Automated Separation of Ultra-trace Actinides from Urine by Ion Chromatography ICP-MS

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Possible Radionuclides from a RDD or IND

- Sources are from nuclear power generation, industrial, nuclear medicine nuclear weapons, IND, RDD, etc.
- Some examples: ^{60}Co, ^{90}Sr, ^{137}Cs, ^{192}Ir, ^{210}Po, ^{241}Am, ^{238}Pu, ^{239}Pu, ^{244}Cm, ^{252}Cf, others…

The DOE/NRC Interagency Working Group on Radiological Dispersal Devices, "Radiological Dispersal Devices: An Initial Study to Identify Radioactive Materials of Greatest Concern and Approaches to their tracking, tagging, and disposition", May 2003.

Radionuclide Analytical Methods (typical in DOE / DOD facilities)

- Requires a 24 hour Urine Collection.
- Most results available in 3-21 days.
- Limited radionuclide analytical methods.
- Sample throughput of 5-40 samples/day/lab.

Urgent Needs for Evaluation of a Population Exposed to a IND / RDD

- Analytical methods that require only 1-50 mL of urine.
- Analytical methods for a wide variety of radionuclides.
- Results available in 4-36 hours.
- Sample throughput of 100-500+ samples/day/lab.

Actinides by ICP-MS: The issues

Polyatomic ions

^{236}UH and ^{237}Np

^{237}NpH and ^{236}U

^{238}UH and ^{239}Pu

^{240}PuH and ^{241}Am

^{242}PuH and ^{243}Am

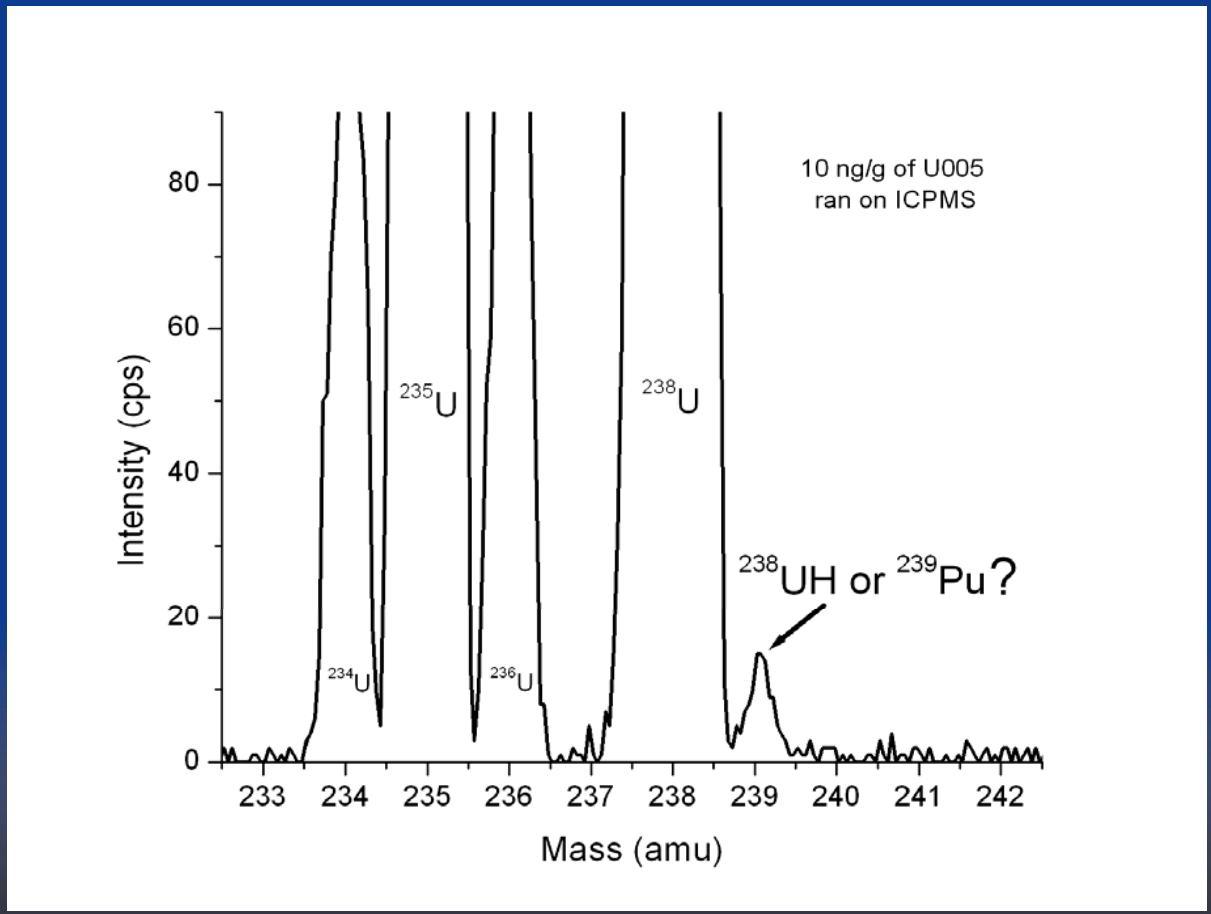
Isobars

^{236}U and ^{236}Np

^{238}U and ^{238}Pu

^{241}Pu and ^{241}Am

^{242}Pu and ^{242}Am

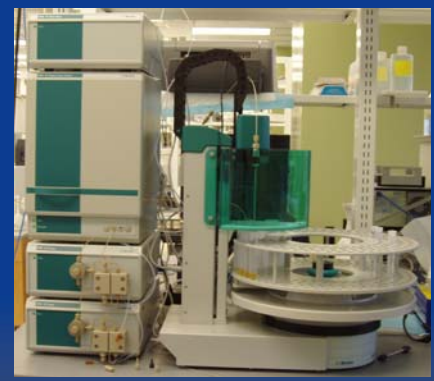


Approach

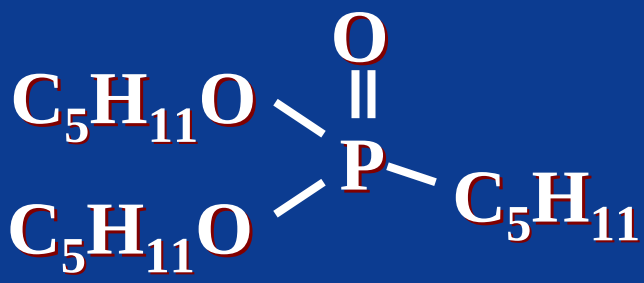
- Utilize small urine sample
- Pre-concentrate lanthanides and actinides on column
- Wash urine's organics and salts from the column to minimize detrimental effects on ICP-SFMS
- Elute lanthanides and actinides from column to ICP-SFMS for quantitation

Instrumentation

- Ion Chromatography
  - Dionex
    - GS50 gradient pump, AS50 autosampler, LC30 oven
  - MetrOhm
    - 818 IC Pump, 820 IC Separation Center, 830 IC Interface, 838 Advanced Sample Processor
- ICP-SFMS
  - Thermo Finnigan Element 2

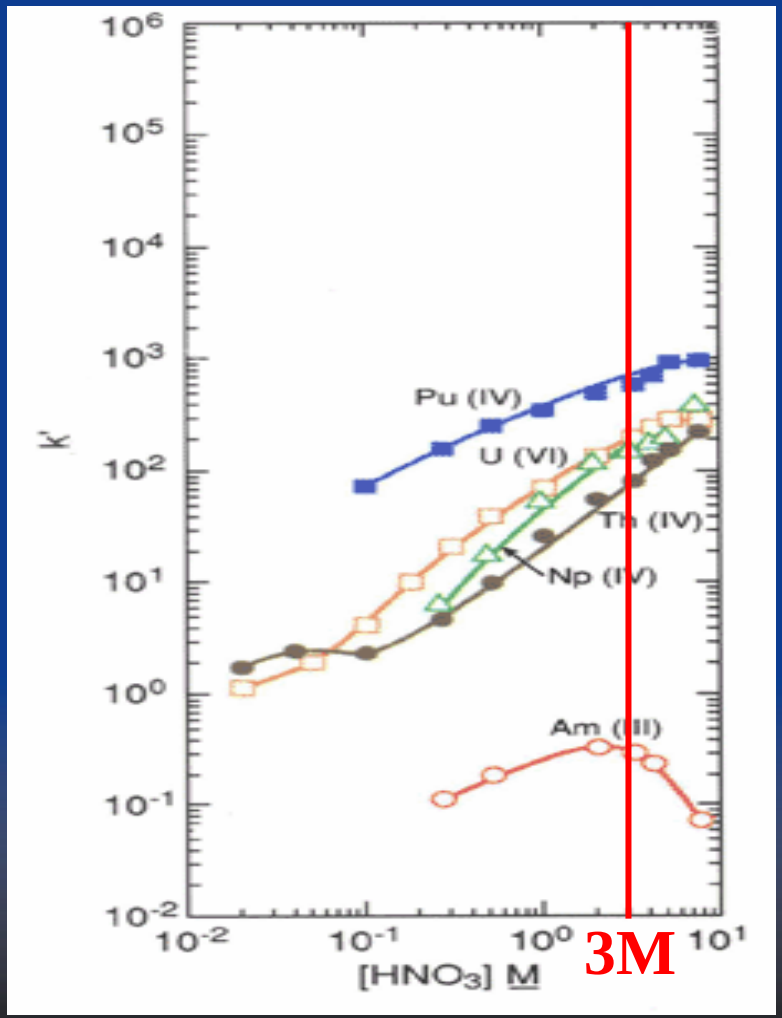


UTEVA



- UTEVA forms nitrato complexes with actinides.
- Retention of actinides dependent on conc. of HNO_3.

UTEVA Acid Dependency of k' in HNO_3



- 3M HNO_3 efficiently retains actinides.
- Low conc of HNO_3 should be efficient at eluting actinides. But in practice, another elute is required.

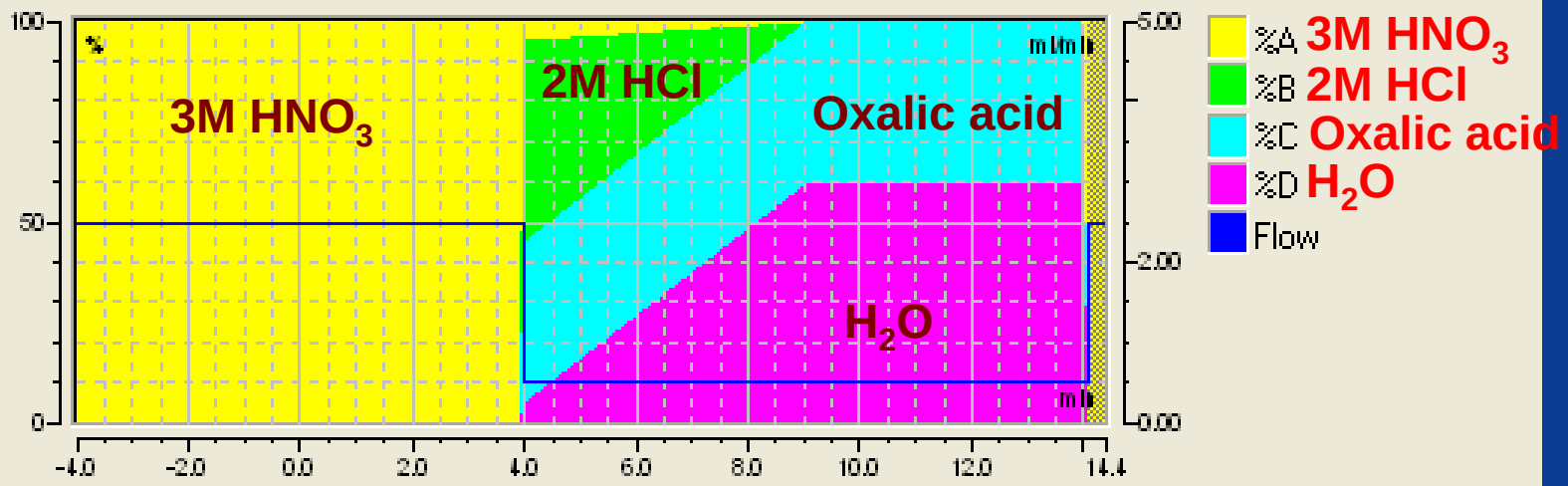
Horwitz, E.P., et al, Separation and preconcentration of uranium from acidic media by extraction chromatography, Analytica *Chimica Acta, Vol.266, pp. 25-37(1992)*

Sample Preparation

- Vortex original Urine sample
- Pippette into autosampler vial
  - 1mL urine
  - 0.27mL conc. HNO_3
  - 0.13mL Internal Standard
- Seal autosampler vial
- Vortex mixture
- Final mixture is urine in 3M HNO_3

Oxalic Acid-HCl Gradient Elution

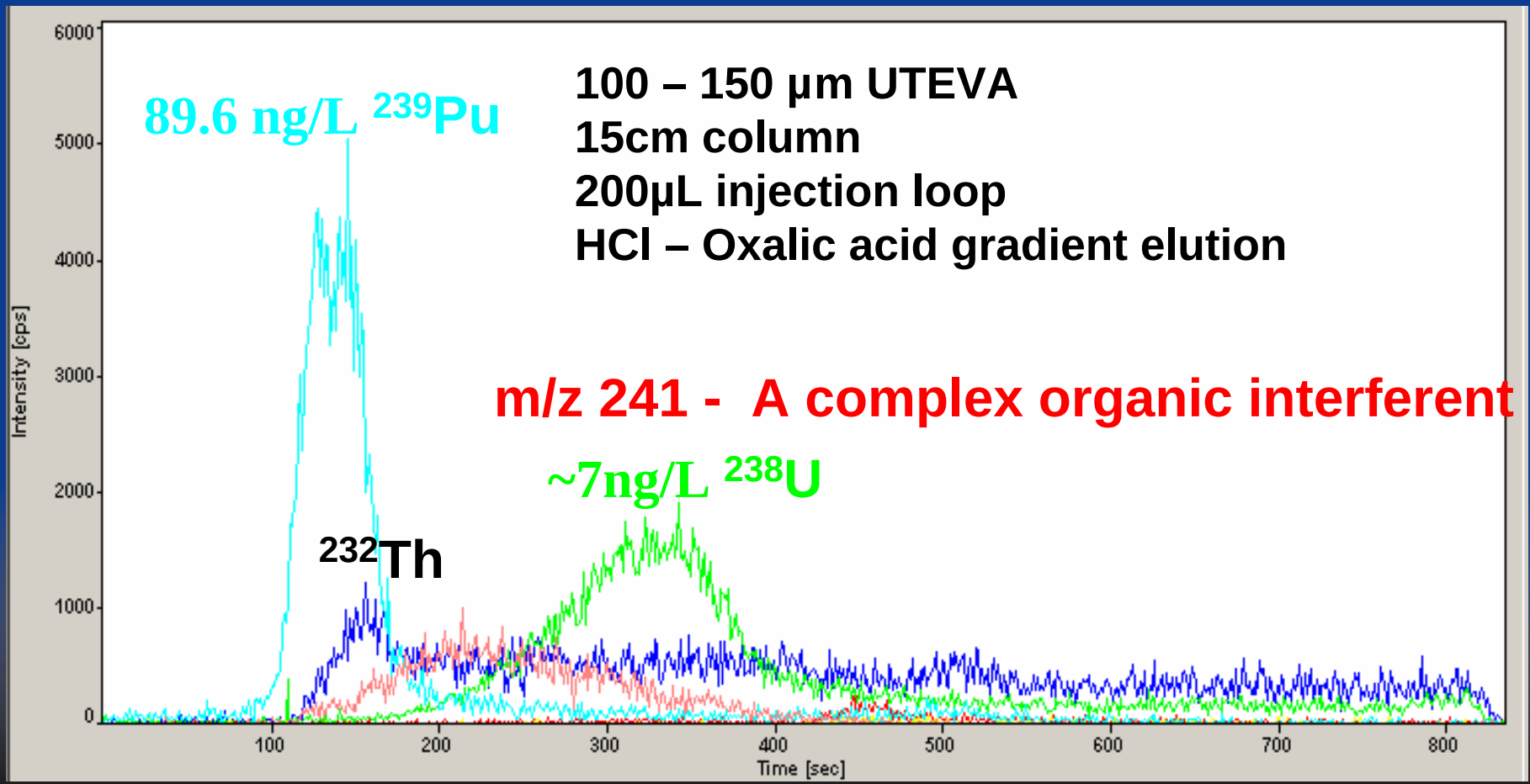
Flow | Flow Gradient | Multi-Step Gradient



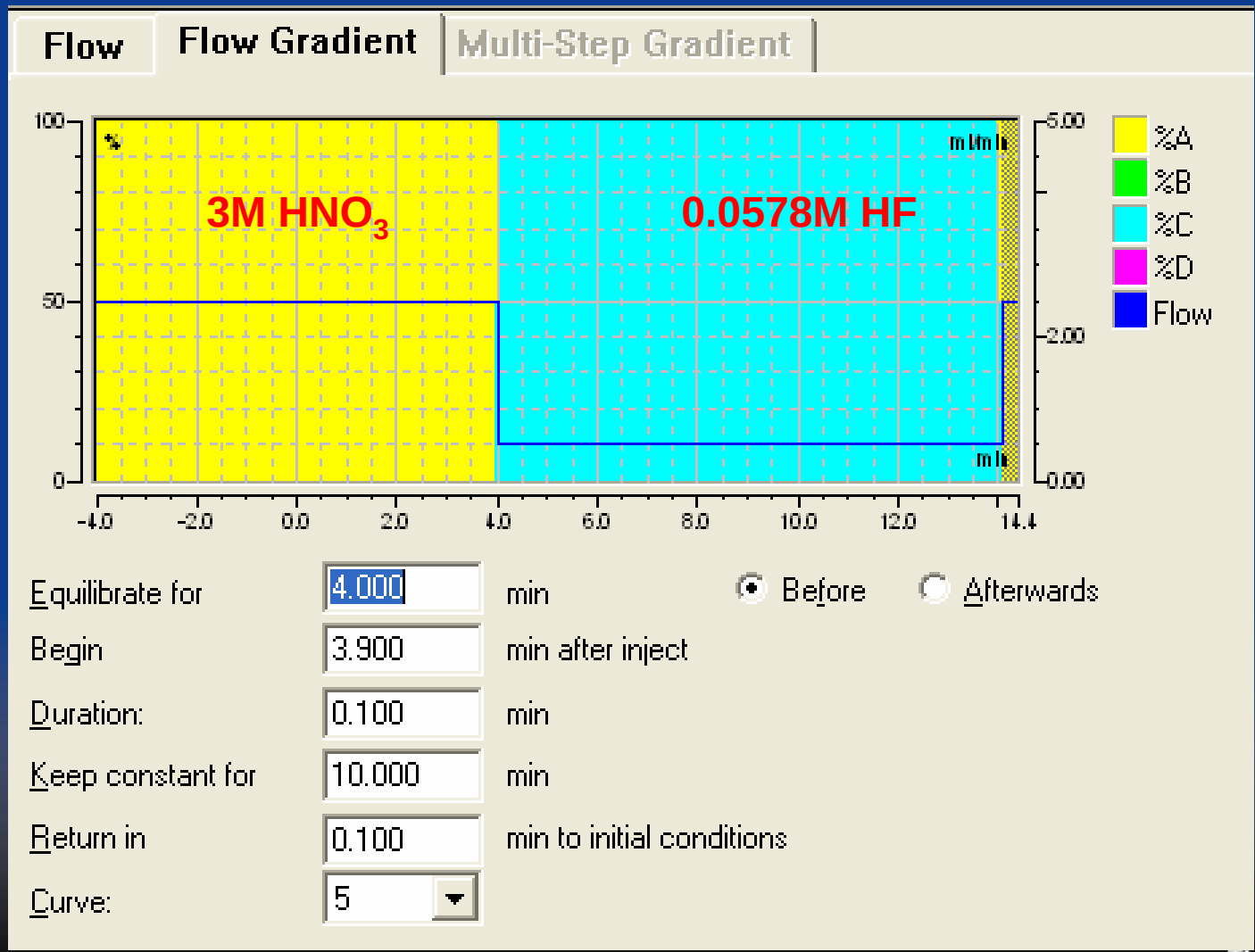
	Retention	Flow	%B	%C	%D	Curve
1	-4.000	2.50	0.0	0.0	0.0	
2	3.900	2.50	0.0	0.0	0.0	5
3	4.000	0.50	50.0	40.0	5.0	5
4	9.000	0.50	0.5	40.0	59.5	5
5	14.000	0.50	0.5	40.0	59.5	5
6	14.100	2.50	0.0	0.0	0.0	5

Insert Line
Delete Line
Clean Up
Interpolate

Separation of Pu, Th, U in Urine



HF Isocratic Elution



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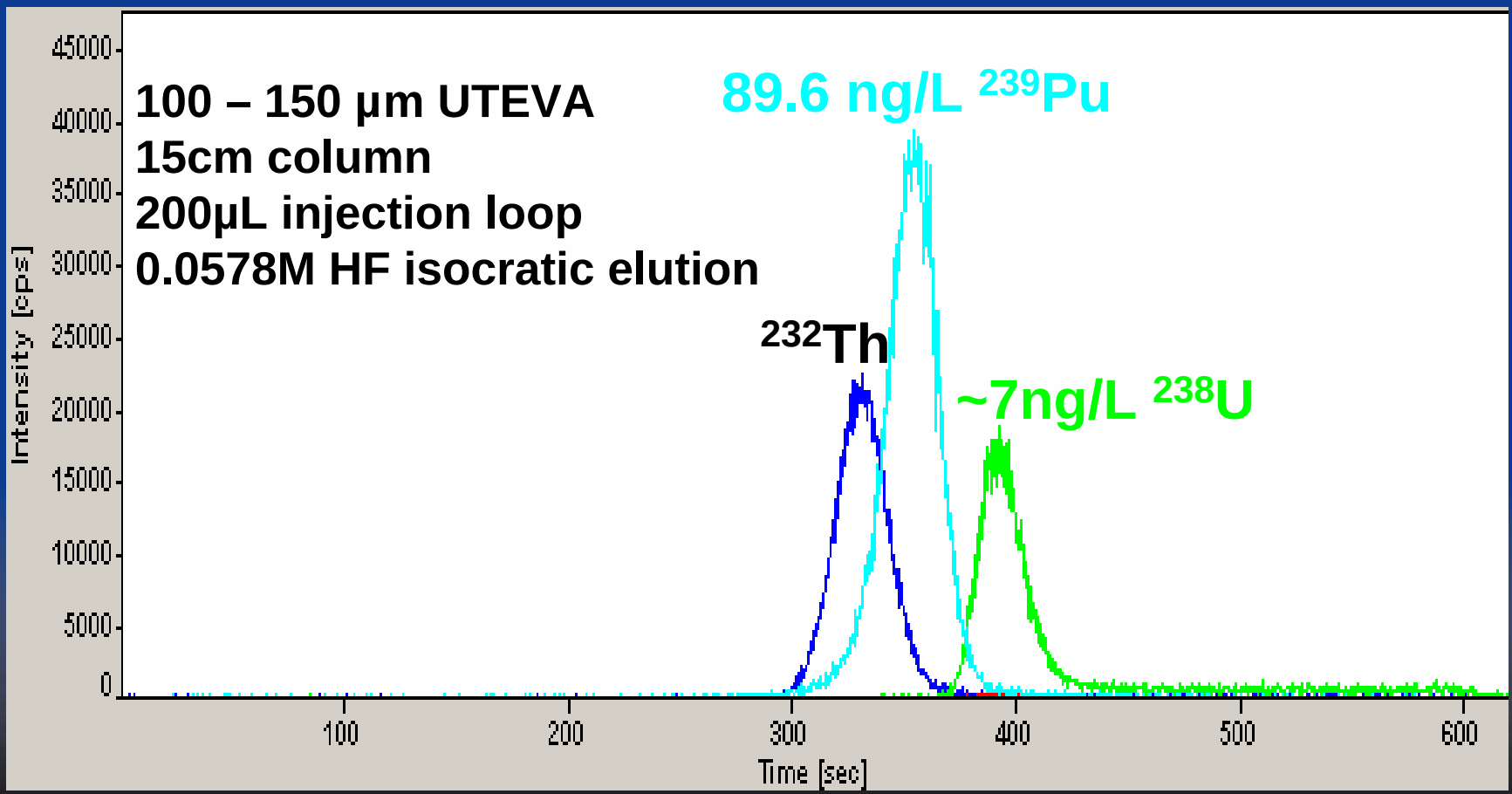
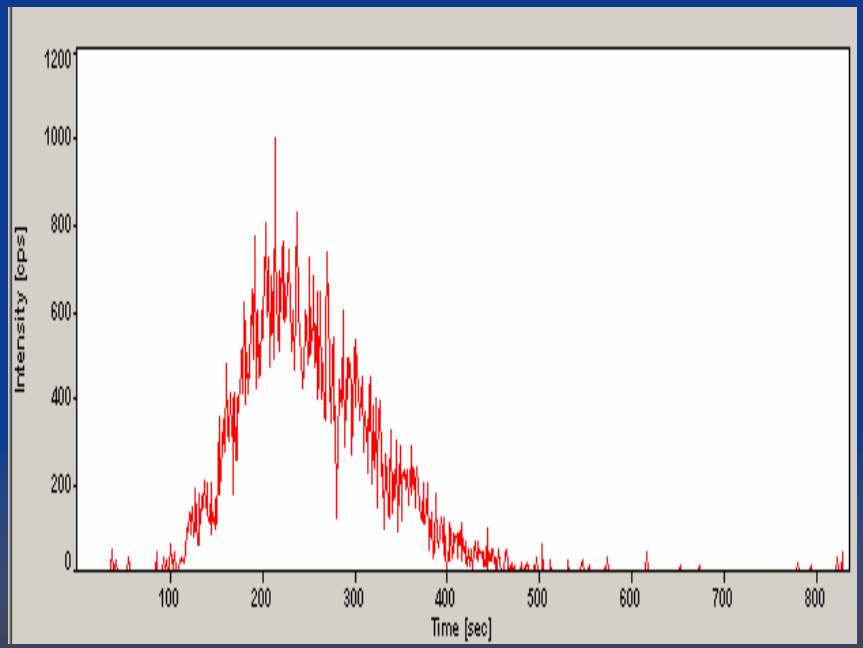
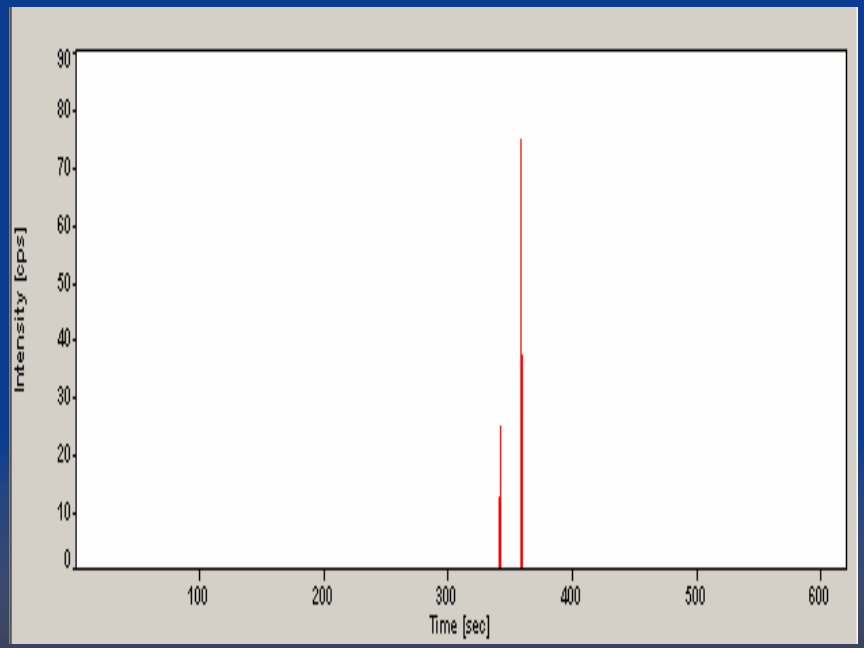


m/z 241 Interference

HCl – Oxalic acid elution

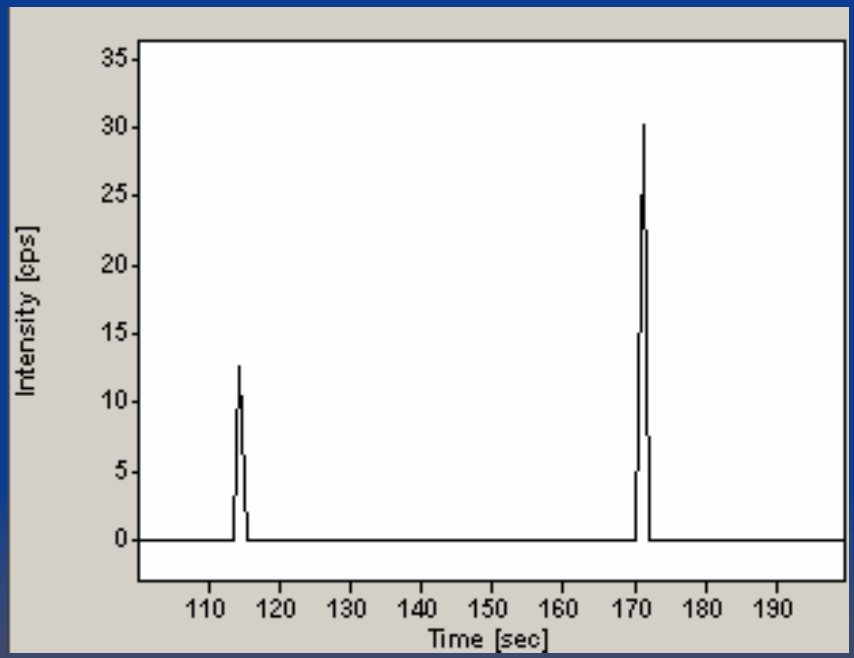


HF elution

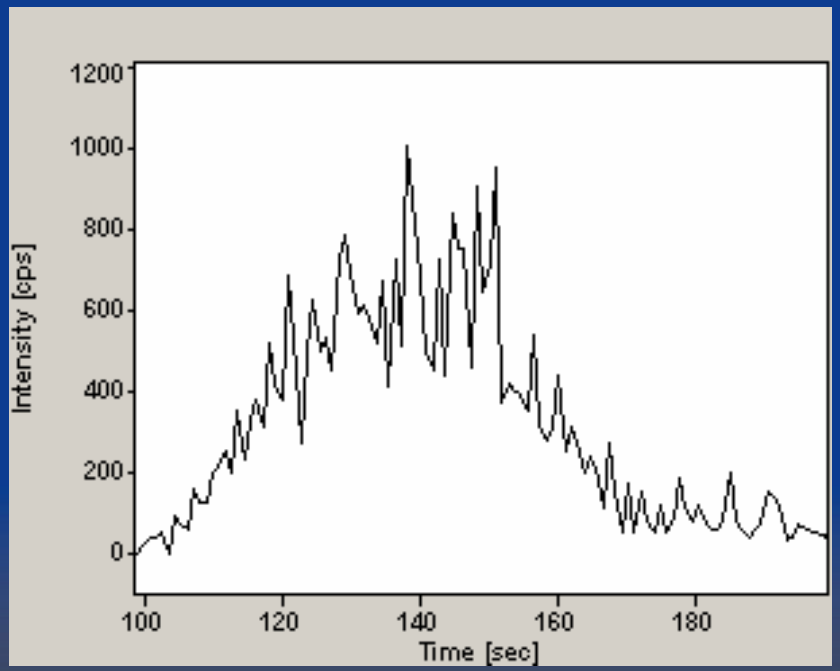


^{239}Pu Separation

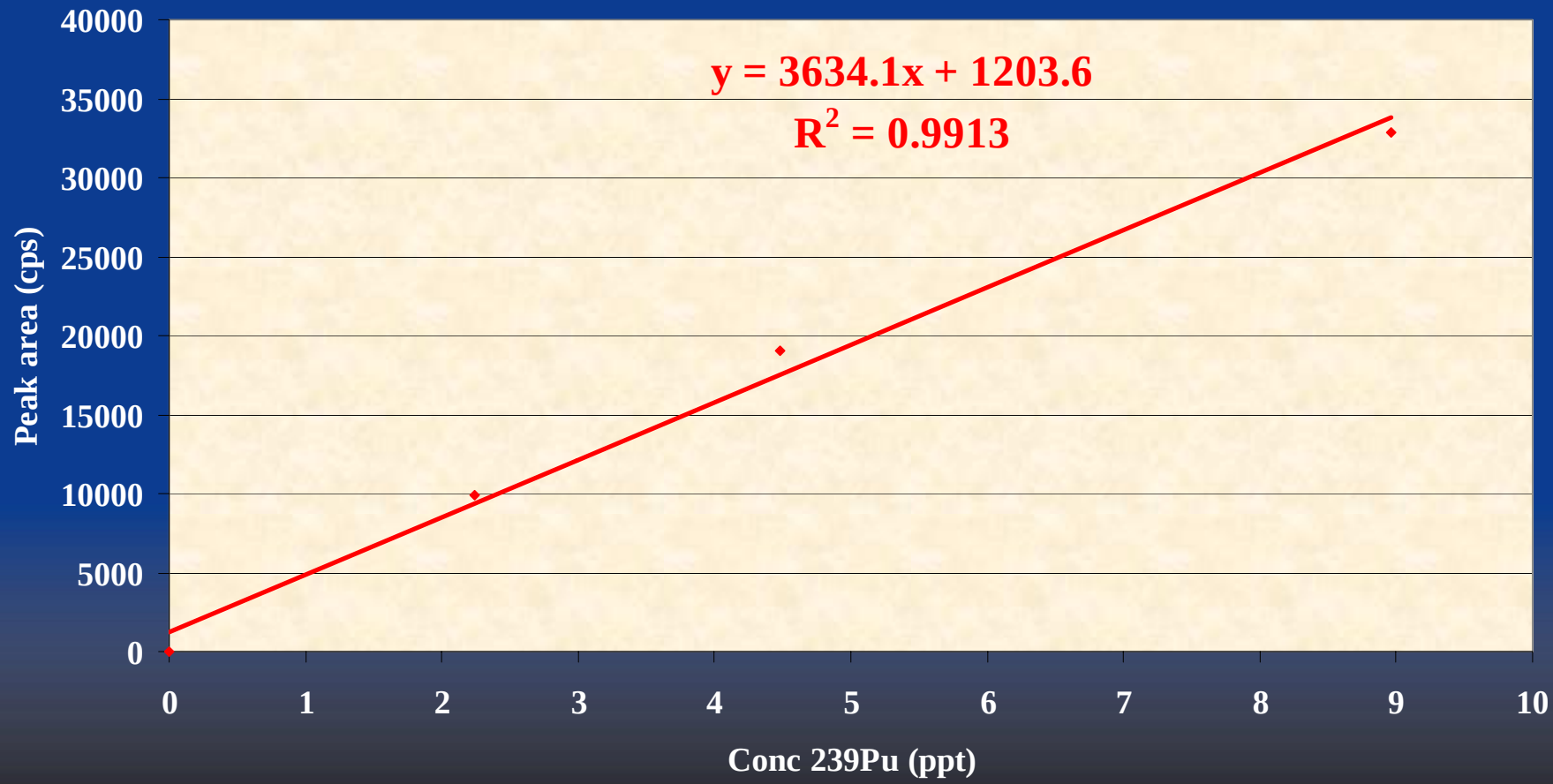
Urine Blank



Urine with 8.962 ng/L ^{239}Pu

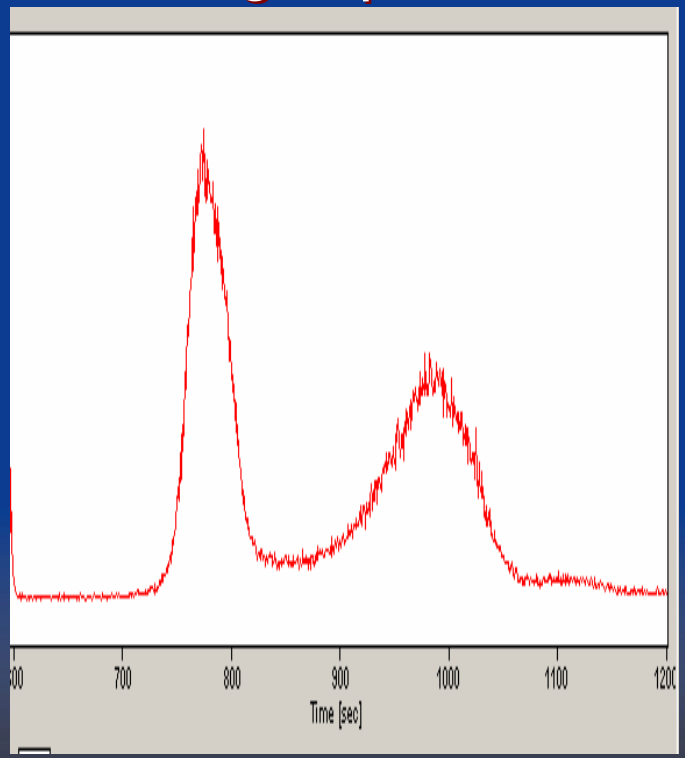


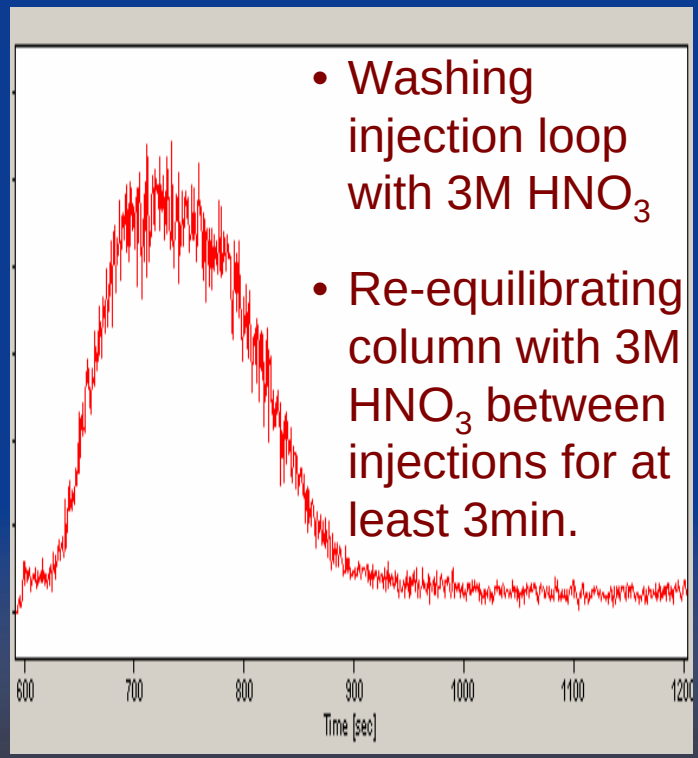
^{239}Pu Calibration



238U Separation Problems

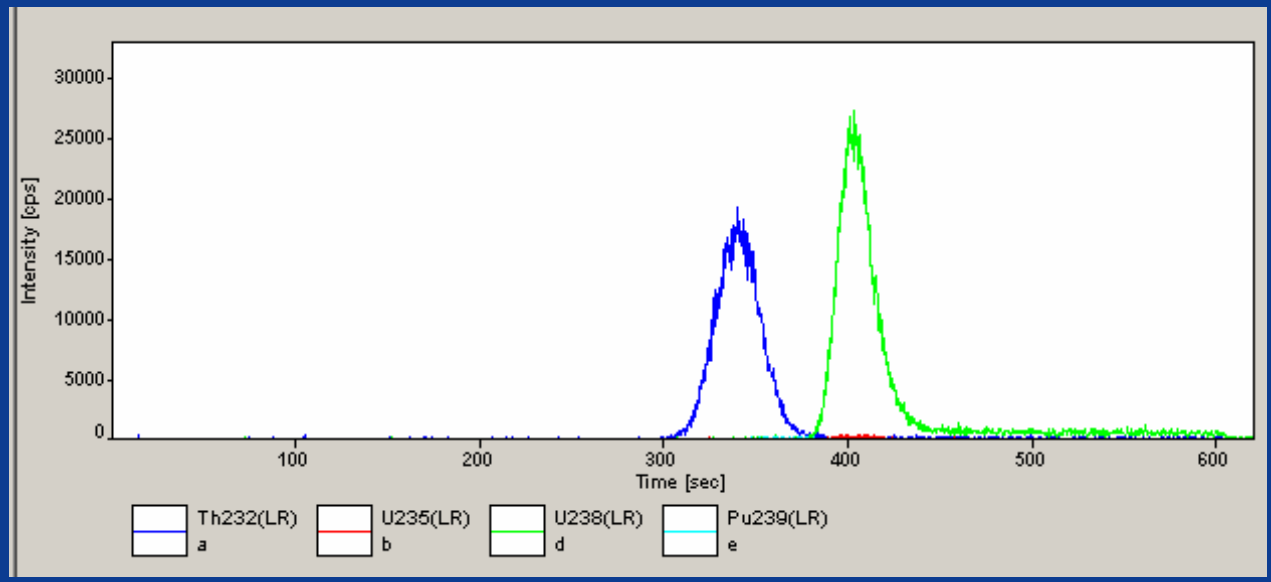
Uranium reducing during separation

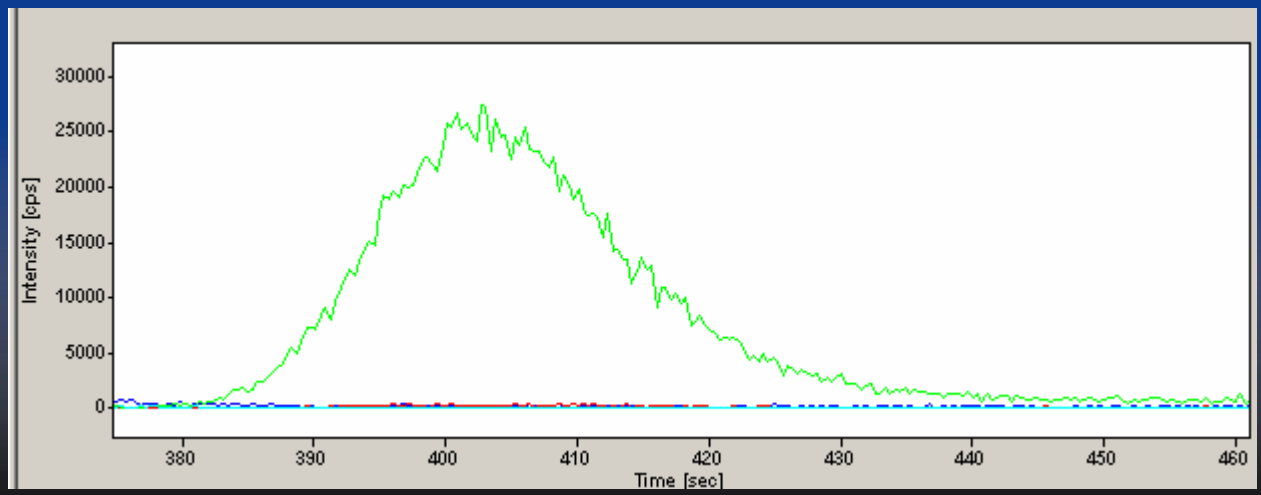




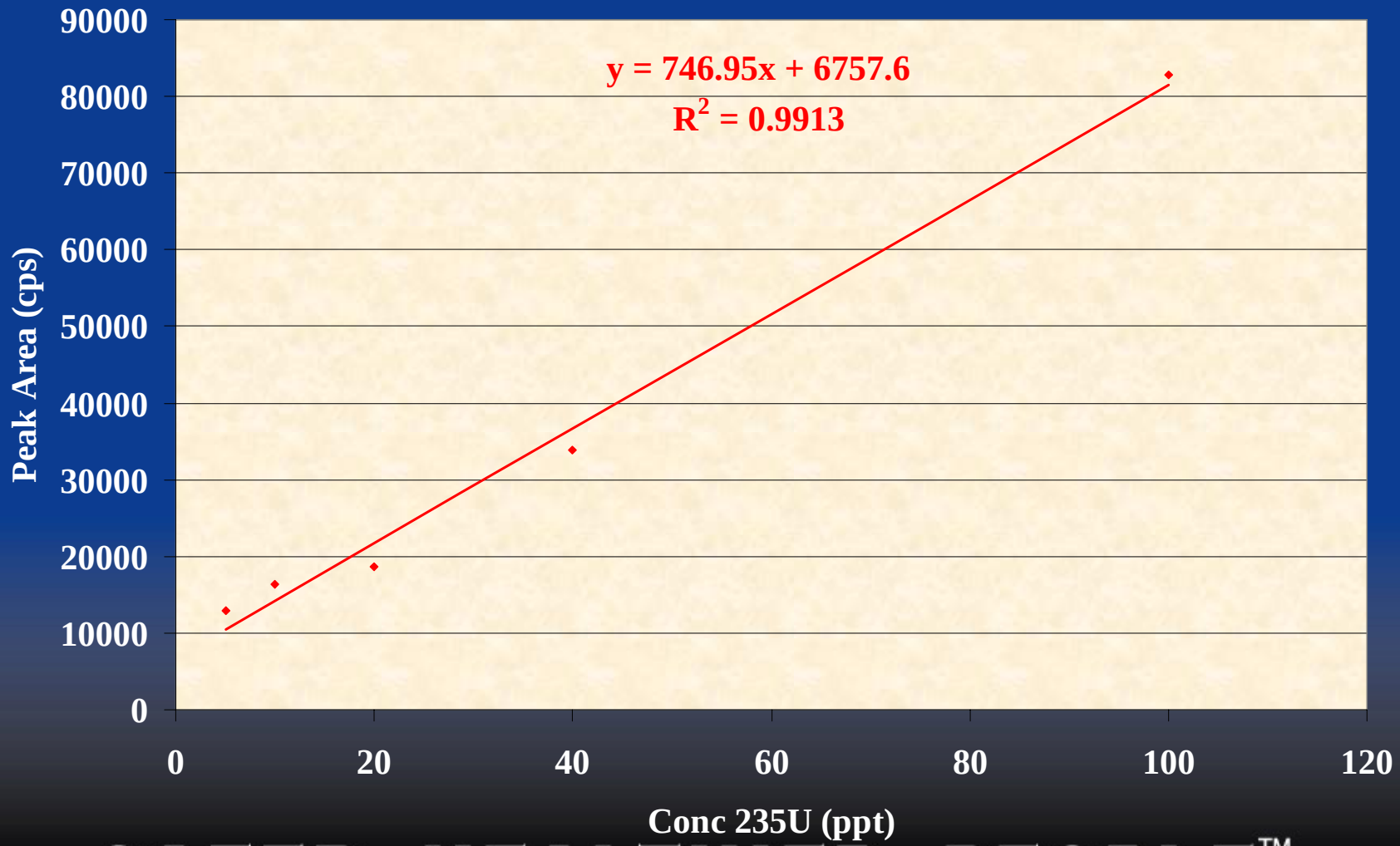
- Washing injection loop with 3M HNO_3
- Re-equilibrating column with 3M HNO_3 between injections for at least 3min.

238U Separation

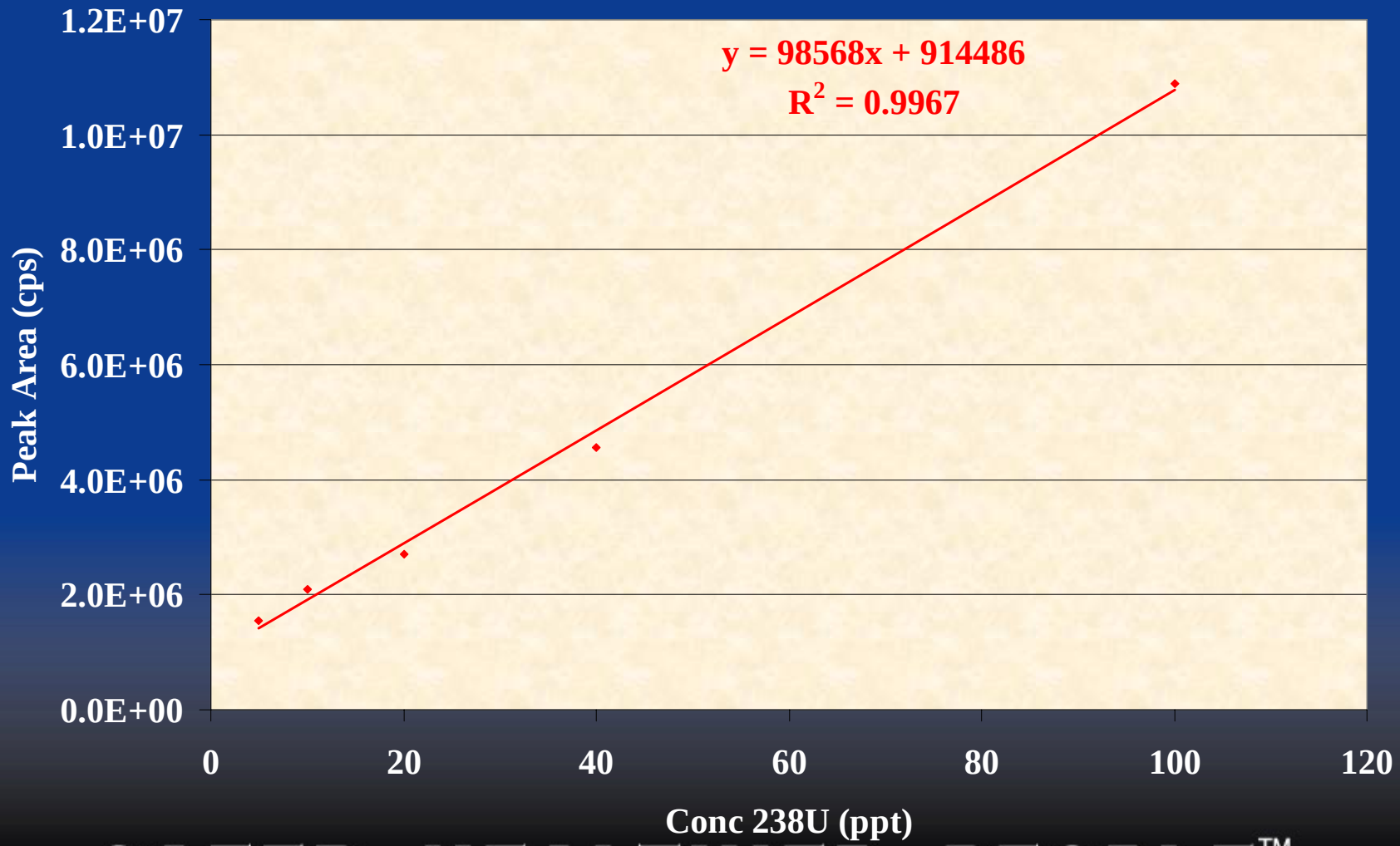




^{235}U Calibration Curve



^{238}U Calibration Curve



Conclusions

- HCl-Oxalic acid elution has wide peaks, slow build-up of uranium background, and is the source of organic backgrounds detected at m/z 241.
- HF efficiently removes all actinides from UTEVA resin.
- Efficient separation of actinides with HF eluent.
- Fast screening method which meets our emergency response needs.