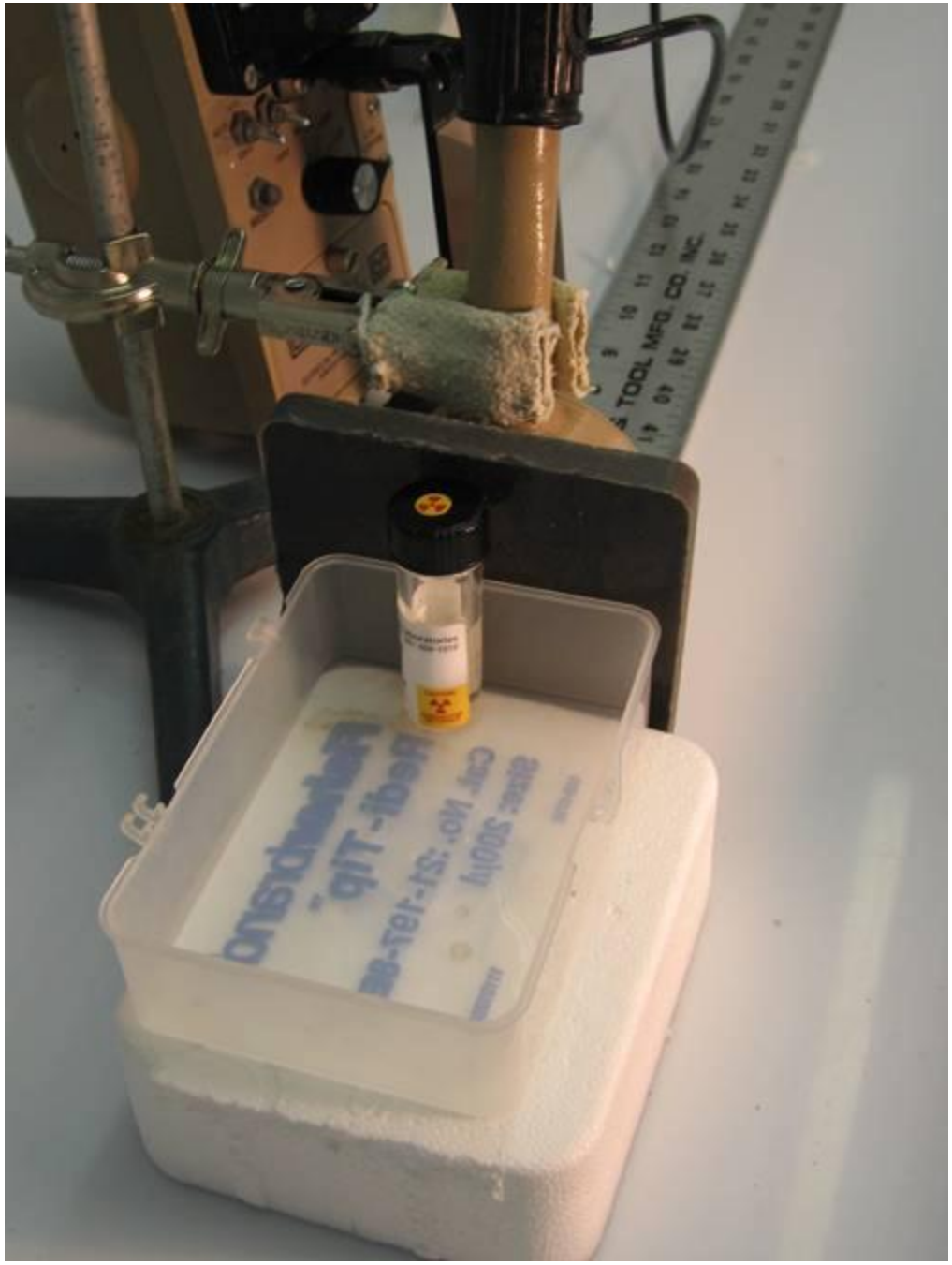
ENVIRONMENTAL AID — E. Philip Horwitz (CHM), left, and David M. Einolf of EIChroM Industries inspect a chemical resin that can help clean up radioactive wastes. EIChroM manufactures and markets the new resins, which are based on research by Horwitz and Mark Dietz (CHM).

Eichrom / NPO

- Founded in 1990

  - 2008 Eichrom Technologies acquired Nuclear Power Outfitters

  - 2009 Eichrom moved entire company into one facility in Lisle, IL just ~30 miles of downtown Chicago



eichrom

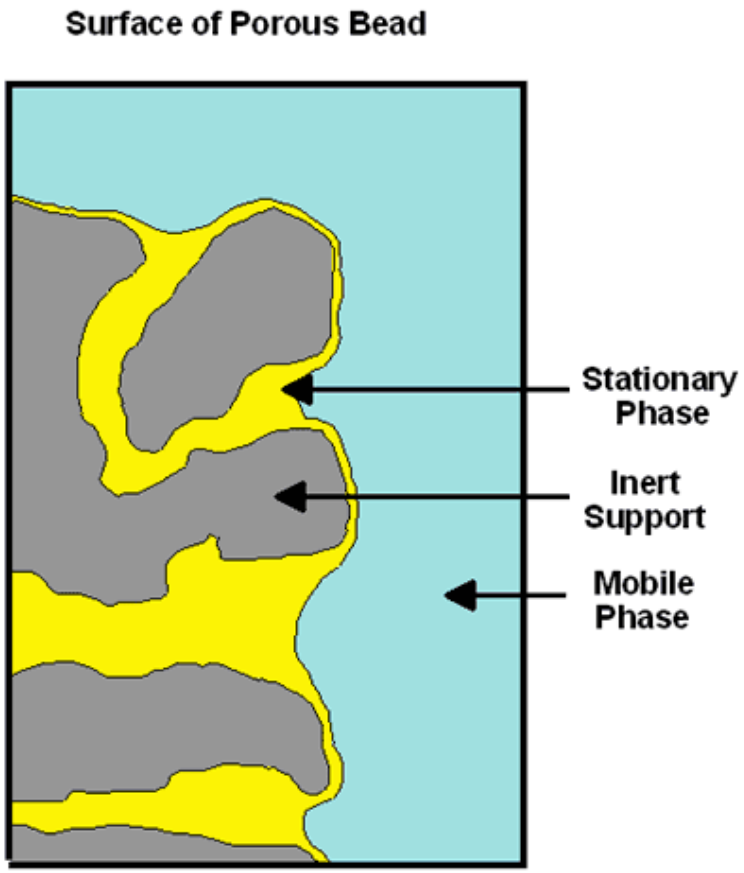
Extraction Chromatography

Solvent Extraction

+

Column Chromatography

Extraction Chromatographic Resin



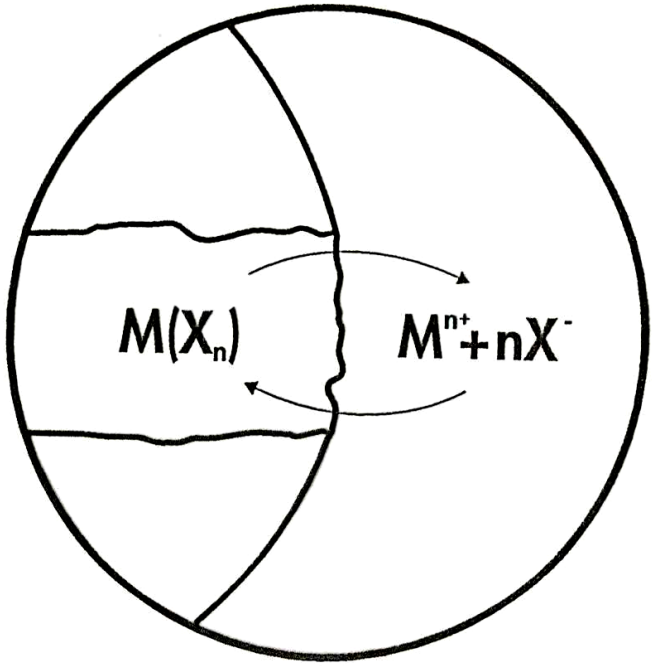
Inert support =

Macroporous Acrylic Resin

Example Stationary Phases

- **Crown Ether (Sr)**
- **CMPO (TRU)**
- **DAAP (UTEVA)**

Metal Anion Complex Formation

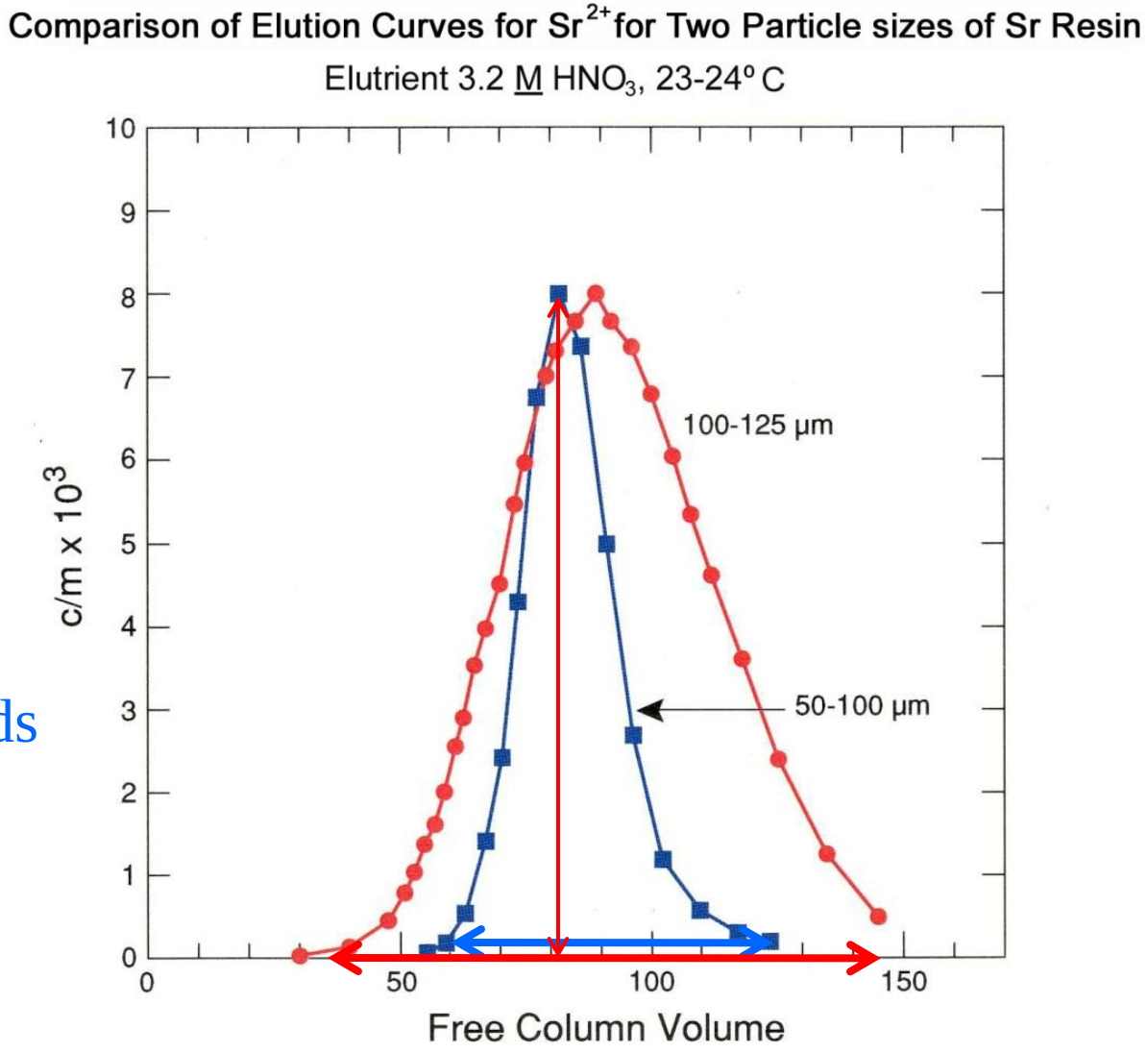


$$\text{Metal} + \text{Anion} \rightleftharpoons \text{Complex}$$

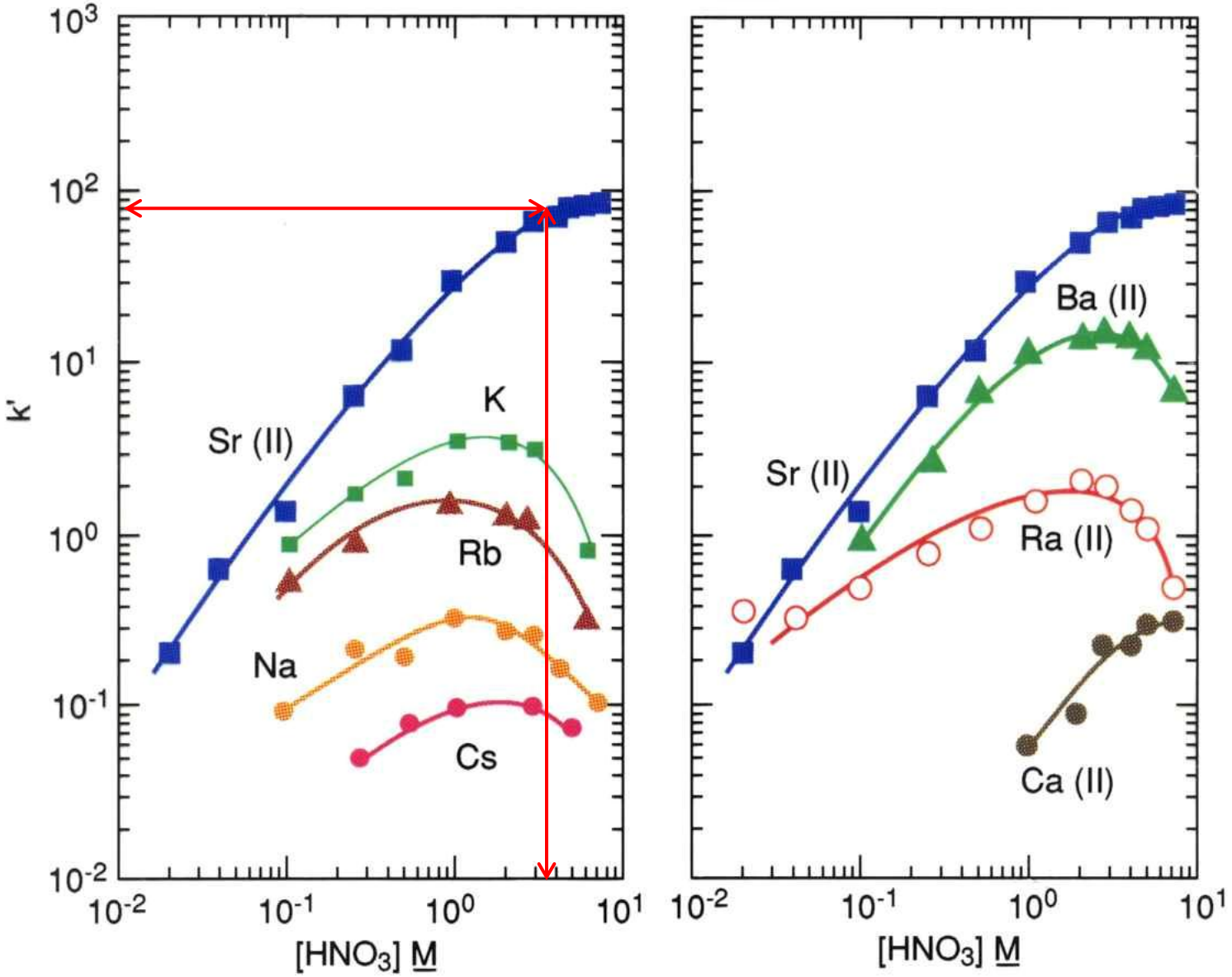
$$\text{Complex} + \text{Organic} \rightleftharpoons \text{Extracted}$$

eichrom

- Smaller particles, sharper elution bands
- Peak maximum corresponds to k'



Acid dependency of k' for various ions at 23-25°C.
Sr Resin



First Wave Response

- http://www.epa.gov/epahome/sciencenb/video/merl/MerlVideo.swf
- US EPA, Mobile Environmental Radiation Laboratory, MERL
- 4 HP Ge gamma detectors,
  2 alpha beta counters and an LSC
- Air filter and swipe samples
- Alpha and Beta isotopes can not be reliably identified, only quantified

- Radioactive Air Monitoring Issues:
  - Capturing Radioactive Particles
  - Detecting the emissions from the Particles
    - Contribution from filter media to the background
    - Loss & degradation of signal due to attenuation by filter media
  - Suitability of filter media for sampling conditions

Filter Backgrounds
Via Gas Flow proportional counting

	α - alpha Background MDA=2.24 (dpm)	**β - beta Background MDA=4.20 (dpm)**
Cellulose	0.78 ± 1.12	0.17 ± 1.30
Glass Fiber	2.00 ± 1.56	4.52 ± 3.44
PTFE Filter	0.24 ± 0.70	0.31 ± 3.54

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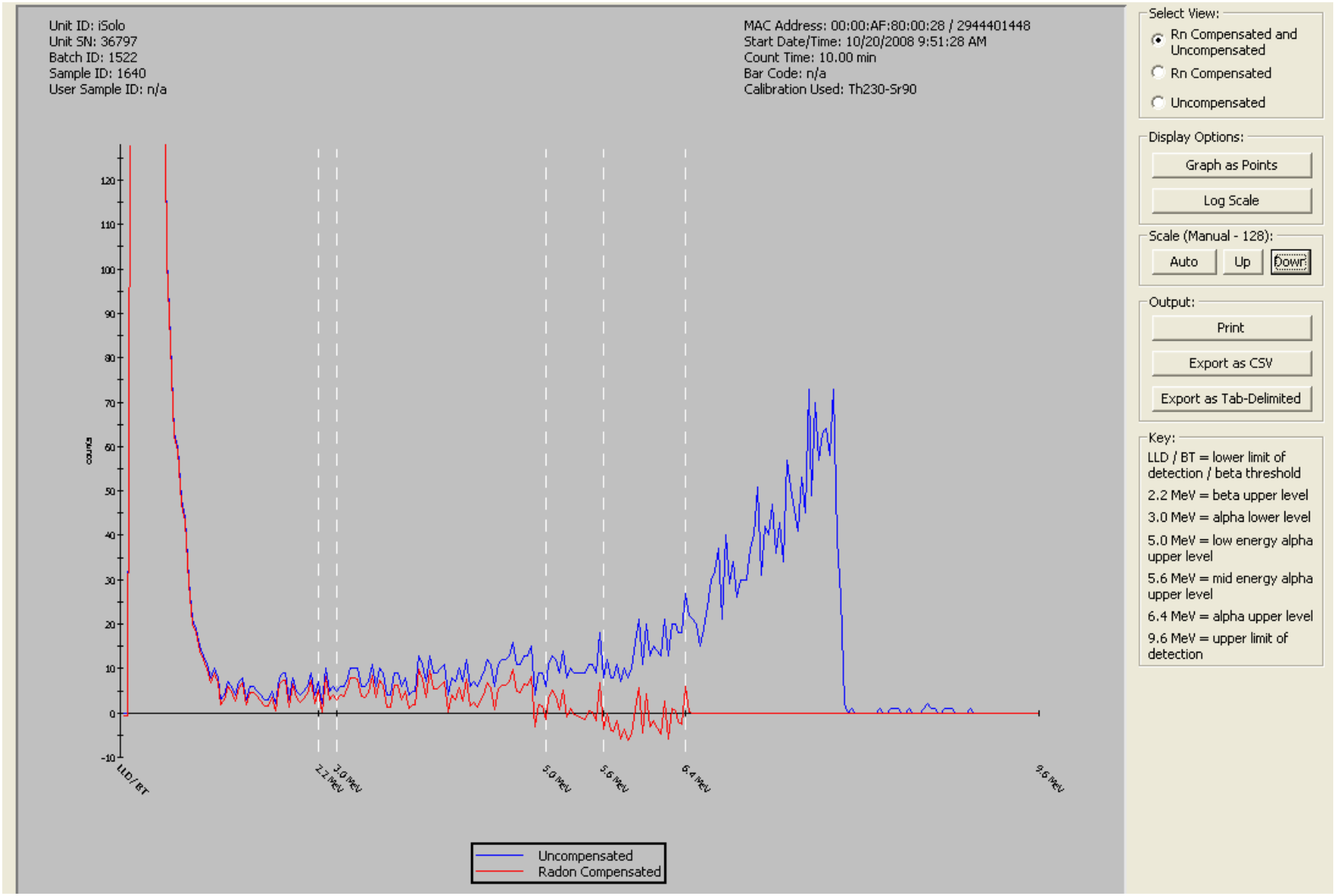
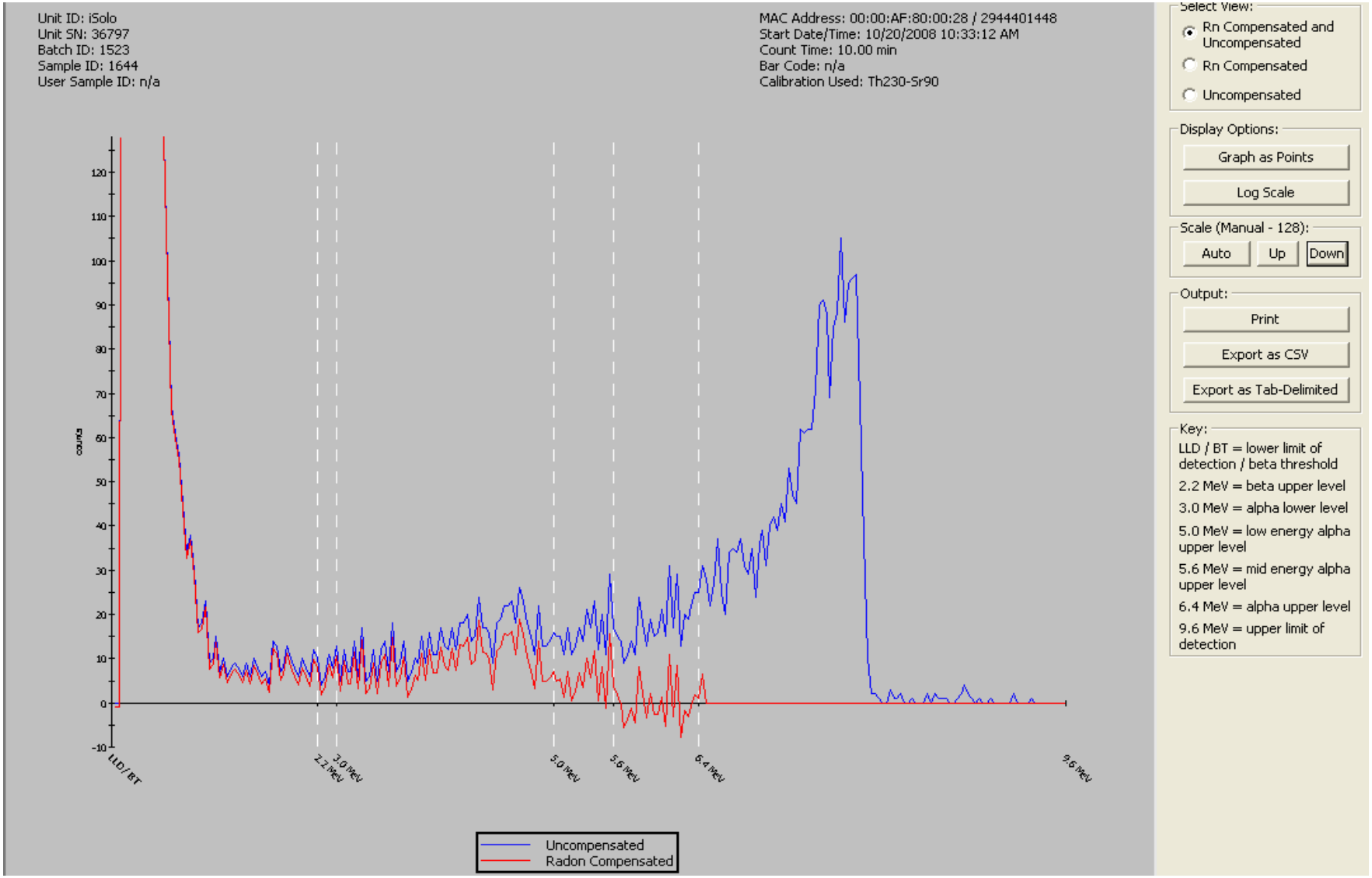
Filter Spiked with U-233 + Am-241 Alpha Analyze Part 2: Post-Air Sampling Spike Recovery (3 replicates)

Filter type	Alpha spike (dpm)	Measured before air sampling Alpha (dpm)	Initial % Recovery	Measured Alpha (dpm) after air sampling	% Recovery
Cellulose	474	106 ± 3.4	22 %	35.9 ± 20.2	8 %
Glass	474	237 ± 5.1	50 %	225 ± 18.8	47 %
PFTE	474	415 ± 6.9	88 %	397.8 ± 14.2	84 %

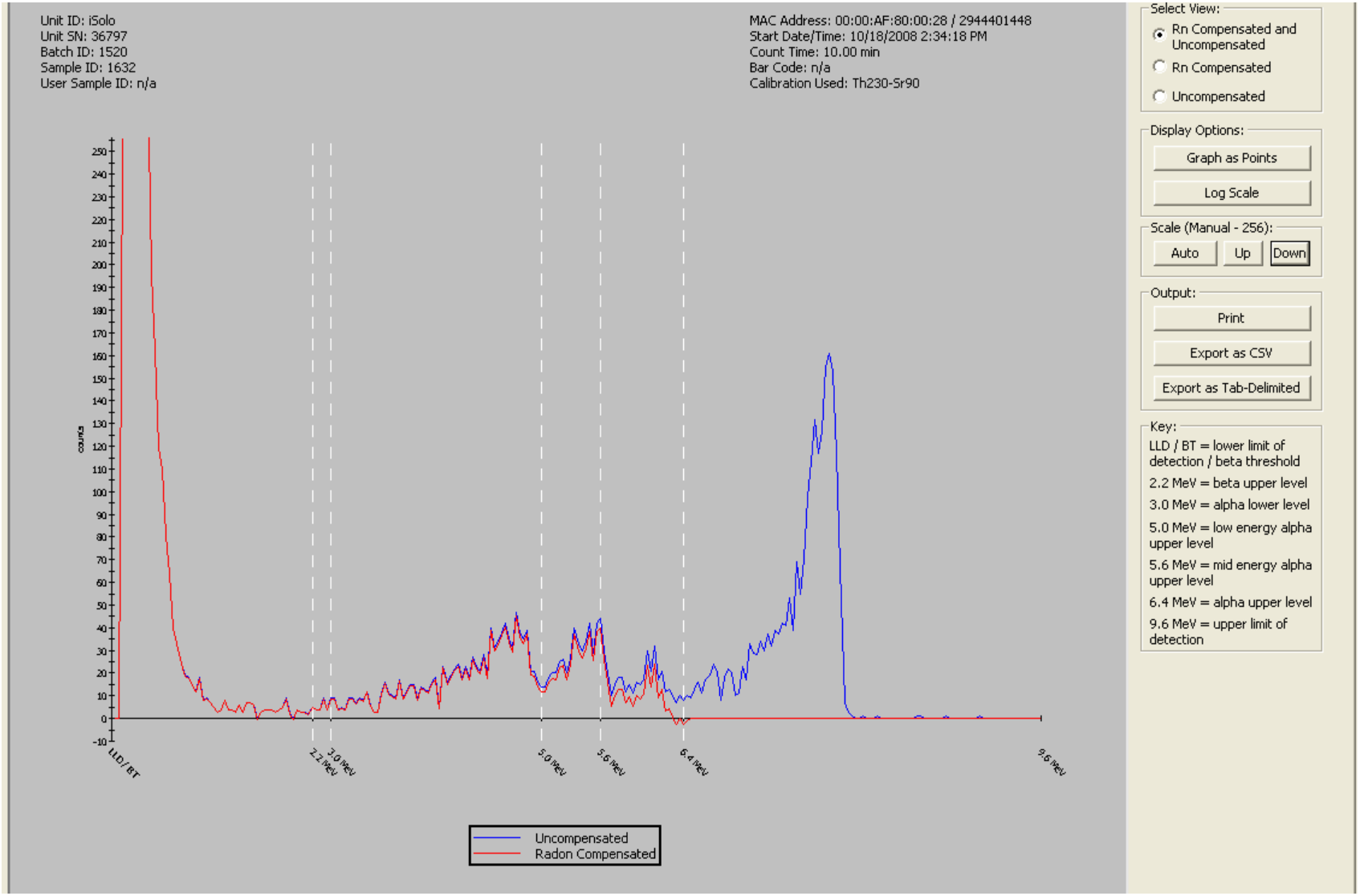
Spiked Cellulose filter
Post Air Sampling



Spiked Glass Fiber Filter Post Air Sampling

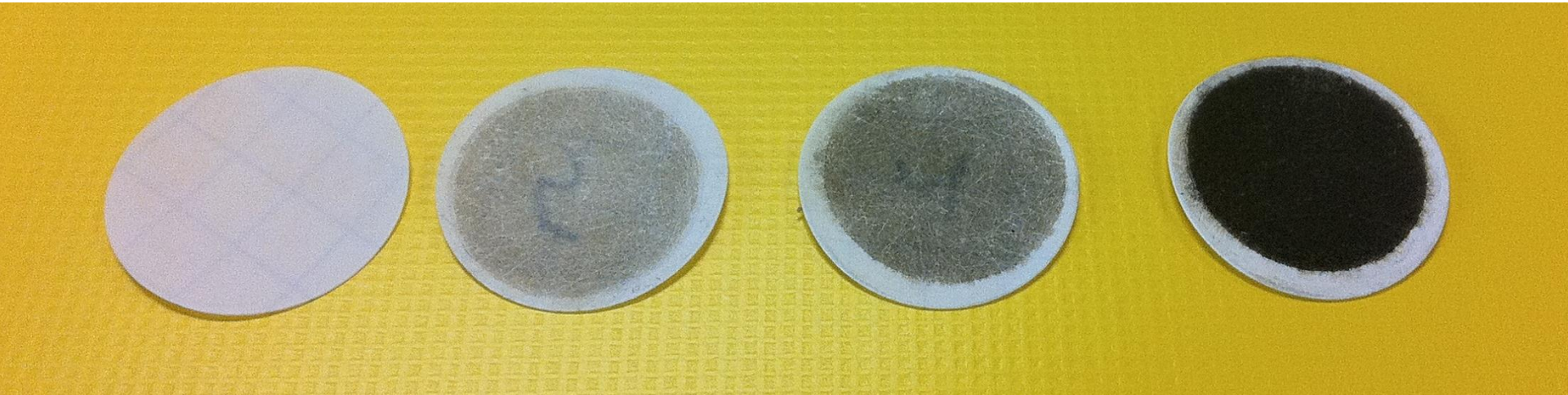


Spiked PTFE Filter
Post Air Sampling – 1st 10 min



Eichrom's Resolve® PTFE Laminate Filters

- Volumetric Flow
  - Resolve 47mm PTFE Filters have maintained a DOP 99.99% efficiency testing rating up to 9 CFM = 254 LPM
  - PTFE Filters maintain integrity even with mg of material loaded on the filter for your harshest applications.



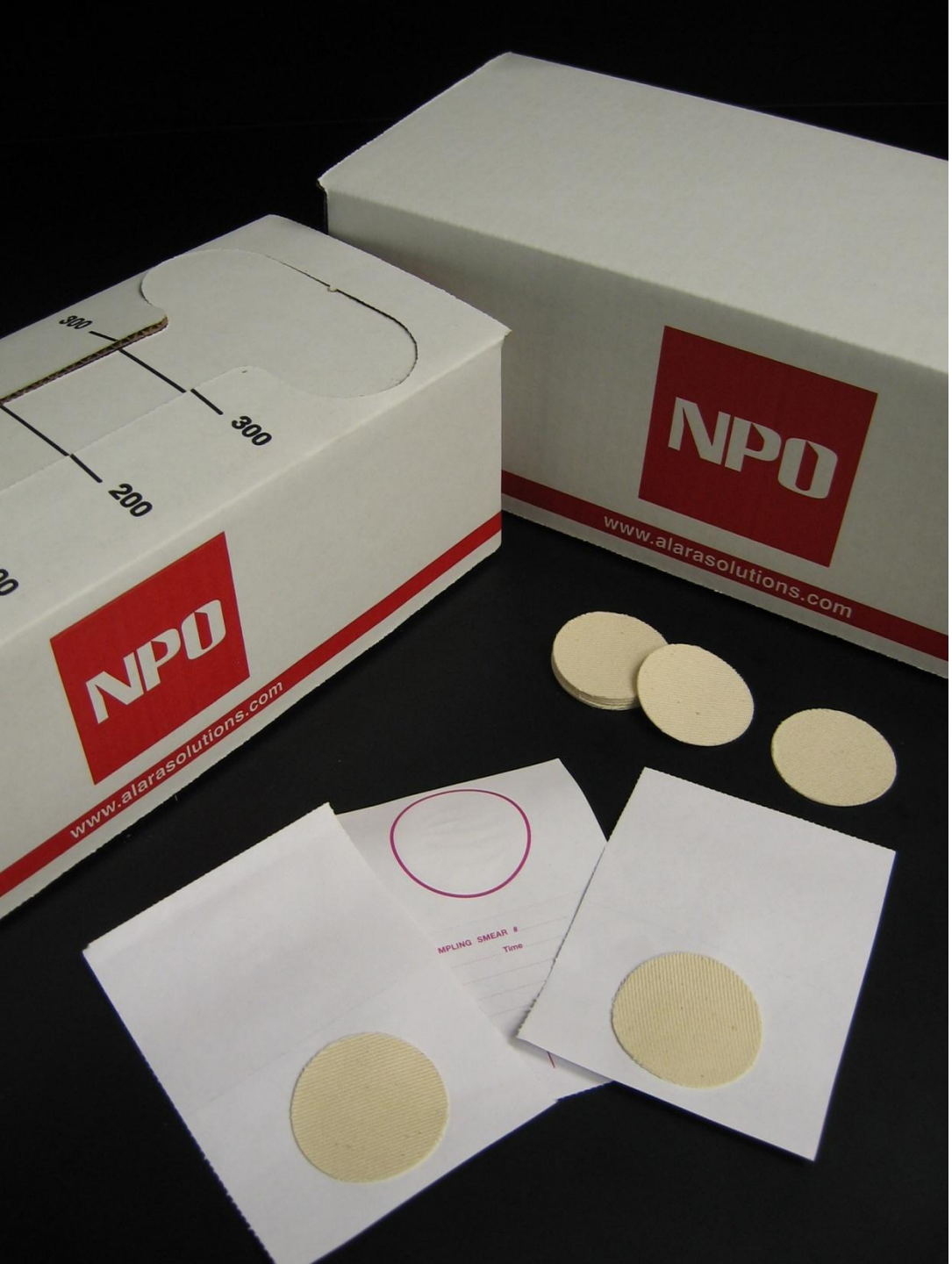
Resolve PTFE Filter

3.0 µ PTFE Laminate

47mm dia. (50 to a package)

- Quality Control Specification:
  - Background < MDA for α & β
  - Resolution verified <60 KeV FWHM
  - Minimal curling <4.0 mm deflection
- The filters have a easy to determine orientation:

  “Grid side down, Opposite Air flow”
- Performance demonstrated at Eichrom and externally
  - Lee Reagan of Canberra uses,
  - Peter Olsen of Washington Closure Hanford



Health Physics Sampling Smears

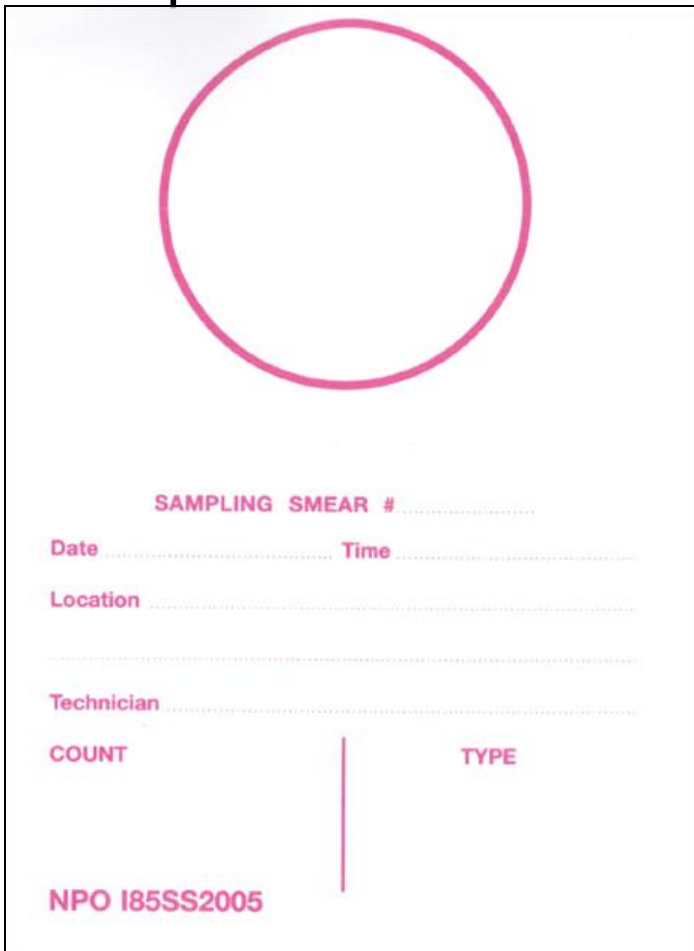
Swipe/Smears for contamination monitoring.

Two Formats:

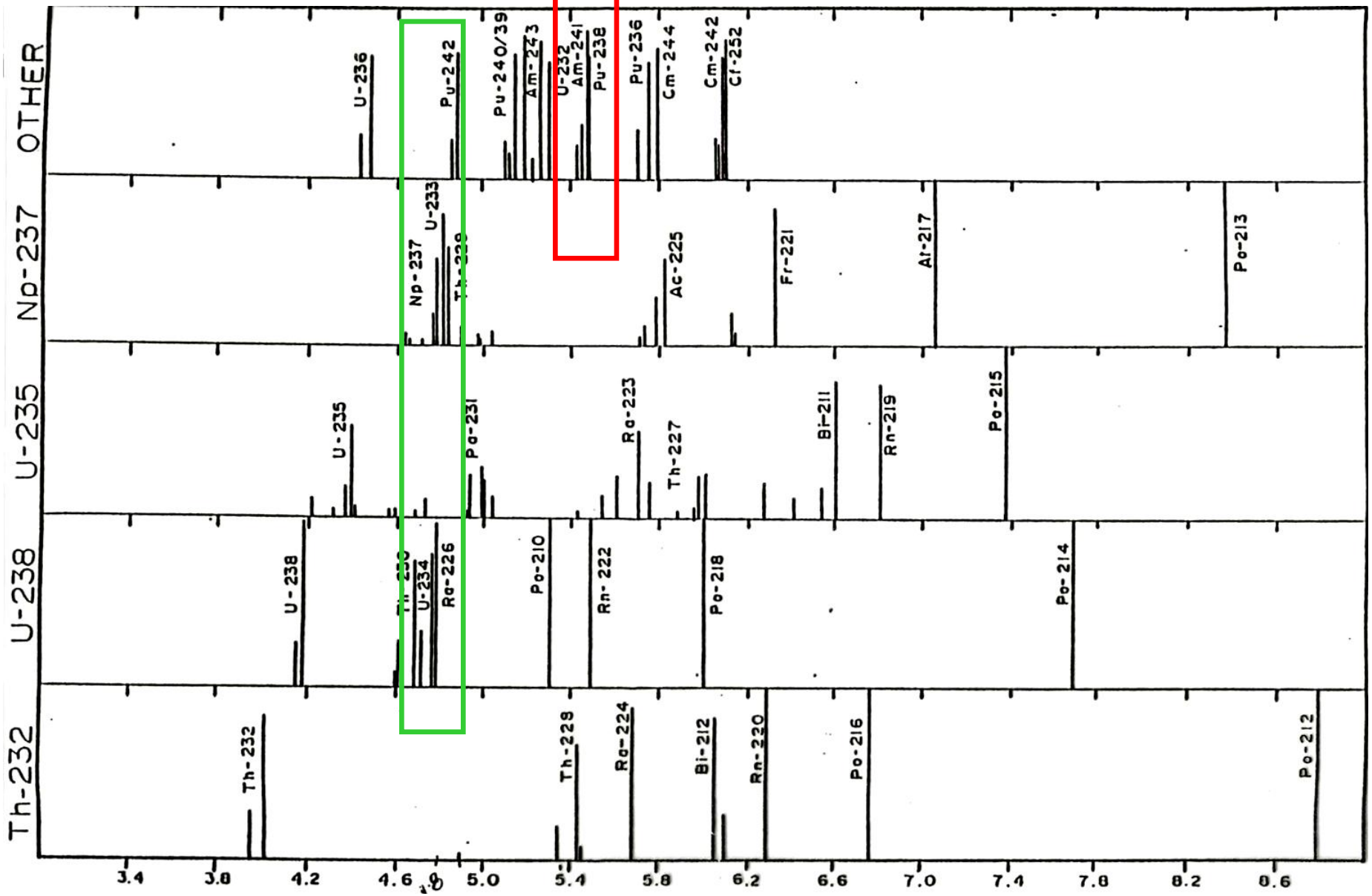
- Paper Backed with recorder paper
- Bulk Packaged

Features of Swipe / Smears

- 44.4mm (1 ¾ inch) in Diameter Cloth Smear
- Pressure Sensitive adhesive backing/support
  - Allows for easy reattachment to support or planchet
- Backing and Smear can be removed together from support for analysis

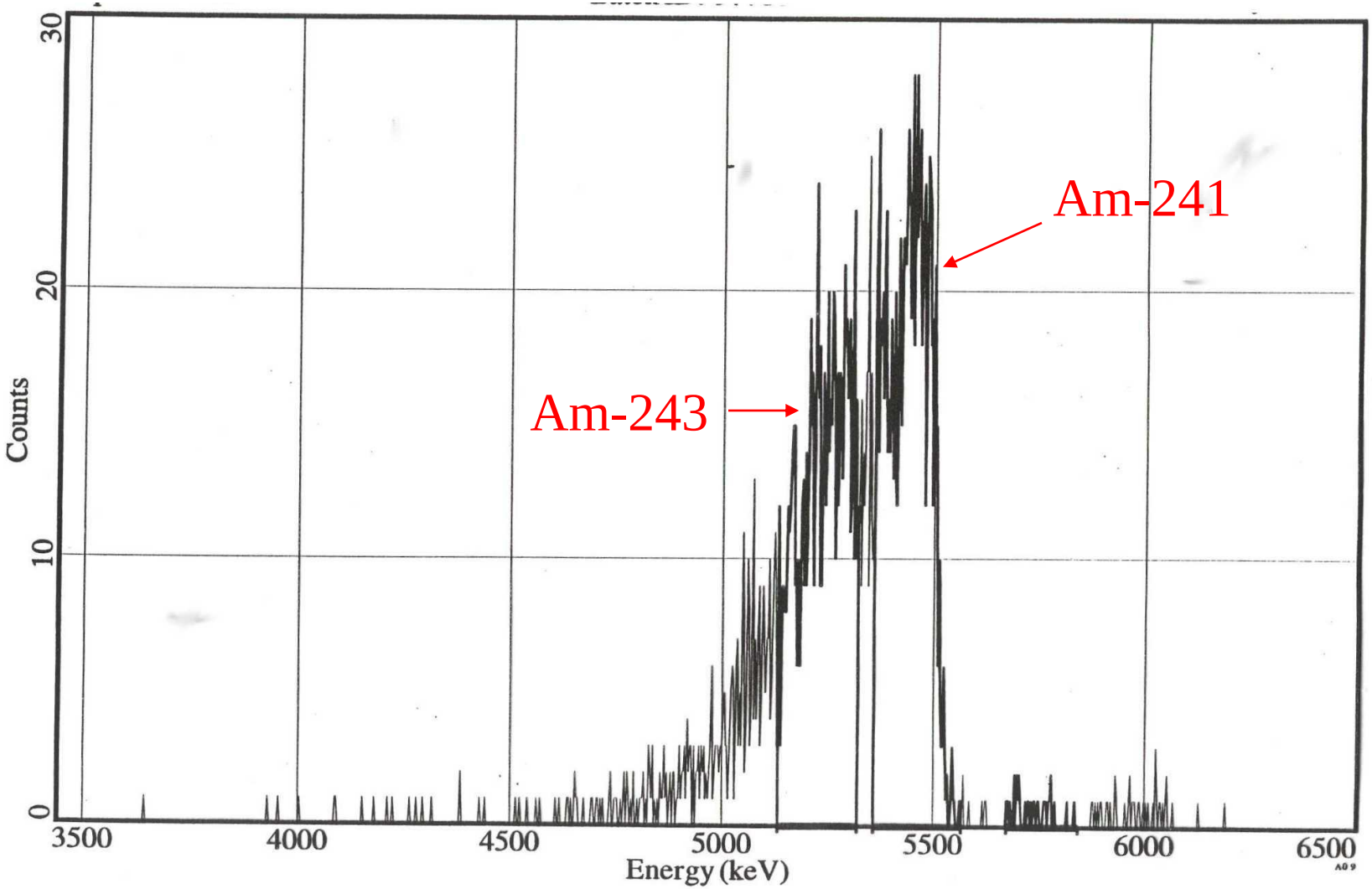


Measurement of Alpha Energy



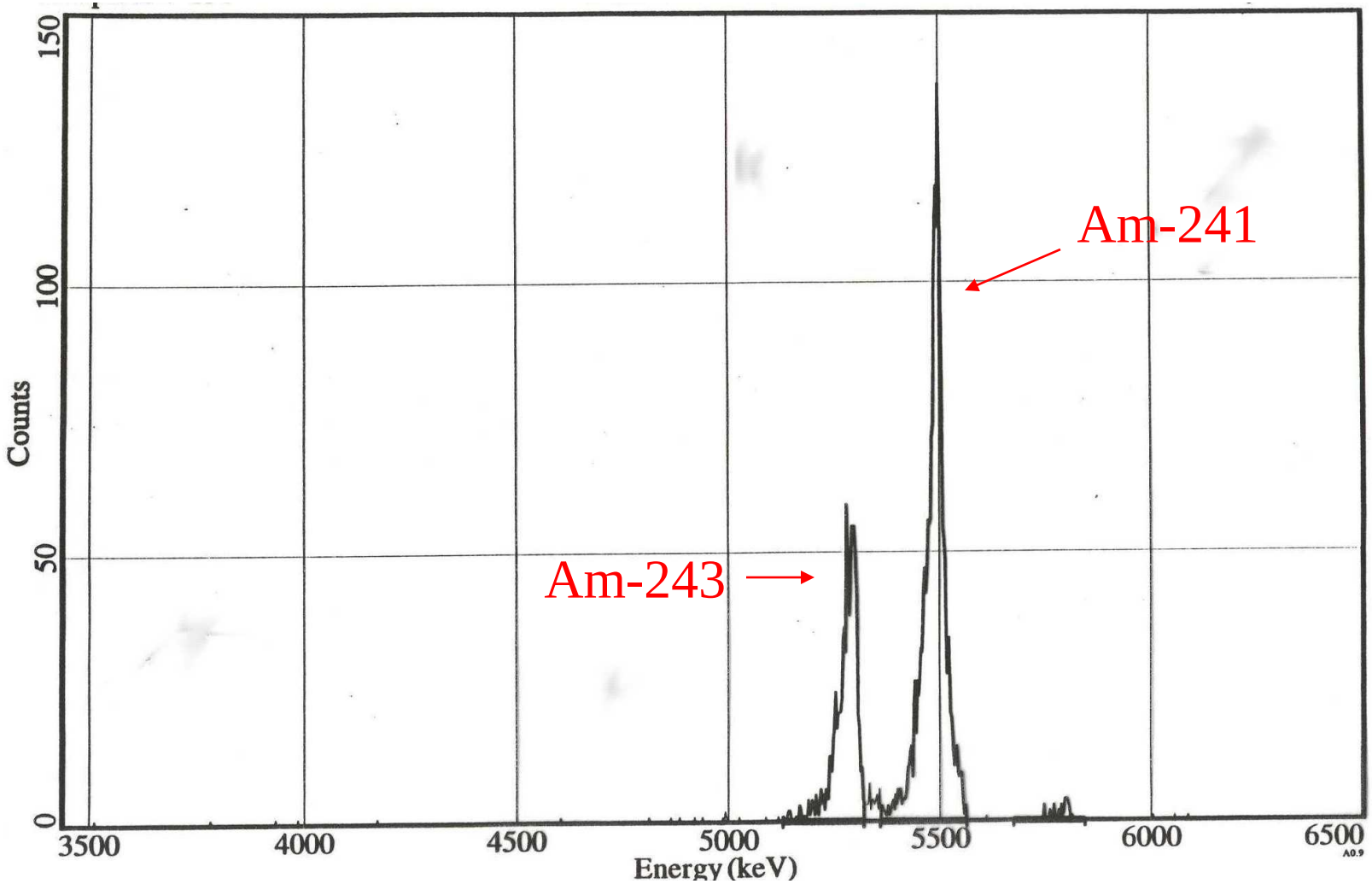
Americium Spectrum after TRU Resin Separation

presence of rare earths degrades spectrum- self absorption issues



Am Spectrum after TEVA Resin Separation

Lanthanide elements removed - cleaner spectrum



Approaches to alpha and beta Emergency Response Measurements

- FDA- food
  - DGA Resin for Sr via Y, Am and Pu
- CDC-urine
  - TRU Resin for Th, U, Pu, Np and Am
- EPA-water
  - UTEVA + TRU Resin for U, Pu and Am
  - Sr Resin for Sr
  - MnO_2 Resin + Diphonix® Resin for Ra-226

RadEx2011 Matrix Extension Study on Rapid Screening of Alpha/Beta Radionuclides in Foods

Zhichao Lin, Stephanie Healey, and Zhongyu Wu

Food and Drug Administration
Winchester Engineering and Analytical Center

- Study included 90 foods
  - Dairy, Vegetables, Composite Meal, Meat, Grain
  - 396 Matrix Spikes + 117 matrix alpha blanks and 133 beta blanks
  - Pu, Am and Y/^{90}Sr measured by LSC

INTRODUCTION

The Problem: FERN currently does not have rapid method and surge capacity for screening alpha/beta radionuclides in foods

The Solution: Development of method using high selectivity solid-phase extraction and discriminative liquid scintillation spectrometry for alpha/beta radioactivity detection

The Approach: Identify radionuclides of most concern → Single laboratory development → Collaborative matrix extension study → Proficiency testing → Proven network capability and capacity

The Objective: Develop and implement a robust high-throughput alpha/beta screening method that ensures effective FERN radiological emergency response

INTRODUCTION

FERN Recourses for Screening Food Alpha/Beta Radioactivity

FDA Alpha/Beta Screening Coverage

Participants	Contributors
1. Maryland Department of Health and Mental Hygiene	√ ●
2. Virginia Division of Consolidated Laboratory Services	√ ●
3. Wisconsin State Laboratory of Hygiene	√ ●
4. New York State Department of Health	√ ●
5. Washington State Department of Public Health Laboratory	√ ●
6. Sandia Staffing Alliance, Sandia National Laboratories*	√ ●
7. FDA Winchester Engineering and Analytical Center	√ ●
8. Texas Department of State Health Services Laboratory	○
9. Illinois Emergency Management Agency	○
10 University of Iowa Hygienic Laboratory	○
11. Indiana Department of Health	○

* Non-FERN Laboratory

Current Status:

- ► 10/36 FERN rad labs equipped for α/β analysis
- ► 7/36 FERN rad labs having ability analyzing foods
- ► Limited α/β national coverage and surge capacity

Assumed Resources:

11 Labs
24 Analysts WEAC(8), CAPLAB(10), NONCAPLAB(6)
8 samples/analyst/day
7 days/week

Potential Surge-Capacity:

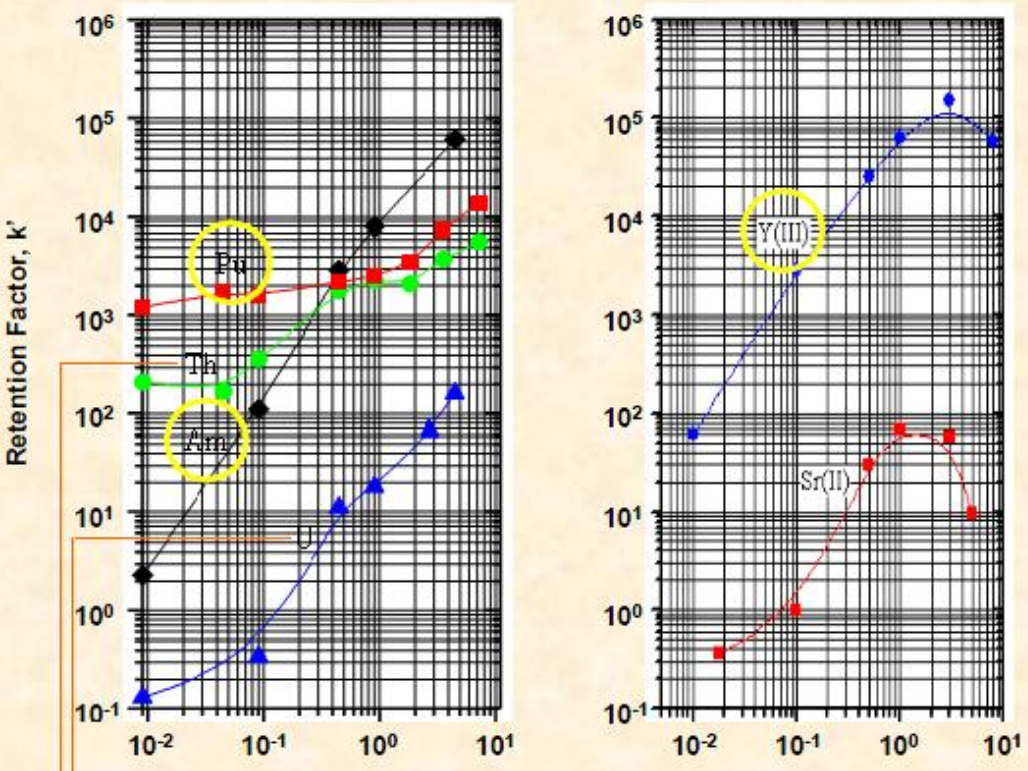
~1344 samples/week (Counter limited)
~2688 samples/week (24/7) (Counter limited & Unsustainable)

Preferred Surge-Capacity:

2500 samples/week

METHOD DETAILS

Target Radionuclides Retained by DGA Resin



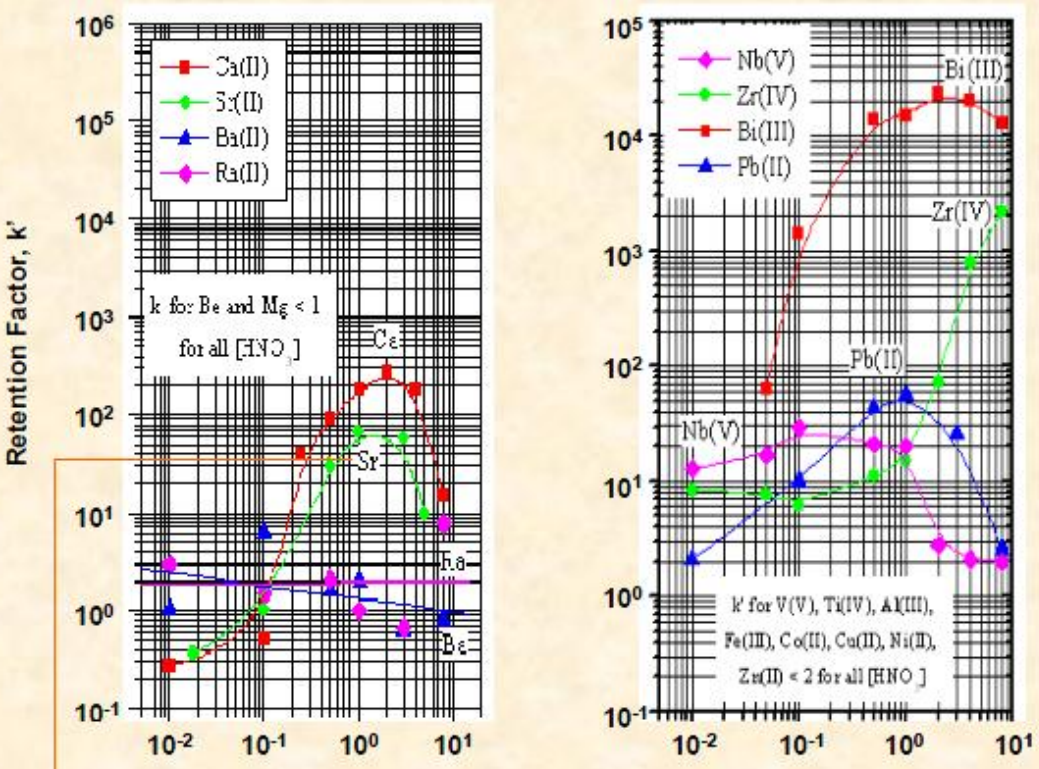
(Courtesy of Eichrom Technologies)

Target radionuclides are Selectively extracted with $k' > 10^4$ @ 8M

Potential interfering radionuclides U & Th
Low concentration due to their relative insolubility in environment
Low specific activity due to their long half-life

METHOD DETAILS

Matrix & Radiometric Interferences Removed by DGA Resin



(Courtesy of Eichrom Technologies)

Most interfering elements are removed with k'<10 @ 8M

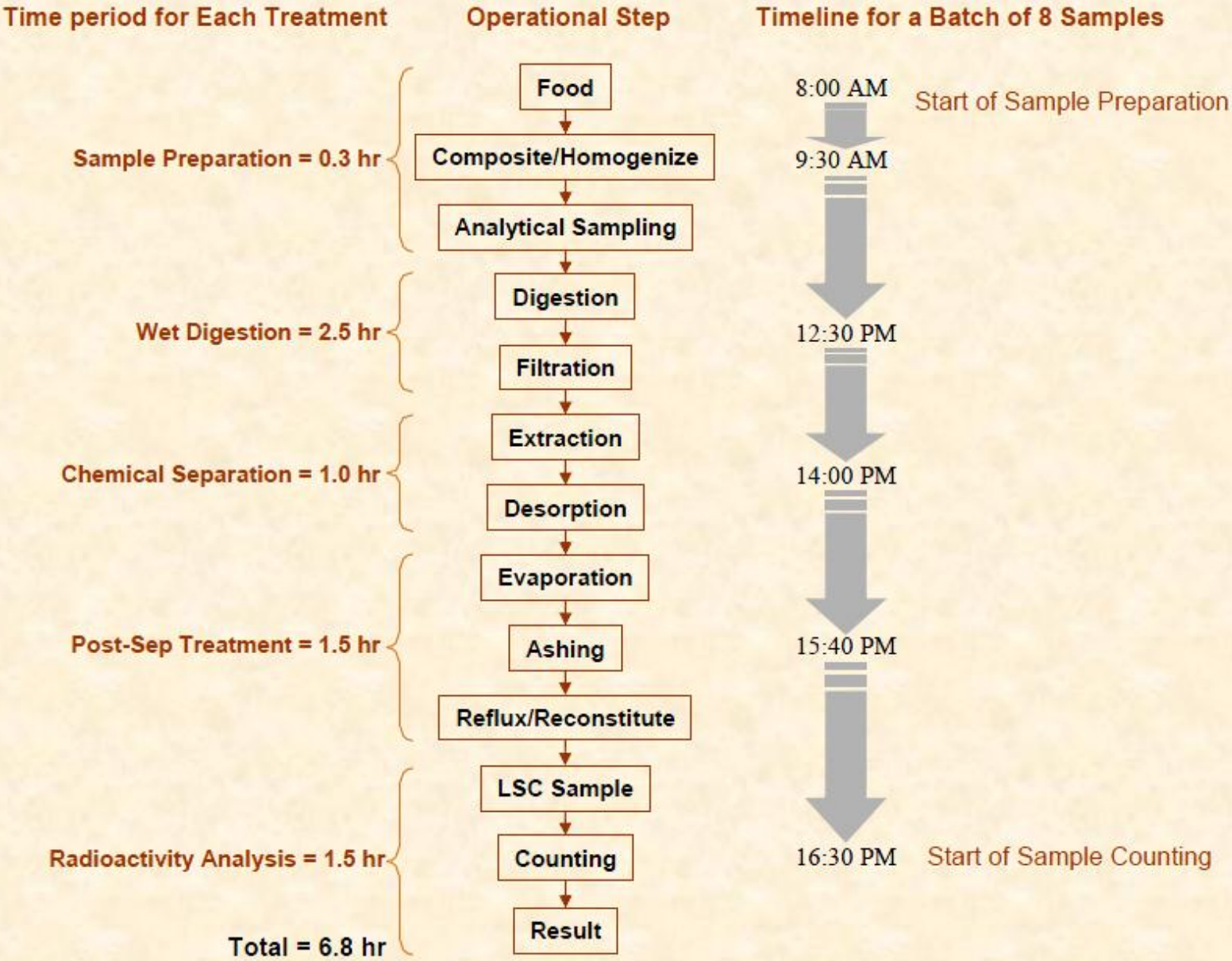
Sr/Y separation improves with increasing HNO_3 concentration. However, $Sr(NO_3)_2 \downarrow$ may occur @ HNO_3 >60% unless the sample is analyzed right after post-digestion filtration, the ^{90}Sr result may subject to low bias.

FDA DGA Resin Separation Method for Food

- After Digestion with Concentrated Nitric Acid and 10 mL of 30% H_2O_2 load onto 1 gram of 50-100µ DGA Resin, Normal
  - Nitric > 4 M, batch uptake
- 10 mL of 3 M HNO_3 Rinse
- Extract Pu, Am and Y with 0.1 M Oxalate + 0.1 M HCl
- Ash to destroy oxalate for 20 minutes at 400°C
- Re-disolve in Conc. HNO_3, Evaporate
- Dissolve in 3 mL of 0.5 M HCl add 17 mL Ultima Gold A/B
- Count by LSC
- No yield monitor

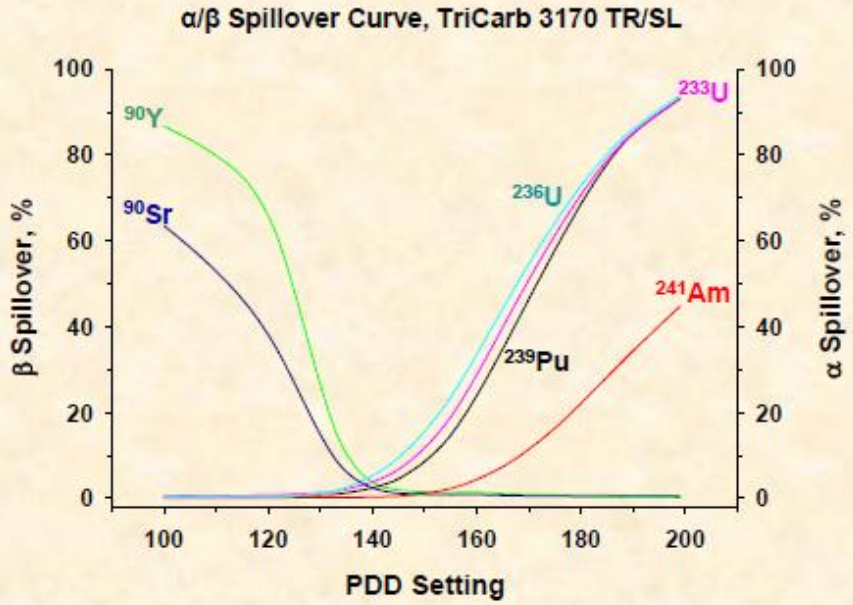
METHOD DETAILS

Procedure Flow



ANALYSIS of STUDY RESULTS

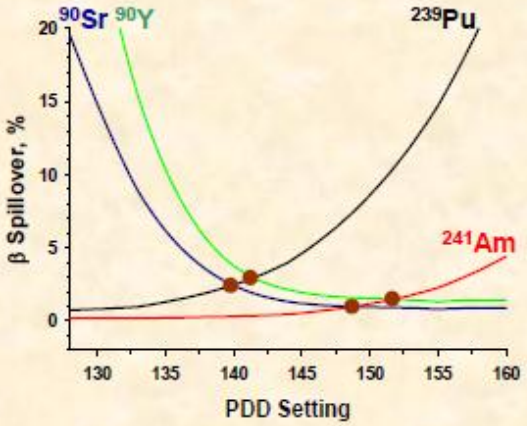
Energy Dependence of α/β Spillover Correction



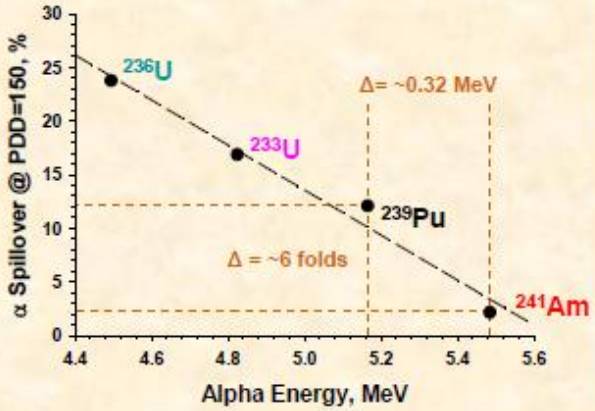
Observation/Action:

- While analyzing the samples mixed with $^{239}Pu/^{90}Sr$, use of $^{241}Am/^{90}Sr$ spillover curve to correct α/β counts may result in high bias for ^{90}Sr & low bias for ^{239}Pu
- The energy effect of using ^{90}Sr and purified ^{90}Y on β spillover calibration is relatively small
- The suspected outliers are confirmed and excluded from data analysis

Beta Energy Effect

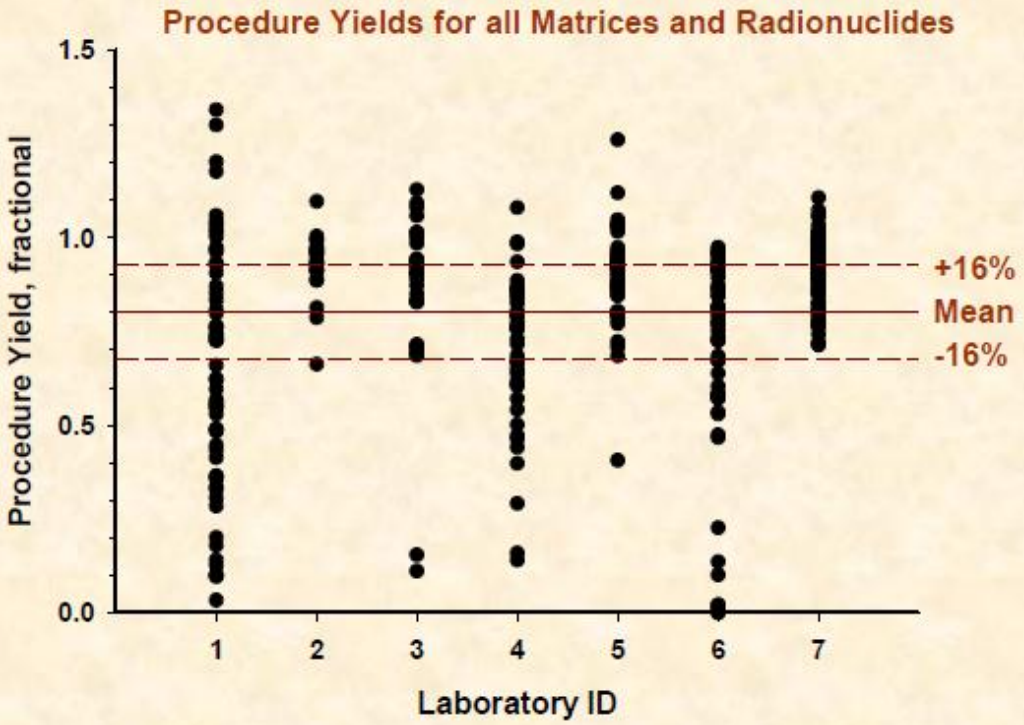


Alpha Energy Effect



ANALYSIS of STUDY RESULTS

Matrix Spike Results without Outliers



Observation/Action:

- The plot shows that the procedure yields have a grand mean of ~80% with an inter-laboratory variability of ±16%
- The within-laboratory variation is greater than laboratory mean variation
- The significant difference in laboratory means may justify use of lab-specific yield
- The factors contribute to yield discrepancy and variability must be determined

QUANTITATIVE DETERMINATION OF ULTRA-TRACE ACTINIDES IN URINE BY ON-LINE HPLC-ICP-MS

Yongzhong Liu[1], David P Saunders[2], Kathleen Caldwell[2] and Robert Jones[2]

[1]Battelle Memorial Institute
[2]Inorganic Radiation & Analytical Toxicology Branch
National Center for Environmental Health, CDC;

57th Annual RRMC

October 30 – November 4, 2011

Disclaimer

Mention of company or product names does not constitute endorsement by the National Center for Environmental Health (NCEH),
Centers for Disease Control and Prevention (CDC),
or the Public Health Service (PHS).

CDC'S URINE RADIONUCLIDE SCREEN

Urine Sample "Spot"

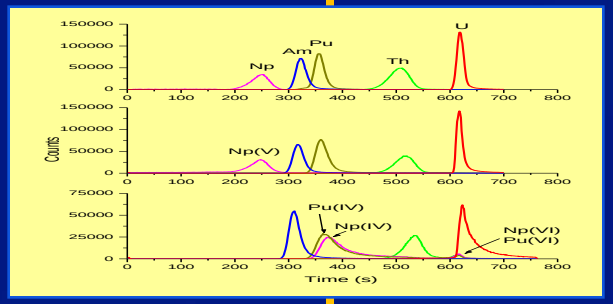
Gamma Radionuclide Screen

Gamma Radionuclide Quantification

Alpha/Beta Radionuclide Screen/Quantification

Alpha Spectroscopy Quantification

Alpha (Long Lived) ICP-MS Screen



Mass Spectroscopy Quantification

High Resolution Mass Spectroscopy Quantification

PROBLEMS – ACTINIDES DETECTION IN URINE

- Ultra-trace concentration levels
  - sub- pg/ml to ng/ml, technique with low LOD
- Complicated matrix with large amount of salts
  - sample pre-treatment
- Multi-element analytical requirement

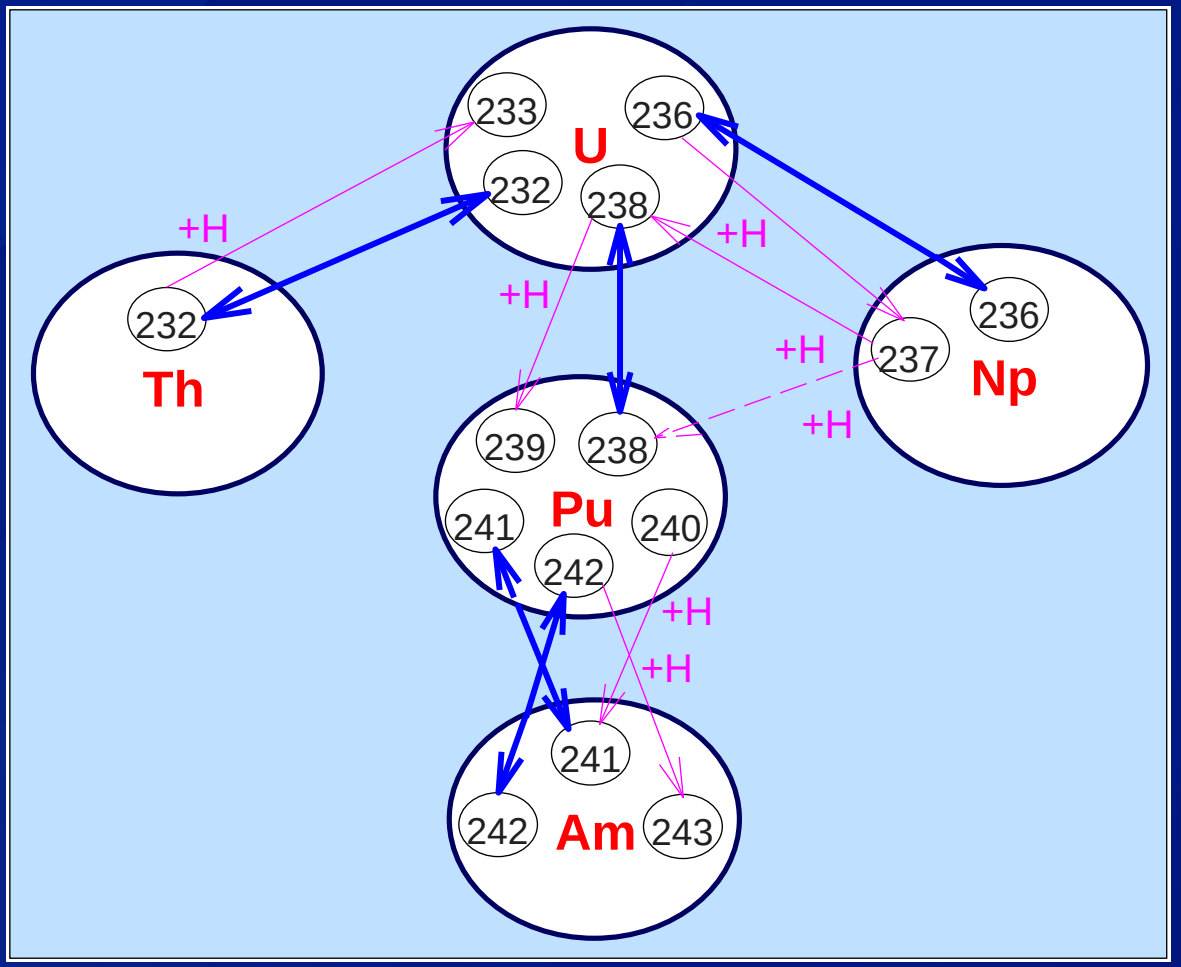
ACTINIDE ANALYTICAL TECHNOLOGIES

- Separation: On-line extraction chromatography
  - Extraction chromatography is stationary-phase solvent extraction, and it is a modified liquid-liquid extraction.

- Detection: Quadrupole ICP-MS
  - ICP-MS has low limits of detection for long-lived radionuclides, short analytical time and multi-element analytical ability.

ACTINIDE DETECTION BY ICP-MS
THE PROBLEMS

- **Polyatomic ions:**
  - ^{236}UH and ^{237}Np
  - ^{238}UH and ^{239}Pu
  - ^{237}NpH and ^{238}U
  - ^{232}ThH and ^{233}U
  - ^{240}PuH and ^{241}Am
  - ^{242}PuH and ^{243}Am
  - ^{237}NpH and ^{238}Pu
- **Isobars:**
  - ^{232}U and ^{232}Th
  - ^{236}U and ^{236}Np
  - ^{238}U and ^{238}Pu
  - ^{241}Am and ^{241}Pu
  - ^{242m}Am and ^{242}Pu



EXPERIMENTAL

TRU columns

- TRU resin (Eichrom Inc.) particle size of 20-50 µm
- PEEK column with an id of 4.6 mm and length of 50 mm

EXPERIMENTAL

Sample preparation

a) 0.5 ml urine + 0.2 ml conc. nitric acid (2 ml centrifuge tube, screw cap with O-ring)

b) Sand bath at 85° C for 45 min.

c) Cool down, open tube, add DI water and shake with Vortex mixer

d) Centrifuge at 15,000 g (RCF) for 10 min.

e) Transfer 1.4 ml supernate to Dionex sample vial

f) Add 50 µl 2.5% $FeSO_4$ to the sample vial

EXPERIMENTAL

Elution procedures

a) The column was washed with 3 M nitric acid to remove urine matrix and precondition for 3+ min.

b) 1ml sample injection

c) Am, Np and Pu were eluted by gradient run in steps 4 to 5

d) Th and U were eluted by isocratic run in steps 6 to 7

EXTRACTION CHROMATOGRAPHY ELUTION

Step	Time	Eluent				Separation Process
		HNO_3 (%)	HCl (%)	H_2O (%)	Oxalic acid (%)	
1	INIT	100				Column precondition
2	0	100				Sample injection and matrix removal
3	3	100				
4	3.1		40	40	20	Elution of Am, Np and Pu
5	7.0		1.0	79	20	
6	7.1		0.3	79.7	20	Elution of Th and U
7	14		0.3	79.7	20	
8	14.1			100		Column cleanup
9	18			100		

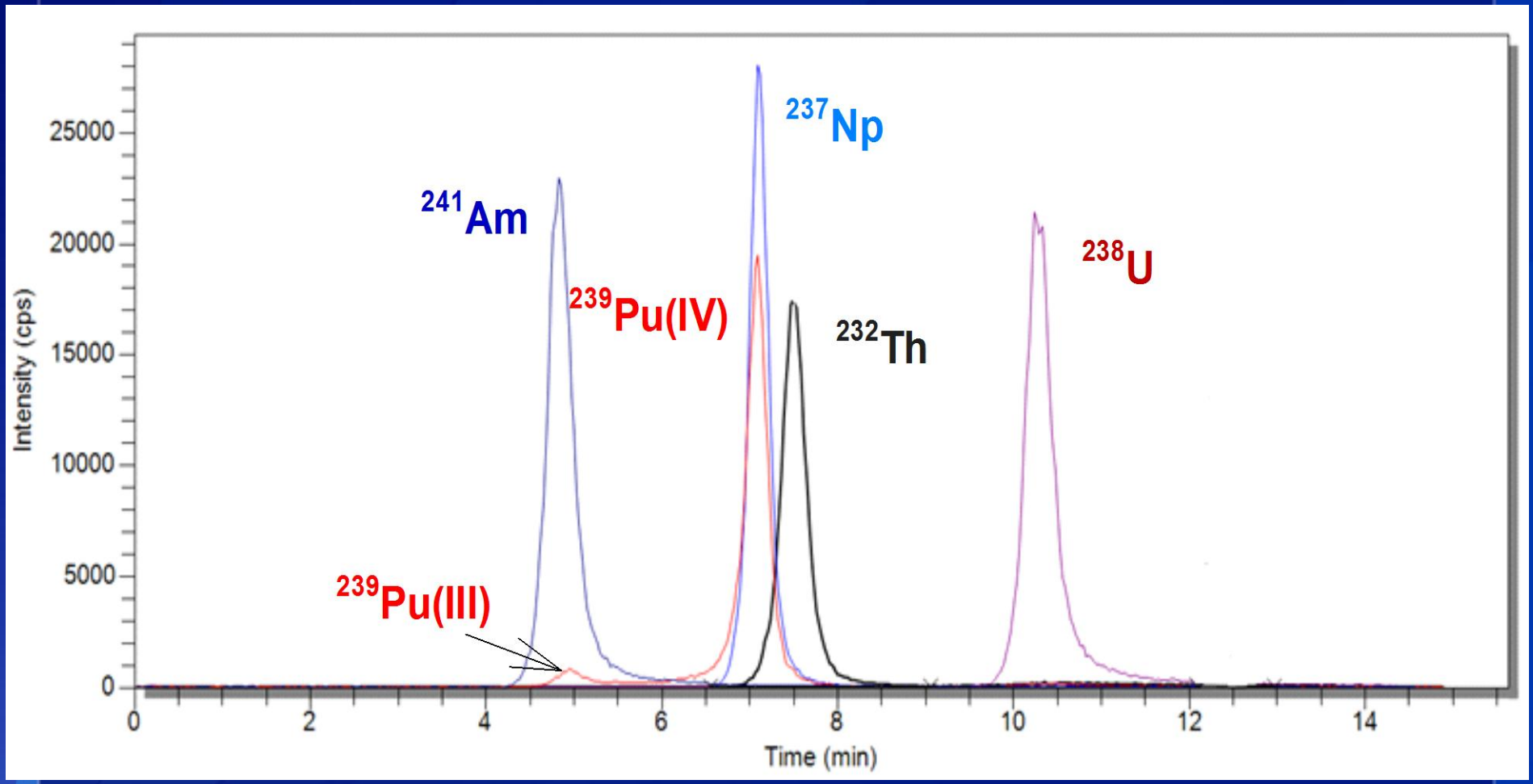


Fig. 7. Actinides (0.1 ng/ml) in diluted urine sample by adding 50 µl 2.5% iron (II) sulfate.
Two Pu peaks Pu(III) and Pu(IV) can be integrated together.

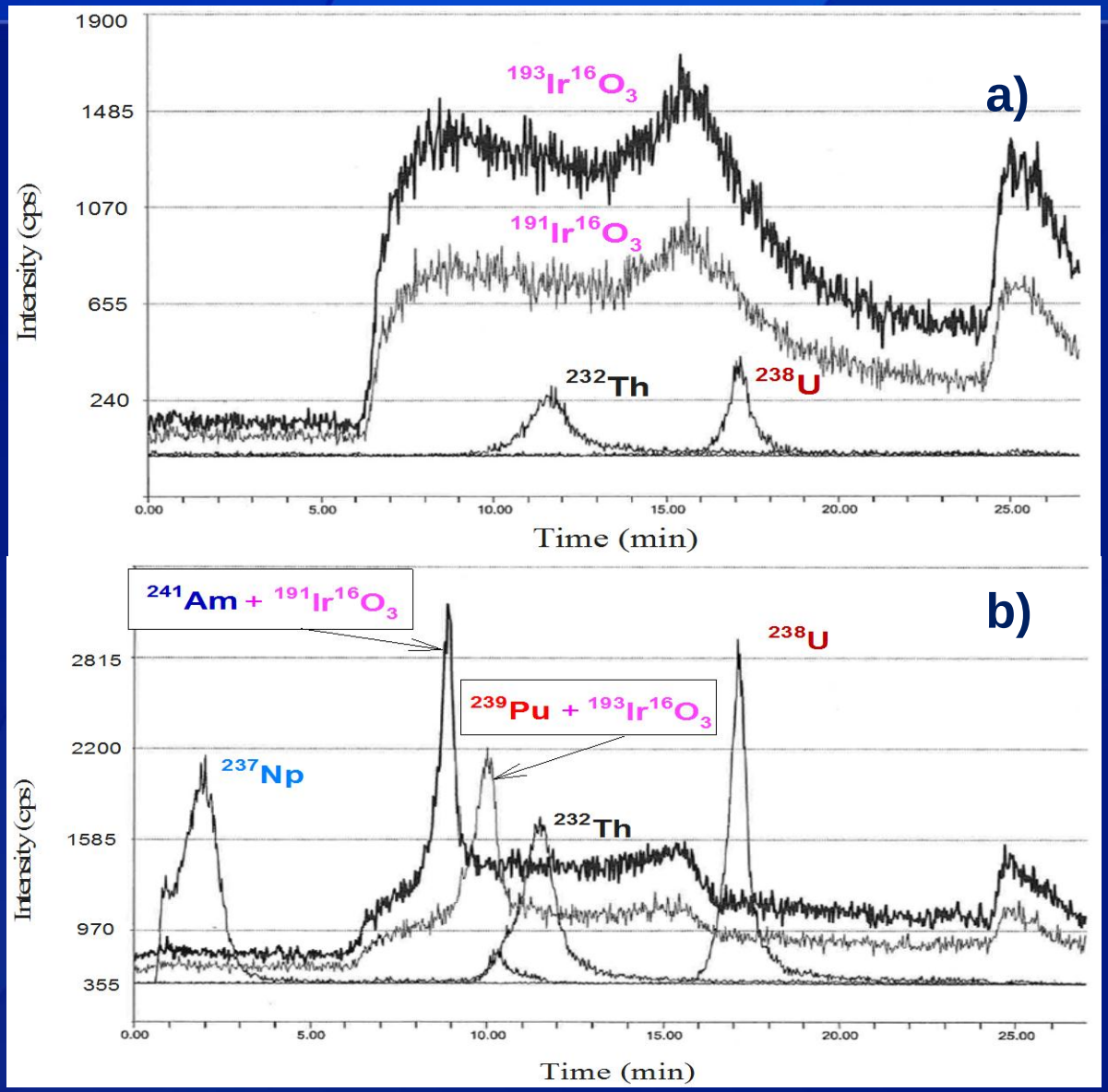


Fig. 10. a) Iridium oxides in a blank sample; b) iridium oxide interference with ^{241}Am and ^{239}Pu.

QUANTIFICATION

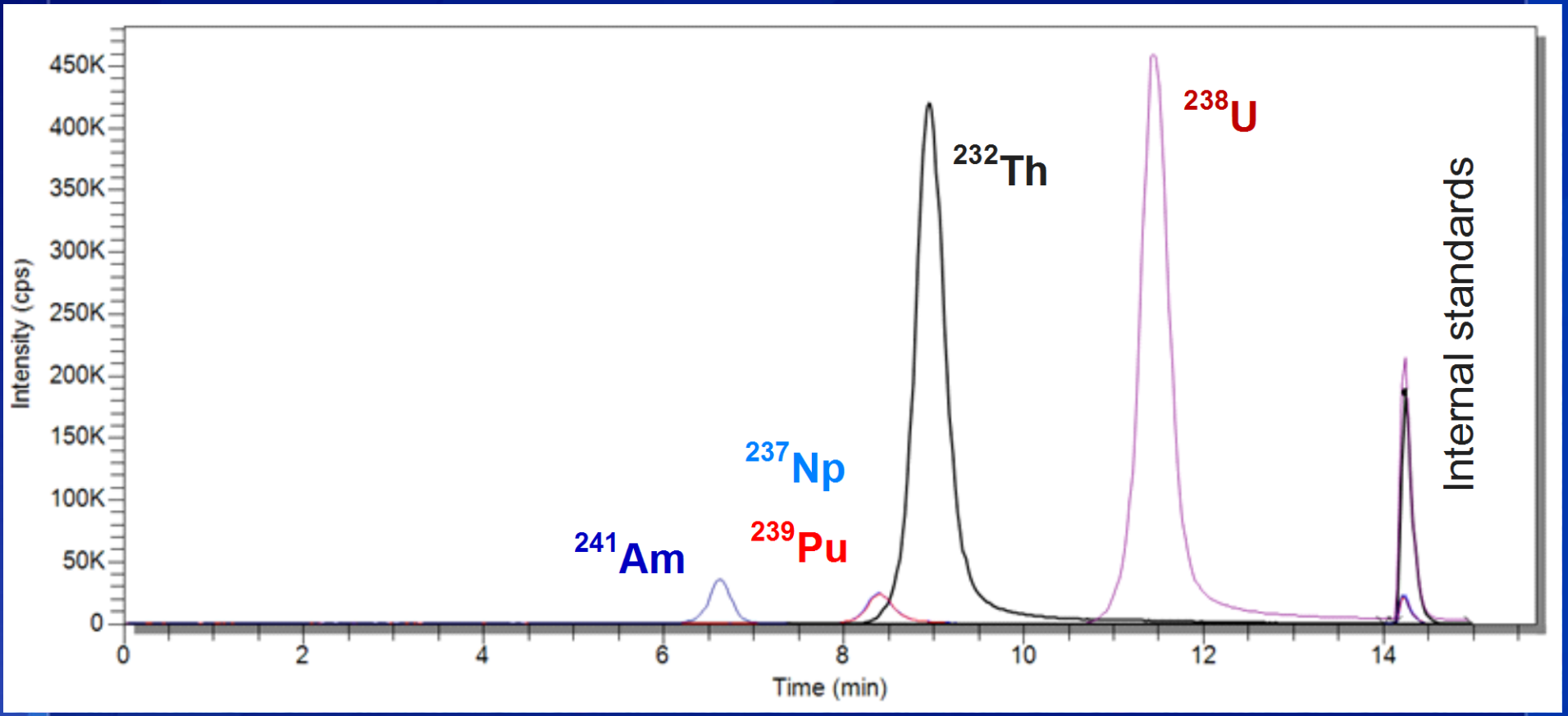


Fig. 12. Chromatogram of actinide quantification analysis with post-column internal standard injection.

Conclusions

- Ultra-trace actinides (Am, Pu, Np, Th and U) in urine matrix can be sufficiently separated and quantified using a single TRU resin packed extraction chromatography column combined with an quadrupole ICP-MS.

  1 ml sample injection → sub-pg/ml to pg/ml levels

- Shortened sample analytical time, long column life and a stable instrumentation system were achieved in this study.

  20 min. per sample

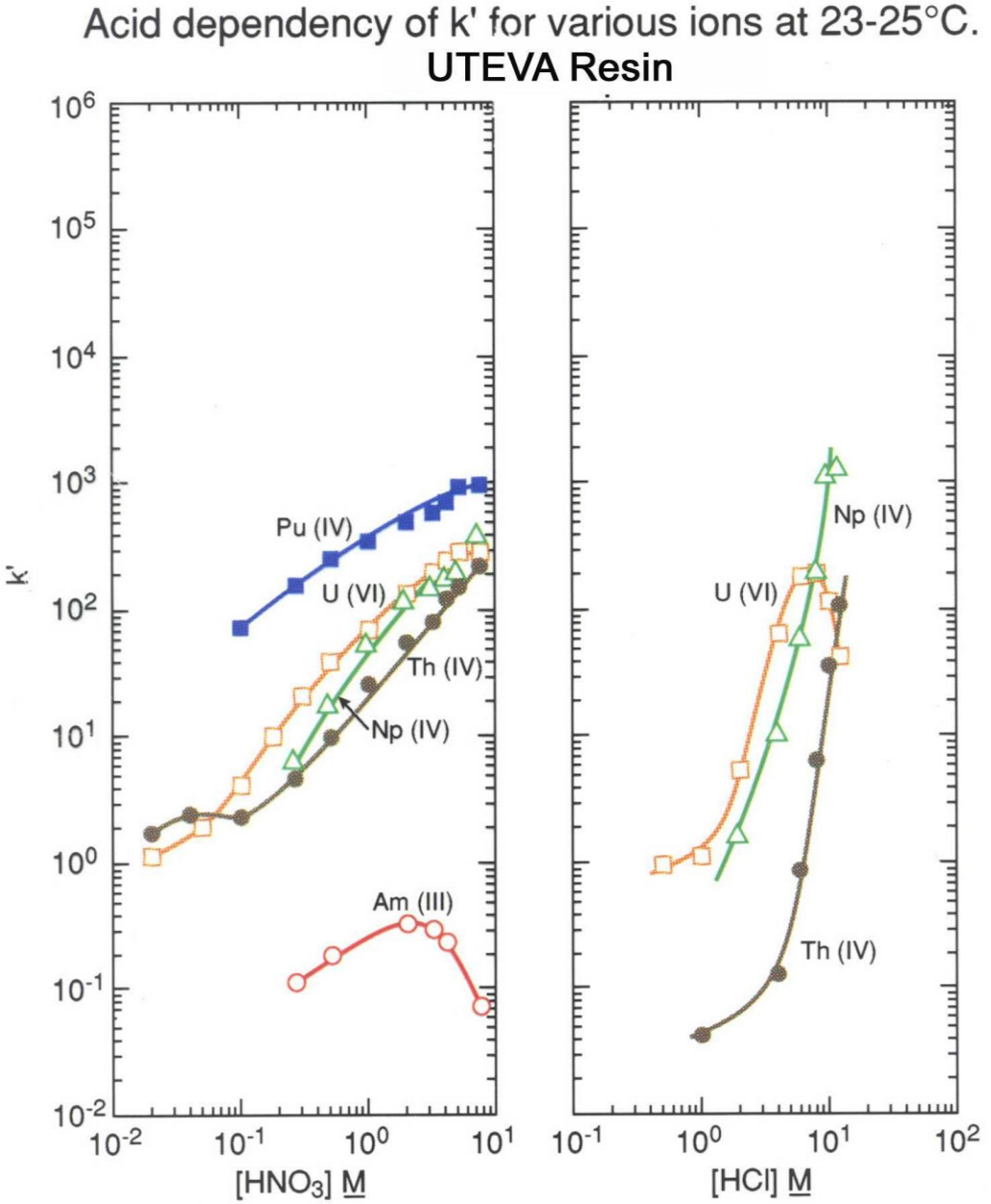
US EPA

- Published “Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events” in February 2010
- Methods use Vacuum Box System, 24 sample capacity
- DQO’s follow MARLAP guidance
  - Relative method uncertainty of 13% at or above a default analytical Action Level
    - 15 pCi/L for ^{241}Am and $^{238,\ 239/240}$Pu; 20 pCi/L for ^{234,235,238}U; 5 pCi/L for ^{226}Ra and 8 pCi/L for ^{90}Sr
  - Sample batch processing time 8-38 hours
  - Single Operator Testing conducted to validate the method, but not part of published records

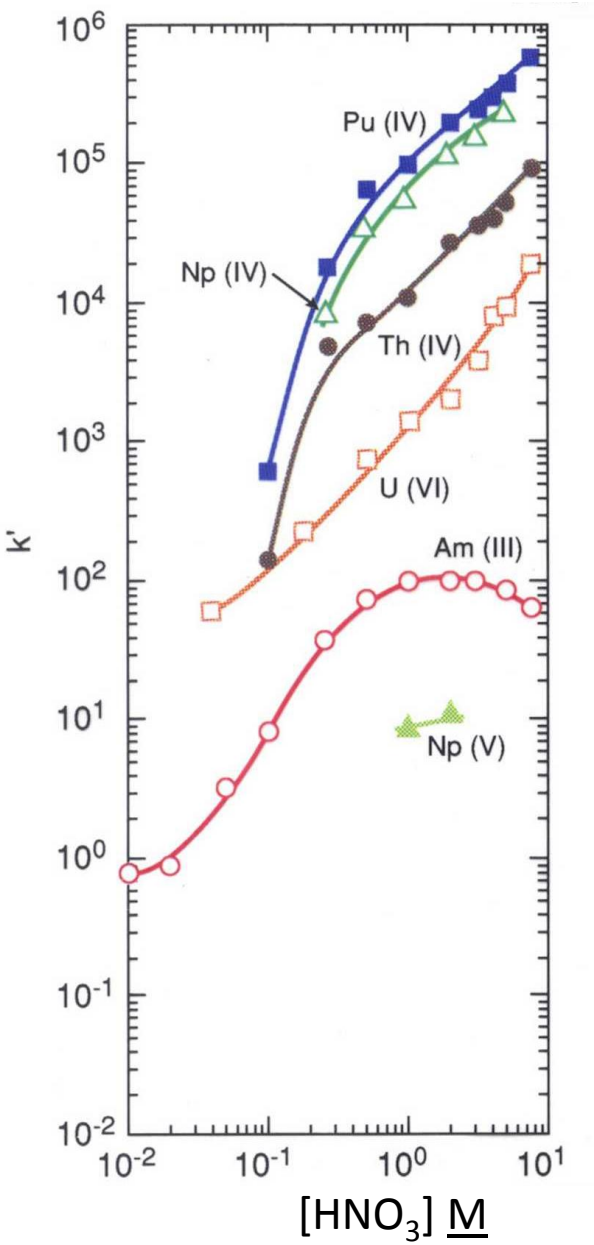
EPA Methods

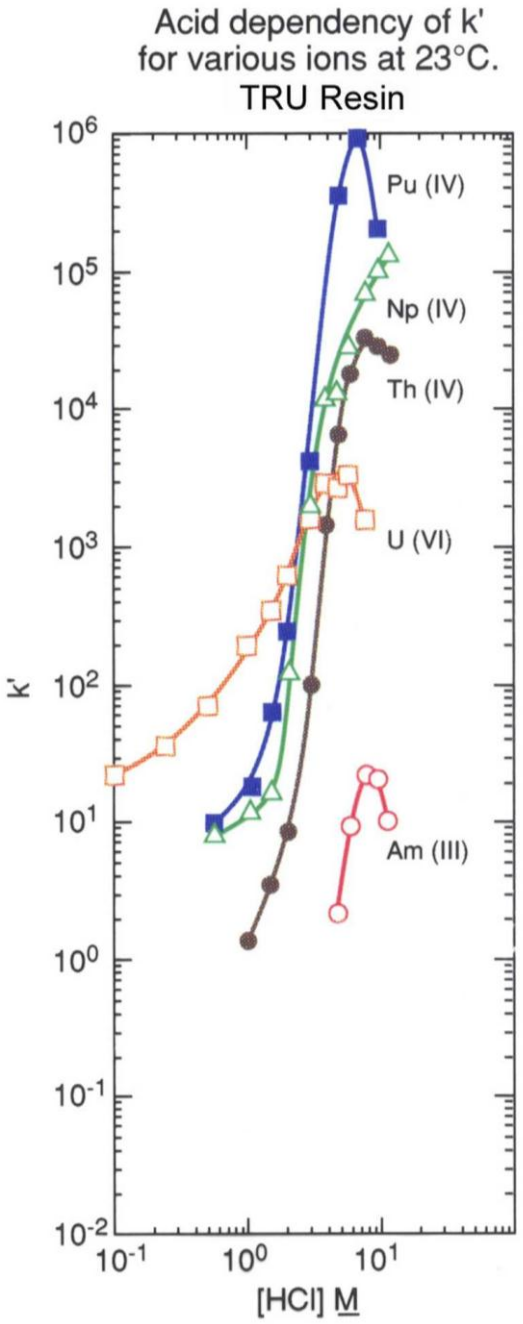
- U, Pu and Am are written as individual methods, but may be performed in tandem
- Patterned after Eichrom ACW03 VBS
- Water Sample is precipitated with calcium phosphate and then dissolved into Nitric acid with Pu reduced to (III)
- Source is prepared using neodymium fluoride ppt and alpha counted

- Sample is dissolved into 3 M HNO_3 with ferrous sulfamate and ascorbic acid
- U is Retained on UTEVA
- Pu(III) and Am are loaded onto TRU
- U is eluted with 1 M HCl



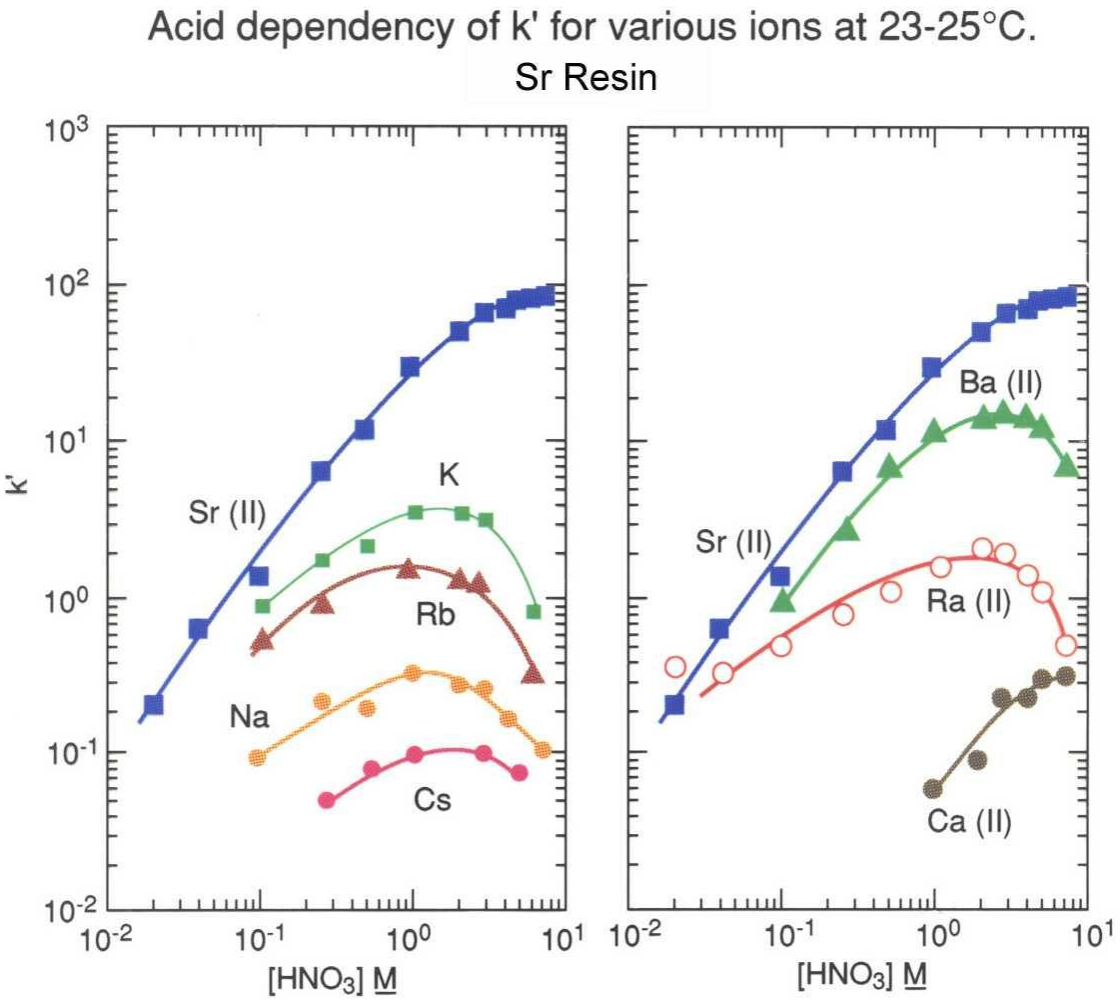
- Pu is oxidized to (IV) with $NaNO_2$
- Am is eluted with 4 M HCl
- Pu is eluted with 0.1 M ammonium bioxalate





EPA Sr Analysis

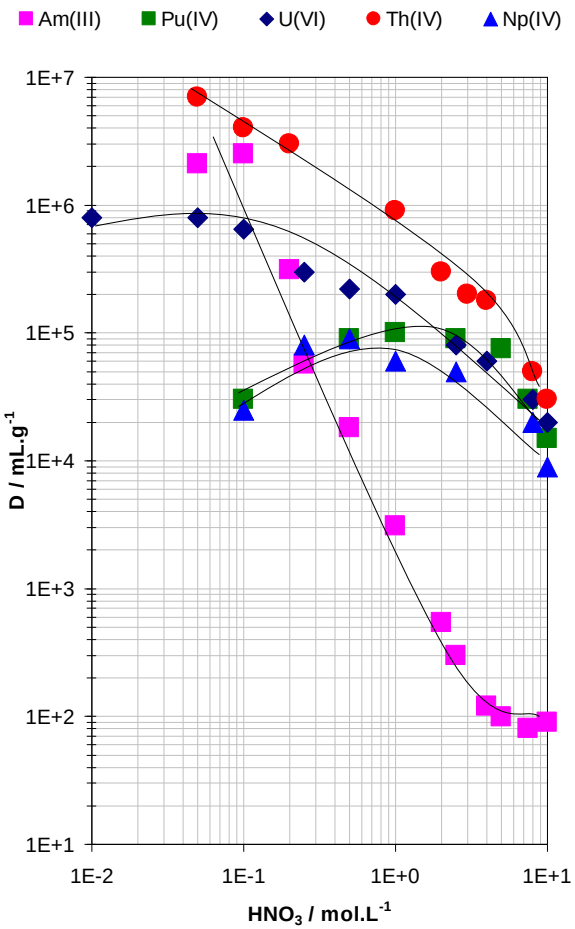
- Carbonate precipitation of water sample
- Load resin with 8 M HNO_3
- Rinse with 3 M nitric+0.05 M oxalic acid
- Elute with 0.05 M HNO_3
- Count by proportional counter



EPA Radium-226 Analysis

Diphonix® Resin

- Yield traced with Ra-225
- From neutral pH, load sample onto 1 g MnO_2 Resin- batch extraction option, or column
- Resin is stripped with 10 mL 2 M HCl + H_2O_2
- Load onto 1 g of Diphonix Resin
- Rinse with 2 X 5mL 2 M HCl and collect the Ra
- The Diphonix retains/removes any Th, Ac, or other higher valance elements



Ra-226 Continued

- Diphonix Rinse containing the Ra and Ba is precipitated as the sulfate
- 5 mL of isoproanol is added
- Sample is placed in ultrasonic cold water bath- 20 minutes
- Pre-wet a 0.1 micron filter with methanol or ethanol and filter sample
- Rinse with 20% isopropanol to dissolve residual $(NH_4)_2SO_4$

Ra-226 continued

- Allow at least 24 hours for ^{217}At (Astatine) to grow in
- Count by Alpha spectrometry

Matrix Considerations-Maxwell et al.

- **5 Papers-Emergency Response**
  - Air Filters
  - Soil
  - Concrete/Brick
  - Vegetation
  - Food

Fukushima Air Filters/ Sr Analysis

- **Cellulose nitrate filters**
  - HNO_3, H_2O_2, HF digestion
    - Repeat HNO_3/H_2O_2 to dryness several times, then with 3ml 3M HNO_3 -boric acid
  - Redissolve in 20 ml 8M HNO_3
  - Took 10 ml aliquot/held back 10 ml in reserve
  - Added 2 ml 2M $Al(NO_3)_3$
- **Separate using 2 ml Sr Resin**
  - twice for very high total beta samples (>1000 pCi/filter)
  - Important to ensure all beta interferences were removed
- **High, consistent Sr gravimetric yields (85-95%)**
- **Gas flow proportional counting**
  - Simultaneous drawer counting system
- **Results within hours!**

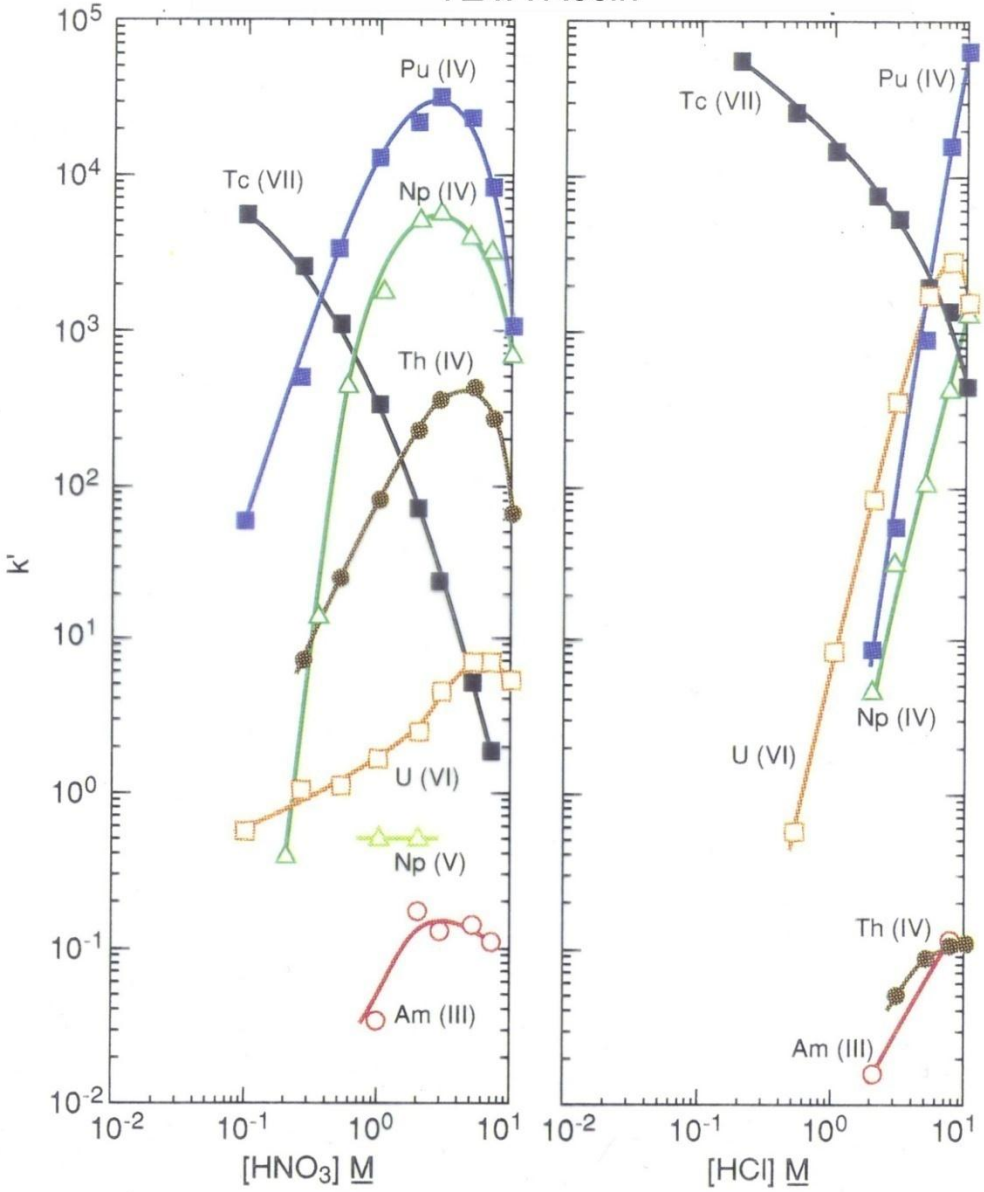
Approach

- Actinides (Pu,Np, Am, Cm, U) and Sr-89/90
  - **Air Filters**
    - **HNO_3+ HF digestion**
    - **Rapid and quantitative**
    - **TEVA Resin +TRU Resin + Sr Resin**
    - **CeF_3 microprecipitation-alpha spectrometry**
    - **Sr-89/90- gas proportional counting**
      - **Gravimetric recovery-Sr carrier (4mg)**

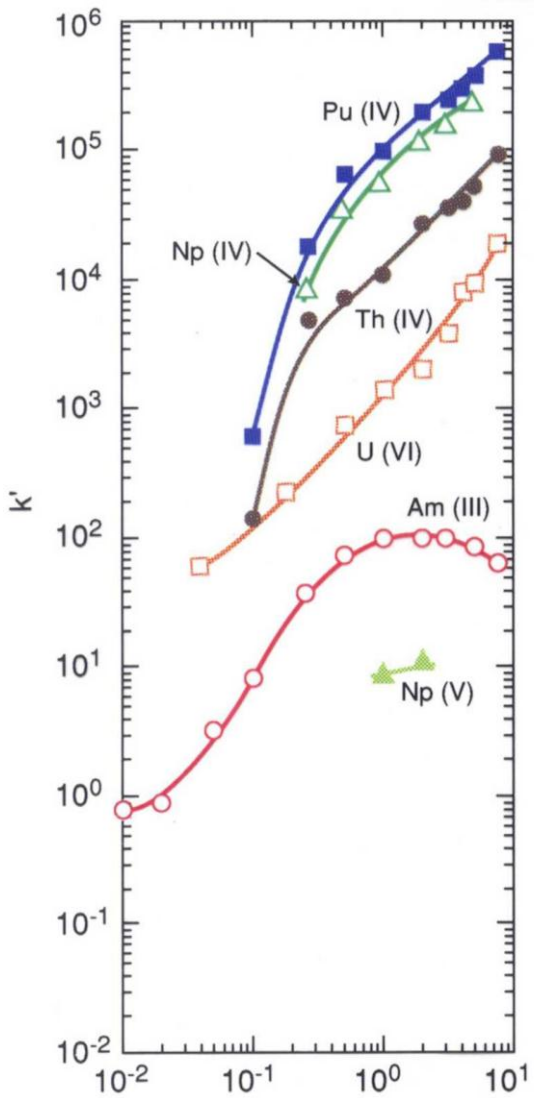
Maxwell, S., Culligan, B. and Noyes, G. Applied Radiation and Isotopes Vol. 68, Issue 12, December 2010, Pages 2125-2131

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

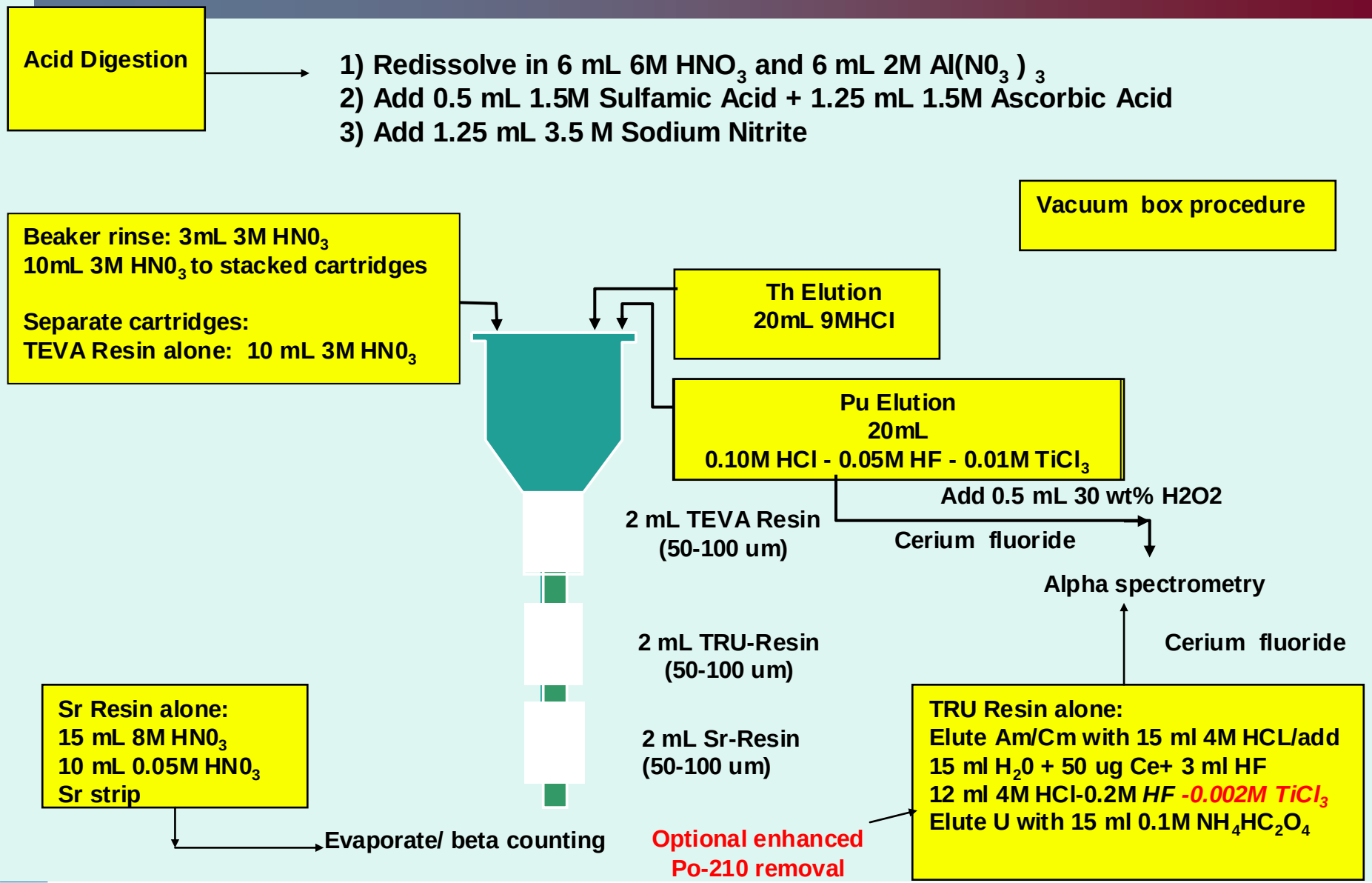
TEVA Resin



TRU Resin



Actinides and Sr-90 in Air Filters



NRIP-2009 Air Filters Turnaround Times

Nuclide	Turnaround Time (Hrs.)
^{238}Pu	3.9
^{240}Pu	3.9
^{241}Am	3.6
^{238}U	3.7
^{234}U	3.7
^{90}Sr	3.3

NRIP -2009 Air Filters Performance vs. NIST

Nuclide	Avg. Difference (%)
^{238}Pu	3.3
^{240}Pu	-7.3
^{241}Am	7.6
^{238}U	-3.1
^{234}U	-3.4
^{90}Sr	-9.9

Sr-89/90 Fukushima Air Filter Work

AF Batch	N	Avg. Sr. Carrier % Recovery	+/- 1 sigma	% Recovery LCS	Approximate MDC (pCi/filter)
A	14	60.0	15.0	82.5	1 - 2
B	14	92.3	5.3	100.1	1 - 1.5
A`	16	91.1	7.3	88.6	1
B`	16	91.6	4.3	94.6	1
C`	16	92.7	7.3	104.0	1
ARF19	17	79.9	4.7	92.0	0.7
AF/Swipes A	7	93.3	4.0	94.1	0.5
AF/Swipes B	7	80.2	10.7	102.7	0.5
Avg.		85.1		94.8	

for the air filter batches A, B, A`, B` and C` - analyzed only 10 of the 20ml dissolved aliquot

ARF19 used 15 of 20 ml

AF/Swipe batches used the entire sample

Fukushima Soil Samples - Actinides

- **Actinides**
  - **Screening with rapid fusion method (2g)**
  - **Analysis of large sample aliquots to achieve lower MDAs**
    - **Volcanic island soil contains high levels of Fe**
    - **Limited sample aliquot size**
  - **Used multiple aliquots and loaded to TEVA+TRU+DGA**
    - **Recombined final purified solutions from multiple purified aliquots into a single CeF_3 micro-ppt**
      - **removes uranium with H_2O_2 present (U^{6+})**
  - **Needed to determine actinides isotopes by alpha/ICP-MS**
    - **Could not split purified aliquots between alpha and ICP-MS since we needed lowest MDA possible for Pu**
    - **so we counted 100% of aliquot by alpha spectrometry 1st**
    - **And then….**

Fukushima Soil Samples - Actinides

- Further processing for ICP-MS
  - Redissolved actinides after alpha counting filters using HNO_3-boric acid
  - Loaded onto TEVA Resin, rinsed with 3M HNO3, and eluted Pu with ICP-MS friendly solution (0.25M HCL-0.005M HF-0.001M$TiCl_3$)
- Did not need to move Pu to DGA to remove U*
  - *since micro-CeF_3 ppt. with H_2O_2 present used to prepare counting sources removes 1000x uranium*
- Having a range different rapid separation 'tools' allowed us to adapt to specific sample needs

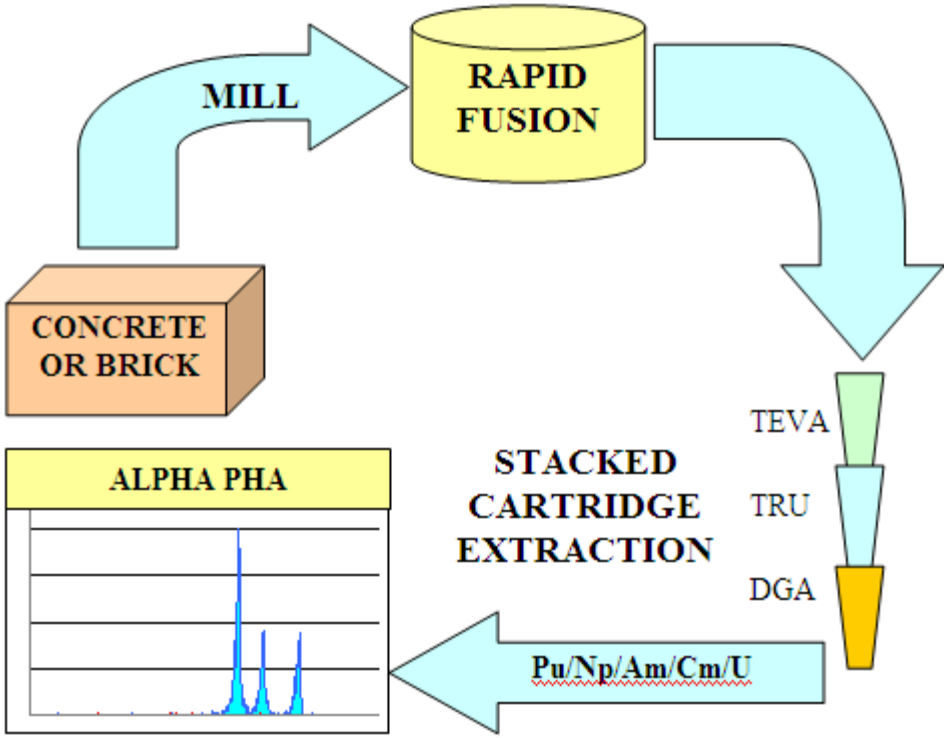
- * Health Physics: August 2011 - Volume 101 - Issue 2 - pp 180-186, Rapid Determination of 237Np and Plutonium Isotopes in Urine By Inductively-Coupled Plasma Mass Spectrometry and Alpha Spectrometry, Maxwell, Sherrod L.; Culligan, Brian K.; Jones, Vernon D.; Nichols, Sheldon T.; Noyes, Gary W.; Bernard, Maureen A.* [>10E6 U decontamination of Pu)

Actinides in Soil: Summary of SRS Approach

- **0.5 -2 grams** **direct fusion (NaOH)**
- **2 -10 grams** **HNO_3-HF Si removal, then fusion**
- **10 -100+ grams** **acid leach**

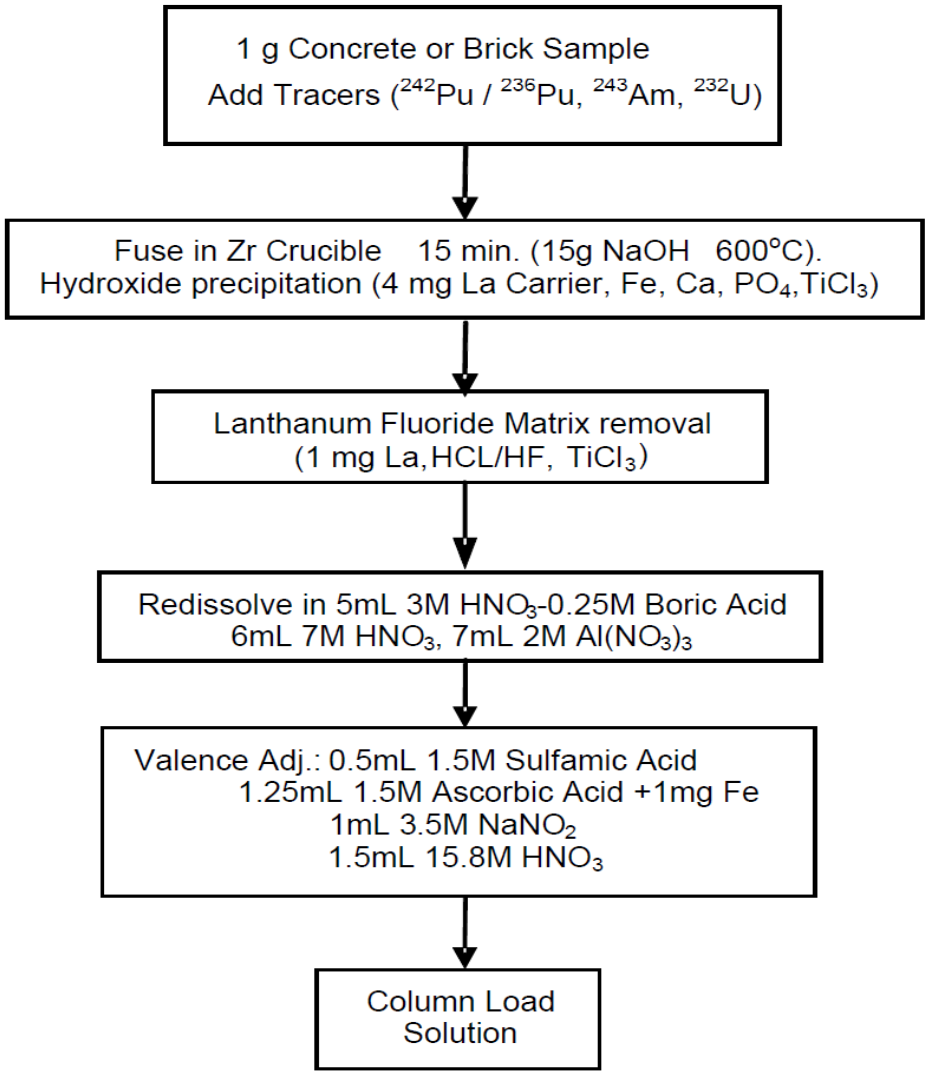
- **In all cases we use Fe/Ti OH precipitation followed by LaF_3 precipitation**
  - to preconcentrate actinides and eliminate soil matrix
    - Silicates, Fe
  - Sr-89/90 can be collected also (Ca + PO4)

Rapid Fusion Application for Concrete and Brick



Anal Chim Acta. 2011 Sep 2;701(1):112-8. Epub 2011 Jun 15.
Rapid radiochemical method for determination of actinides in emergency concrete and brick samples.
Maxwell SL, Culligan BK, Kelsey-Wall A, Shaw PJ.

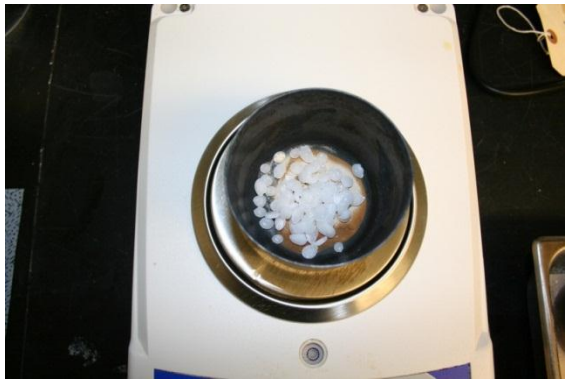
Rapid Concrete and Brick Sample Preparation

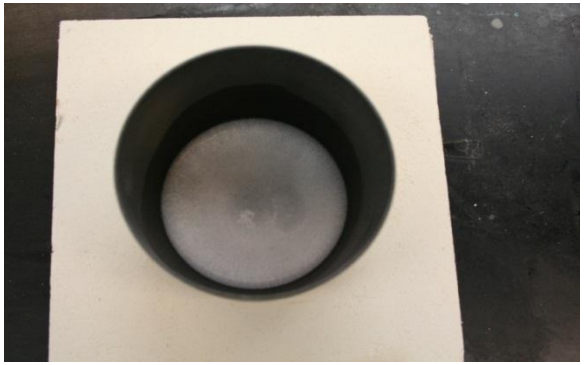


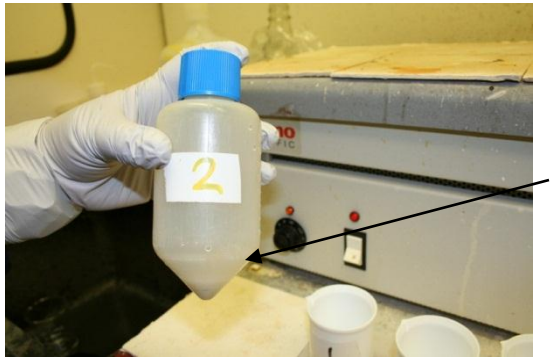
We now add Ca and PO4 for soil, concrete and brick

Rapid Sodium Hydroxide Fusion

- Great for silicates
- ~10 minutes







The Magic of DGA

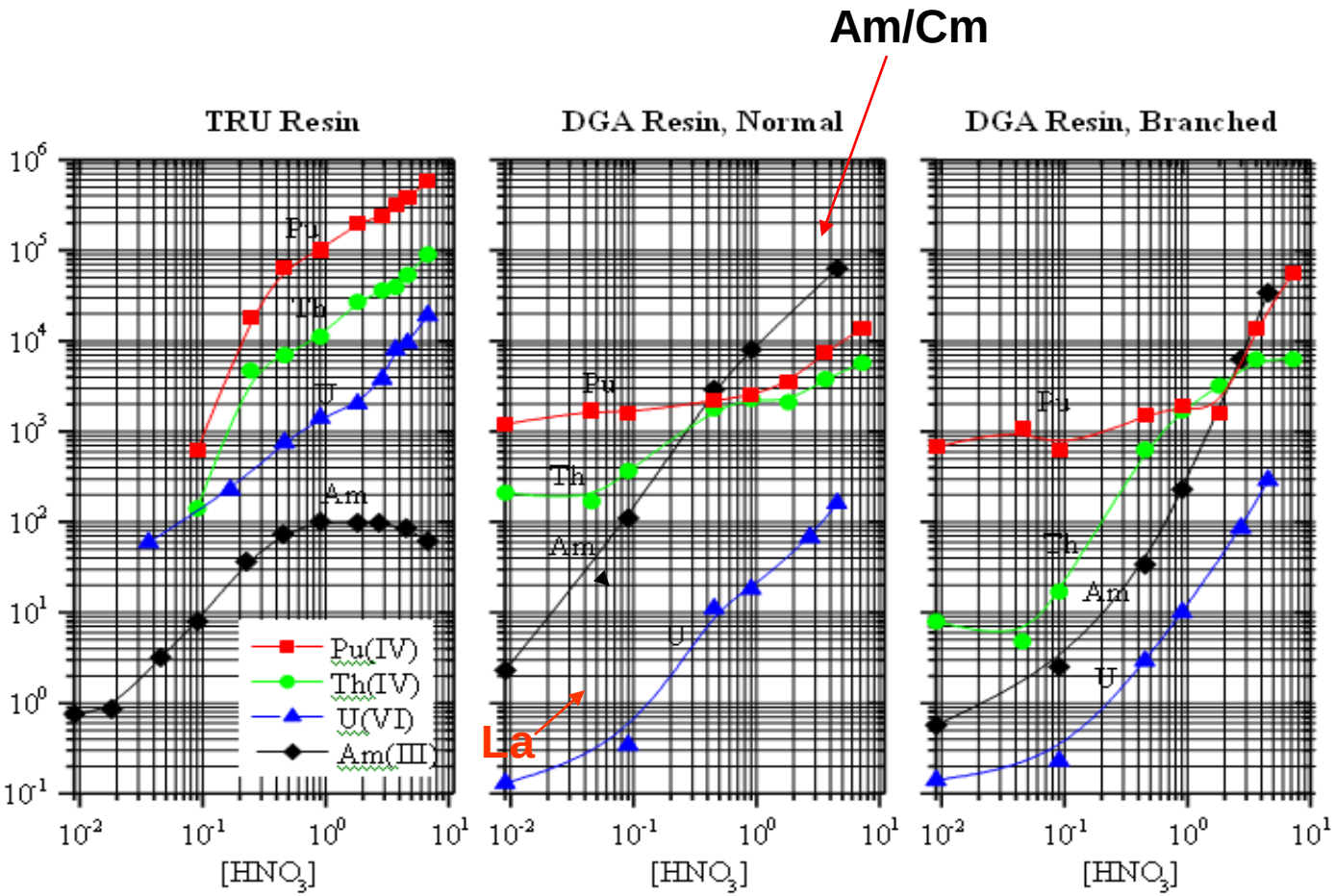
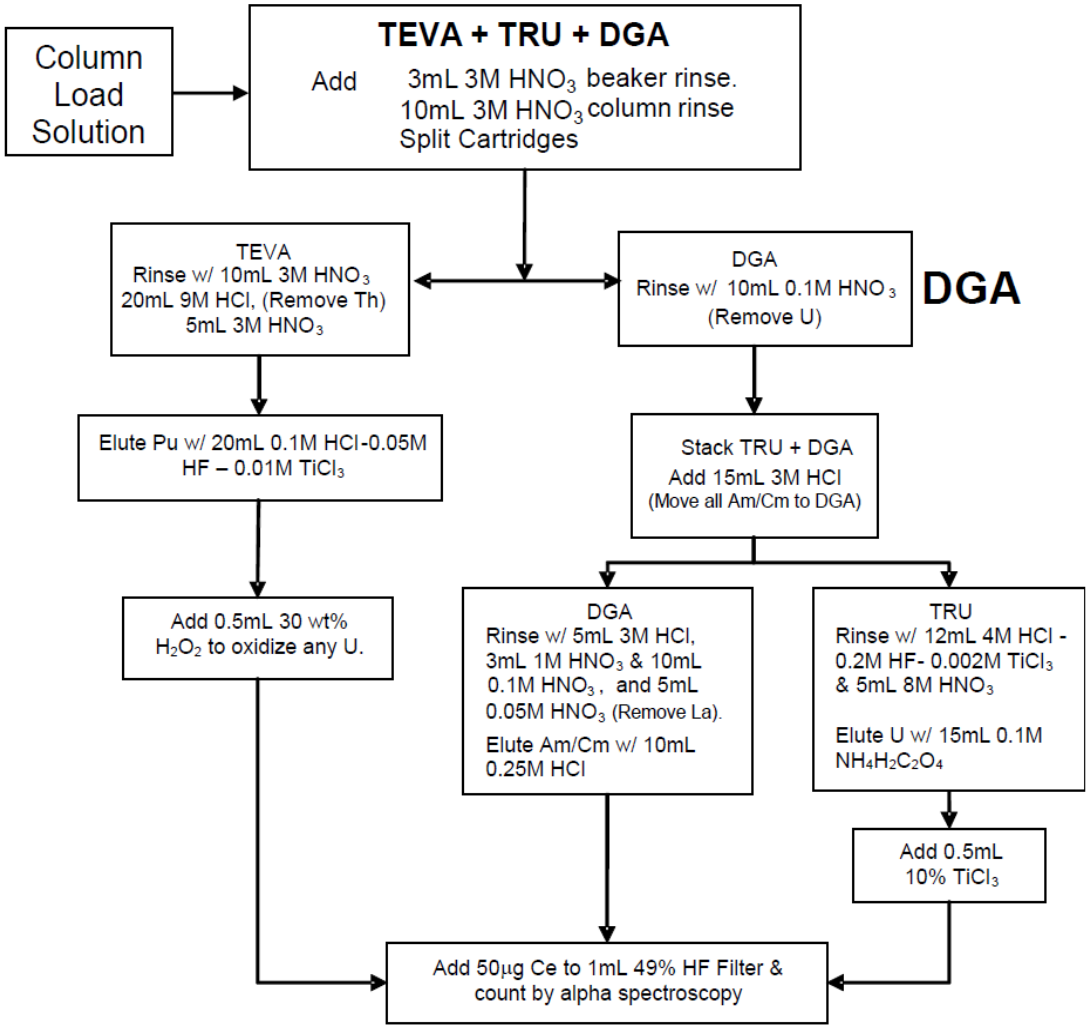


Figure 2

Source: http://www.eichrom.com/products/info/dga_resin.cfm

Rapid Column Separation



Pu and Np results for brick samples (with MAPEP 18 standard)

Sample ID	^{236}Pu Yield (%)	^{238}Pu Measured mBq g^{-1}	^{239}Pu Measured mBq g^{-1}	^{237}Np Measured mBq g^{-1}
1	95.9	15.4	20.6	34.3
2	89.5	16.6	16.5	35.2
3	107.6	13.7	18.0	32.2
4	85.0	14.0	14.8	33.4
5	95.7	15.6	16.2	40.3
Avg.	94.7	15.1	17.2	35.1
1SD	8.5	1.2	2.2	3.1
%RSD	9.0	7.9	12.8	8.9
Reference		14.8	18	37
% Difference		1.8	-4.3	-5.2

Pu-239 is refractory in MAPEP 18 soil standard

Am and Cm results for brick samples (with MAPEP 18 standard)

Sample ID	^{243}Am Yield (%)	^{241}Am Measured mBq g^{-1}	^{244}Cm Measured mBq g^{-1}
1	91.5	22.6	38.1
2	92.0	24.5	35.8
3	94.8	24.3	34.6
4	92.4	26.2	34.9
5	98.0	23.3	34.4
Avg.	93.7	24.2	35.6
1SD	2.7	1.4	1.5
%RSD	2.9	5.7	4.3
Reference		25.4	35
% Difference		-4.8	1.6

U results for brick samples (with MAPEP 18 standard)

Sample ID	^{232}U Yield (%)	^{234}U Measured mBq g^{-1}	^{238}U Measured mBq g^{-1}
1	81.1	31.5	26.9
2	85.7	27.8	31.4
3	89.3	27.8	29.9
4	91.4	21.5	28.8
5	92.8	25.2	27.7
Avg.	88.1	26.7	28.9
Corr. Avg.		25.7	28.0
1SD	4.7	3.7	1.8
%RSD	5.4	13.8	6.1
Reference		28.4	29.6
% Difference		-5.9	-2.3

avg ^{238}U in unspiked 1g sample = 0.94 mBq
avg ^{234}U in unspiked 1g sample = 1.02 mBq

[A] average spiked sample result corrected for unspiked content

Summary

- **Rapid fusion method is effective for concrete and brick**
  - Stack cartridges with vacuum flow
  - TEVA (Pu,Np) +TRU (U) +DGA (Am,Cm)
  - TEVA (Pu, Np)
  - TEVA+DGA (Pu+Am,Cm)
  - TEVA+TRU (Pu, U)
- **Alpha spectrometry or ICP-MS**

Food-Approach

- Could we apply rapid fusion technology we have used for NRIP emergency vegetation samples to food ?
  - Previous method: furnace, wet-ash, acid leach digestion
    - Residual ash/solids
    - Lower tracer recoveries
  - Now: furnace, wet-ash, *rapid fusion*
  - Why: eliminate lower, inconsistent yields and improve quality
  - TEVA Resin +TRU Resin + DGA Resin, then Sr Resin
  - CeF_3 microprecipitation-alpha spectrometry
  - Sr-89/90- gas proportional counting
    - Gravimetric recovery-Sr carrier (4mg)
  - Results in <8 hours

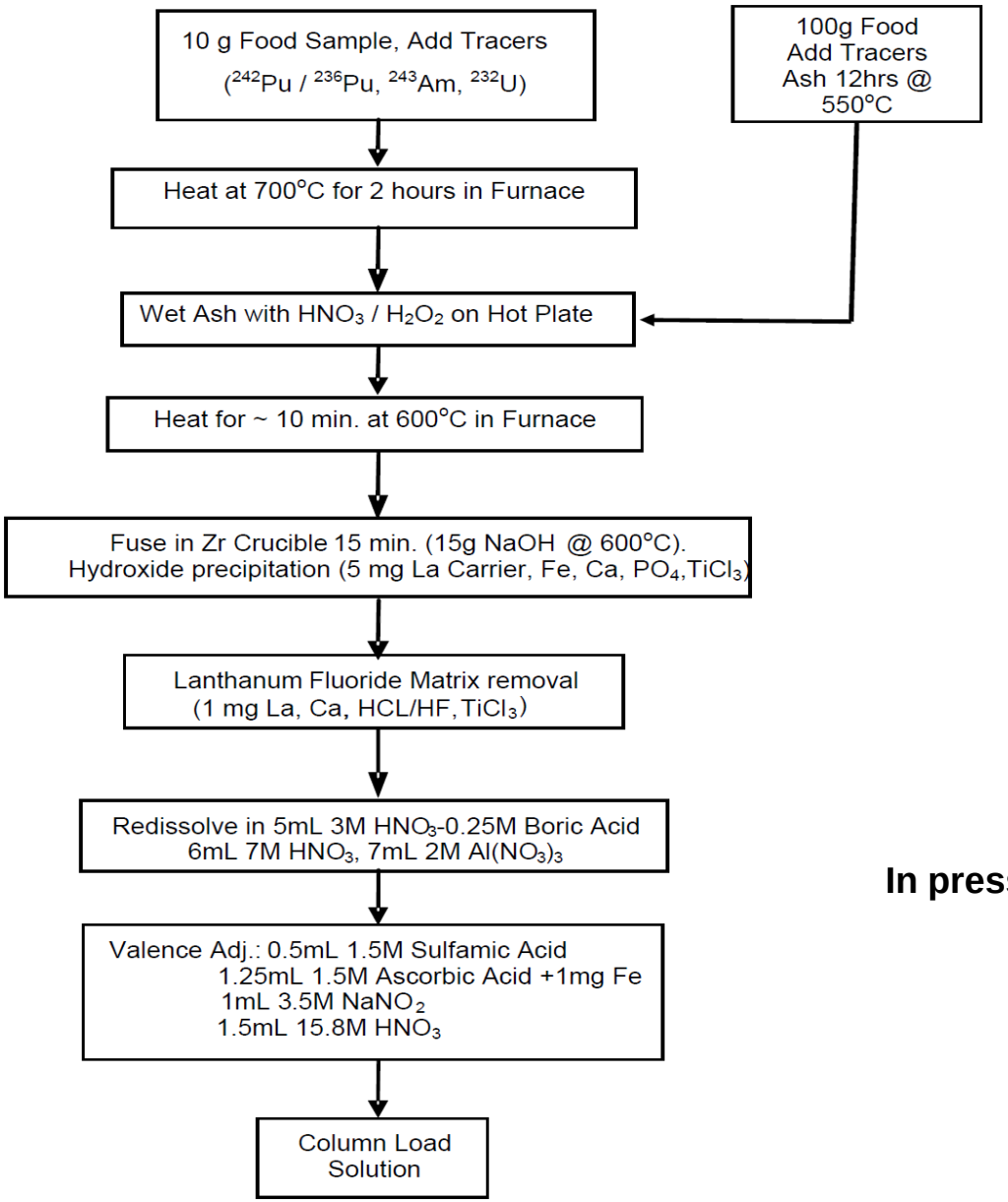
Maxwell, S., Culligan, B. and Noyes, G., Rapid Separation of Actinides and Radiostrontium in Vegetation Samples, J. Radioanal. Nucl. Chem, (2010), 286:273–282

FDA Requirements

- **U.S Food and Drug Administration (FDA) has provided guidance regarding accidental contamination of foods to state and local agencies so that protective actions may be taken**
- **FDA Derived Intervention Level (DIL) for ^{238}Pu+ ^{239}Pu + ^{241}Am is 2 Bq/kg (2 mBq/g or 0.054 pCi/g).**
  - DILs were calculated to help protect even the most vulnerable segments of the population by limiting radiation dose from ingestion.
- **Rapid and effective analysis methods are essential to allow responsible officials to apply protection actions.**

  - U.S Department of Health and Human Services, Food and Drug Administration, Accidental Radioactive Contamination of Human Food and Animal Feeds: Recommendations for State and Local Agencies, Center for Devices and Radiological Health, August 13, 1998, http://www.fda/cdrh

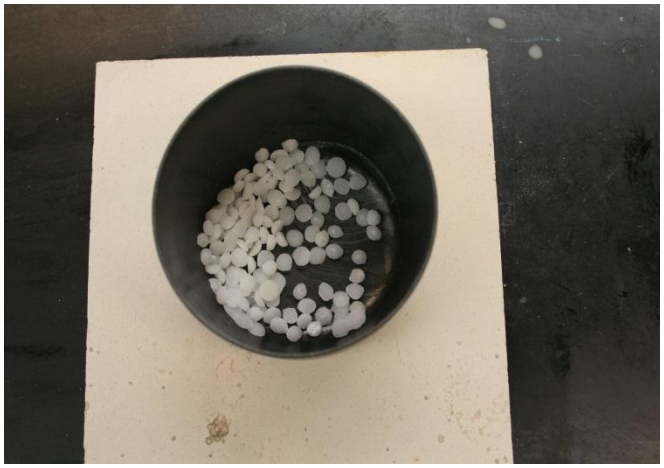
Actinides in Food

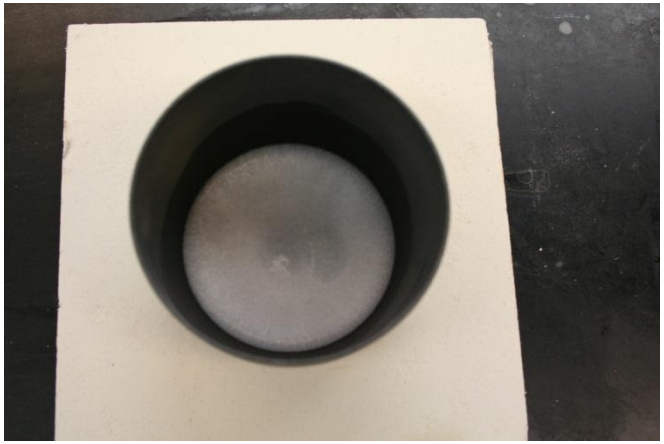


In press JRNC

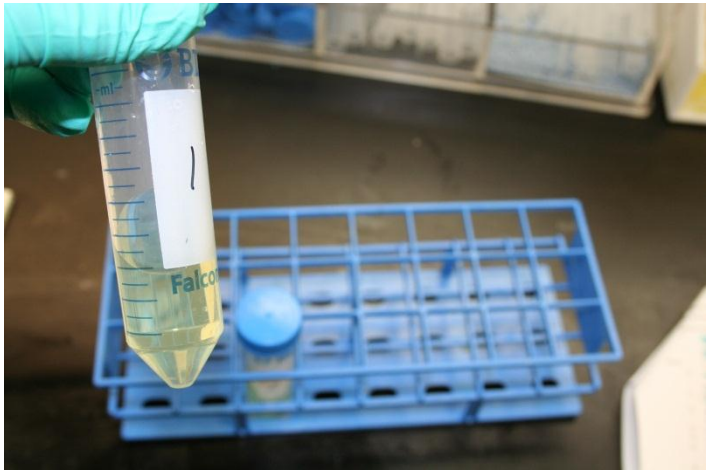
Rapid Furnace Heating of Food Aliquots

Rapid Sodium Hydroxide Fusion

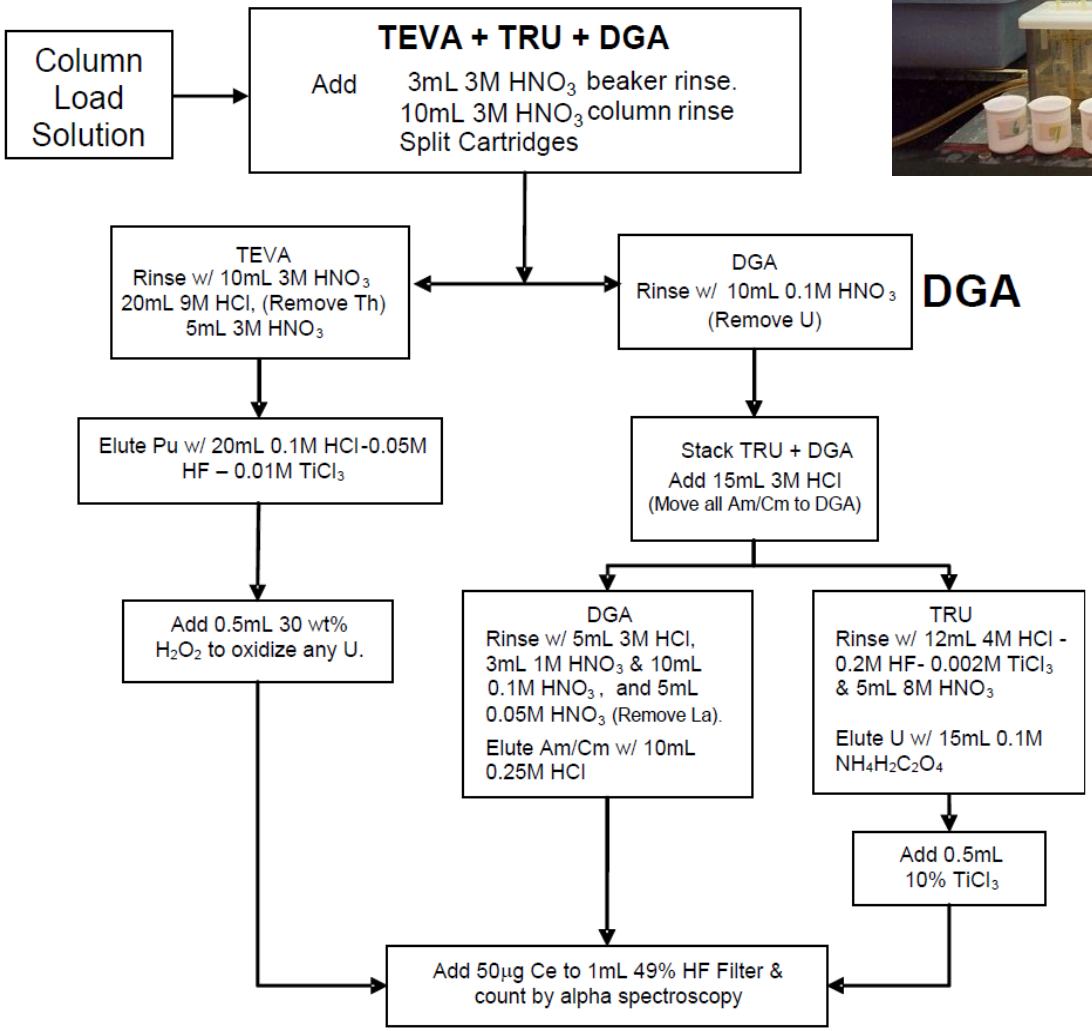




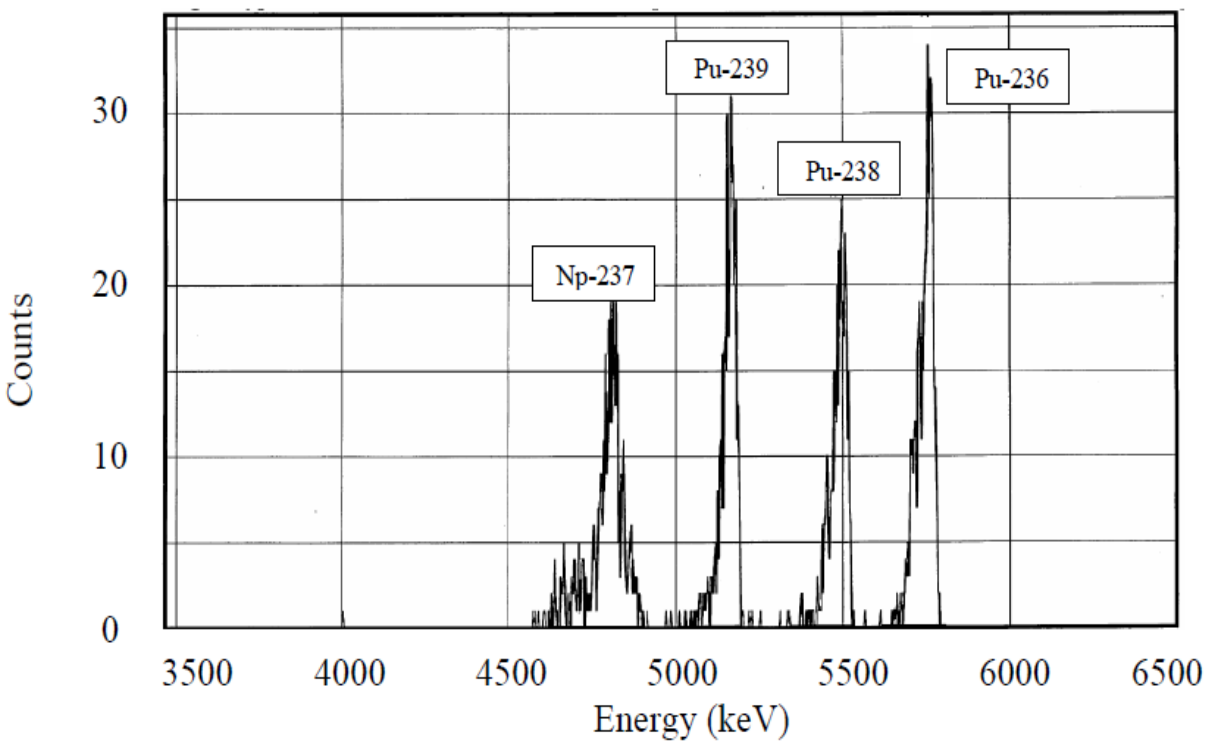
Preconcentration Steps



Rapid Column Separation

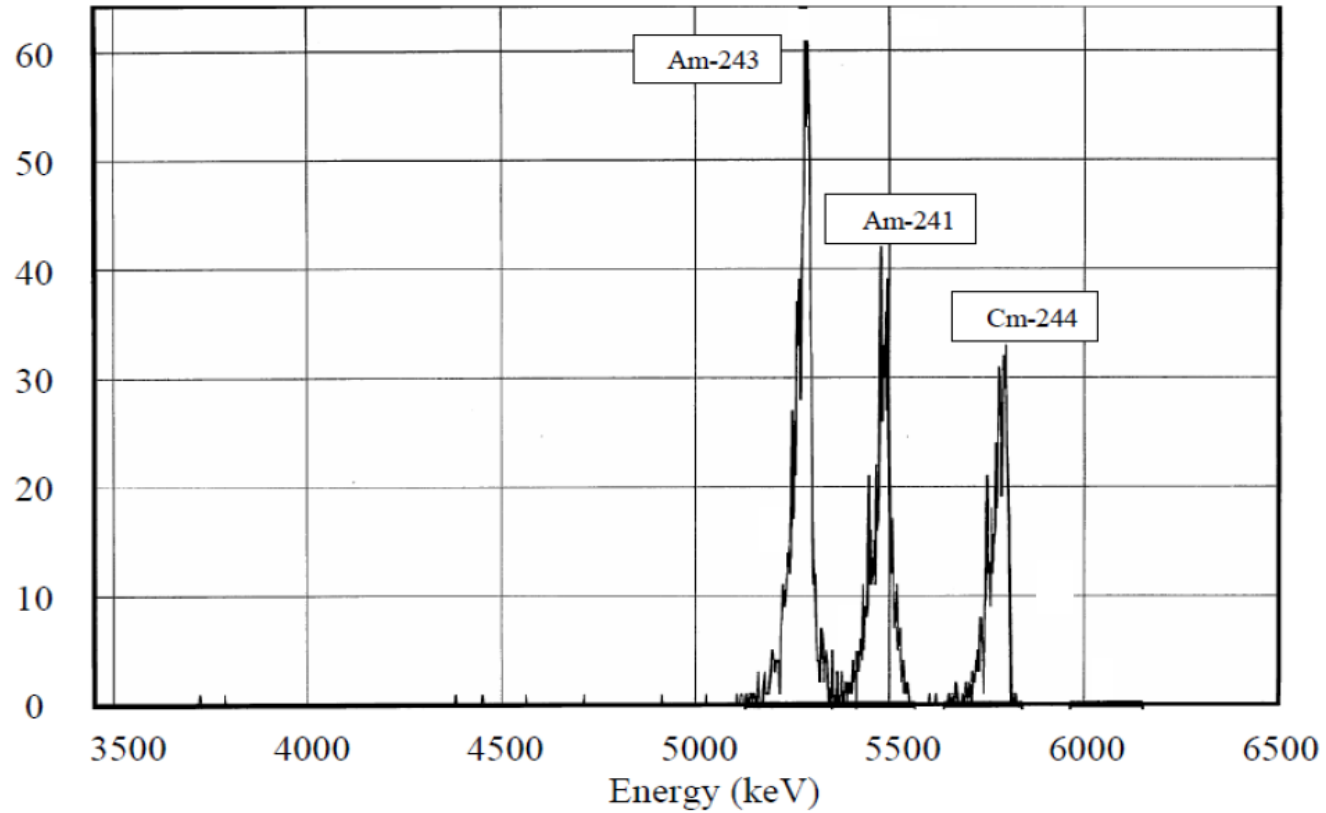


Pu and Np Alpha Spectra Food Sample



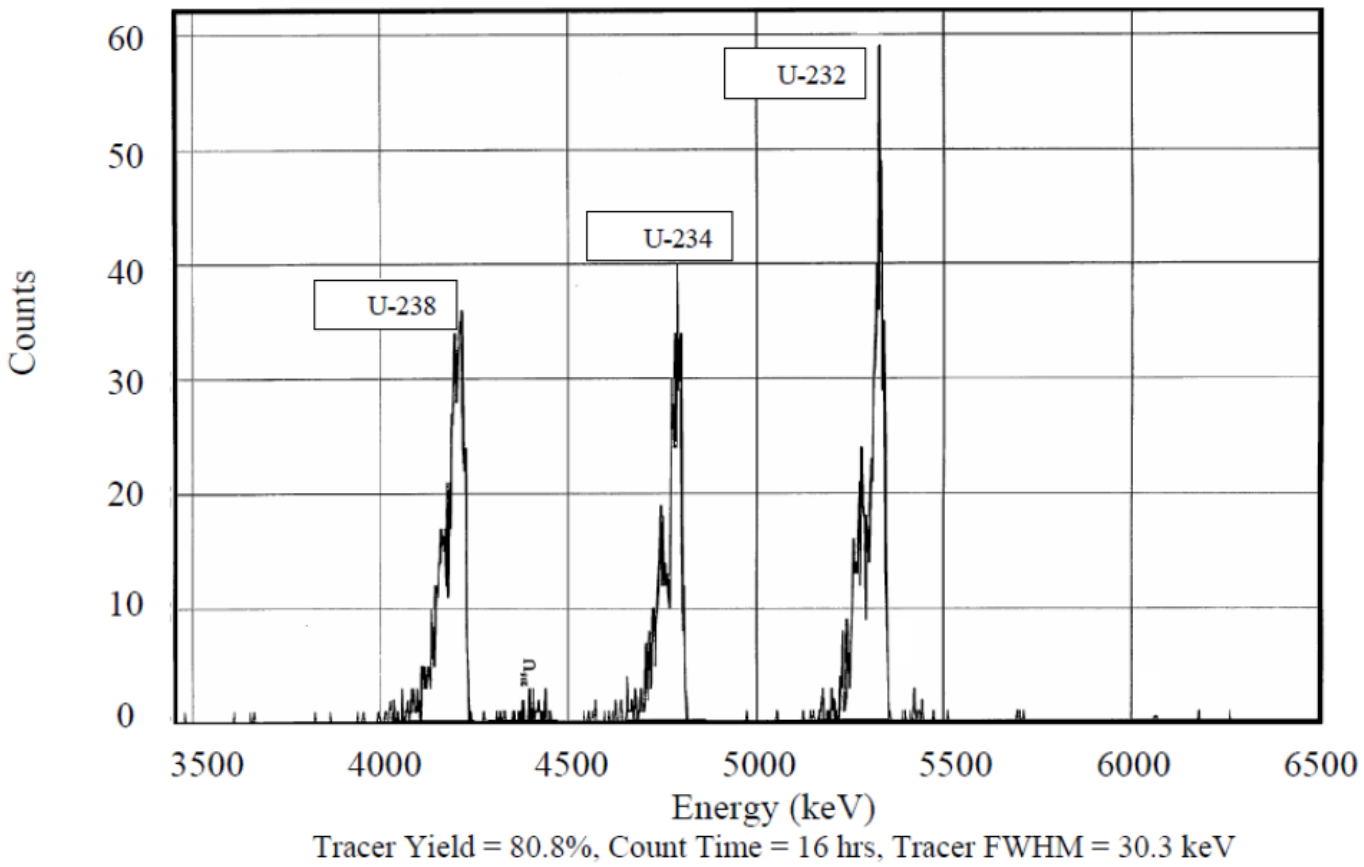
Tracer Yield = 100.5%, Count Time = 16 hrs, Tracer FWHM = 49.3 keV

Am and Cm Alpha Spectra Food Sample



Tracer Yield = 93.2%, Count Time = 16 hrs, Tracer FWHM = 42.6 keV

U Isotope Alpha Spectra Food Sample



Tracer Yield = 80.8%, Count Time = 16 hrs, Tracer FWHM = 30.3 keV

Emergency Response Methods

Reference Number	MS510
Analytes	Actinides, Cm, Am, Pu, U
Matrix	Soil, Emergency Response Methods
Authors	Maxwell, S.L., Culligan, B.K., Noyes, G.W.
Title	Rapid separation method for actinides in emergency soil samples
Journal	Radiochimica Acta
Year	2010
Reference	Vol. 98, No. 12, pp. 793-800
Detectors	Alpha-spec
Resins	UTEVA Resin, TRU Resin, DGA Resin
URL	http://www.oldenbourg-link.com/doi/abs/10.1524/ract.2010.1785?journalCode=ract
Digital Object Identifier	10.1524/ract.2010.1785

Emergency Response Methods

Reference Number	MS112
Analytes	Actinides, Pu, Np, Am, Cm, U
Matrix	Food, Emergency Response Methods
Authors	Maxwell, S.L., Culligan, B.K., Kelsey-Wall, A., Shaw, P.J.
Title	Rapid determination of actinides in emergency food samples
Journal	Journal of Radioanalytical and Nuclear Chemistry
Year	2012
Reference	Vol. 292, No. 1, pp. 339-347
Detectors	Alpha-spec
Resins	TEVA Resin, TRU Resin, DGA Resin
URL	http://www.springerlink.com/content/qj242h7q7442j252/
Digital Object Identifier	10.1007/s10967-011-1411-5

Emergency Response Methods

Reference Number	MS212
Analytes	Ra
Matrix	Vegetation, Air Filters, Brick, Concrete, Soil, Water, Emergency Response Methods
Authors	Maxwell, S.L., Culligan, B.K.
Title	Rapid determination of 226Ra in environmental samples
Journal	Journal of Radioanalytical and Nuclear Chemistry
Year	2012
Reference	Online 03 February 2012
Detectors	Alpha-spec
Resins	Cation Exchange Resin, Sr Resin, Ln Resin
URL	http://www.springerlink.com/content/c8184647k630r1k8/
Digital Object Identifier	10.1007/s10967-012-1627-z

Emergency Response Methods

Reference Number	MS111
Analytes	Actinides, Pu, Np, Am, Cm, U
Matrix	Concrete, Brick, Emergency Response Methods
Authors	Maxwell, S.L., Culligan, B.K., Kelsey-Wall, A., Shaw, P.J.
Title	Rapid radiochemical method for determination of actinides in emergency concrete and brick samples
Journal	Analytica Chimica Acta
Year	2011
Reference	Vol. 701, Issue 1, pp. 112-118
Detectors	Alpha-spec
Resins	TEVA Resin, DGA Resin, TRU Resin
URL	http://www.sciencedirect.com/science/article/pii/S00032670 1100780X
Digital Object Identifier	10.1016/j.aca.2011.06.011

Emergency Response Methods

Reference Number	MS210
Analytes	Actinides, Sr, U, Pu, Am, Cm, Np, Th
Matrix	Vegetation, Emergency Response Methods
Authors	Maxwell, S.L., Culligan, B.K., Noyes, G.W.
Title	Rapid Separation of actinides and radiostrontium in vegetation samples
Journal	Journal of Radioanalytical and Nuclear Chemistry
Year	2010
Reference	Vol. 286, No. 1, pp. 273-282
Detectors	Alpha-spec, GPC
Resins	TEVA Resin, TRU Resin, Sr Resin
URL	http://www.springerlink.com/content/b424421j7n198186/
Digital Object Identifier	10.1007/s10967-010-0653-y

Emergency Response Methods

Reference Number	US110
Analytes	U, Pu, Am, Sr, Ra
Matrix	Water, Emergency Response Methods
Authors	United States Environmental Protection Agency
Title	Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events
Journal	EPA 402-R-10-001
Year	2010
Reference	EPA 402-R-10-001
Detectors	Alpha-spec, gas flow proportional
Resins	TRU Resin, UTEVA Resin, Diphonix Resin, MnO2 Resin, Sr Resin
URL	http://www.epa.gov/narel/reports/Rapid_Radiochemical_Methods_In_Water_with_cover_06-24-10.pdf