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Rapid Separations for Environmental Level and High Activity Radioactive Solutions

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Outline

- Introduction to Extraction Chromatography
- Three Separation Applications
  - Actinides in Large Soil Samples
    - Work by Sherrod Maxwell, Savannah River Site
  - Se-79 in Savannah Rive Tank Waste
    - Work by Dave and Cecilia DiPrete, SRNL
  - Tc-99 Separation in a Spent Nuclear Fuel Reprocessing System
    - Work by Phil Horwitz and Dan McAlister, PGRF and Gordon Jarvinen, LANL

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Extraction Chromatography

Solvent Extraction

Column Chromatography

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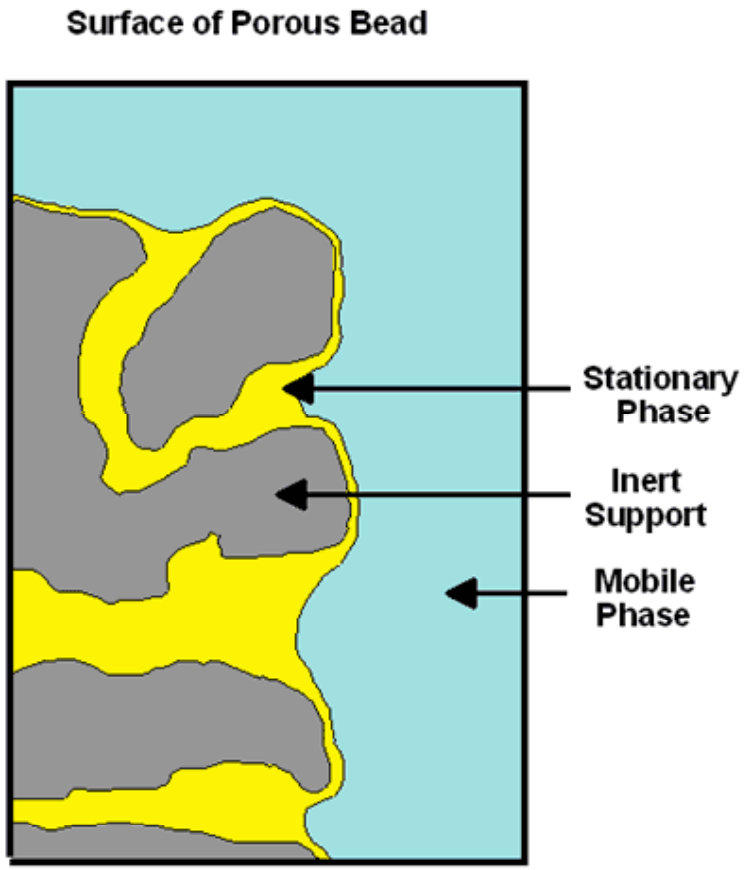
Extraction Chromatographic Resin

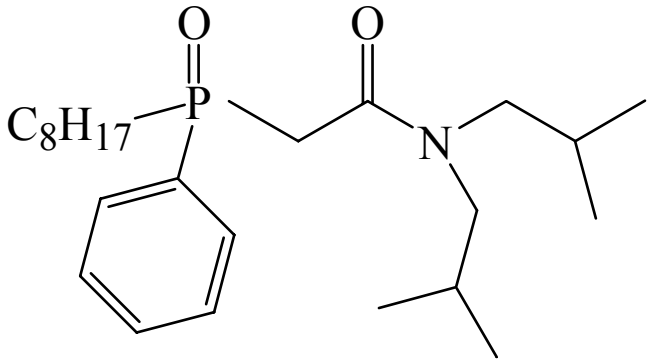


Inert support =

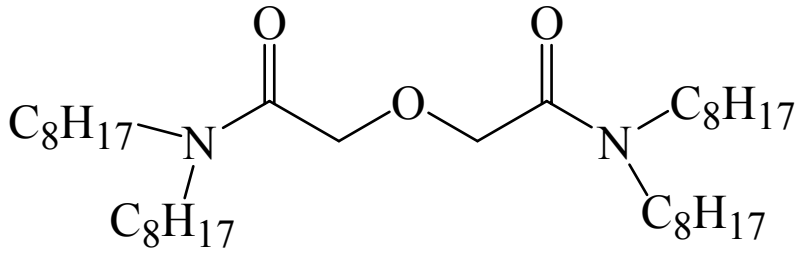
Macroporous Acrylic Resin

Example Stationary Phases = **CMPO, quaternary and tertiary amines, diglycolamide**

Extractants



CMPO (TRU and RE Resin)



Tetraoctyldiglycoloamide (DGA Resin, Normal)

$$Am^{3+} + 3X^{-} + \overline{3E} \leftrightarrow \overline{AmX_3E_3}$$

$$X = Cl^{-} \text{ or } NO_3^{-}$$

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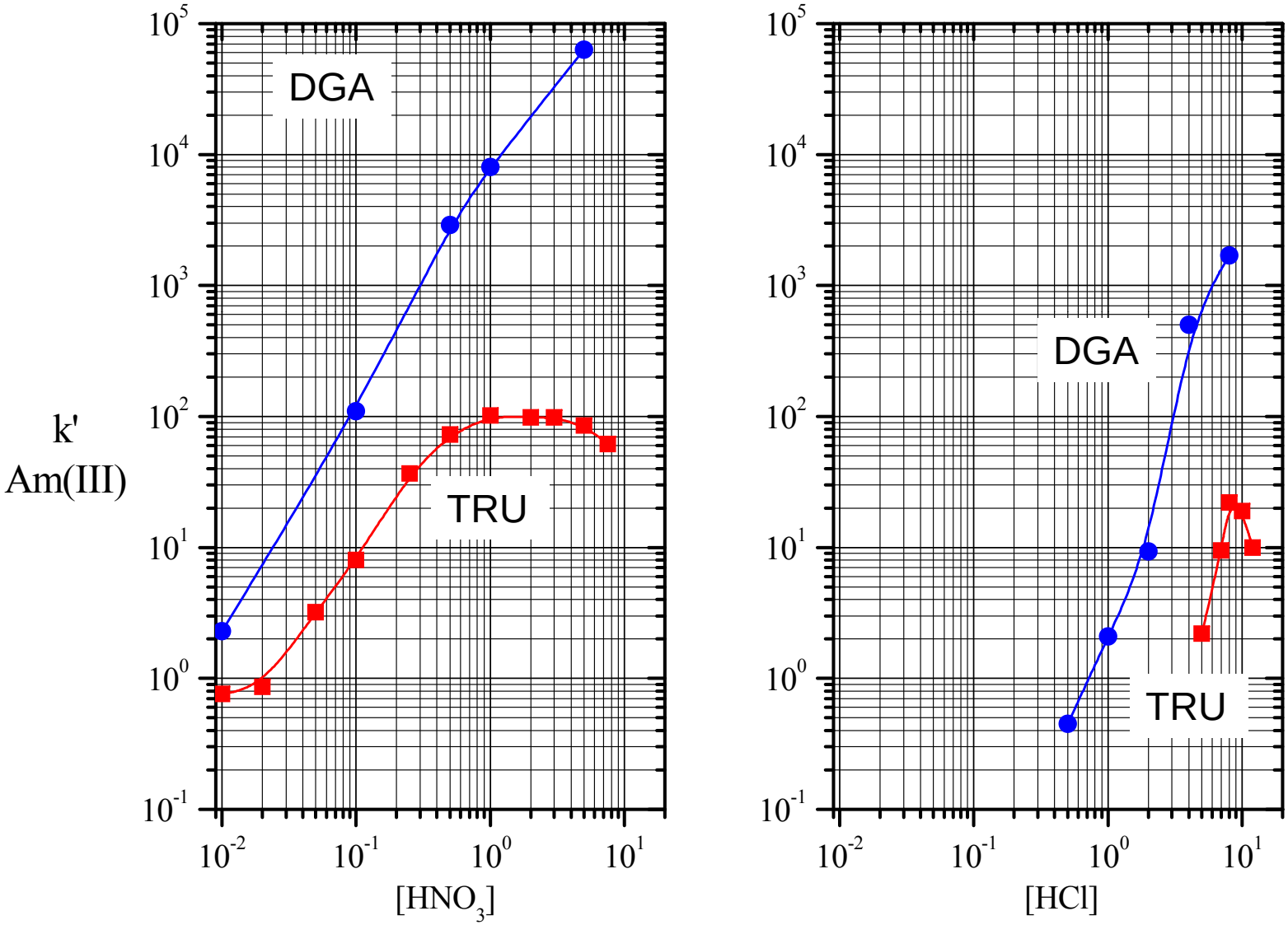
k'_{Am} as a Function of HNO_3 and HCl



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Actinides in Soil Methods

- 5-10 g soil method
  - Lower MDA than typical 1 gram methods
  - Rugged even for refractory soil
  - NaOH Fusion/cerium fluoride precipitation (TEVA+TRU+DGA resins)
  - Pu, Np, Am, Cm, U, Th

"Rapid Column Extraction Method for Actinides in Soil", Journal of Radioanalytical and Nuclear Chemistry, Vol. 270, No. 3 (December, 2006)

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Need to Analyze Larger Sample Aliquots

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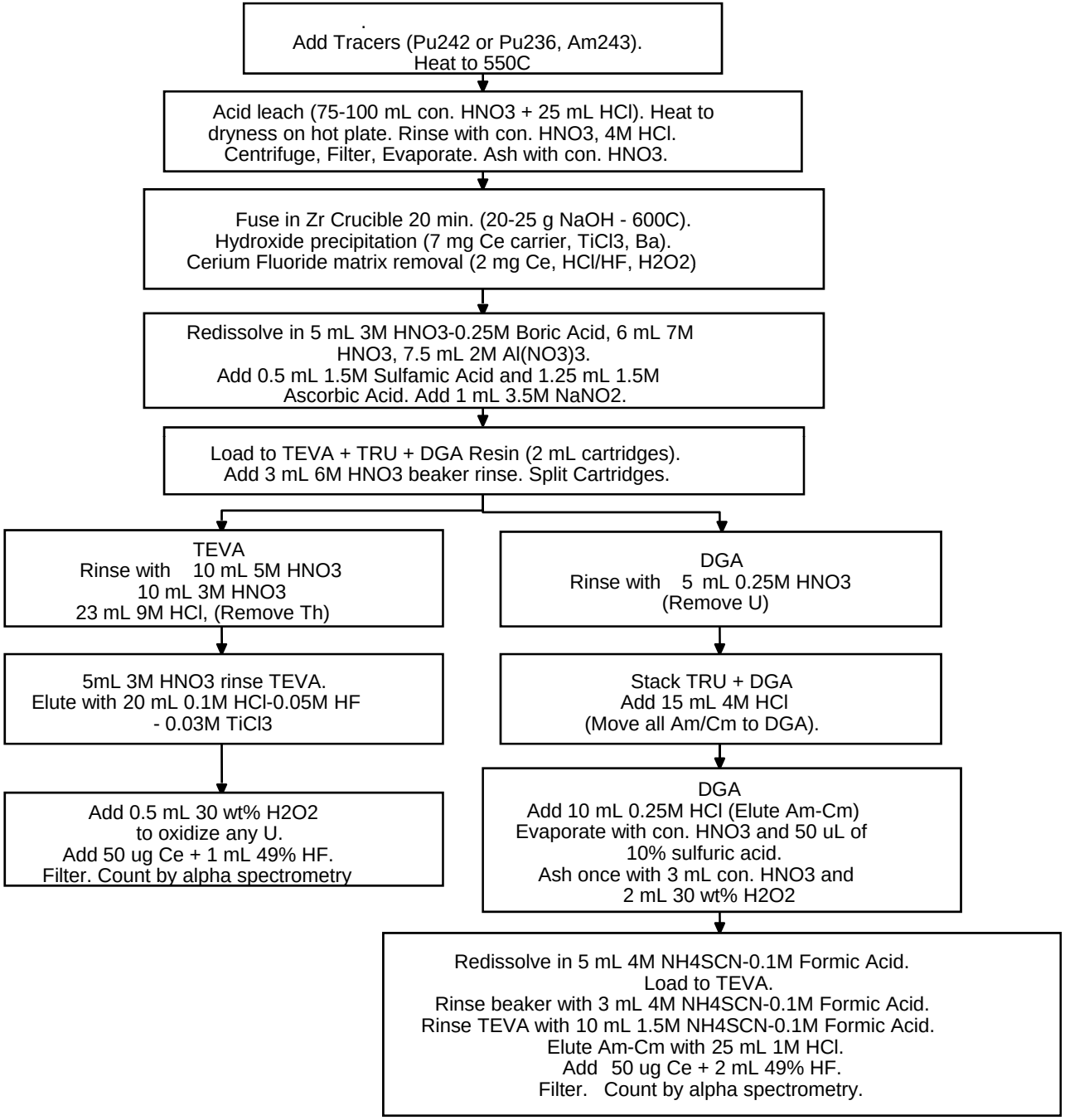
Actinides in Soil Methods

- **100-200g soil method**
  - Pu and Am/Cm
  - Cerium fluoride matrix removal / select against Uranium
  - TEVA+TRU+DGA resins
  - High recoveries (Pu, Am 80-90% for 200 g samples)
  - Very low MDA - 3E-5 pCi/g (0.001 Bq/kg)-16 hour count

Rapid Method for Determination of Plutonium, Americium and Curium in Large Soil Samples, *Journal of Radioanalytical and Nuclear Chemistry, Vol. 275, No. 2(2007)*

100-200g Soil Method



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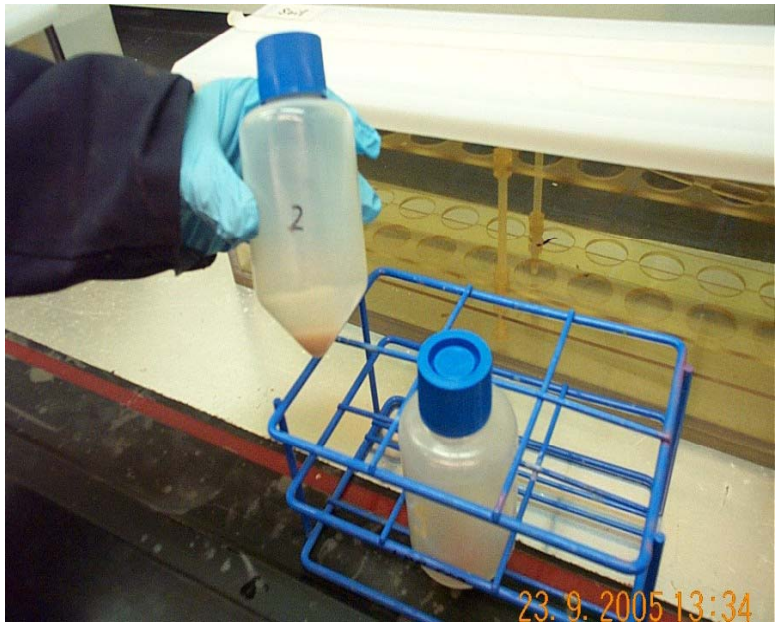
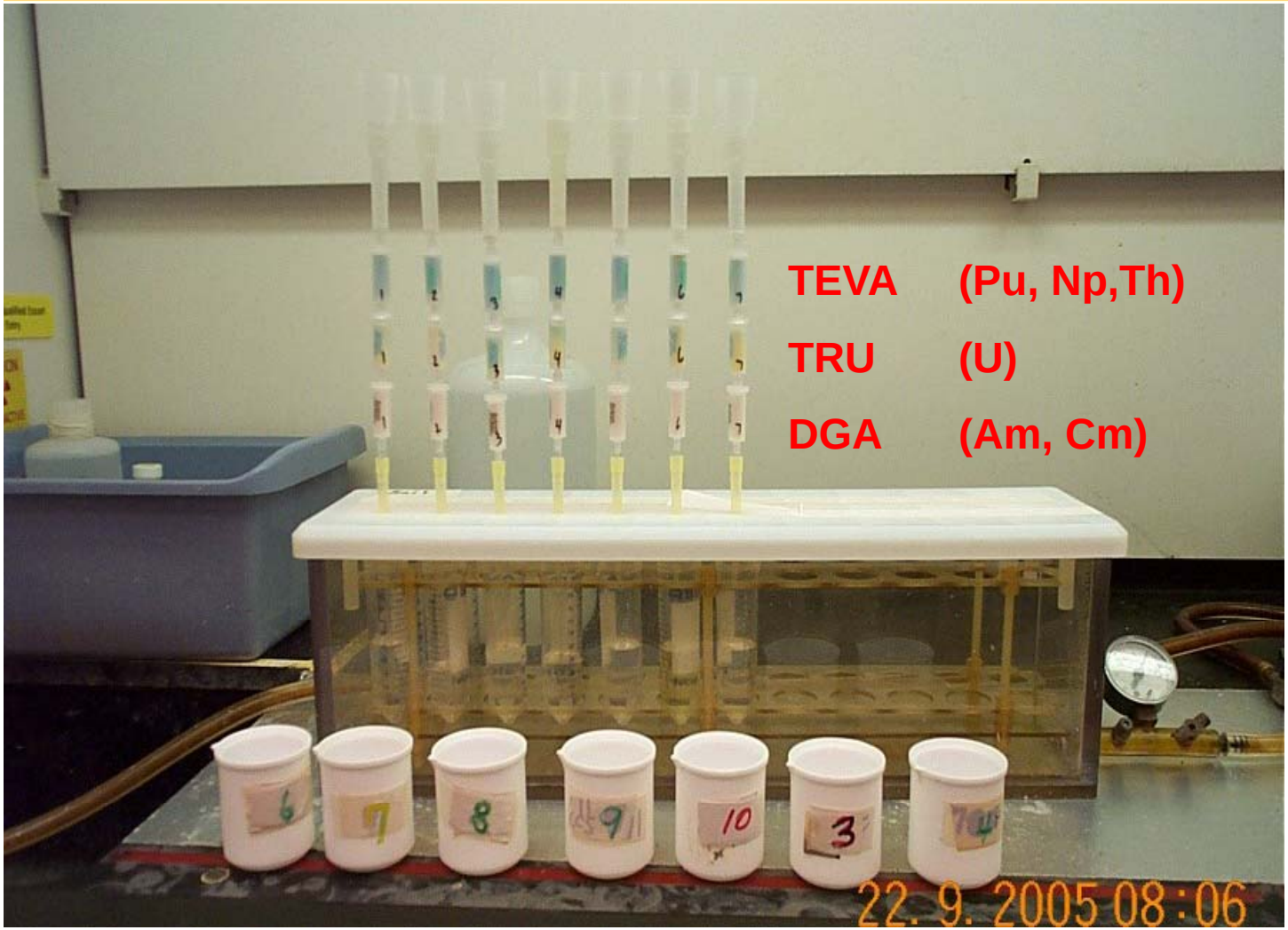
Matrix Removal using Cerium Fluoride



Cerium Fluoride Precipitate

Column load solution

TEVA+TRU+DGA Resins For Soils



Soil (5-10 g)-fusion/CeF3 ppt

Soil (200 g)-leach/CeF3 ppt

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MAPEP MAS-15 Performance

	SRS	REF.	Ratio
Pu-238	56.9	61.15	0.93
Pu-239	41.0	45.85	0.89
Am-241	51.1	57.08	0.90
U-234	35.6	37.00	0.95
U-238	38.9	38.85	1.00

Results in Bq/kg

5 gram sample analyzed

MAPEP=DOE Mixed Analyte Performance Evaluation program standard

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100 g Samples with MAPEP-05-S14 Soil Standard Added

Soil Sample	Pu-242 Tracer Recovery	Pu-238 Measured/ Reference	Am-243 Tracer Recovery	Am-241 Measured/ Reference
100g + 1 g S14	77.2 %	0.99	90.0%	0.95
100g + 3 g S14	91.5%	0.97	97.5%	0.87
100g + 3 g S14	88.2%	0.95	95.3%	0.86
Avg.	85.6%	0.97	94.3%	0.90

Unspiked sample=0.120 Pu-238 Bq/kg and 0.152 Am-241 Bq/kg

0.0608 Bq Pu-238 and 0.0811 Bq Am-241 added per 1 gram of S14

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200 g Samples with MAPEP-05-S14 Soil Standard Added

Soil Sample	Pu-242 Tracer Recovery	Pu-238 Measured/ Reference	Am-243 Tracer Recovery	Am-241 Measured/ Reference
200g + 3 g S14	82.1 %	1.00	96.6%	0.80
200g + 3 g S14	81.4%	1.04	90.0%	0.82
Avg.	81.8%	1.02	93.3%	0.81

Unspiked sample=0.120 Pu-238 Bq/kg and 0.152 Am-241 Bq/kg

0.0608 Bq Pu-238 and 0.0811 Bq Am-241 added per 1 gram of S14

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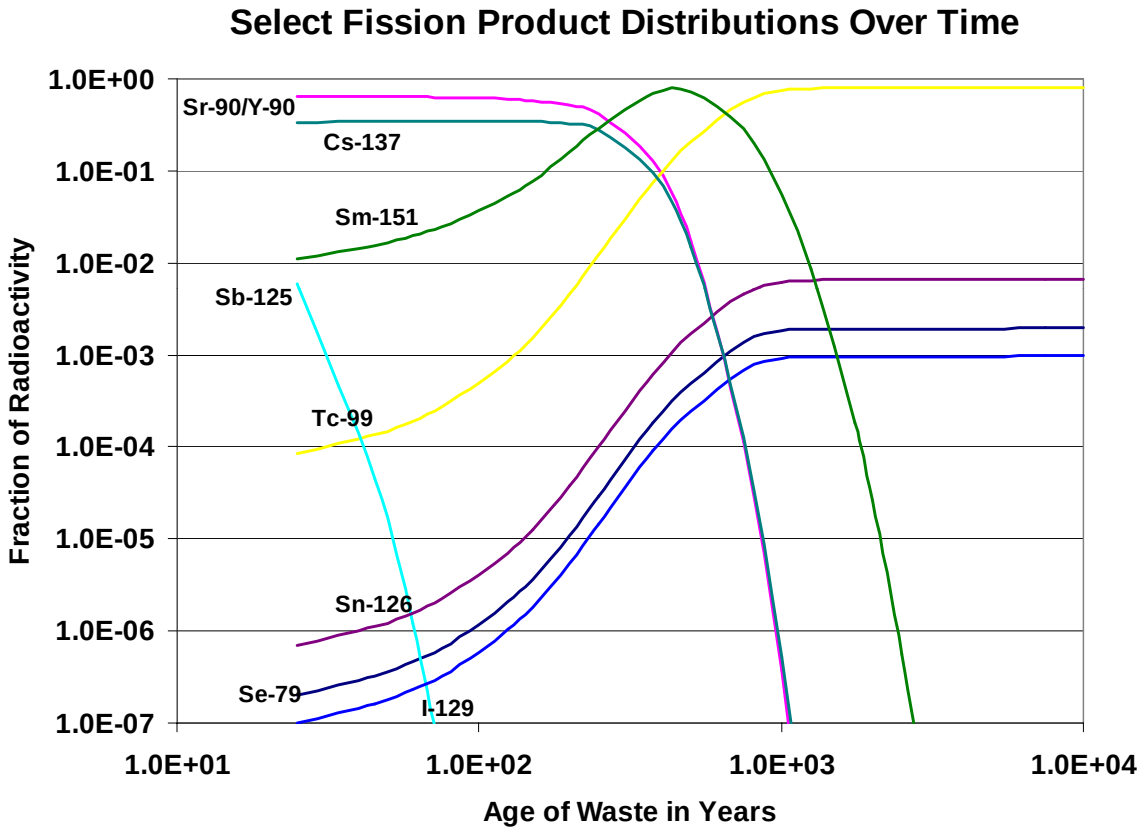
Challenges of SRS Se-79 Measurements in SRS High Activity Samples



Waste Acceptance Criteria requirements of various repositories often call for low level Se-79 measurements in the presence of high levels of interfering beta species.

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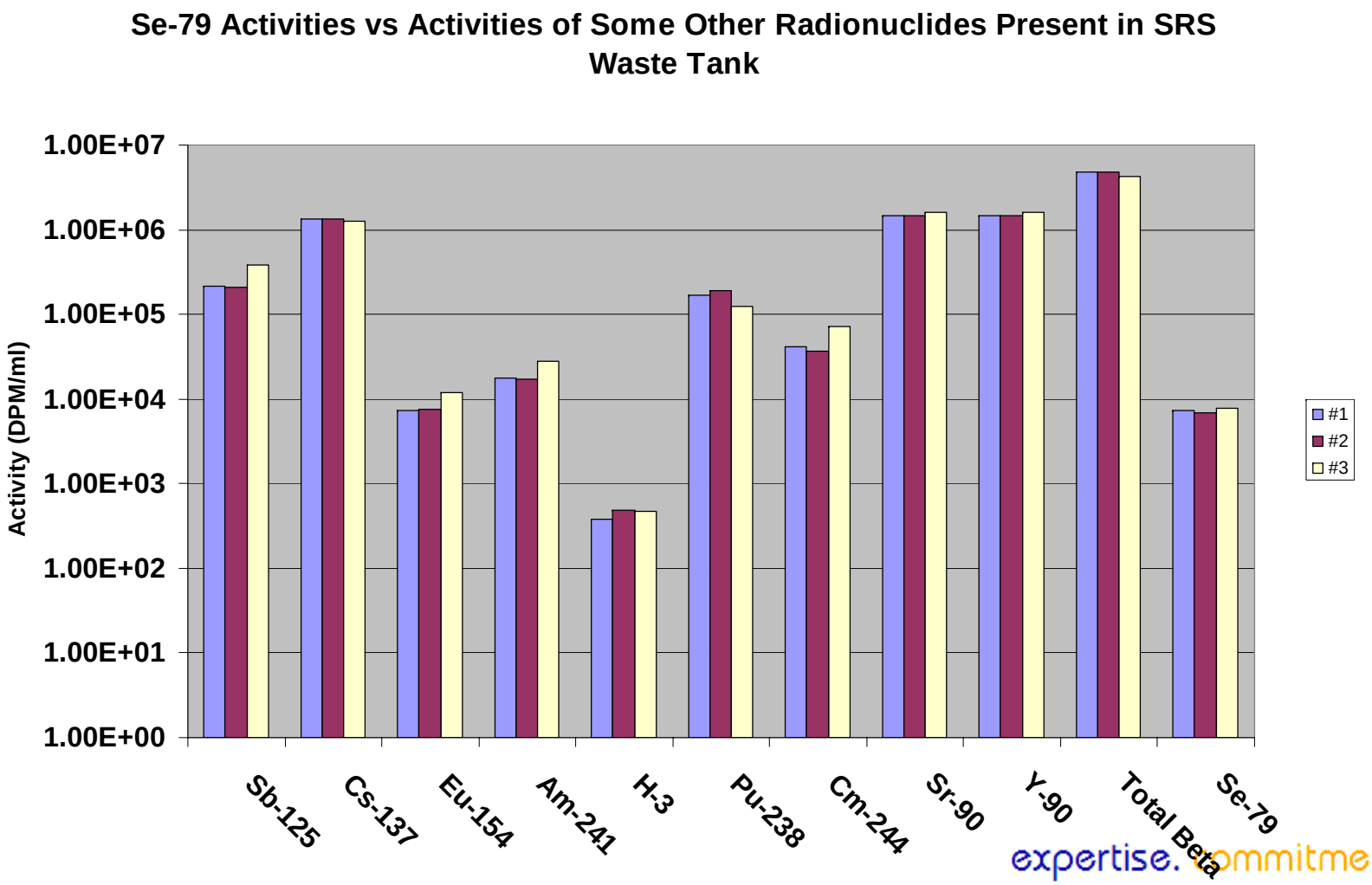
Activities of Various Isotopes Separated from Se-79 in Waste Tank Sample



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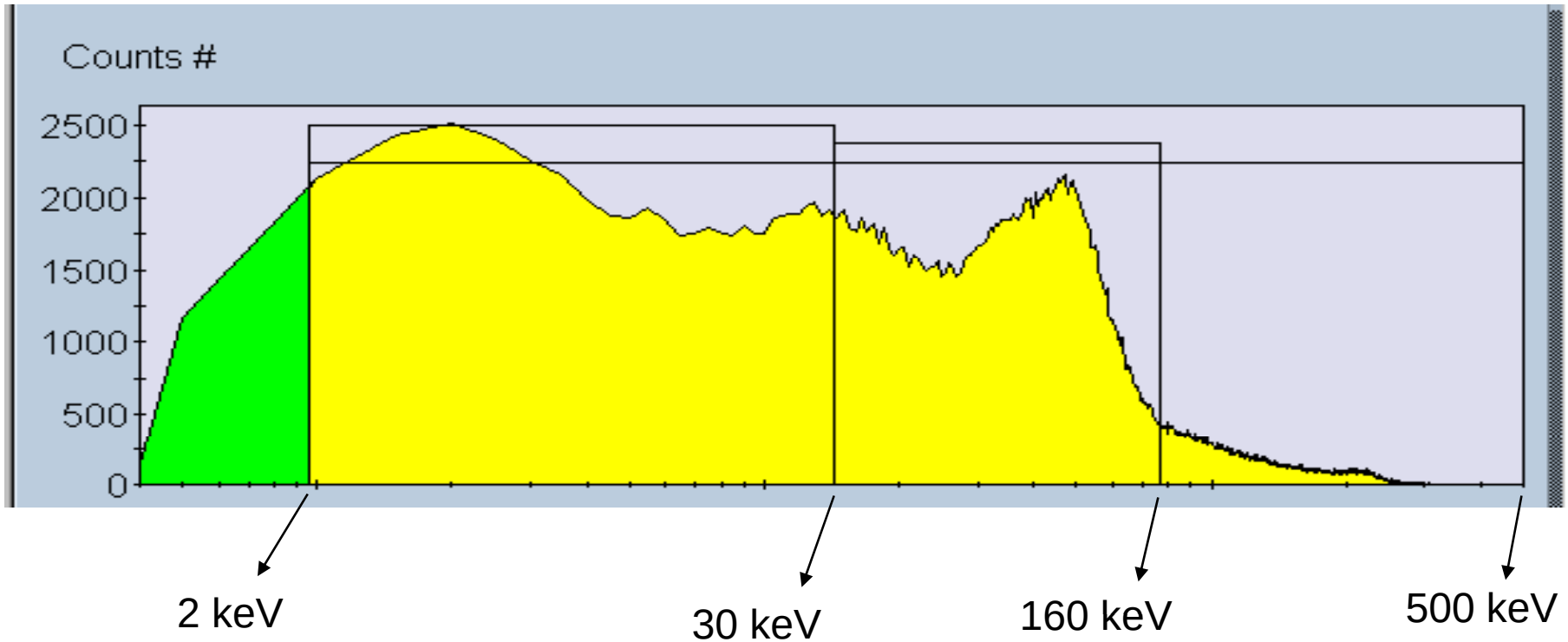
Poor DF for Sb-125 with 30% TBP method



Separation of Sb from Se

- Sb quantitatively extracted in 6M HCl by RE resin, Se not extracted at all (Chloride system)
- Added to beginning of TBP Se procedure

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New Se-79 Extraction

- Sample aliquot spiked with Se carrier, acidified to 6M HCl
- Added to 2 mL RE Resin cartridge, eluate diluted with DI water to 1M HCl
- Se metal precipitated with Titanous Chloride and Hydroxylamine Hydrochloride, precipitate filtered, rinsed
- Re-dissolved in 9 M HBr
- Se extracted with 30% TBP, Se eluted with DI water
- Aliquots analyzed by LSC for Se-79 and Se carrier by NAA

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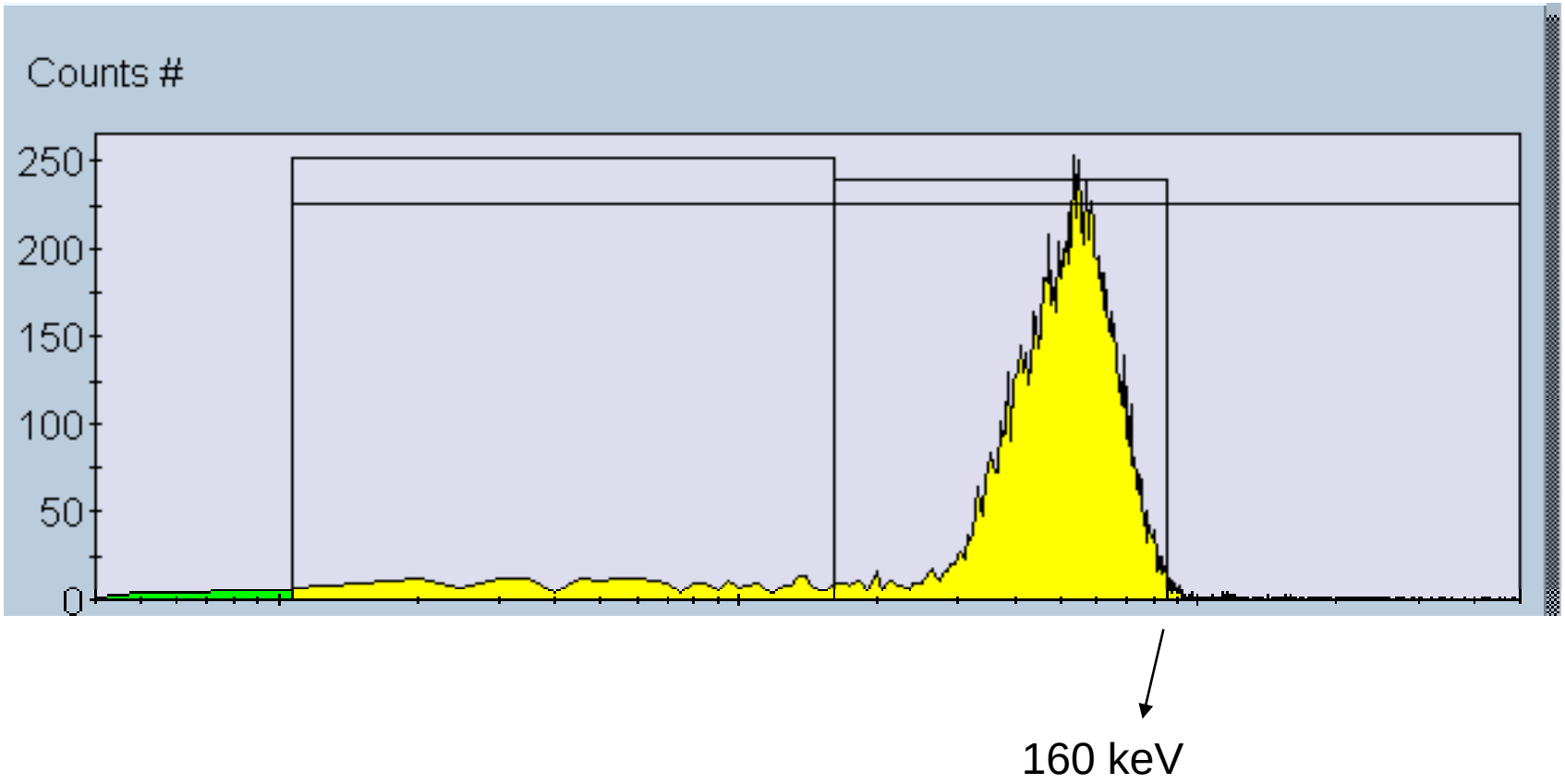
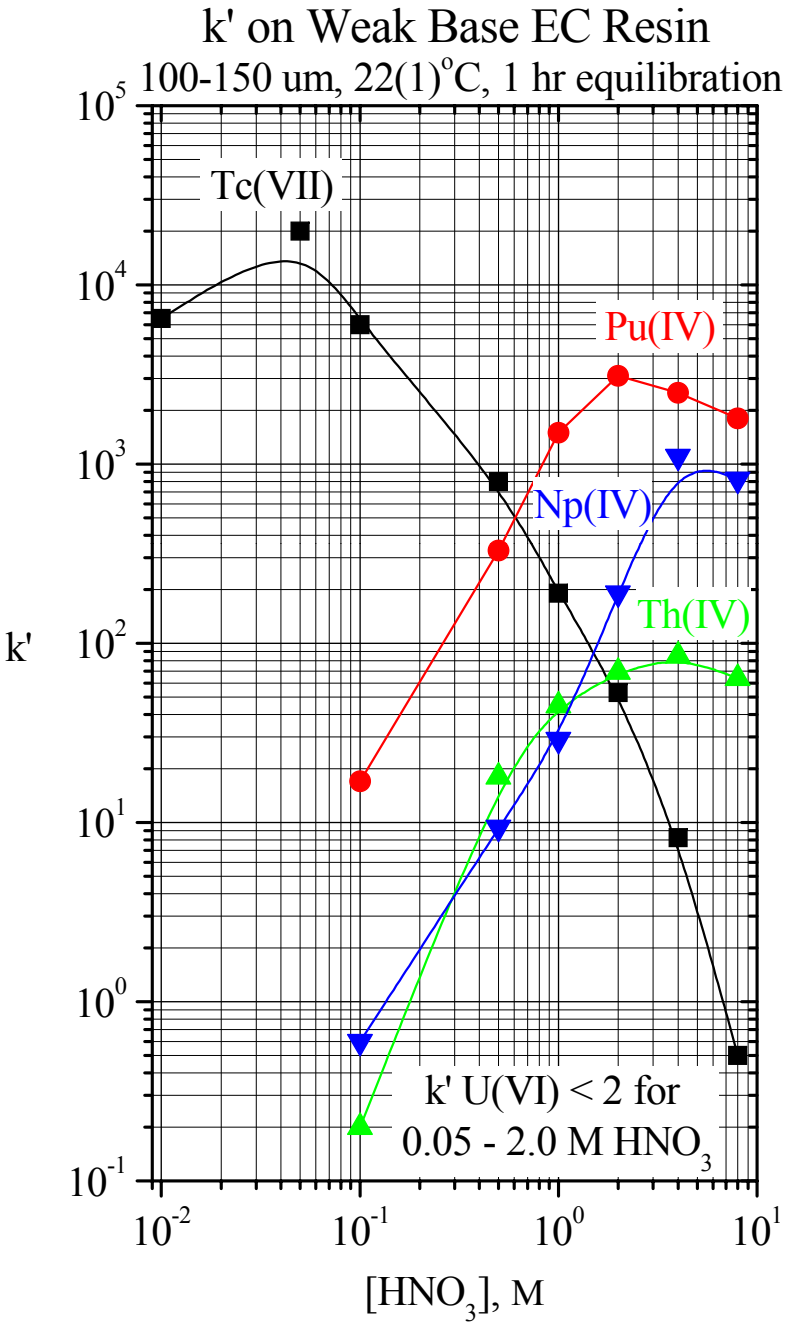
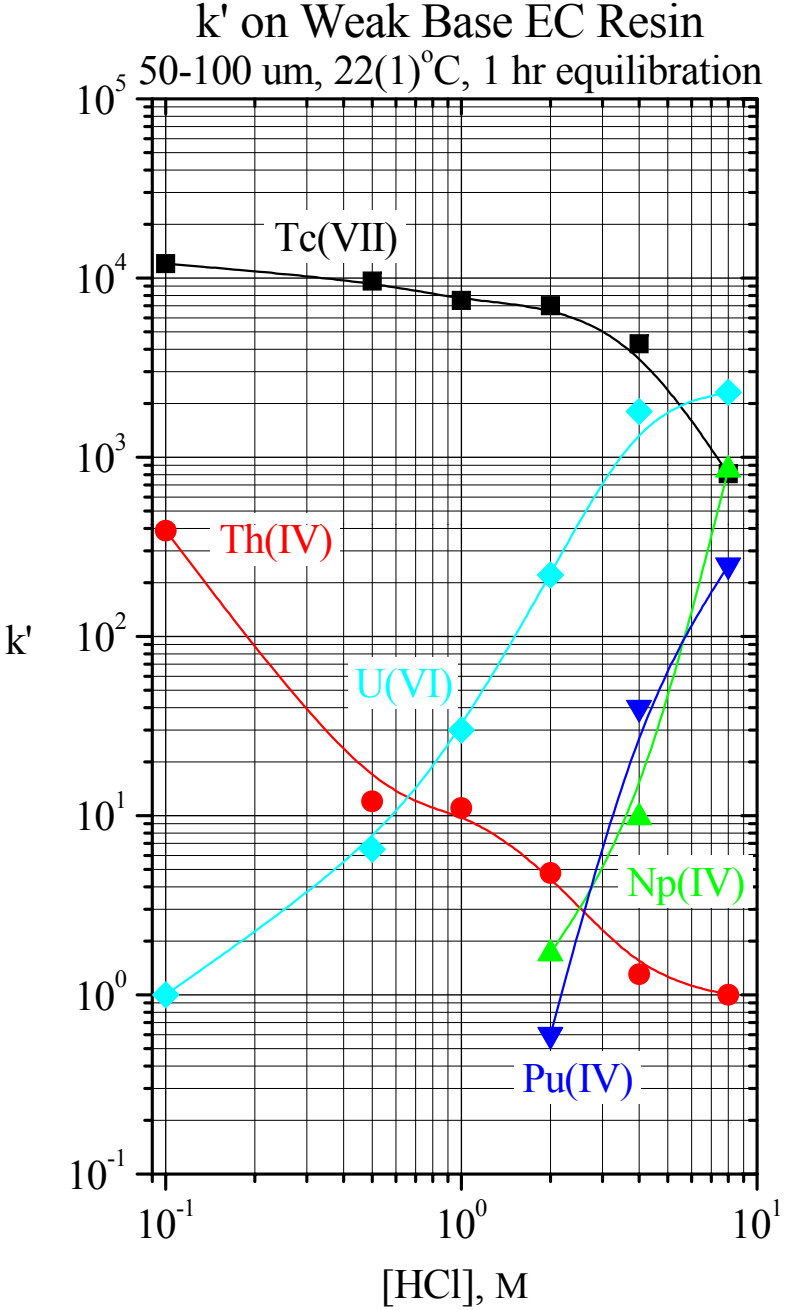
Se-79 Spectrum of Sample Run Through New Procedure



Weak Base EC Resin

- Flow Sheet Development for GNEP
  - Conventional cross-linked macroporous resin removes100 ppm Tc-99 well from 0.01M nitric acid containing 50-100 g/L Uranium
  - Elution efficiency is not great with NH_4OH
- Phil Horwitz suggests an Extraction Chromatographic variation of the anion resin


k' on Weak Base EC Resin
100-150 um, 22(1)°C, 1 hr equilibration
Tc(VII)
Pu(IV)
Np(IV)
Th(IV)
k' U(VI) < 2 for
0.05 - 2.0 M HNO3
k'
[HNO3], M


k' on Weak Base EC Resin
50-100 um, 22(1)°C, 1 hr equilibration
Tc(VII)
Th(IV)
U(VI)
Np(IV)
Pu(IV)
k'
[HCl], M

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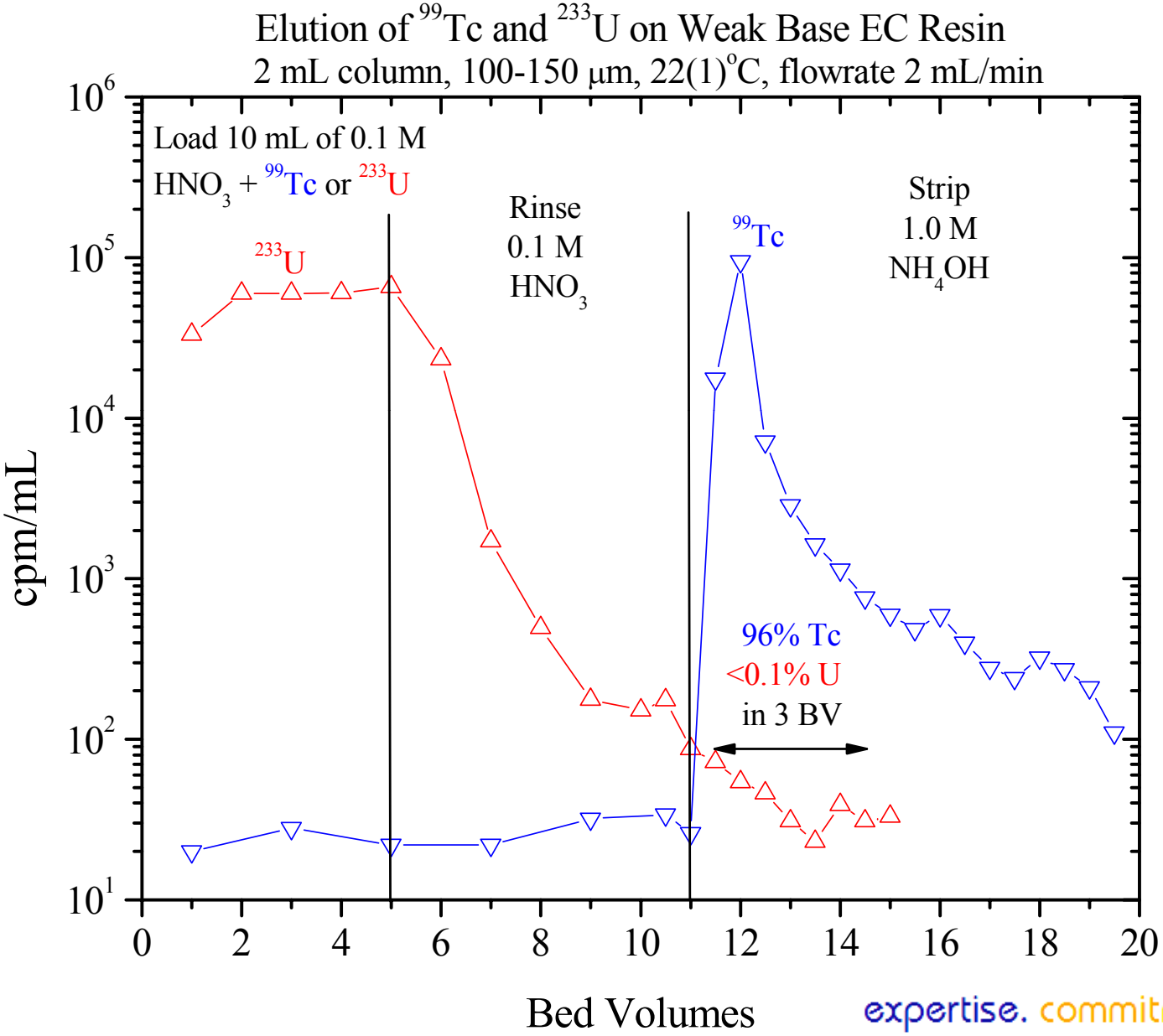

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Conclusions

- Extraction Chromatographic Resins are a flexible separation tool for…
  - Achieving ultra-low detection levels
  - Cleaning up high activity waste
  - High value process separations
- Application areas continue to grow…
  - Radiopharmaceuticals
  - Emergency Response Methods