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Extraction Chromatography Resins and their Use in Food Methods

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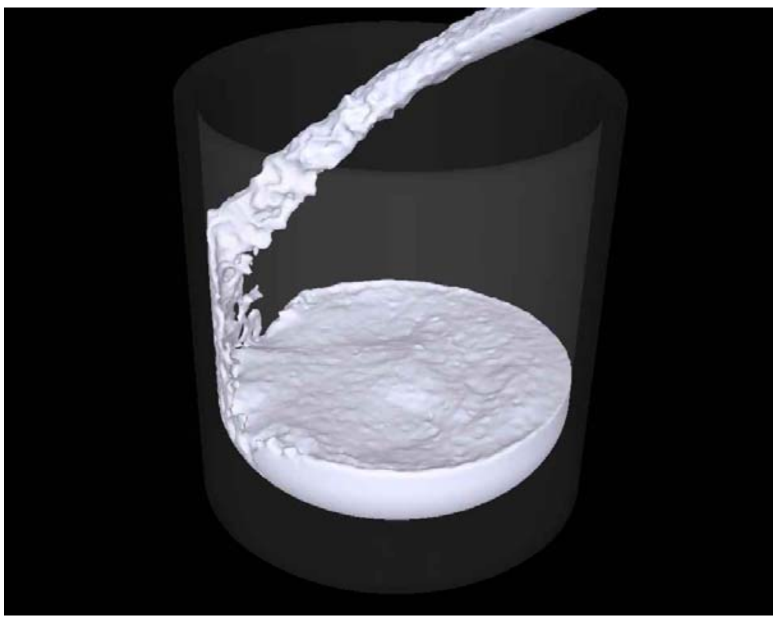
Winchester Engineering and Analytical Center (WEAC)

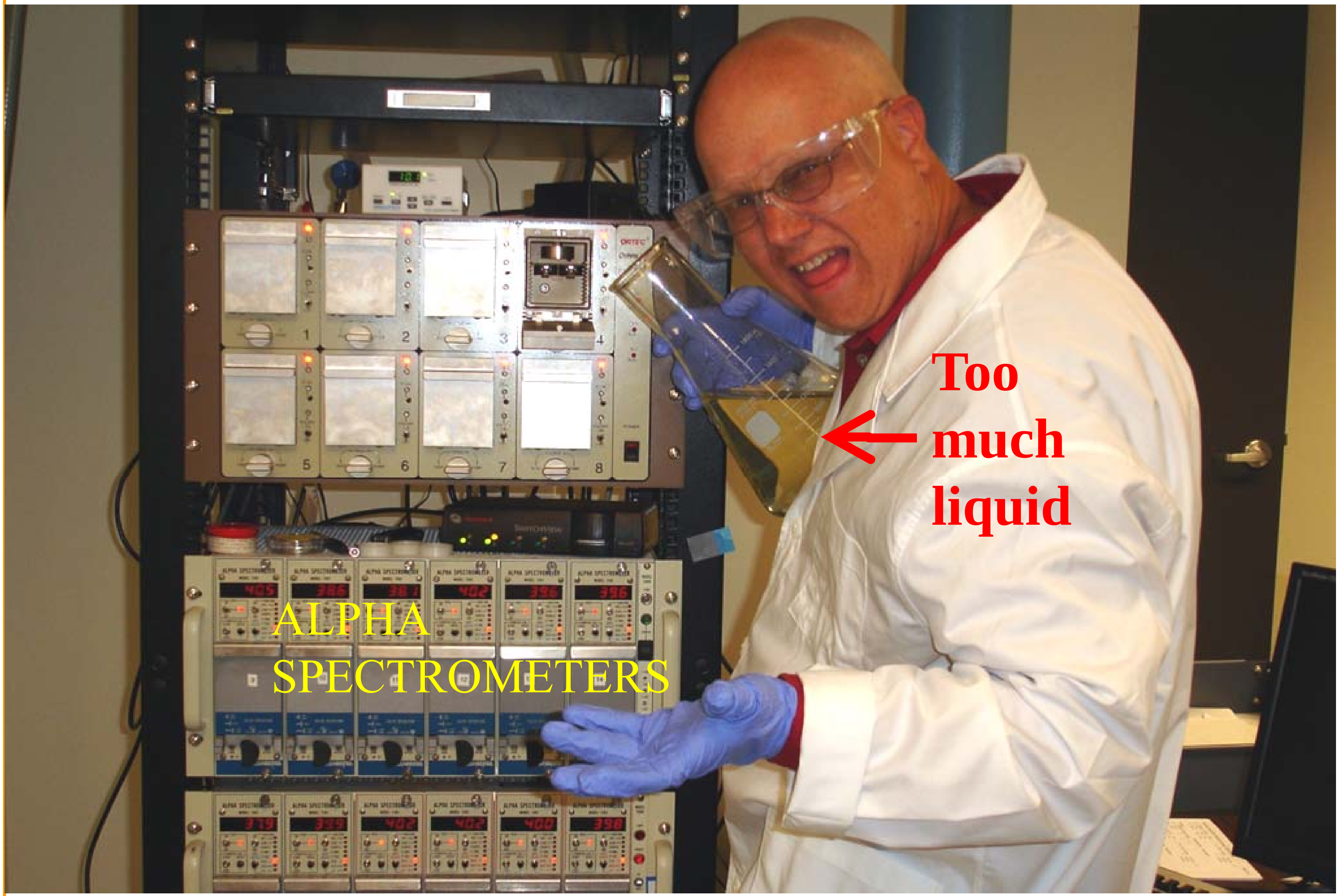
July 15th, 2010

Variety is the spice of life



However, it is a **nightmare** in the Lab

We Need Sample Preparation



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RADIOACTIVE
TENNELEC


varian
varian
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RADIOACTIVE
2550 TR/AB
LIQUID SCINTILLATION ANALYZER
PACKARD

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Your separation resin drawer!

Hows

Versatility

Results

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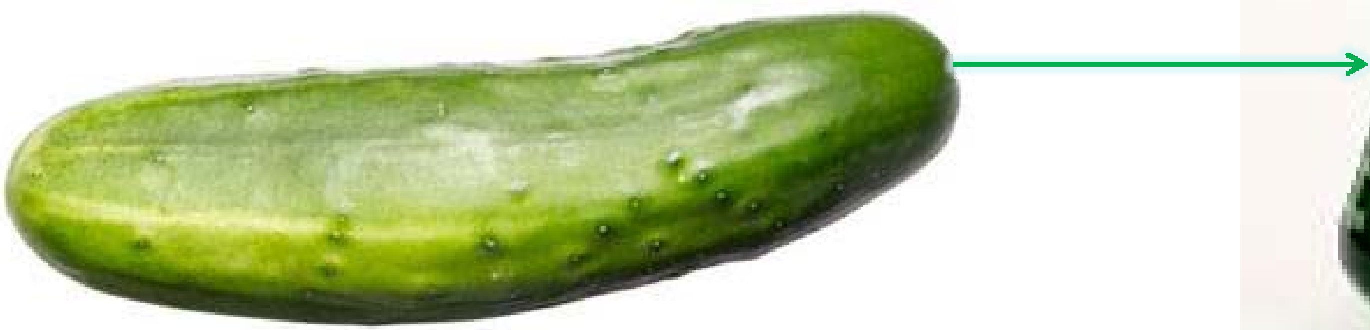
Stops in the Lab/Kitchen along the way

- Why Sample Preparation / Instrumentation Choices
- Matrix Elimination Approaches
- Extraction Chromatography (EXC) Separations
- Some example separations and RESULTS
- Questions ?

Your goals for Sample Preparation

- Minimize sample prep time and waste generation
- Trade offs between
  - sample size, detection level, sample preparation rigor
- Data quality objectives
- Detection instrument selection
- Instrument's capabilities



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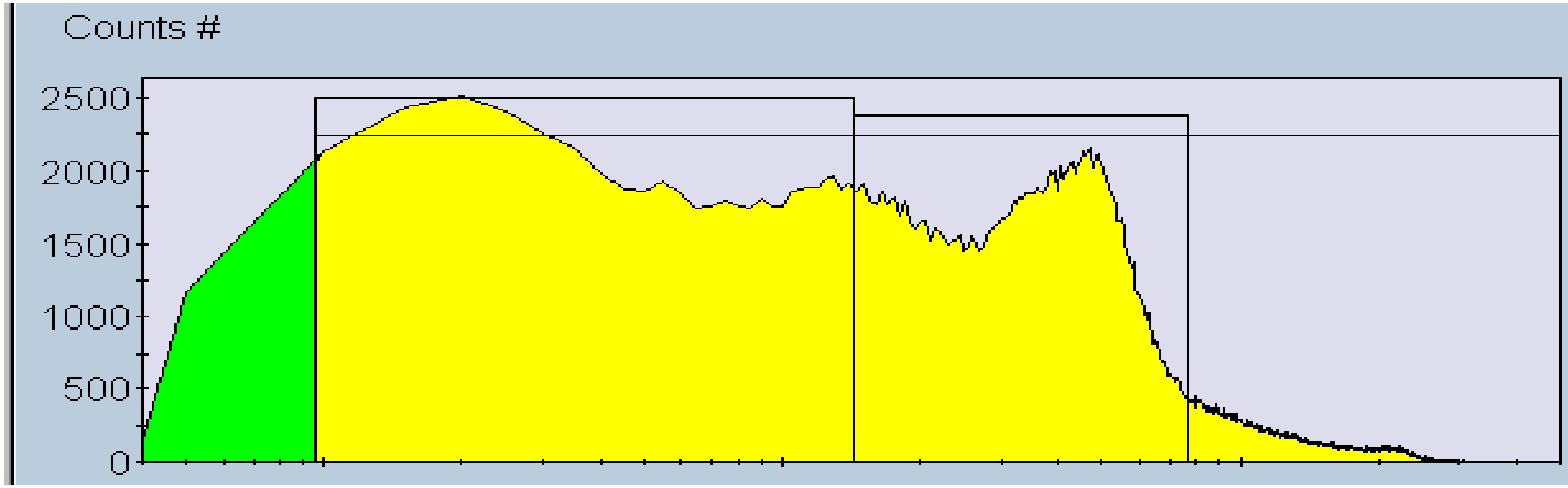
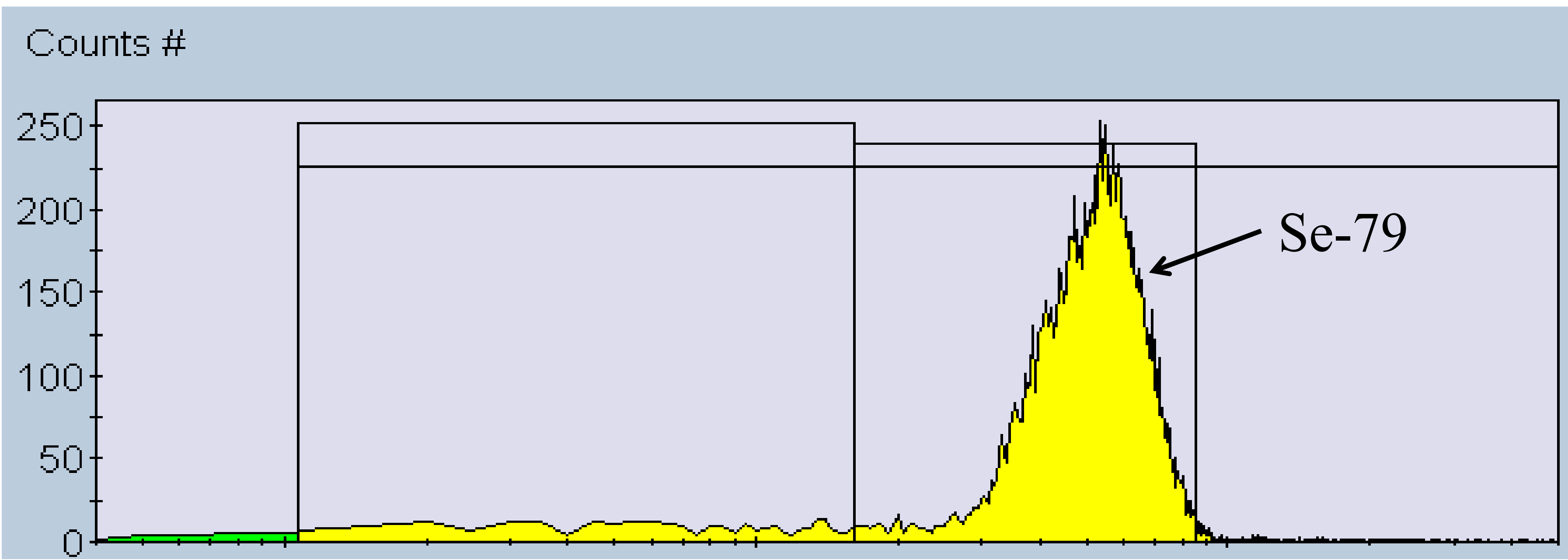
Radiologic Screening Counters

- Gas-Flow Proportional Counters
  - Alpha/Beta Weight Attenuation Curves
  - Alpha/Beta Cross Talk Calibration Curves
  - Alpha/Beta Isotope Calibration

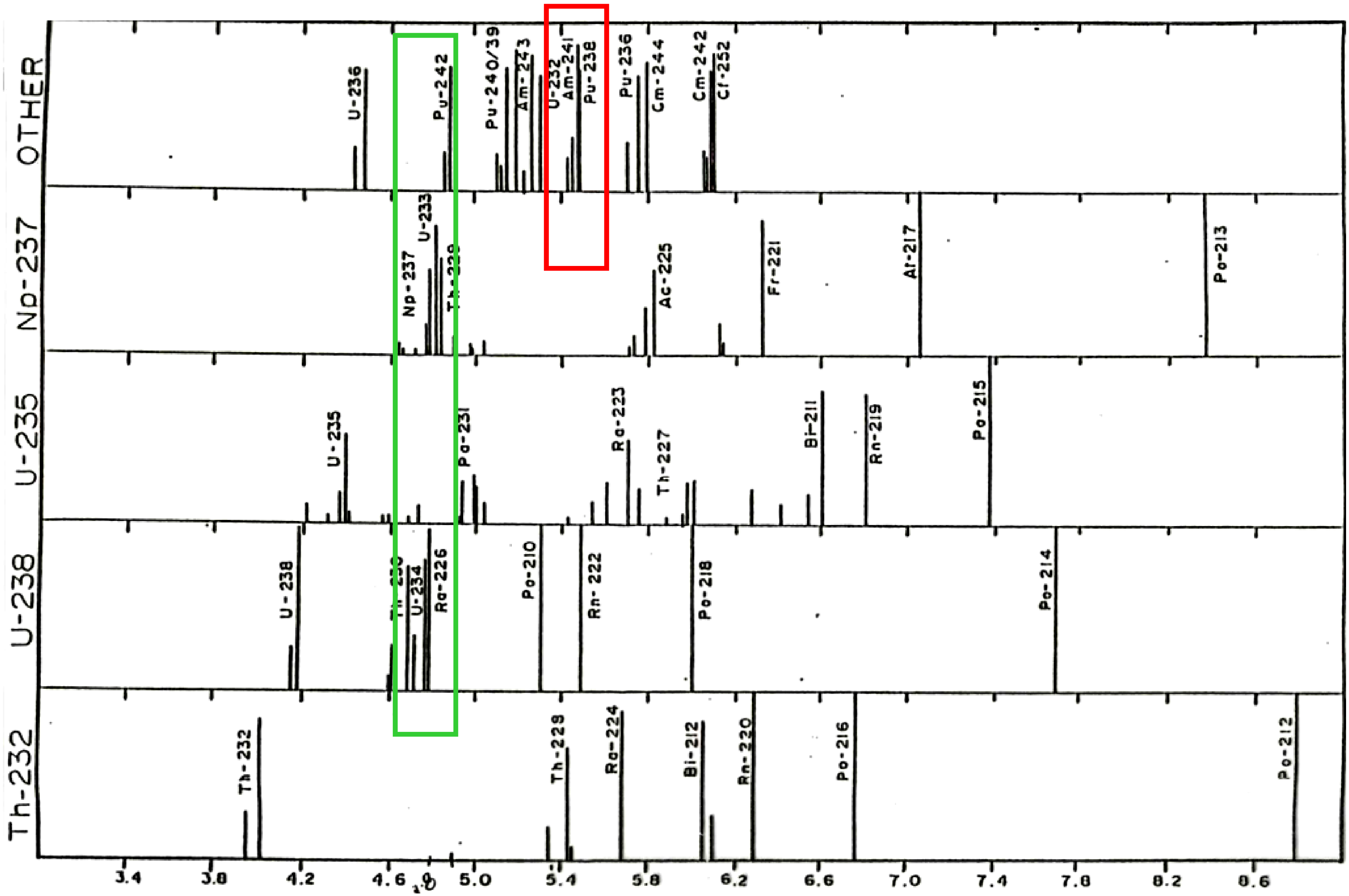
- Liquid Scintillation Counters
  - Alpha/Beta Efficiency Determination
  - Alpha/Beta Cross Talk
  - Alpha/Beta Quench/Color Correction

Measurement of Beta Energy (LSC)





Measurement of Alpha Energy



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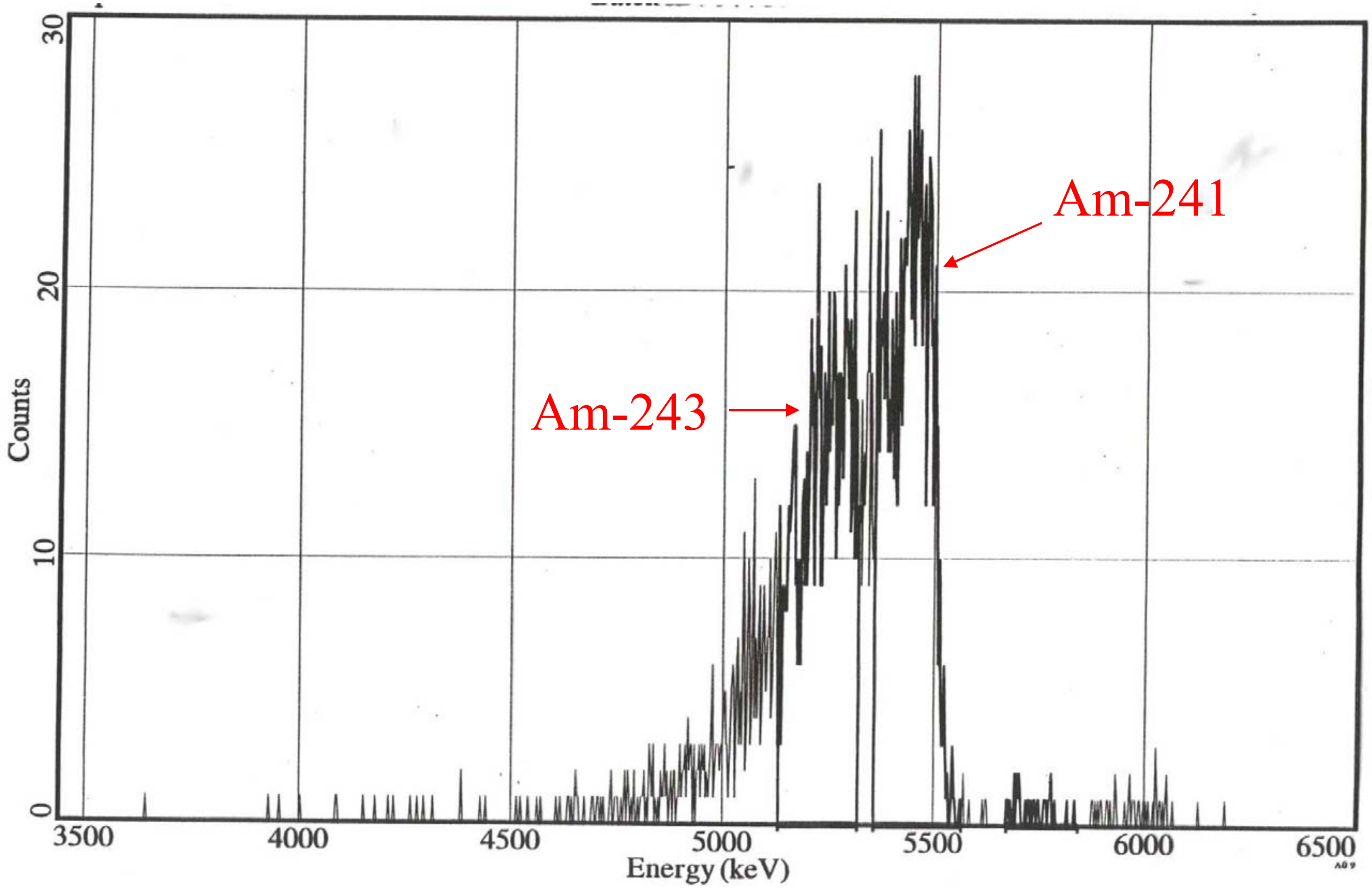
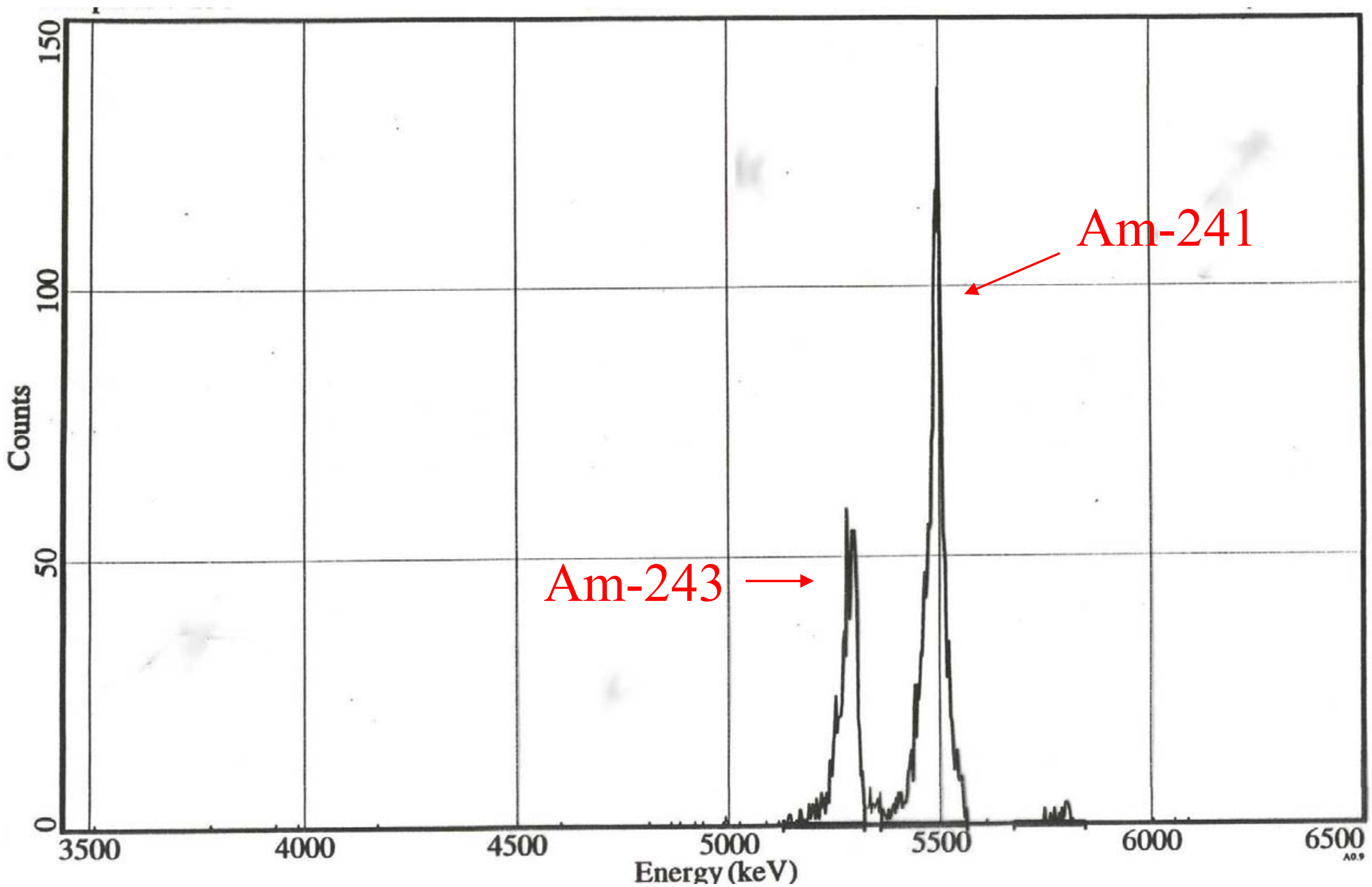
Americium Spectrum after TRU Resin Separation

presence of rare earths degrades spectrum- self absorption issues

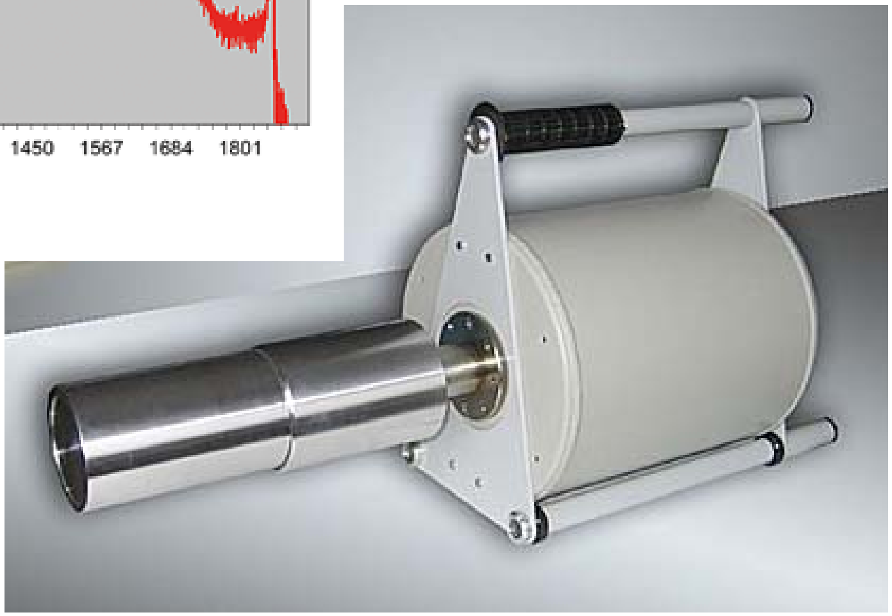


Am Spectrum after TEVA Resin Separation

Lanthanide elements removed - cleaner spectrum



Measurement of Gamma Energy



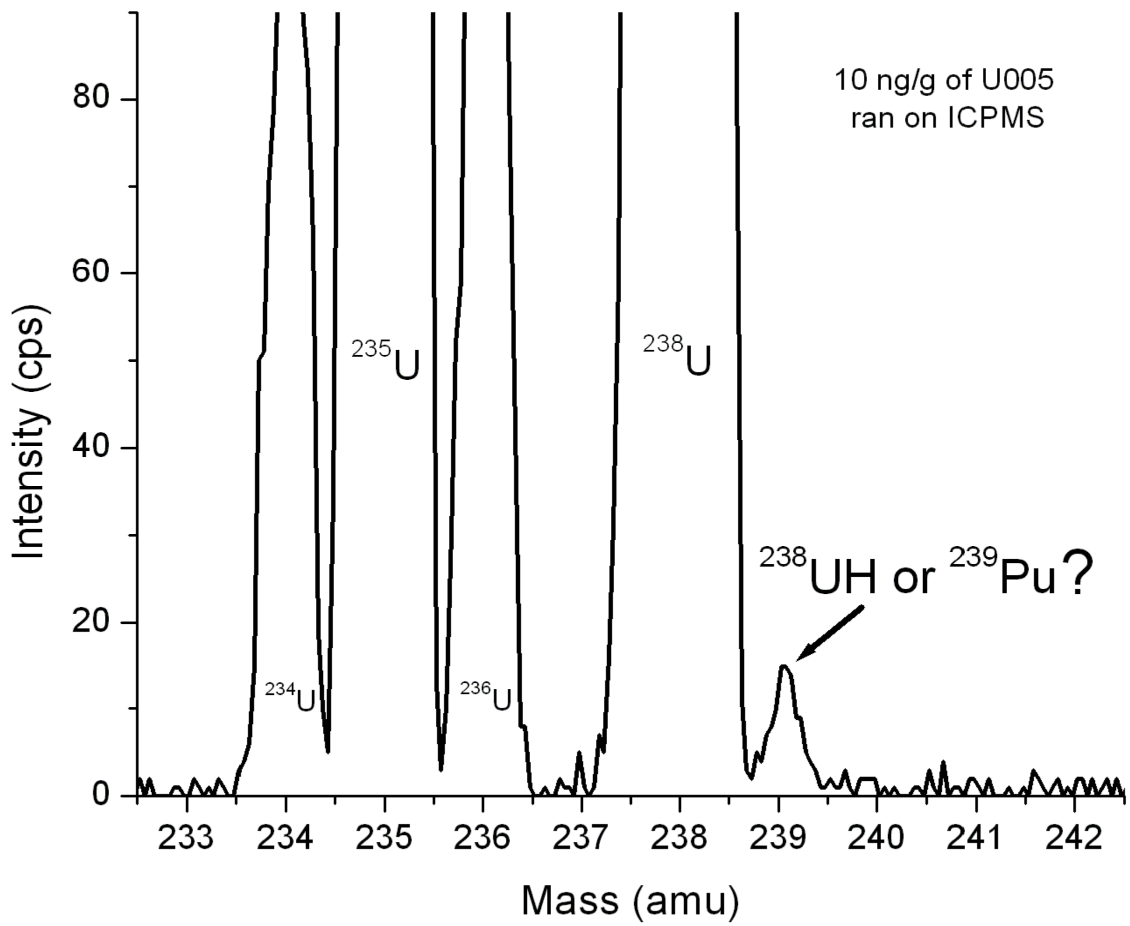
Actinides by ICP-MS: The issues

Polyatomic ions

^{230}ThH and ^{231}Pa
^{236}UH and ^{237}Np
^{237}NpH and ^{238}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

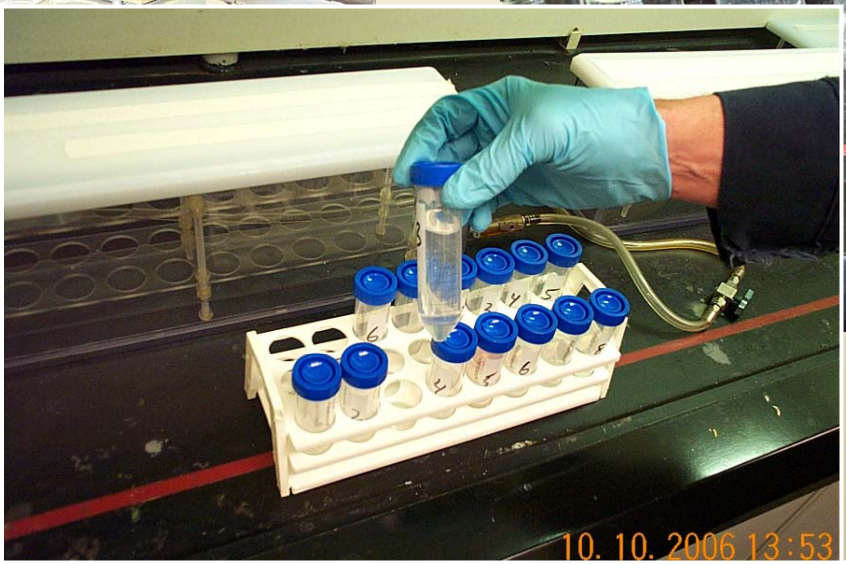


Matrix Elimination Approaches

- Sample Modification
  - Digestion
  - Leach
  - Fusion
- Volume Reduction
  - Precipitation
  - Evaporation
  - Ion Exchange

Actinides/Sr in Fish Method

- 200 g fish
- Wet ash
  - aqua regia/HNO_3/H_2O_2
- Furnace
  - 550°C
- Dissolve in 12 ml 6M HNO_3 +12 ml 2M $Al(NO_3)_3$ + 3M HNO_3 as needed (~40-45 ml load solution)

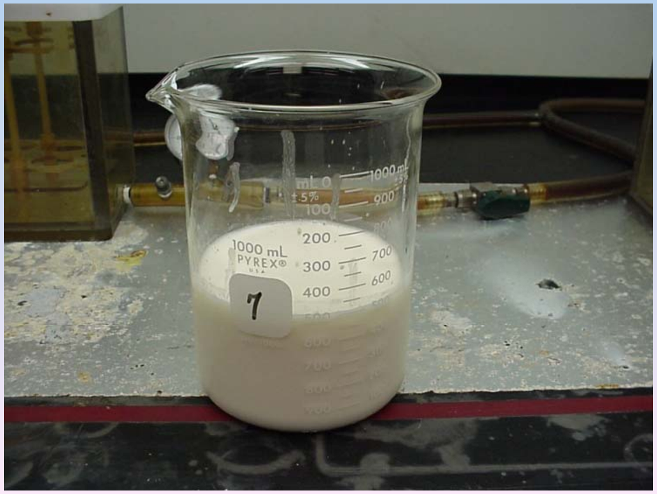


Sr in Milk
Calcium Phosphate Precipitation

- Milk Sample
  - 500 ml aliquot routine
  - 100 mL emergency + 50 mL Water to facilitate separation

- Add 2 mL 1.25M $Ca(NO_3)_2$ and 5 mL $(NH_4)_2HPO_4$
  - Ca added so water blanks will precipitate (not really needed for milk)

500 ml milk



Calcium Phosphate Preciptation

- Add phenolphthalein indicator
- Add NH_4OH to dark pink (pH 10)
- Centrifuge 10 minutes at 3500 rpm
- Discard the supernatant

Acidification of Precipitant

Separate the fat/protein from the Sr

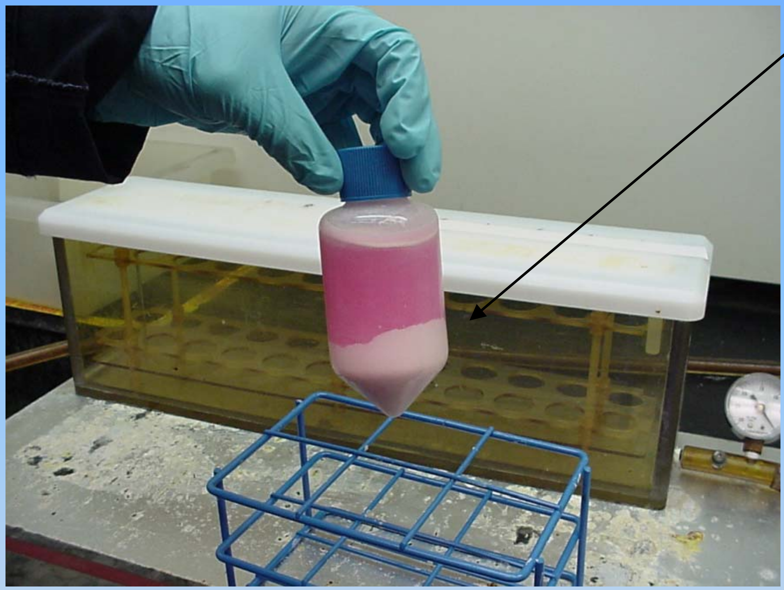
- Add 20 mL of 3M HNO_3 into each tube
- $Ca_3(PO_4)_2$ dissolves
- Fat/protein coagulate
- Centrifuge
- Transfer supernatant to beaker (contains the Sr)
- Rinse solids with 10-15 ml 3M HNO_3
- Transfer supernatant to beaker (remaining Sr)
- Evaporate beaker to dryness

Destruction of the remaining matrix

- Wet ash
  - 15 ml concentrated HNO_3 and 5 ml 30 wt% H_2O_2
- Heat beakers in a furnace
  - at 550C for 30-60 minutes to turn the solids white
- Wet ash
  - 10-15 ml concentrated HNO_3 and 5 ml 30 wt% H_2O_2
- Redissolve in 10 ml 8 M HNO_3 -1M $Al(NO_3)_3$

Sample Preparation

500 ml sample ppt. shown

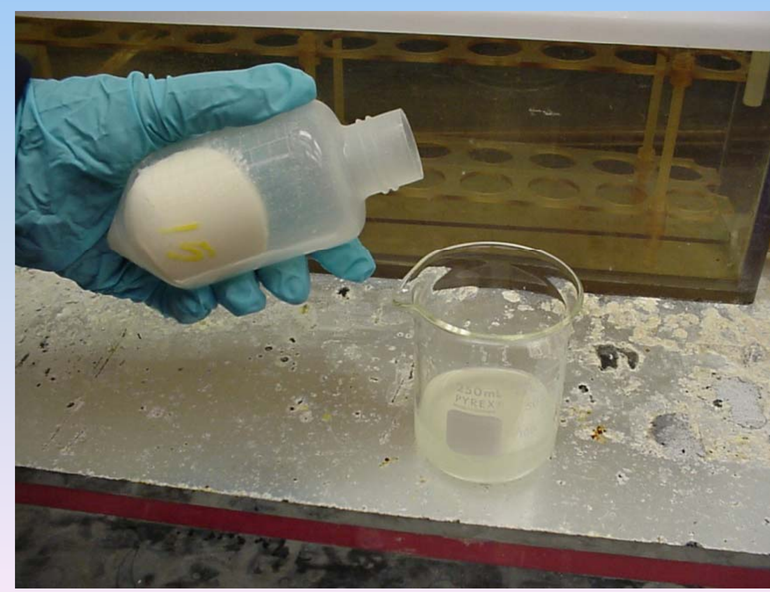


$Ca_3 (PO_4)_2$ and fat/protein

Add 3M HNO3

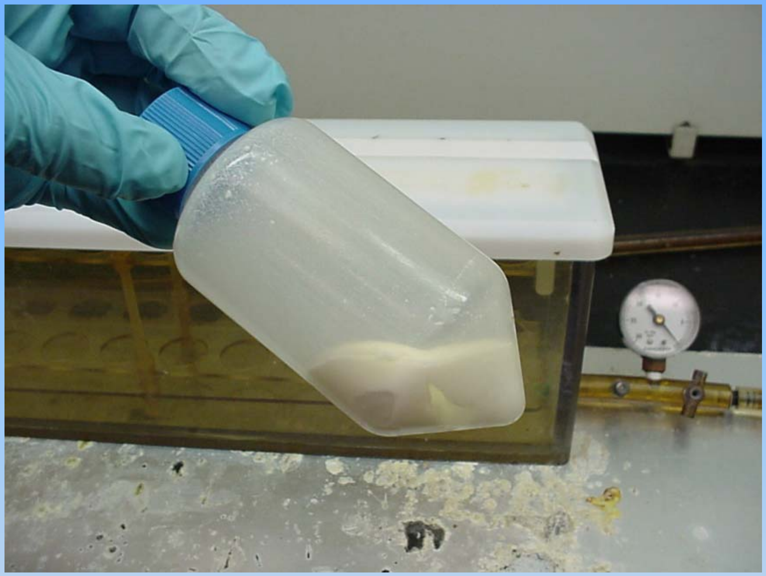
Sample Preparation

Centrifuge



Most fat/protein is removed

Sample Preparation



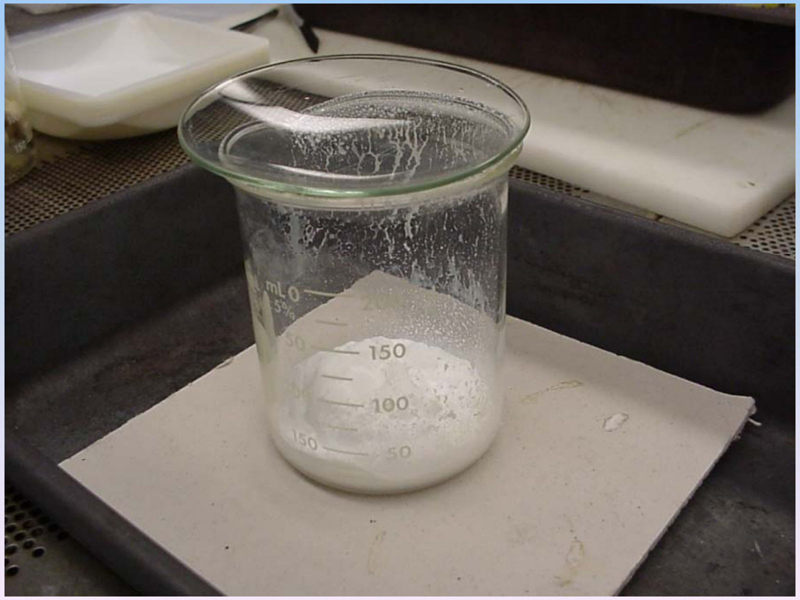
Heat on hot plate

Sample Preparation

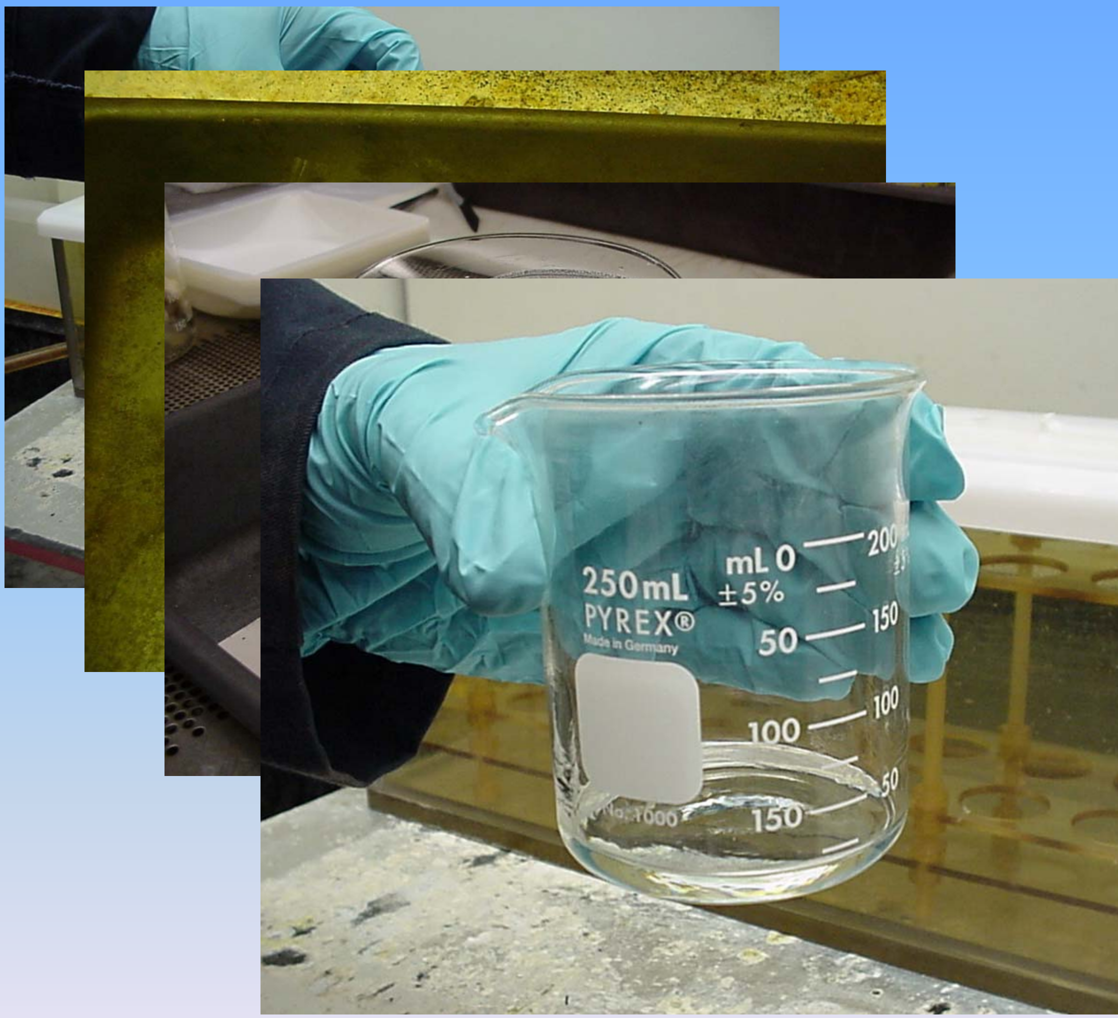
Heat to dryness

Sample Preparation

Heated at 550C 30 min.



Flowchart of with time frames
Radiostrontium Emergency Method At SRS



12 Samples of Milk, 100 mL Aliquots

↓

Calcium Phosphate Precipitation + Acidification and Wet Ash

3 Hours

↓

Furnace @ 550C

30 – 60 Minutes

↓

Separation using Sr-Resin and Mounting

2.5 Hours

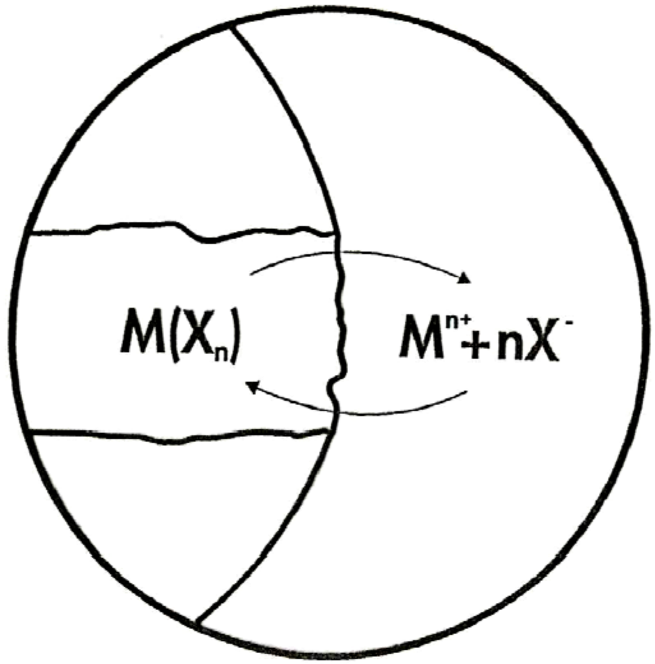
↓

Gas-Flow Proportional Counting

20 – 60 Minutes

Maxwell III, SL and Culligan, B.K., "Rapid Method for Determination of Radiostrontium in Emergency Milk Samples", Journal of Radioanalytical and Nuclear Chemistry, Vol. 279, 3 (2009) 757-760

Metal Anion Complex Formation



Metal + Anion ⇌ Complex

Complex + Organic ⇌ Extracted

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Extraction Chromatography

Solvent Extraction

Column Chromatography

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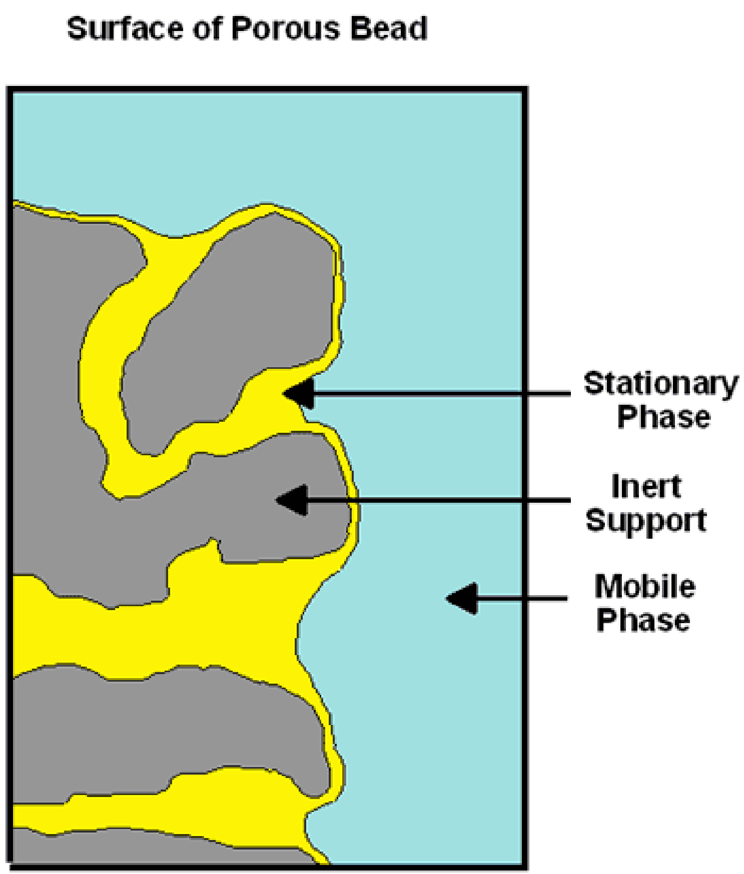
Extraction Chromatographic Resin



Inert support =

Macroporous Acrylic Resin

Example Stationary Phases

- **Crown Ether (Sr)**
- **CMPO (TRU)**
- **DAAP (UTEVA)**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TECHNOLOGIES INC
8205 South Cass Ave, Suite 111
Darien, IL 60561 USA
Tel: 630.963.0320
Fax: 630.963.1928
TEVA Resin
Part #:
Lot:
Amount:
Sr Resin
Part #: SR-B100-A
Lot: SRA03032
Amount: 100 grams
Part #:
Lot:
Amount:

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Batch Reaction / MnO2 Resin for Ra Analysis

Column Format / Gravity Flow

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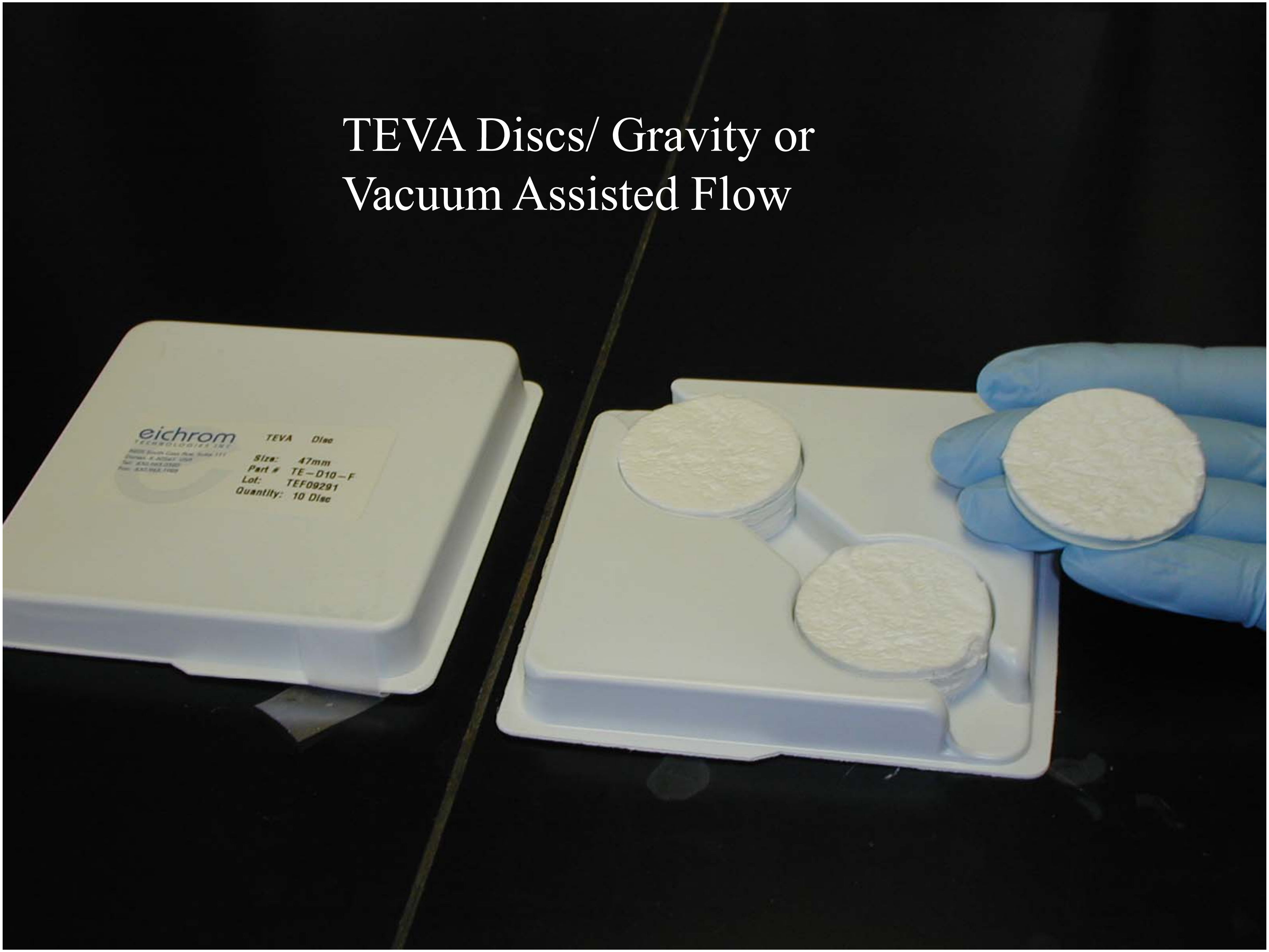
Cartridge Format / Vacuum Assisted Flow

Gravity Flow vs. Vacuum Assisted

TEVA Discs/ Gravity or Vacuum Assisted Flow



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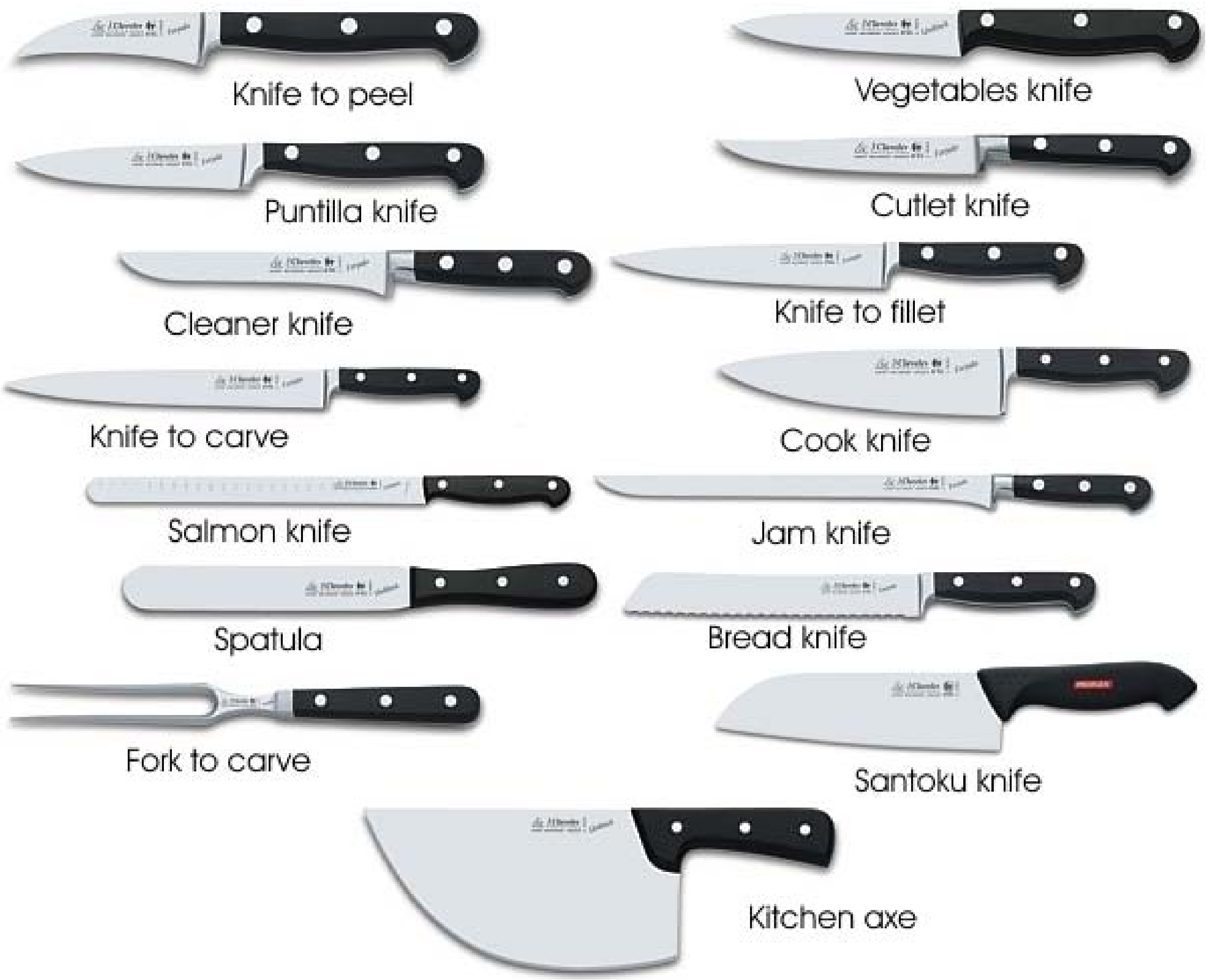
Selecting the right utensil for the job



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Product Name	Color Code	Applications*		
Accessories		Plastic accessories for columns and cartridges	product info	part numbers
Resolve™ Filters		Alpha spectroscopy source preparation	technical info	part numbers
Resolve™ PTFE Filters		• NEW Radiological Air Monitoring	technical info	part numbers
Actinide Resin	● Yellow	**Group actinide separations/gross alpha measurements**	technical info	part numbers
Beryllium Resin		**Be**	technical info	part numbers
DGA Resin		Actinids, Lanthanides, Y, Ra	technical info	part numbers
Diphonix® Resin		Actinides and transition metals	technical info	part numbers
Ion Exchange Resins		Analytical grade cation and anion exchange resins	technical info	part numbers
Ln Resin	● Purple	**Lanthanides, Ra-228**	technical info	part numbers
MnO_2 Resin		**Ra**	technical info	part numbers
Nickel Resin	● Pink	**Ni**	technical info	part numbers
Pb Resin	● Black	**Pb**	technical info	part numbers
Pre-filter Material		**Organics removal**	technical info	part numbers
RE Resin		Th, U, Np, Pu, Am, Cm, **rare earth elements**	technical info	part numbers
Sr Resin	● Red	**Sr**, Pb	technical info	part numbers
TEVA® Resin	● Green	**Tc, Th, Np,** Pu, **Am/lanthanides**	technical info	part numbers
Tritium Column		**^{3}H**	technical info	part numbers
TRU Resin	● Blue	**Fe,** Th, Pa, U, Np, **Pu, Am, Cm**	technical info	part numbers
UTEVA® Resin	● Orange	Th, **U,** Np, Pu	technical info	part numbers

*Primary applications shown in **blue**.

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EXC Resin Extractant Choice

- Ionic Recognition Extractant based resin
  - Analyte retention related to charge and ionic radii
- Neutral and Anionic Extractant based resin
  - Analytes are directly hydrogen ion dependant, although anionic extractant based resins tend to show reduced analyte uptake as the acid competes
- Acidic Extractant based resin
  - Analyte retention is inverse hydrogen ion dependant

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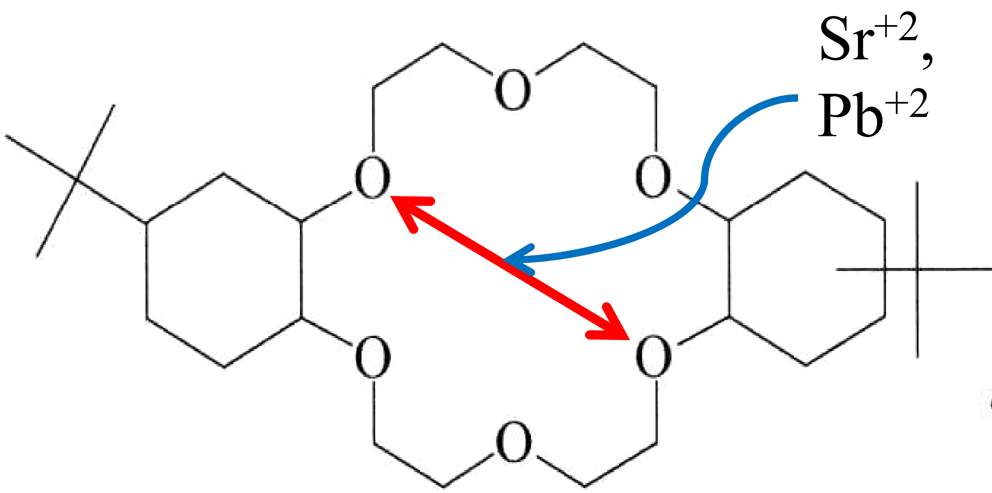
Sr Resin

di-t-butylcyclohexano 18-crown-6

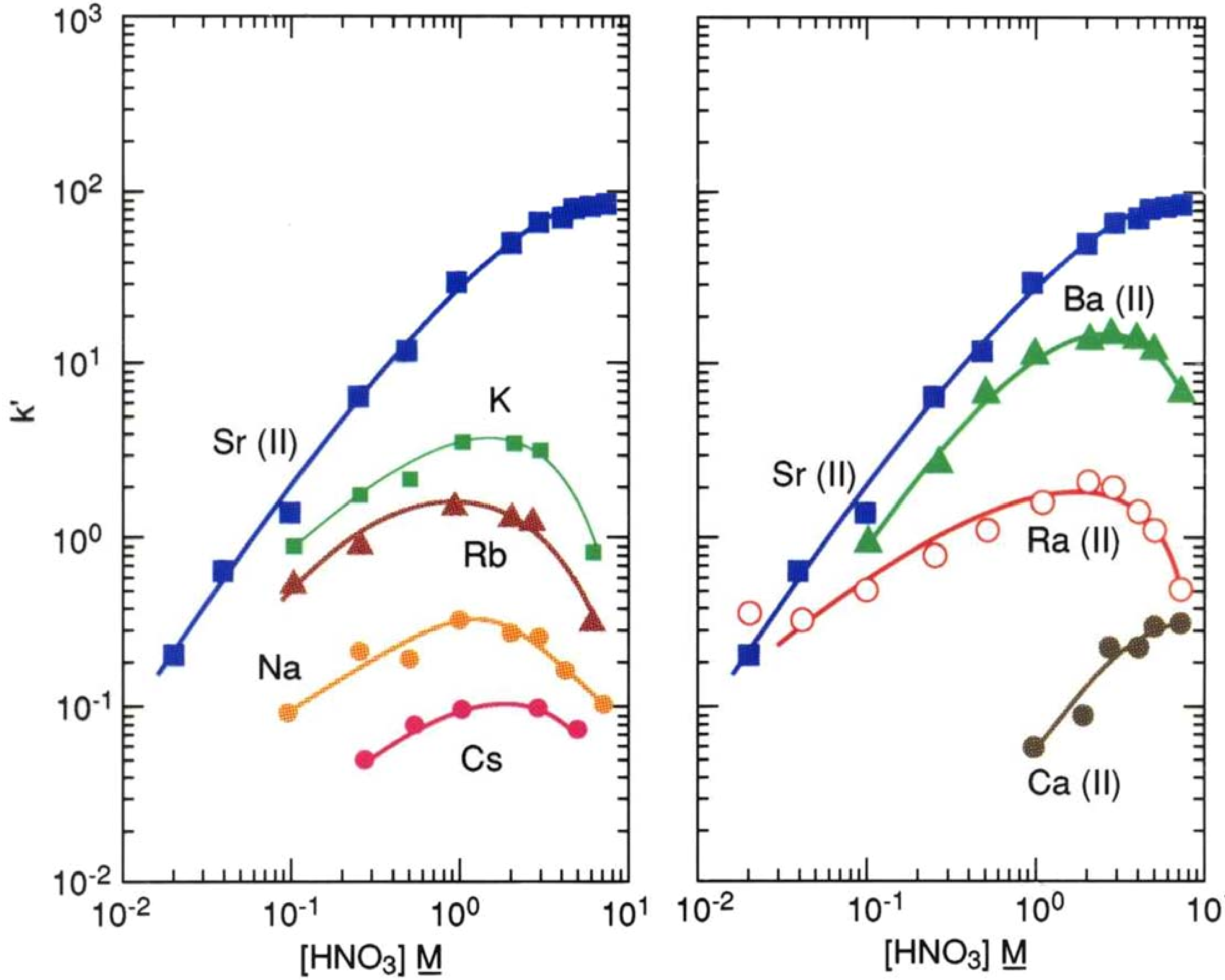


Diluent: 1-octanol

Ionic
Recognition,
size and charge

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

Sr Resin



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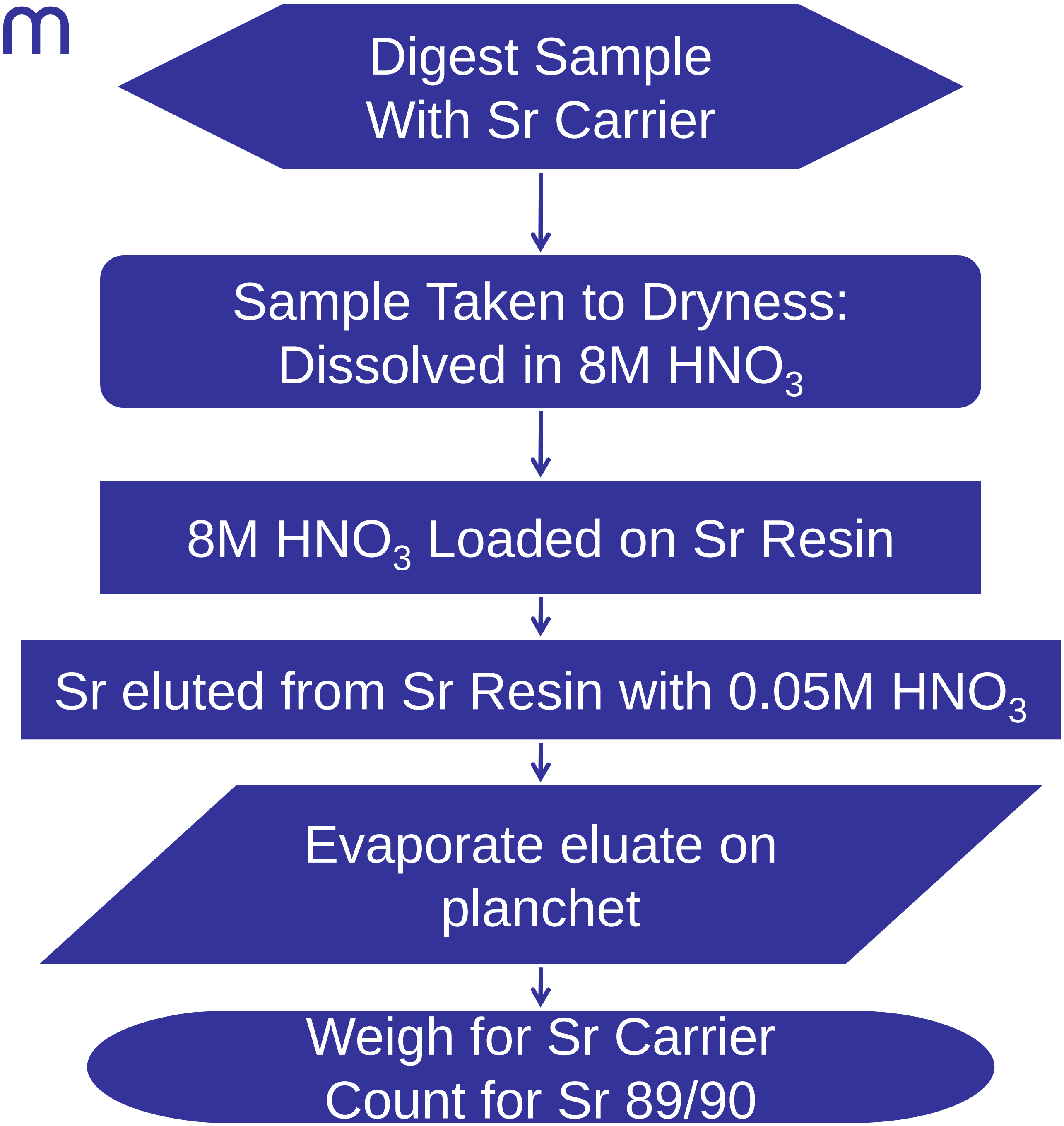

Digest Sample
With Sr Carrier
Sample Taken to Dryness:
Dissolved in 8M HNO_3
8M HNO_3 Loaded on Sr Resin
Sr eluted from Sr Resin with 0.05M HNO_3
Evaporate eluate on
planchet
Weigh for Sr Carrier
Count for Sr 89/90

Sr-89/90 in Milk Column Extraction

- Redissolve in 10 ml 8M HNO_3-1M $Al(NO_3)_3$
- Perform typical Sr Resin Separation using 3 ml Sr resin
  - (2 ml +1 ml cartridges)

- Rinses:
  - o 15 mL of 8M HNO_3
  - o 5 ml 3M HNO_3-0.05M oxalic acid
  - o 7 ml 8M HNO_3
- Sr Elution: 13 ml 0.05M HNO_3

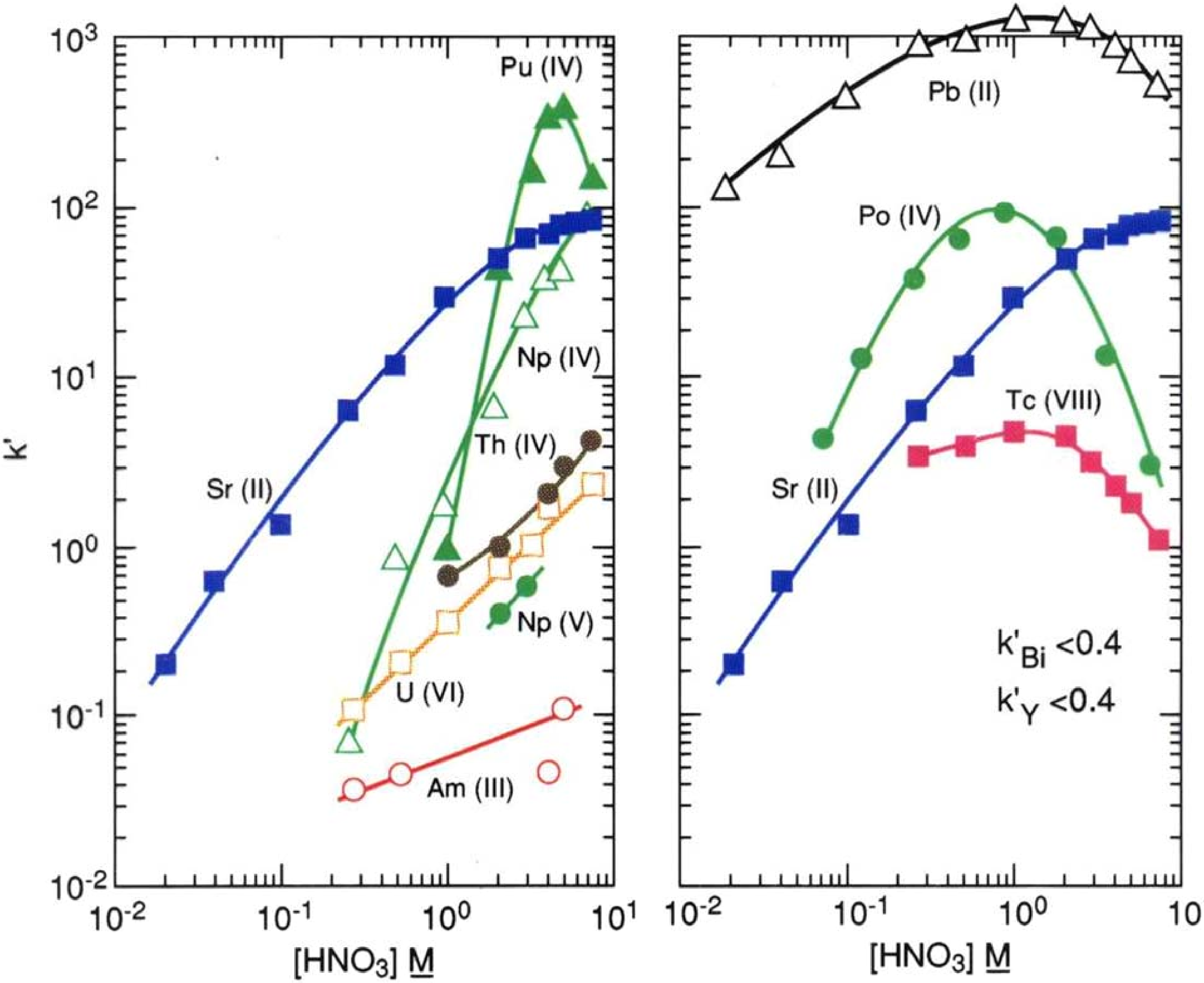
Performance of New Radiostrontium in Milk - 60 minute Count

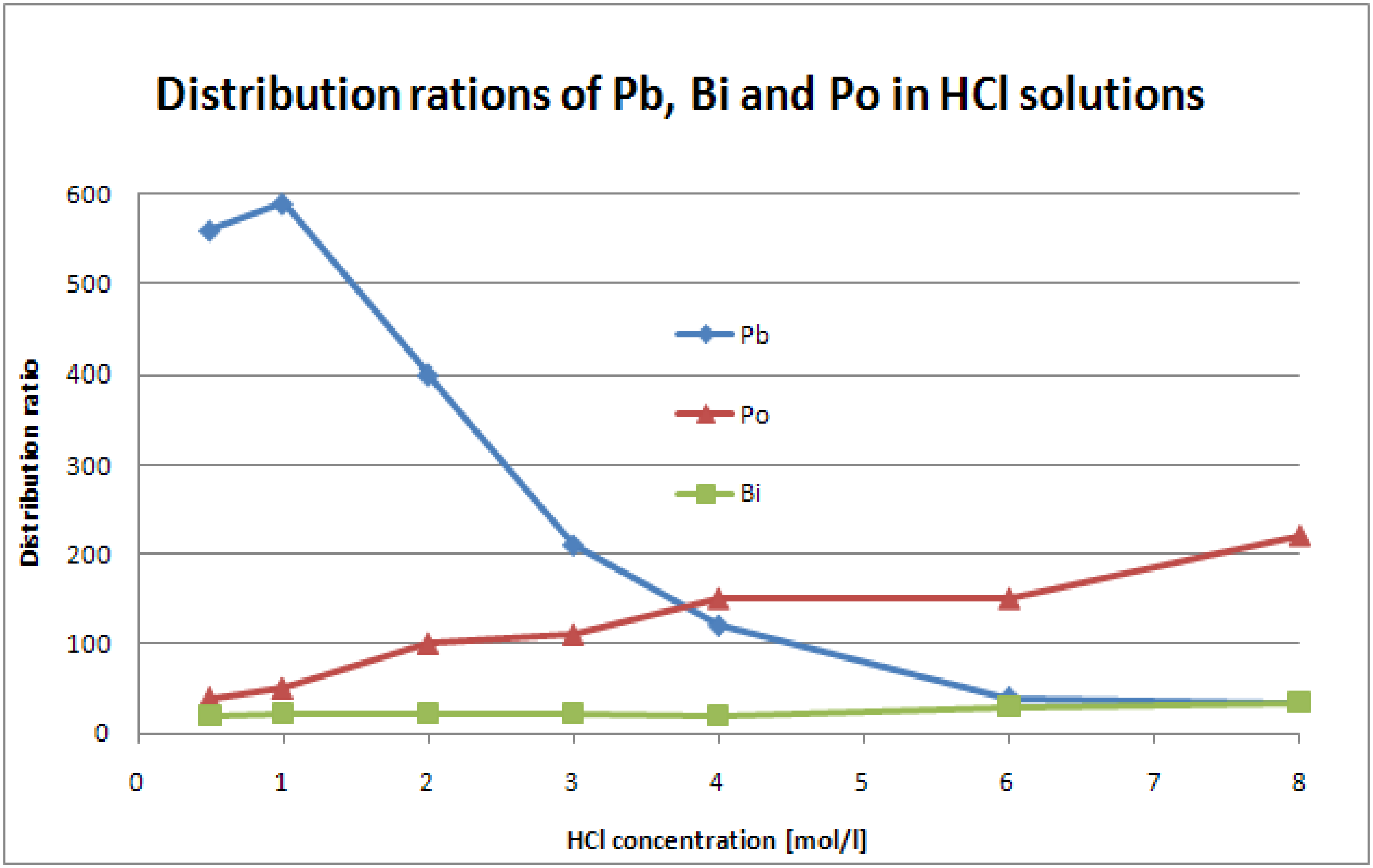
^{90}Sr Added (Bq/L)	^{90}Sr Measured (Bq/L)	Uncertainty (%, K=2)	Difference (%)
0	0.11	130	N/A
0	0.27	59	N/A
2.86*	3.09	13.2	+8.0
2.86*	3.11	16.7	+8.7
2.86*	2.67	13.6	-6.6
2.86*	2.67	11.3	-6.6
5.70	5.85	10.4	+2.6
5.70	5.75	8.3	+0.9
5.70	6.04	8.2	+5.9
14.3	13.6	6.1	-4.9
14.3	14.0	6.1	-2.1
14.3	14.2	6.1	-0.7

* Added using NRIP water standard

Average +0.52

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




Distribution rations of Pb, Bi and Po in HCl solutions
Distribution ratio
600
500
400
300
200
100
0
0
1
2
3
4
5
6
7
8
HCl concentration [mol/l]
Pb
Po
Bi

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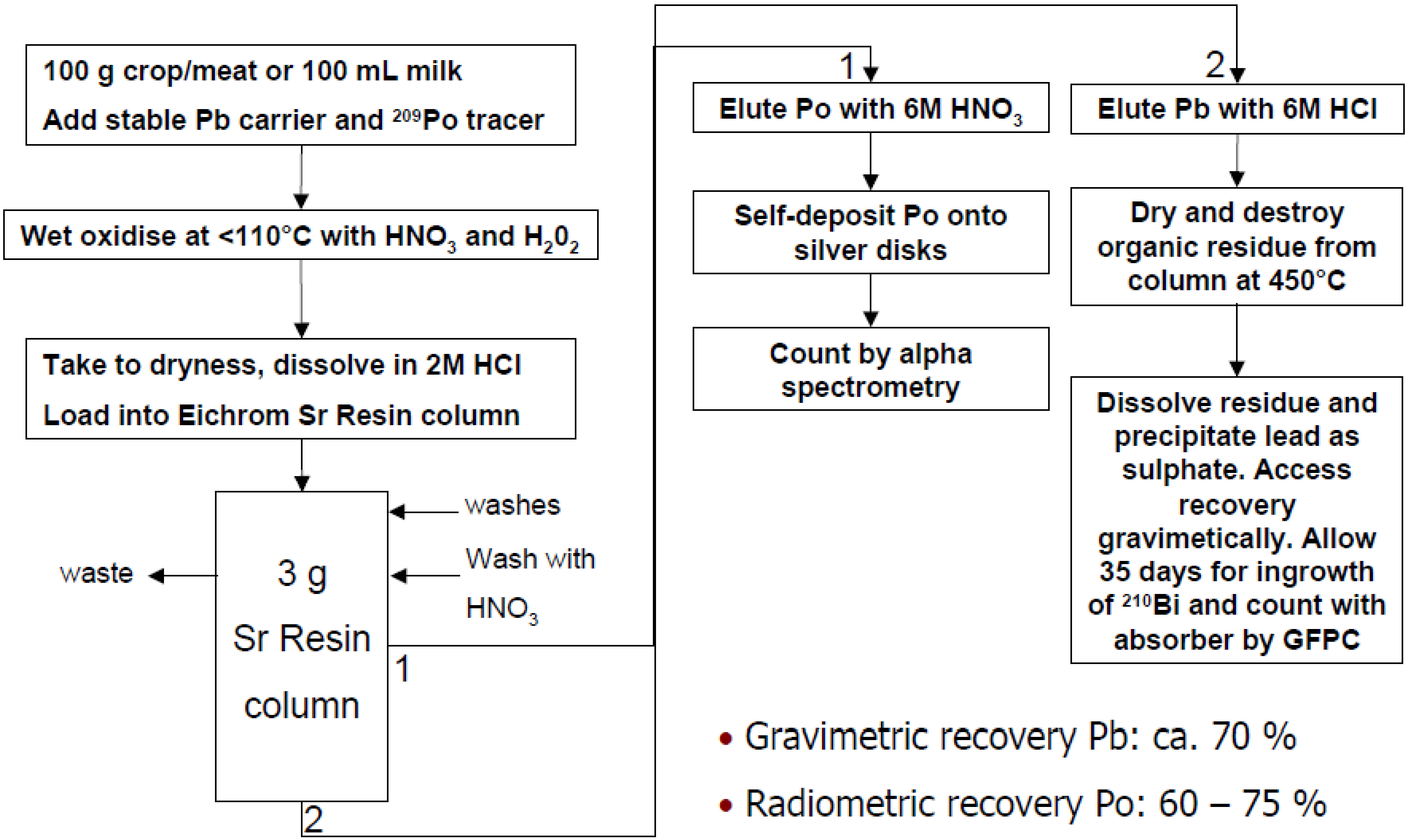
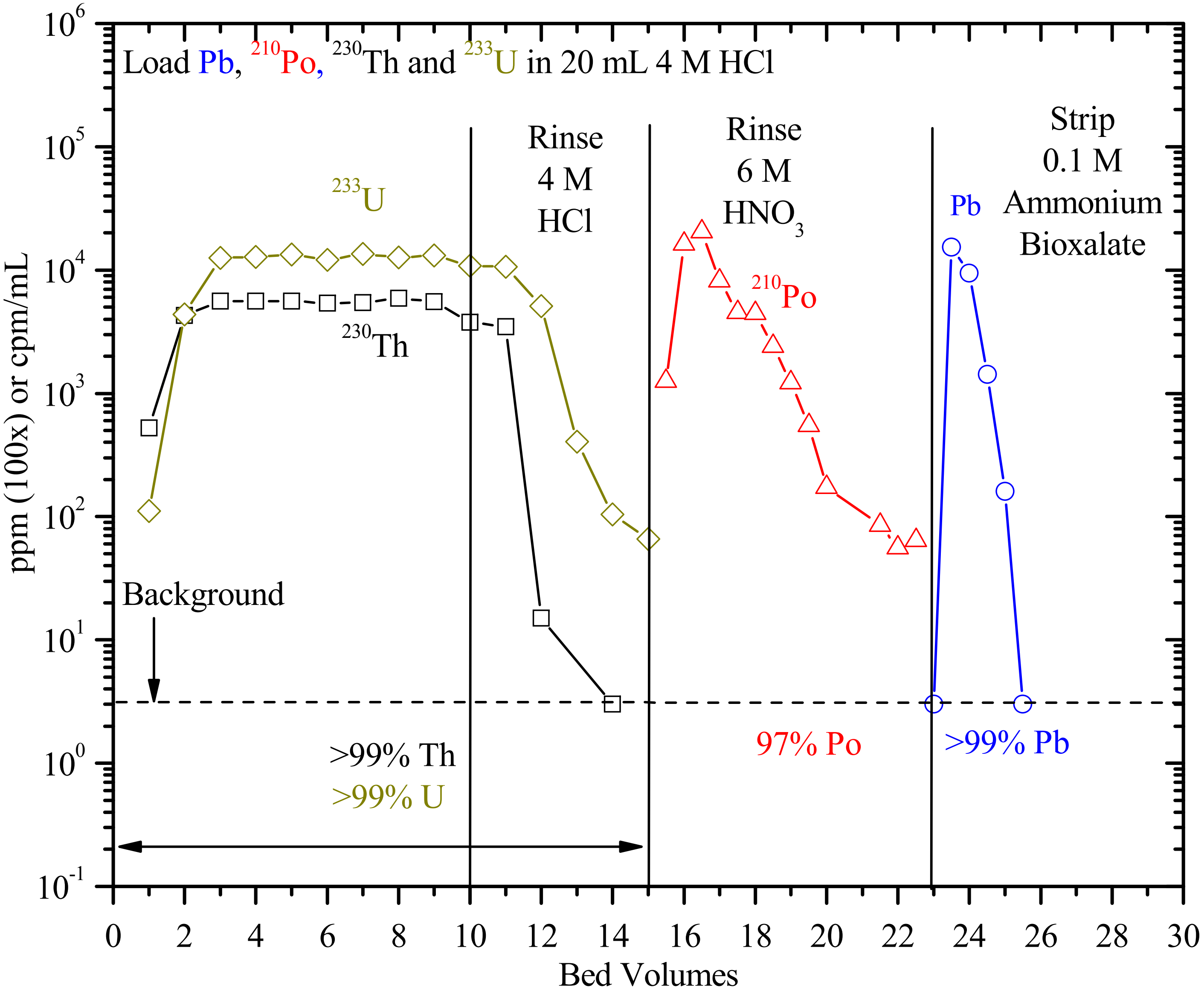
Pb and Po in milk, crop and animal samples (Dell)



- Gravimetric recovery Pb: ca. 70 %
- Radiometric recovery Po: 60 – 75 %

Pb, Po, U, Th, Ra

2.0 mL catridge Sr Resin, 22(1)°C, 50-100 μm, 2 mL/min



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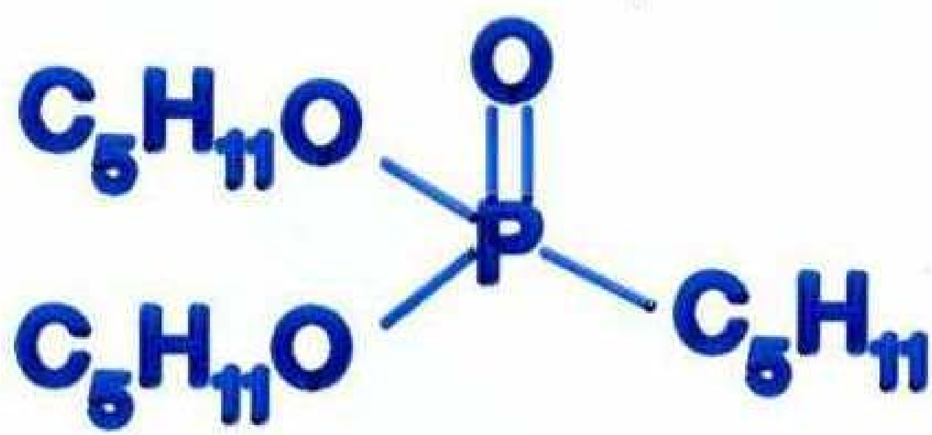
UTEVA Resin / Neutral Extractant

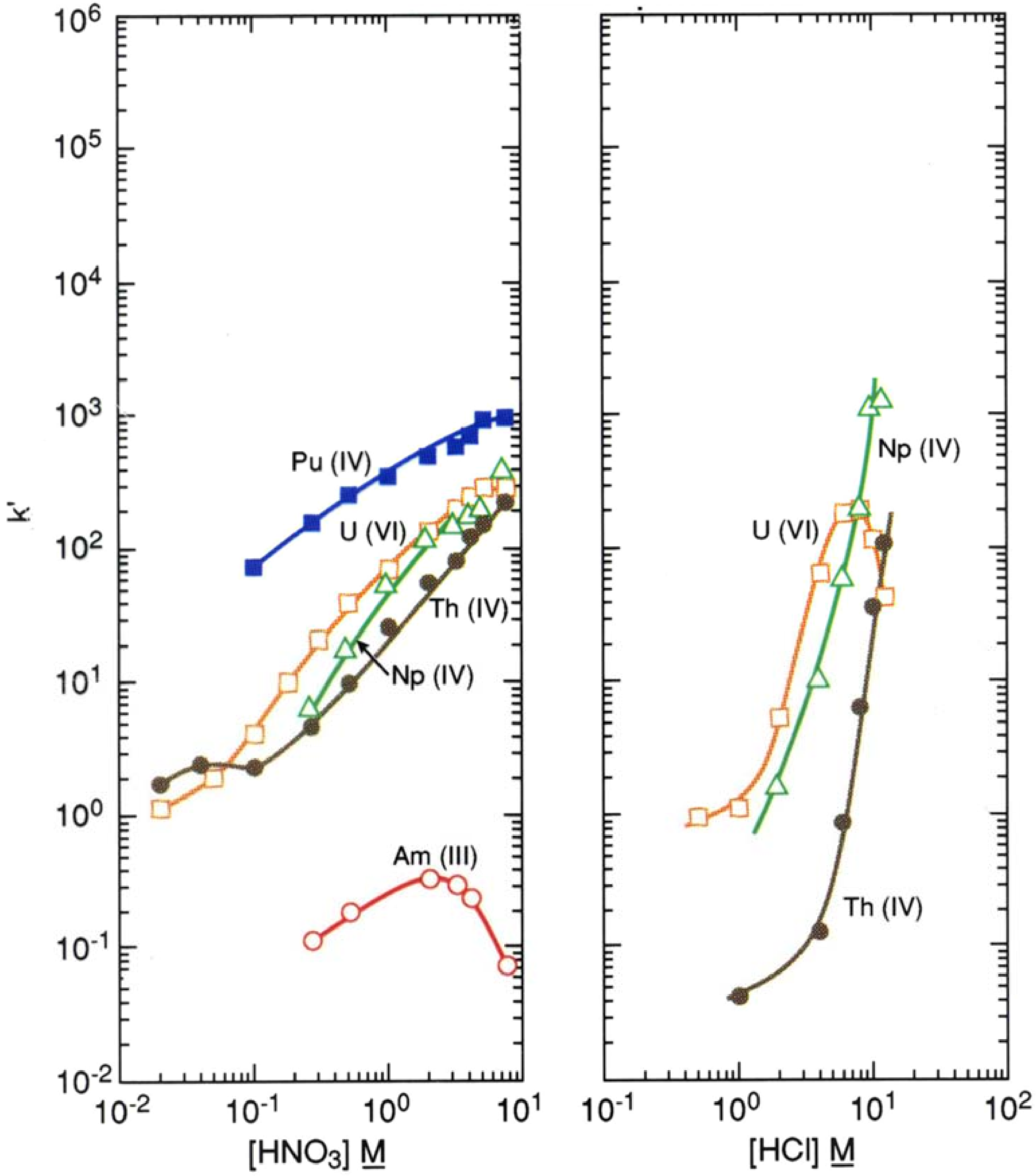
Diamyl Amylphosphonate (DAAP)

a.k.a. Dipentyl Pentylphosphonate (DPPP)



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

UTEVA Resin



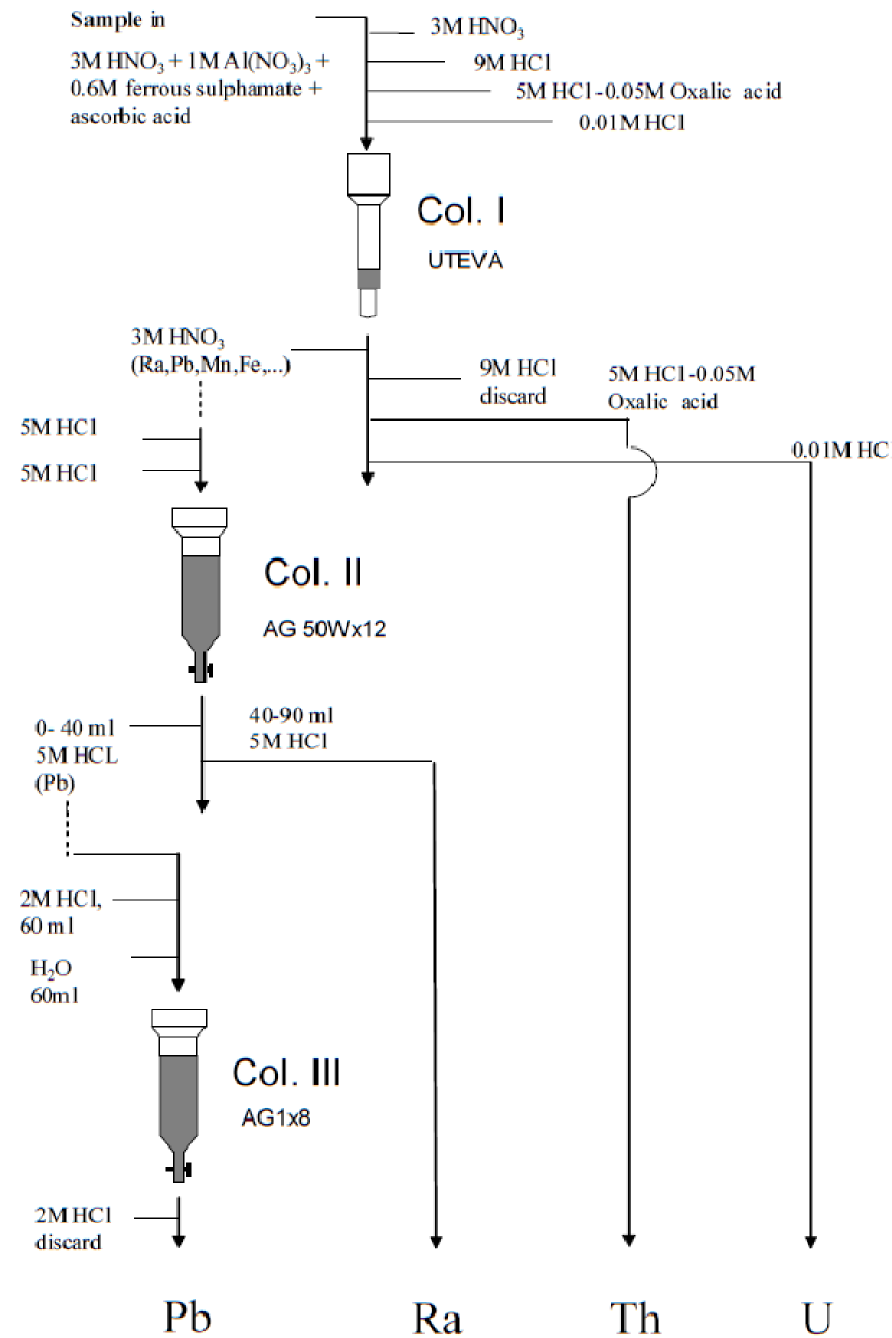
UTEVA

Sequential extraction procedure for determination of U, Th, Ra, Pb and Po radionuclides by alpha spectrometry in Environmental Samples

Isotopic Tracer Recovery Yields (mean ±1σ) for 19 Biota Samples

Analyte	Yield	Uncertainty
U	0.88	±0.12
Th	0.47	±0.18
Ra	0.22	±0.12
Po	0.80	±0.08
Pb	0.28	±0.24

C.J. M. Oliveira and F. P. Carvalho



Absorption of elements from HCl solutions by Anion Resin

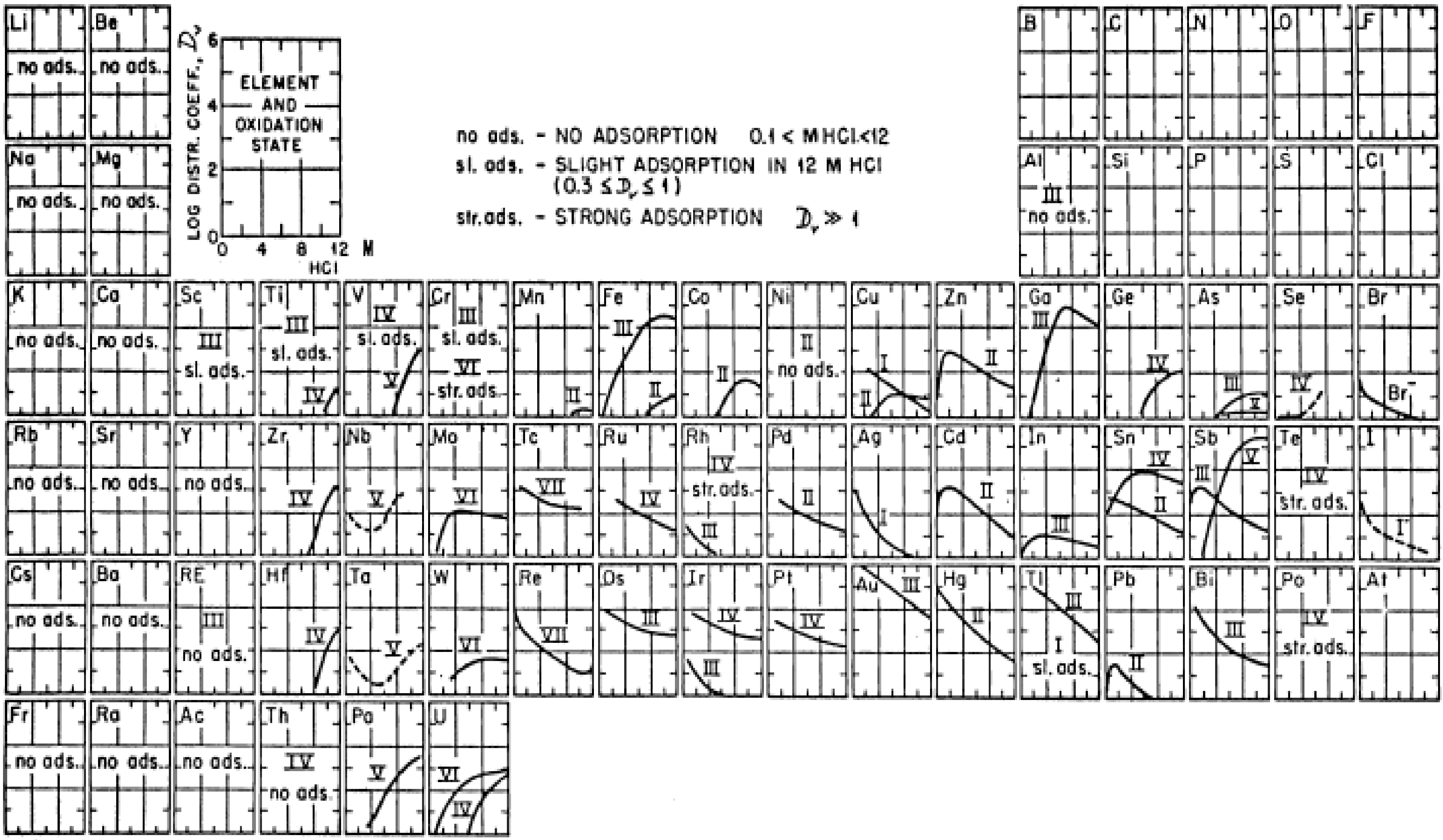


Fig. 6. Anion exchange distribution coefficients in HCl solutions.(Dowex 1-X10) (Ref. 3)

Absorption of elements from HNO_3 solutions by Anion Resin

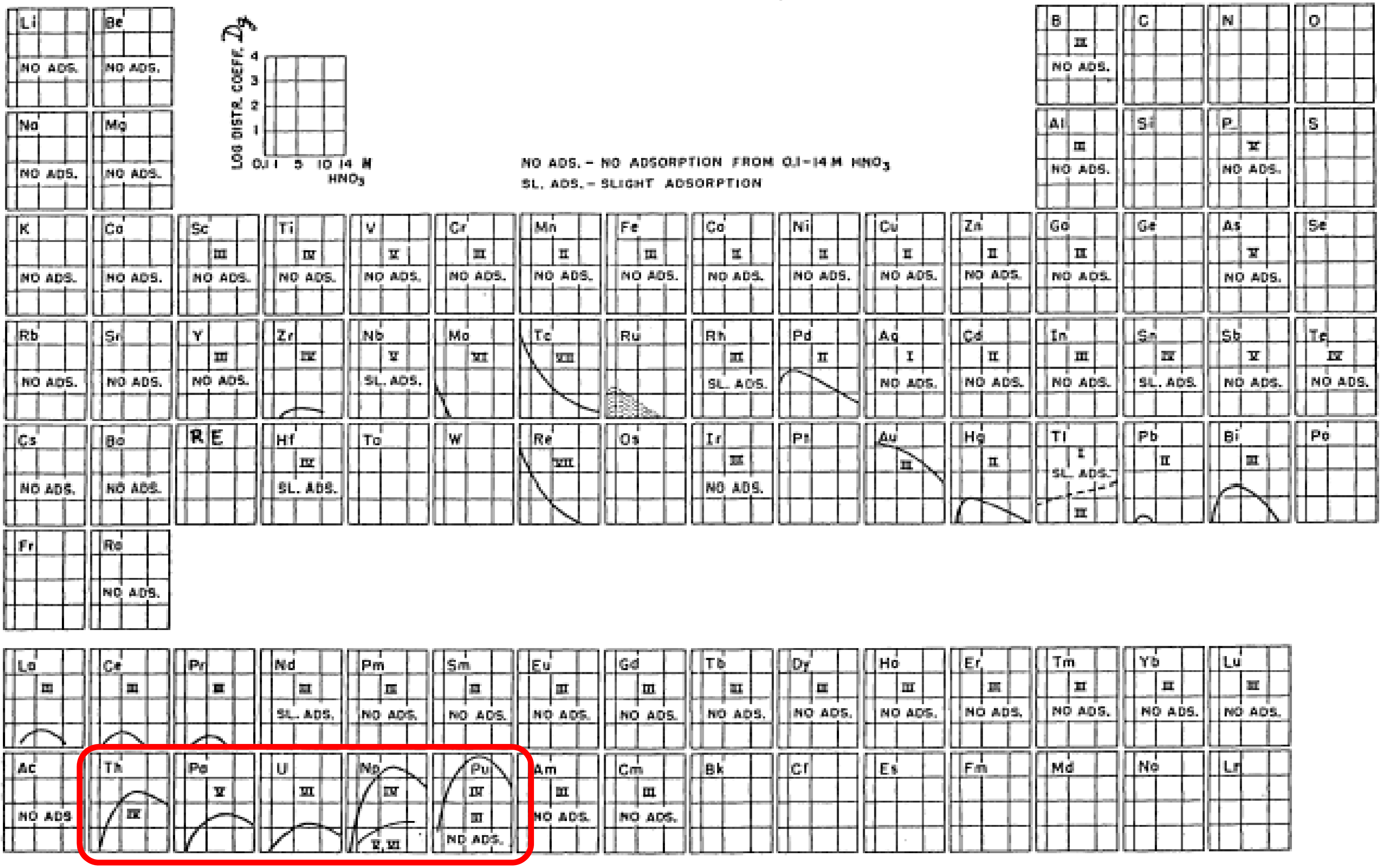


Fig. 7. Anion exchange distribution coefficients in HNO_3 solutions.(Dowex 1-X10) (Ref. 4)

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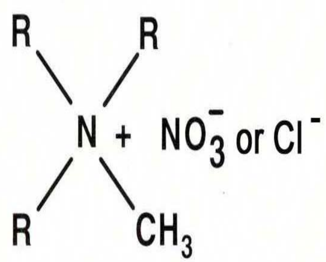
Anionic Extractant TEVA Resin

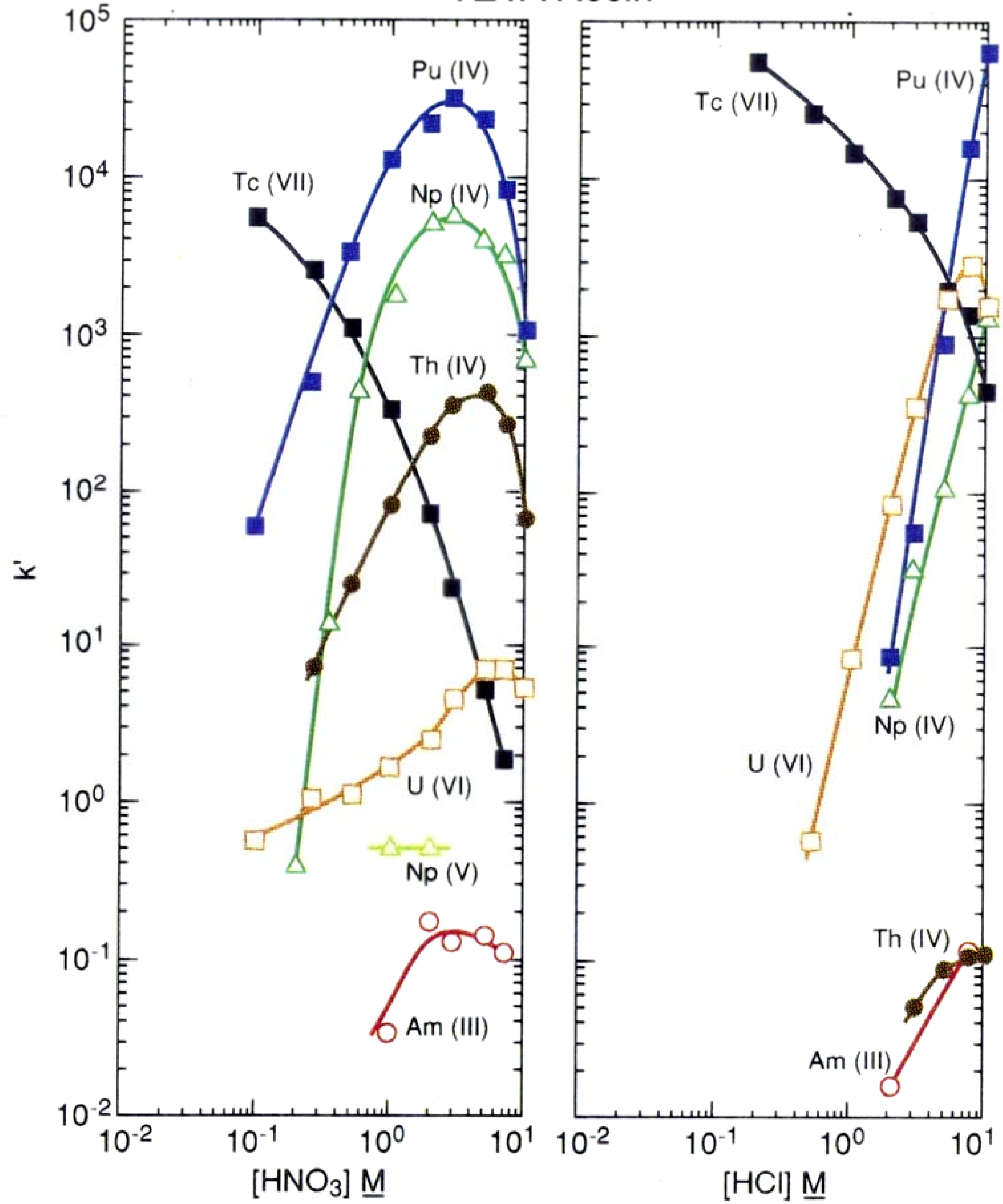
Trialkylmethylammonium Nitrate or Chloride



R = C_8H_{17} and $C_{10}H_{21}$

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

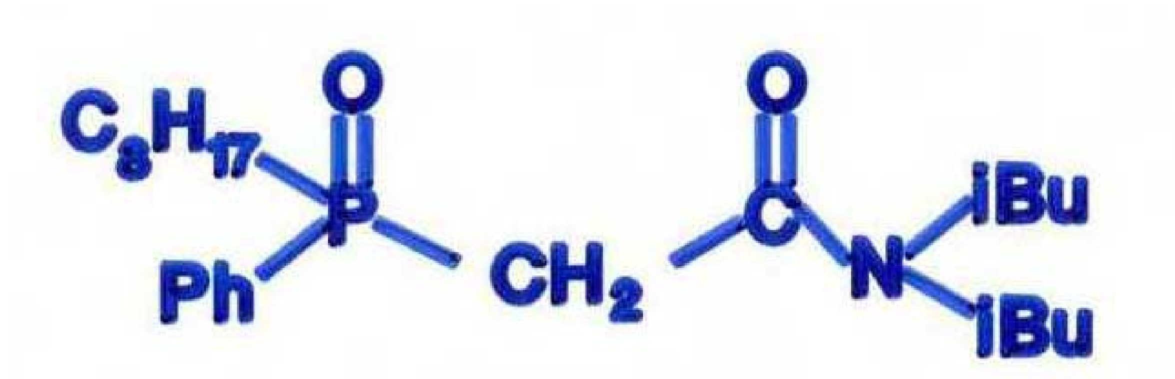
TEVA Resin



Neutral Extractant - TRU Resin,

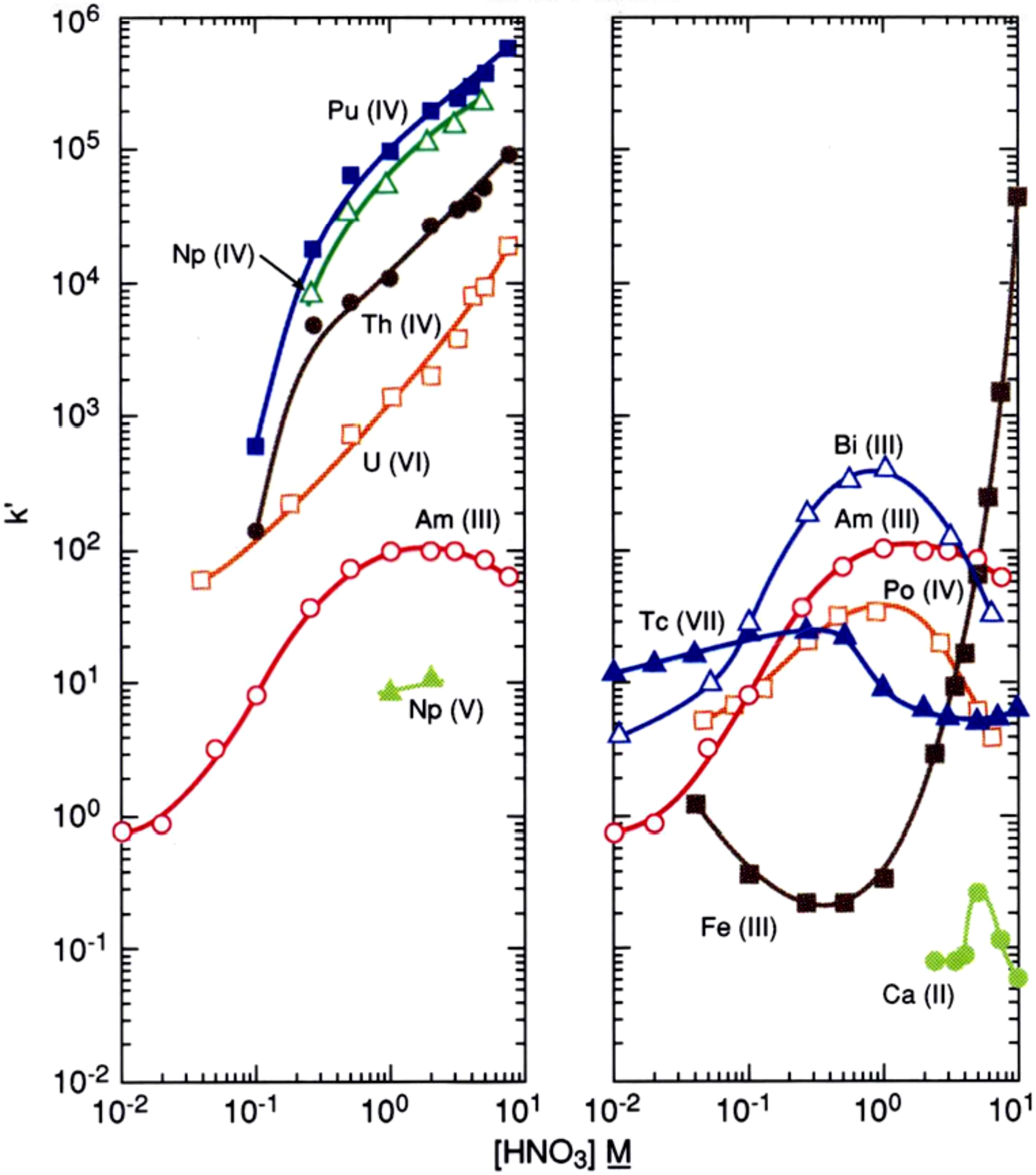
Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide

(CMPO)



Diluent: tri-*n*-butyl phosphate

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



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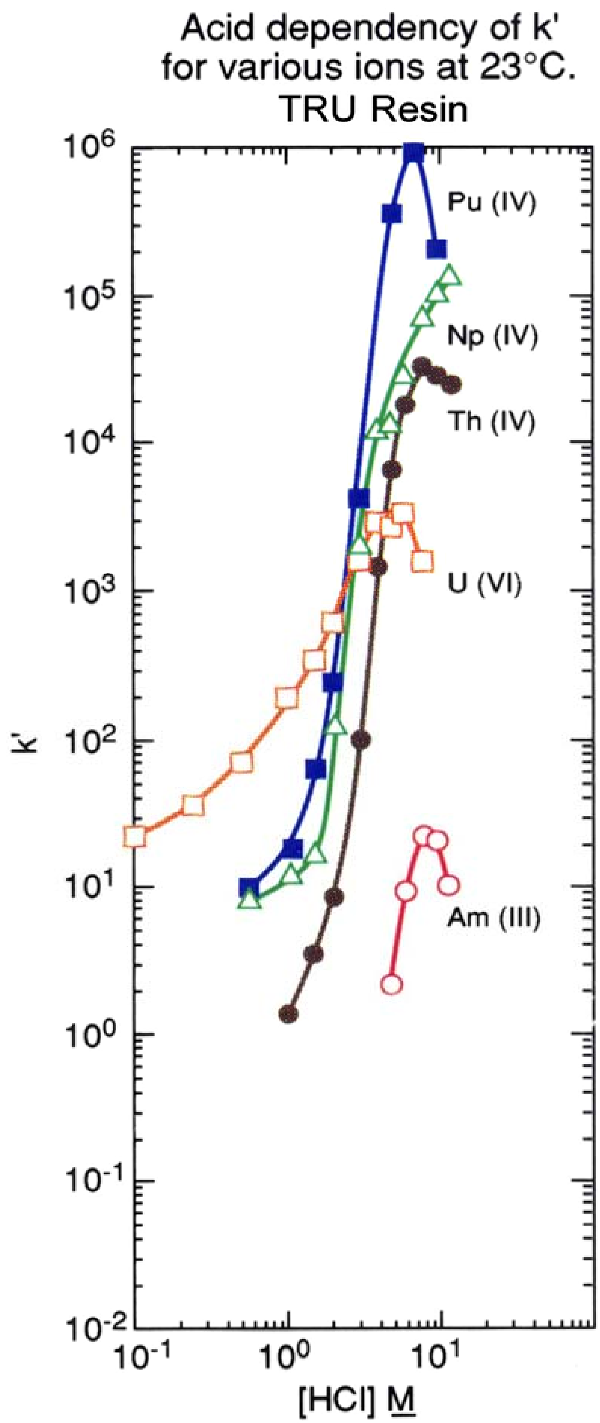
Acid dependency of k'
for various ions at 23°C.
TRU Resin
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
k'
Pu (IV)
Np (IV)
Th (IV)
U (VI)
Am (III)
10^-1
10^0
10^1
[HCl] M

Actinides/Sr in Fish Method

- 3 + 3M

- **Load to TEVA+TRU+DGA**
  - after valence adjustment
    - using sulfamic acid, iron (if Np-237 needed), ascorbic acid, followed by sodium nitrite
- **Collect load/rinse (evaporate and redissolve later in 8M HNO3 for Sr Resin)**

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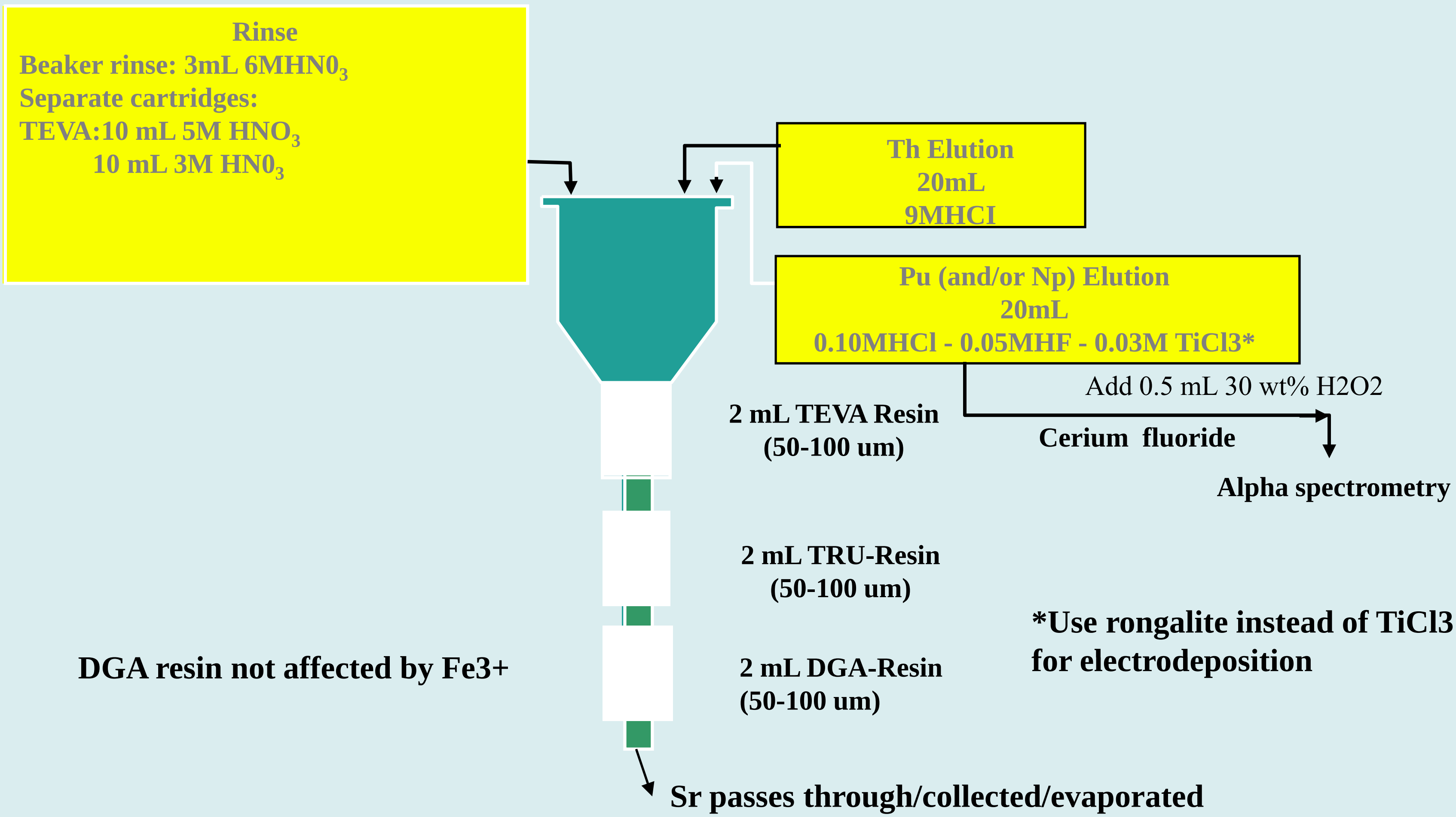
Actinides and Sr-90 in Fish Data

Tracer/carrier Recovery	Avg. Recovery	MS
Pu-236	99.8%	100% (Pu-238) 90.0% (Np-237)
Am-243	109%	94.1% (Am-241) 94.3% (Cm-244)
U-232	97.1%	91.1% (U-235)
Sr carrier	84.9%	97.7% (Sr-90)

Actinide Column Separation

1) Redissolve in 7 mL warm 6M $HN0_3$ and 7mL 2M $Al(N0_3)_3$
2) Add 0.5 mL 1.5M Sulfamic Acid + 1.25 mL 1.5M Ascorbic Acid/ 1 mg Fe (if Np-237 analyzed)
3) Add 1 mL 3.5 M Sodium Nitrite



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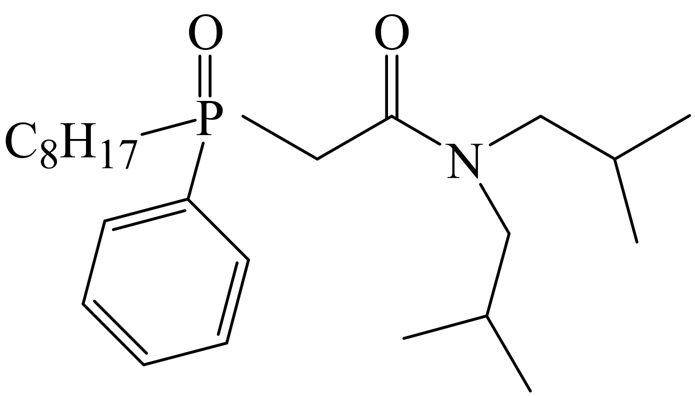
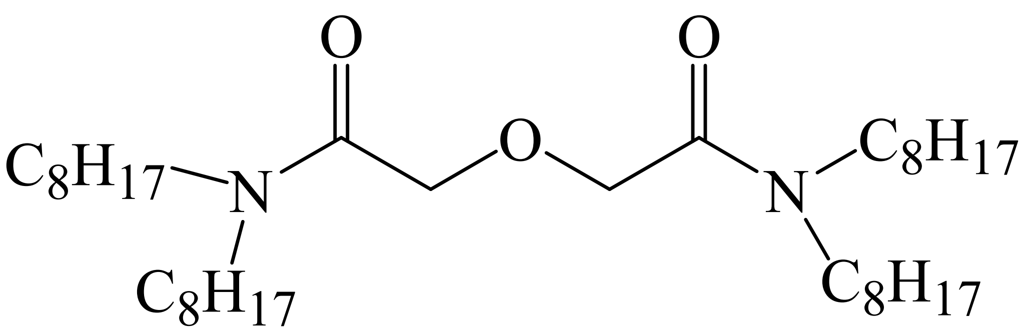
TRU Resin: Neutral Extractant

DGA Resin: Neutral extractant/ ionic recognition



TRU (CMPO)

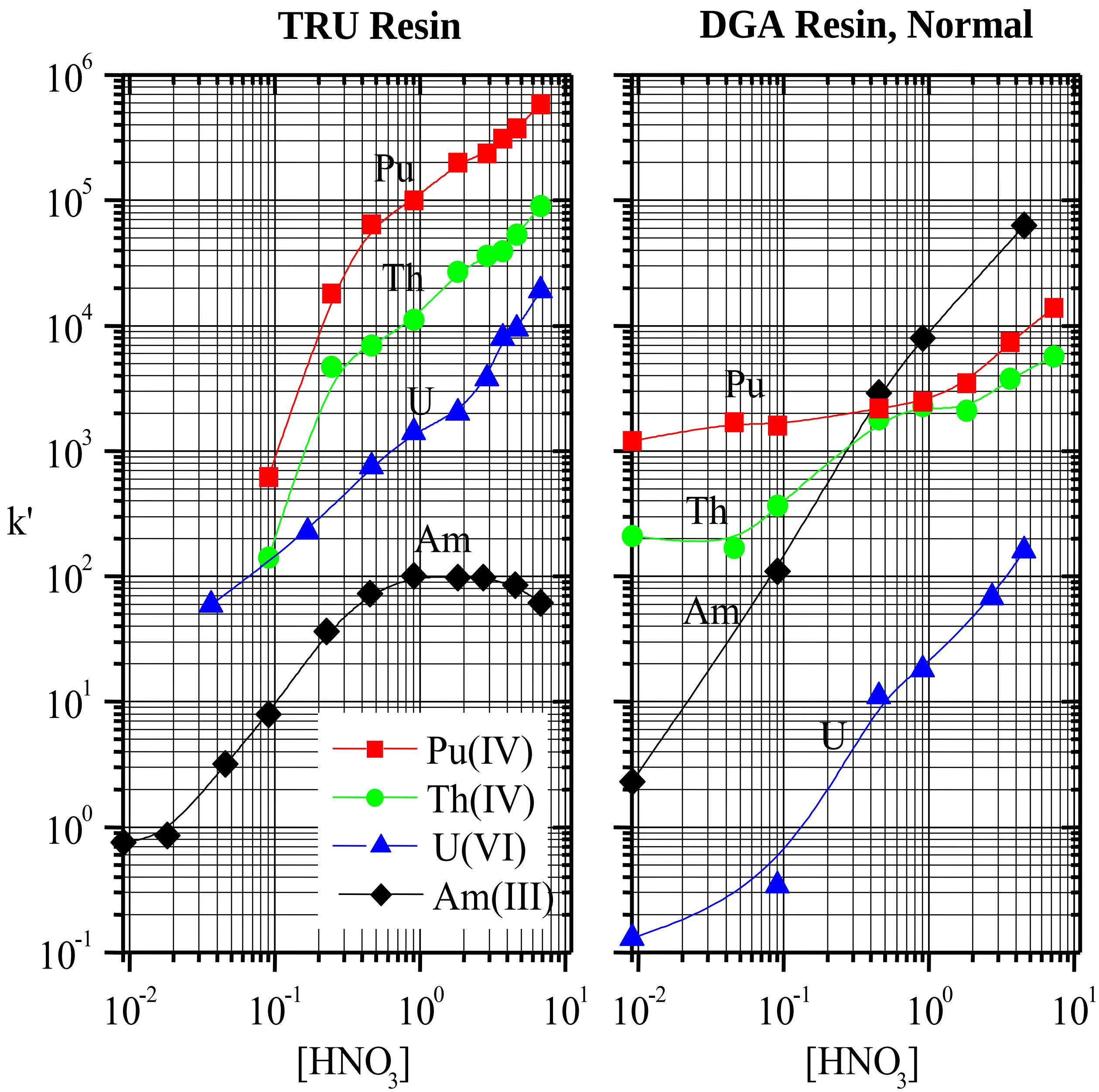


DGA

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

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

Actinides on TRU vs. DGA out of HNO_3



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- DGA alone:
  - Rinse DGA with 8 ml 0.1M HNO3
  - Add rinse to initial load/rinse solution containing Sr and evaporate
    - Contains some Sr
    - Place TRU cartridge above DGA and elute Am/Cm from TRU onto DGA with 15 ml 4M HCL
  - Discard rinse
- Rinse DGA (alone) with 3 ml 1M HNO3/10 ml 0.1M HNO3 to remove interferences
  - Discard rinse
- Elute Am/Cm from DGA with 10 ml 0.25M HCl
  - Cerium fluoride microprecipitation
  - Alpha spectrometry

eichrom Actinides/Sr in Fish Method

- Rinse TRU with 12 ml 4M HCL-0.2M HF
  - Th removal
- Elute U from TRU with 15 ml 0.1M ammonium bioxalate
  - Cerium fluoride precipitation/alpha spectrometry

Typical Actinide Tracers and Sr Carrier Recoveries for Animal Tissue Matrices

Matrix	Pu-236	Am-243	U-232	Sr Carrier
Beef (N=6)	98.7% ±5.7%	97.1% ± 8.4%	93.4% ±4.7%	96.3% ±0.5%
Deer (N=59)	99.3% ±12%	93.4% ±10%	90.4% ±8.0%	83.4%±3.5%
Fish-Bass (N=72)	96.2% ±14%	101.8%±13%	95.1% ±8.1%	89.0% ±16%
Fish-Bream (N=57)	96.6% ±12%	98.4% ±7.7%	91.1% ±6.3%	91.7% ±10%
Fish-Catfish (N=69)	98.3% ±12%	103.7% ±7.6%	89.4% ±12%	89.4% ±17%
Fish-Mullet (N=6)	96.2% ±6.8%	100.4% ±8.9%	91.0% ±8.1%	85.6% ±17%
Fish-Red Fish (N=6)	99.5% ±11%	105.2% ±8.6%	95.7% ±3.2%	77.7% ±21%
Fish-Sea Trout (N=6)	100.5% ±5.0%	102.2% ±7.6%	83.5% ±20%	74.4% ±25%
Hog (N=17)	93.0% ±20%	96.4% ±9.7%	86.4% ±15%	86.0%±7.1%
Shellfish (N=5)	101.3 ±2.2%	97.4% ±7.1%	81.7 ±3.2%	97.5% ±0.89%

Composite tissue samples
100 gram-deer, hog, bream, shellfish
200 gram-catfish, bass, red drum, mullet, sea trout
25 gram- nonedible fish samples including bones

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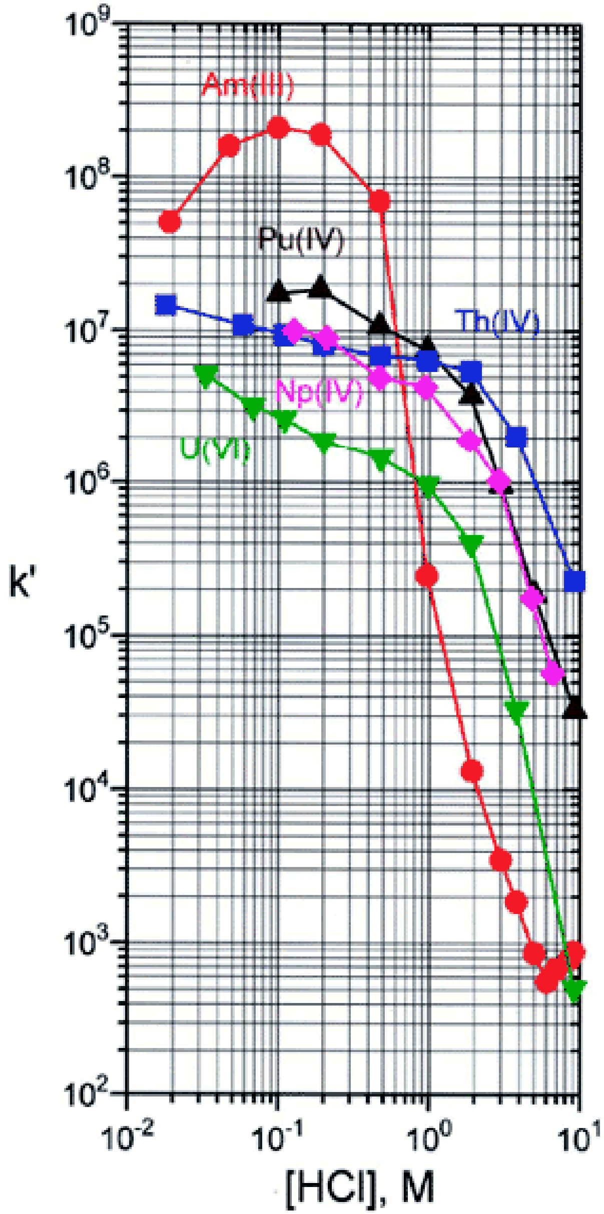
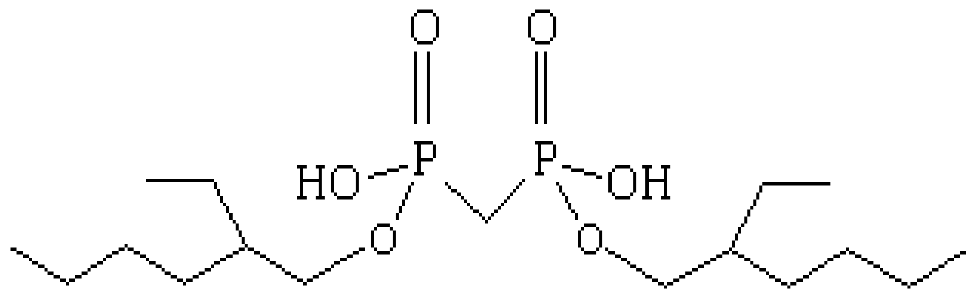


Actinide Resin uptake of various actinides with DIPEX® extractant (Liquid Chelating Exchanger)



Data developed at Argonne National Laboratory, USA

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Your separation resin drawer!

Hows

Versatility

Results

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¿ Questions ?