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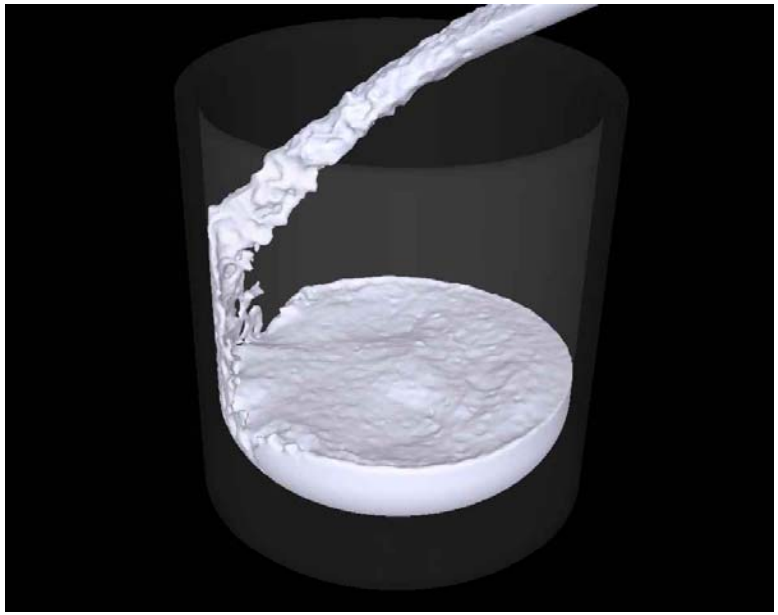
expertise. collaboration. results.

Introduction to Extraction Chromatography Resins and their Use in Rapid Methods

Lawrence Jassin and Terence O'Brien

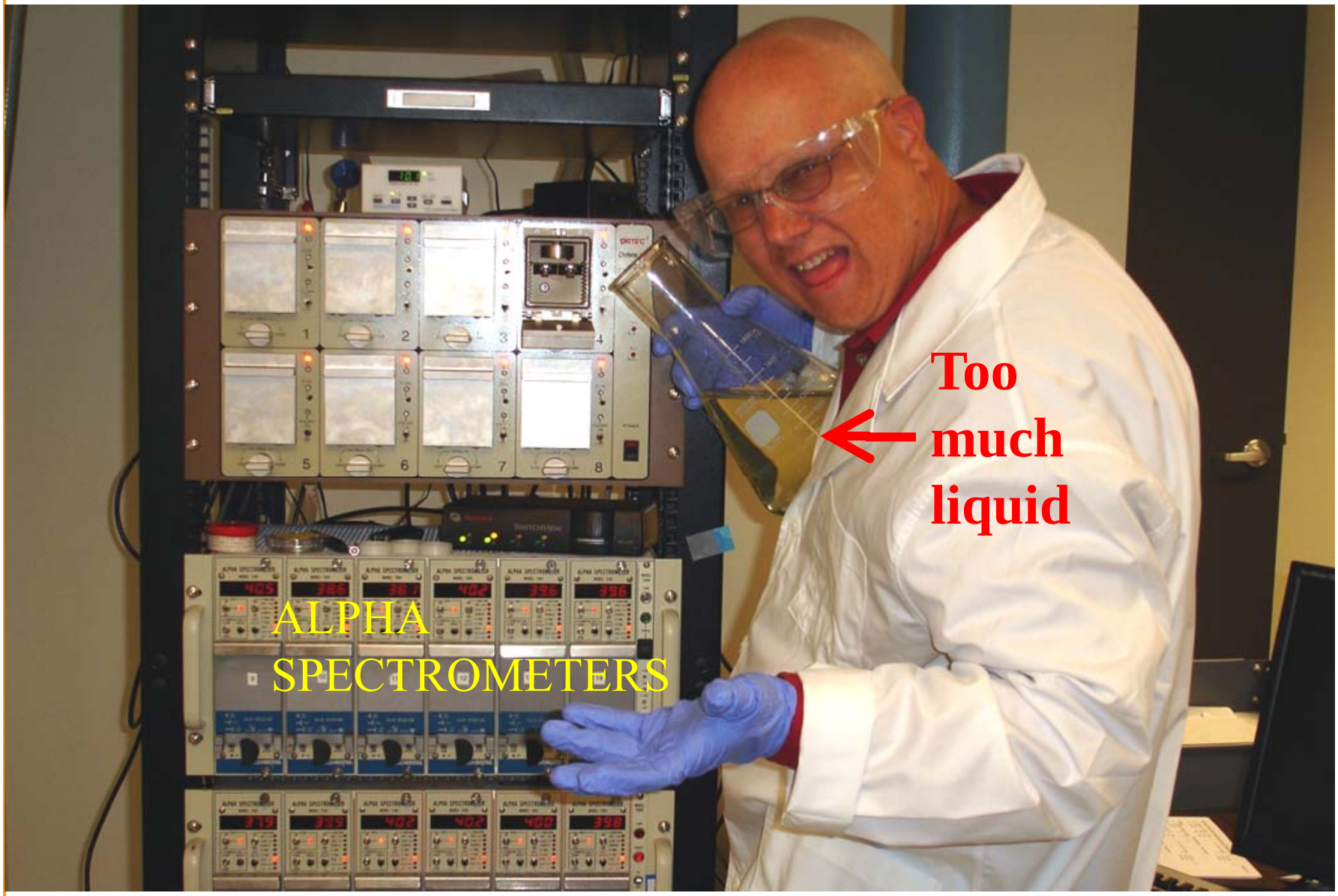
At the FERN National Training Conference
June 30th, 2010

Variety is the spice of life



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

We Need Sample Preparation



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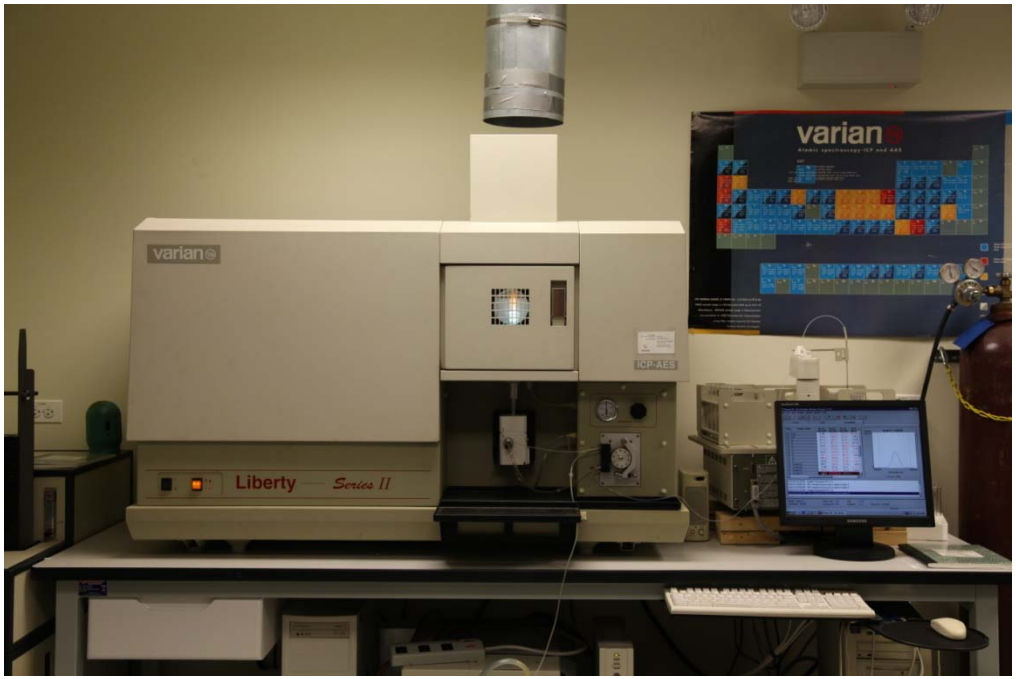
RADIOACTIVE
TENNELEC


varian
varian
Liberty Series II
ICP-AES


TRI-CARB
RADIOACTIVE
#218 Liquid Scintillation Counter
2550 TR/AB
LIQUID SCINTILLATION ANALYZER
PACKARD

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Your separation resin drawer!

Hows

Versatility

Results

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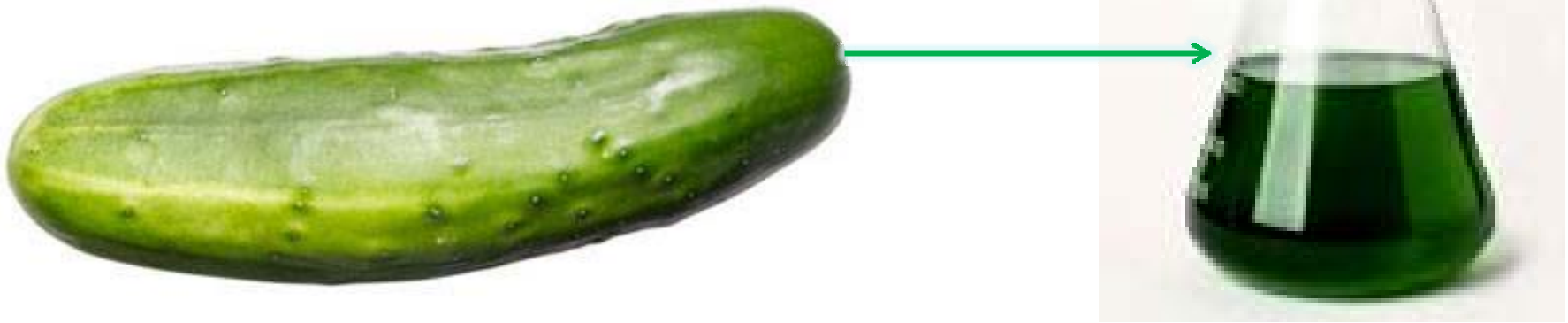
Stops in the Lab/Kitchen along the way

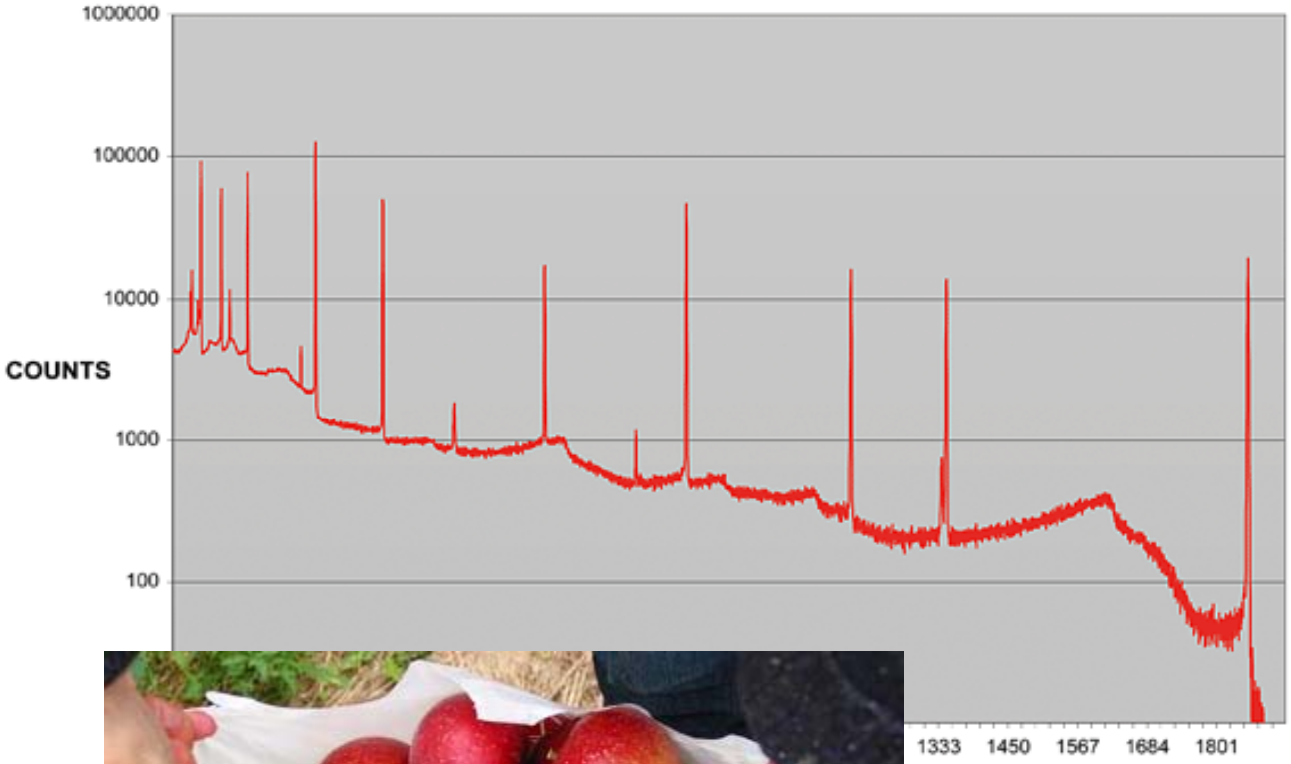
- Sample Preparation Concepts
- Extraction Chromatography (EXC) Fundamentals
- Separation Tools – EXC Uptake Curves
- Some example separations and RESULTS
- Questions ?

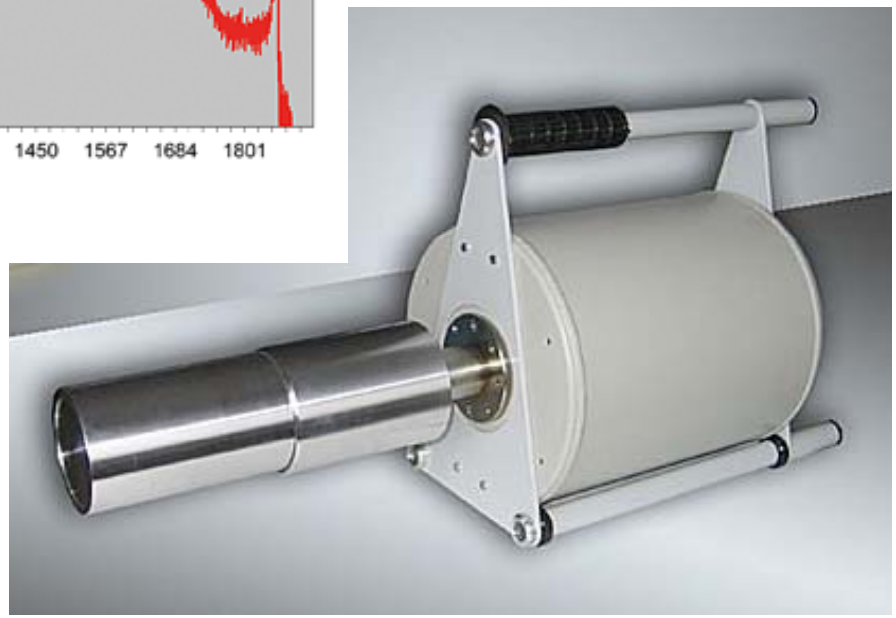
Your goals for Sample Preparation

- 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

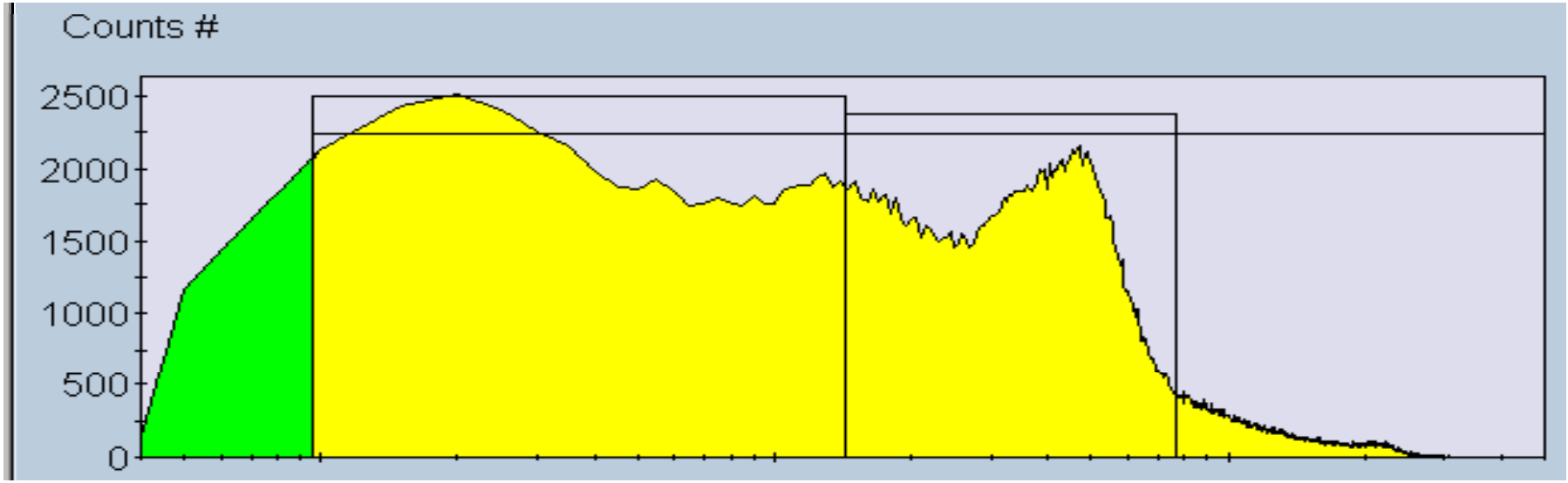


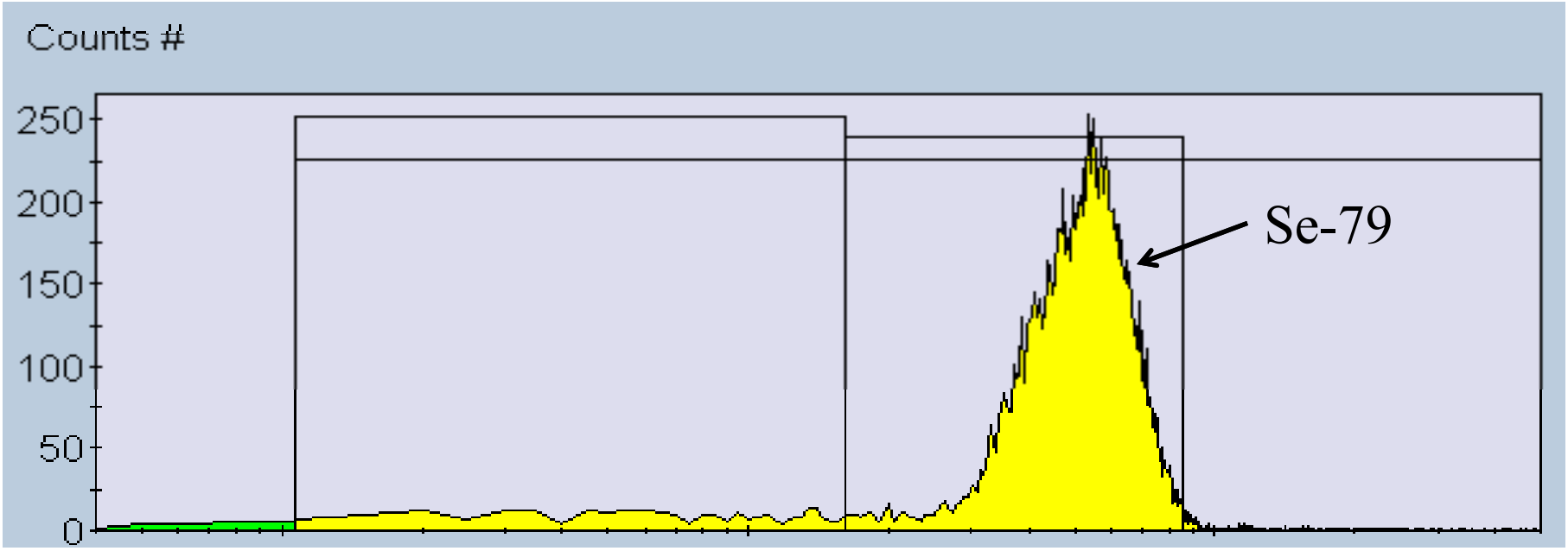
Measurement of Gamma Energy



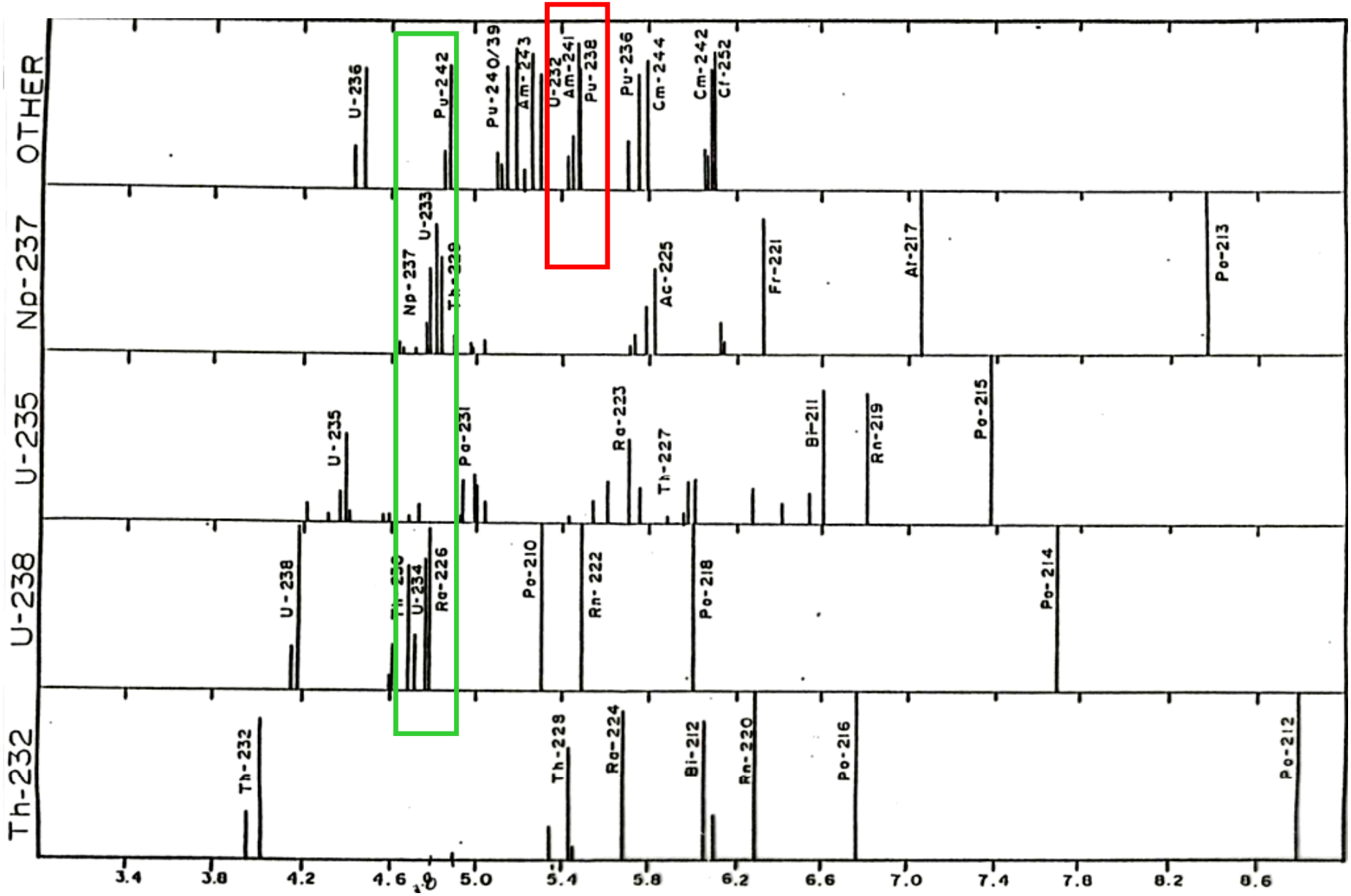


Measurement of Beta Energy (LSC)





Measurement of Alpha Energy



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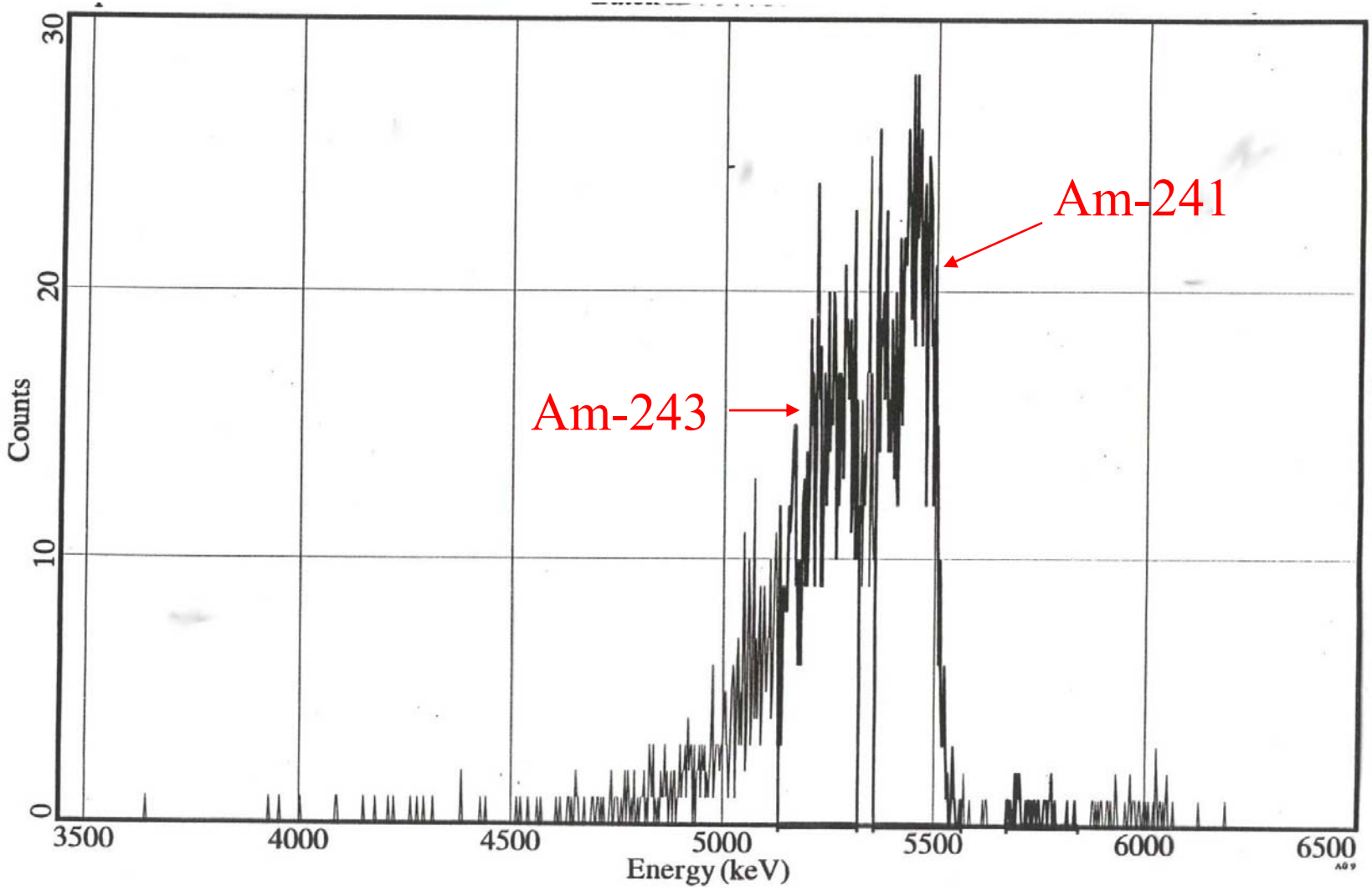
Americium Spectrum after TRU Resin Separation

presence of rare earths degrades spectrum- self absorption issues



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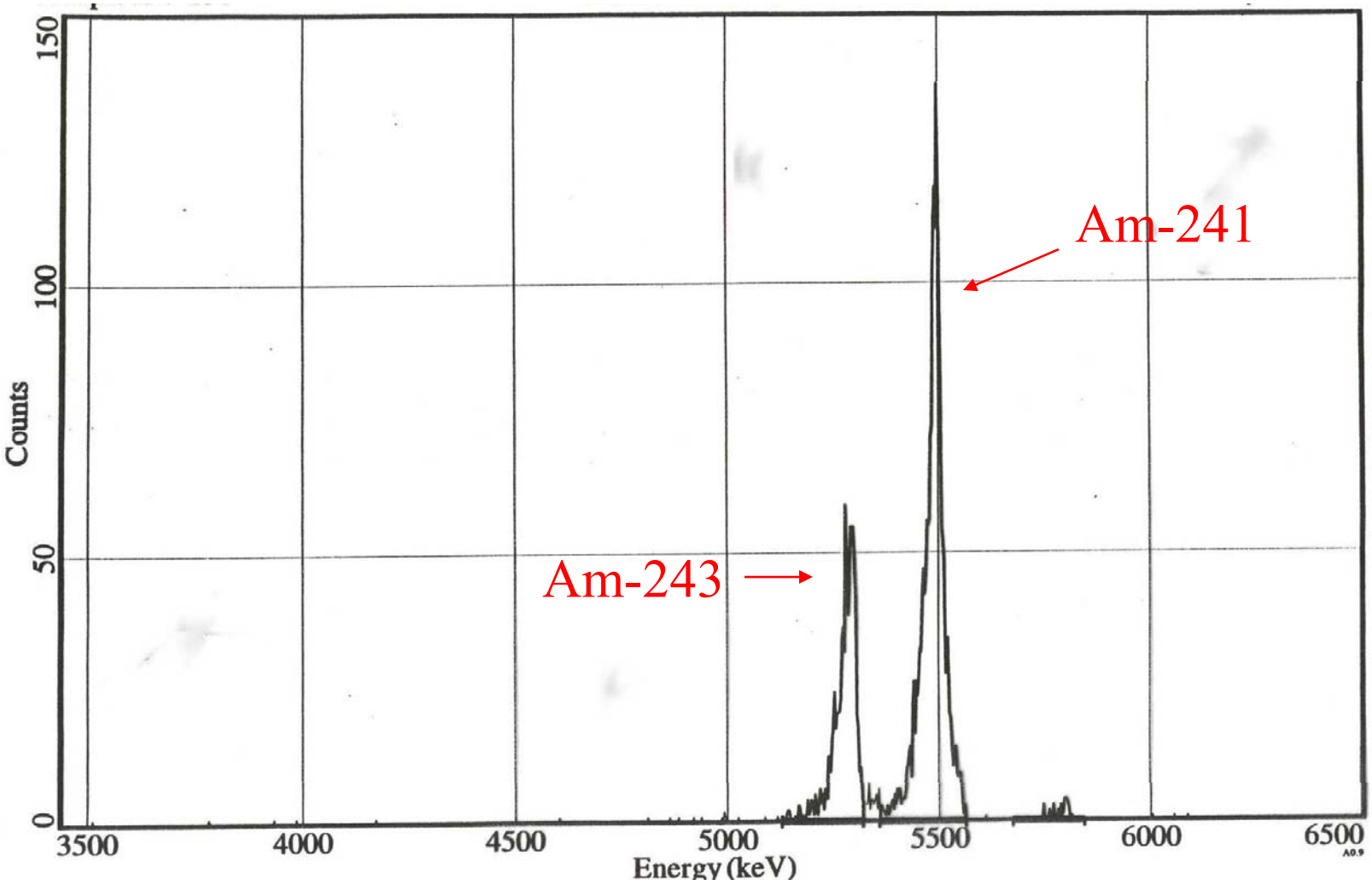
Am Spectrum after TEVA Resin Separation

Lanthanide elements removed - cleaner spectrum



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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

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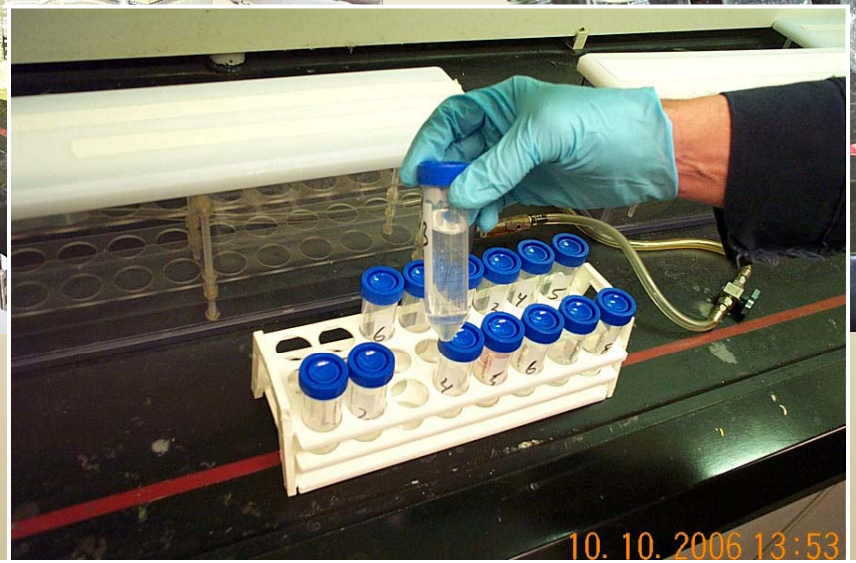
Bulk Sample Preparation Steps

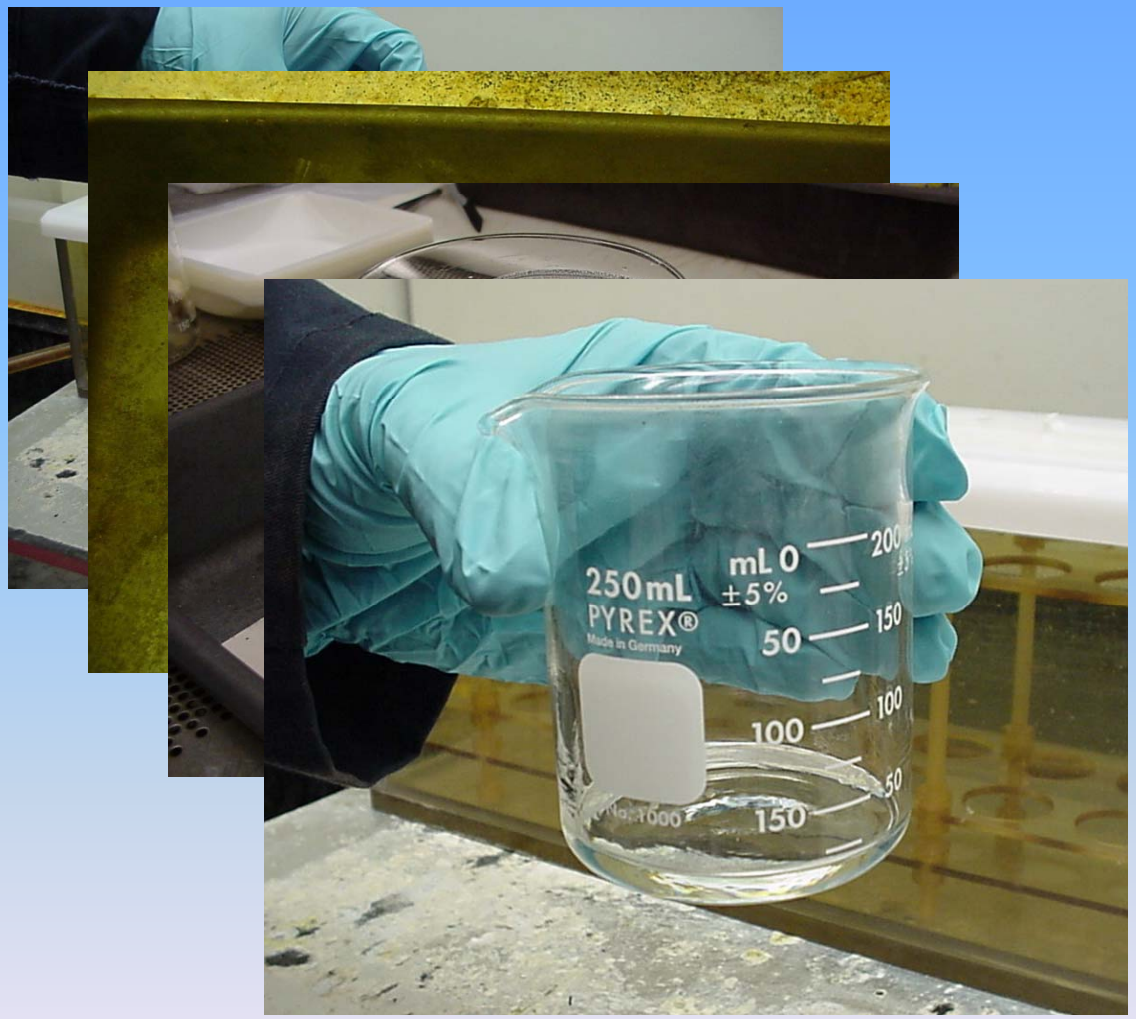
- Volume Reduction
  - Precipitation
  - Evaporation
  - Ion Exchange
- Sample Modification
  - Digestion
  - Leach
  - Fusion

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)



FlowChart of with time frames Radiostrontium Emergency Method At SRS



12 Samples of Milk, 100 mL Aliquots

↓

Calcium Phosphate Precipitation + Acidification and Wet Ash

↓

Furnace @ 550C

↓

Separation using Sr-Resin and Mounting

↓

Gas-Flow Proportional Counting

3 Hours

30 – 60 Minutes

2.5 Hours

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

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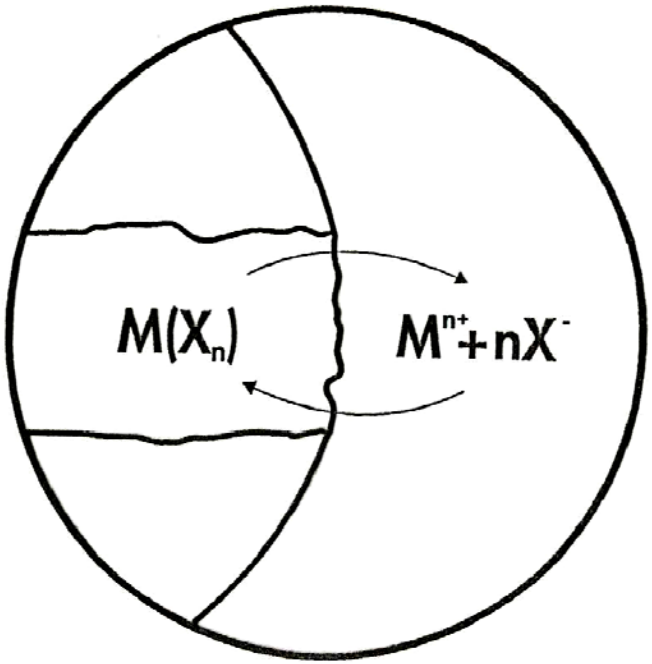
Separation of target analyte(s) from interferences

- Precipitation or Co-Precipitation
  - Adjustment of sample conditions that causes target analytes to fall out of solution
- Ion Exchange
  - Retention of target analytes on a activated support
- Solvent Extraction
  - Liquid to Liquid Extraction Separation
- Extraction Chromatography
  - Retention of target analytes in a supported liquid to liquid system.

Metal Anion Complex Formation



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

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

Absorption of elements from HCl solutions by Anion Resin

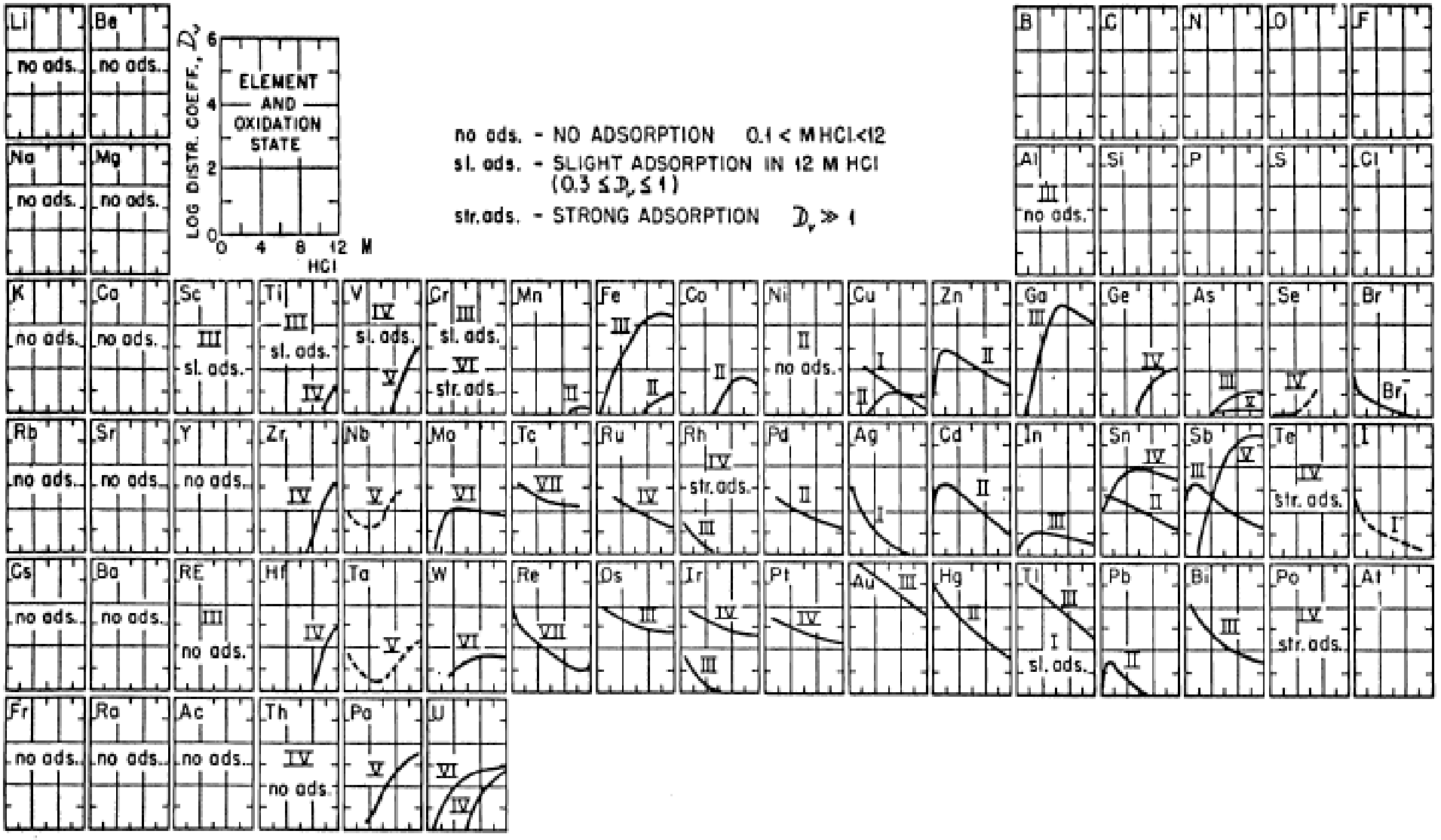


Fig. 6. Anion exchange distribution coefficients in HCl solutions.(Dowex 1-X10) (Ref. 3)

Absorption of elements from HNO_3 solutions by Anion Resin

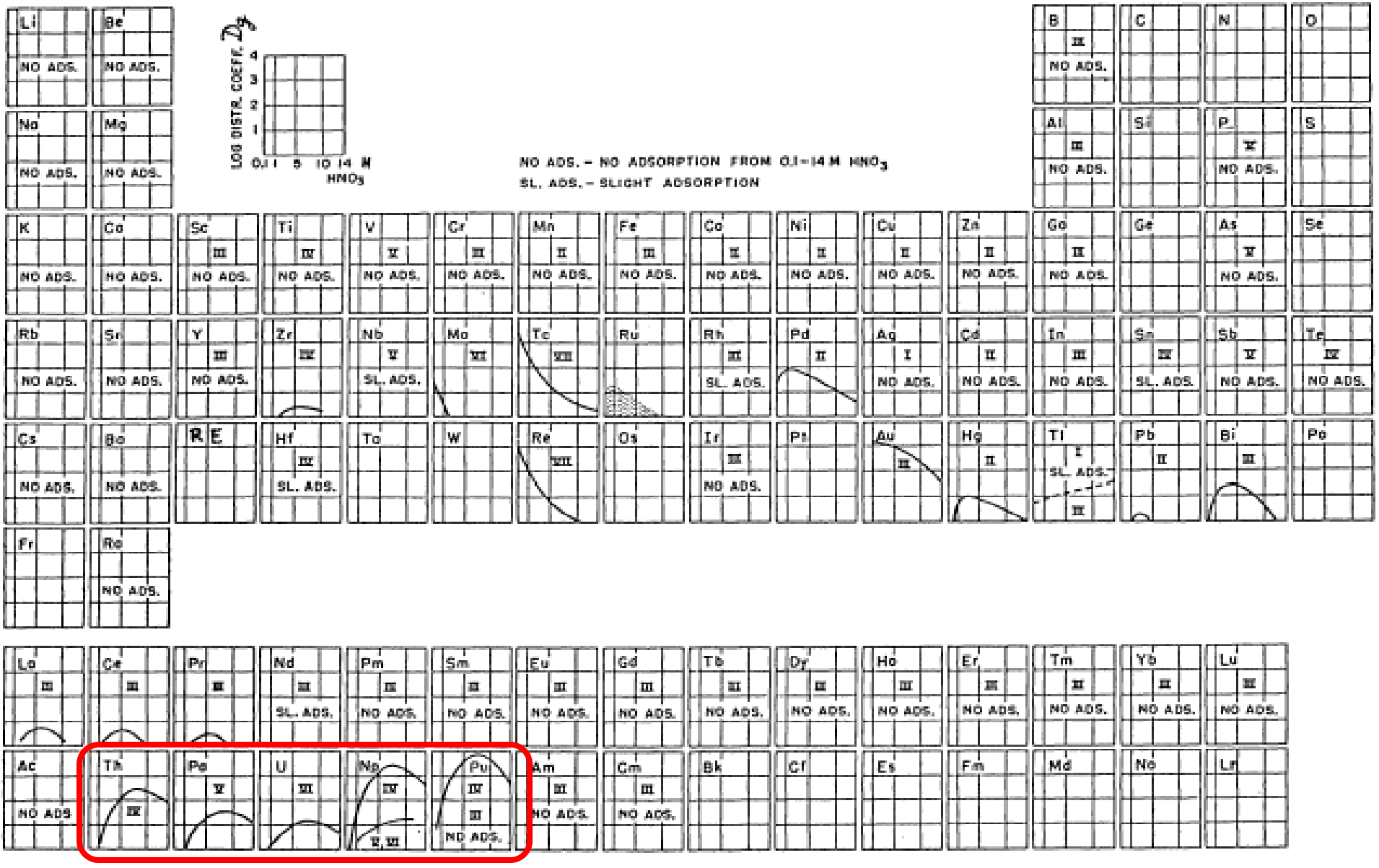


Fig. 7. Anion exchange distribution coefficients in HNO_3 solutions. (Dowex 1-X10) (Ref. 4)

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Extraction Chromatography

Solvent Extraction

Column Chromatography

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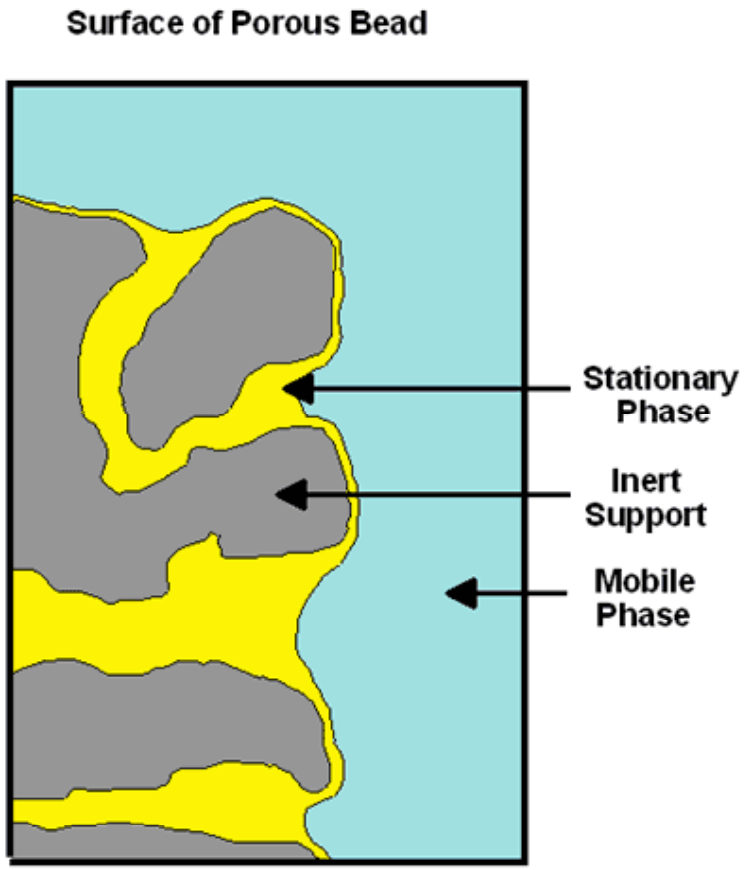
Extraction Chromatographic Resin



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:
TRU Resin SPS
Part #:
Lot:
Amount:
Sr Resin
Part #: SR-B100-A
Lot: SRA03032
Amount: 100 grams

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Batch Reaction / MnO2 Resin for Ra Analysis

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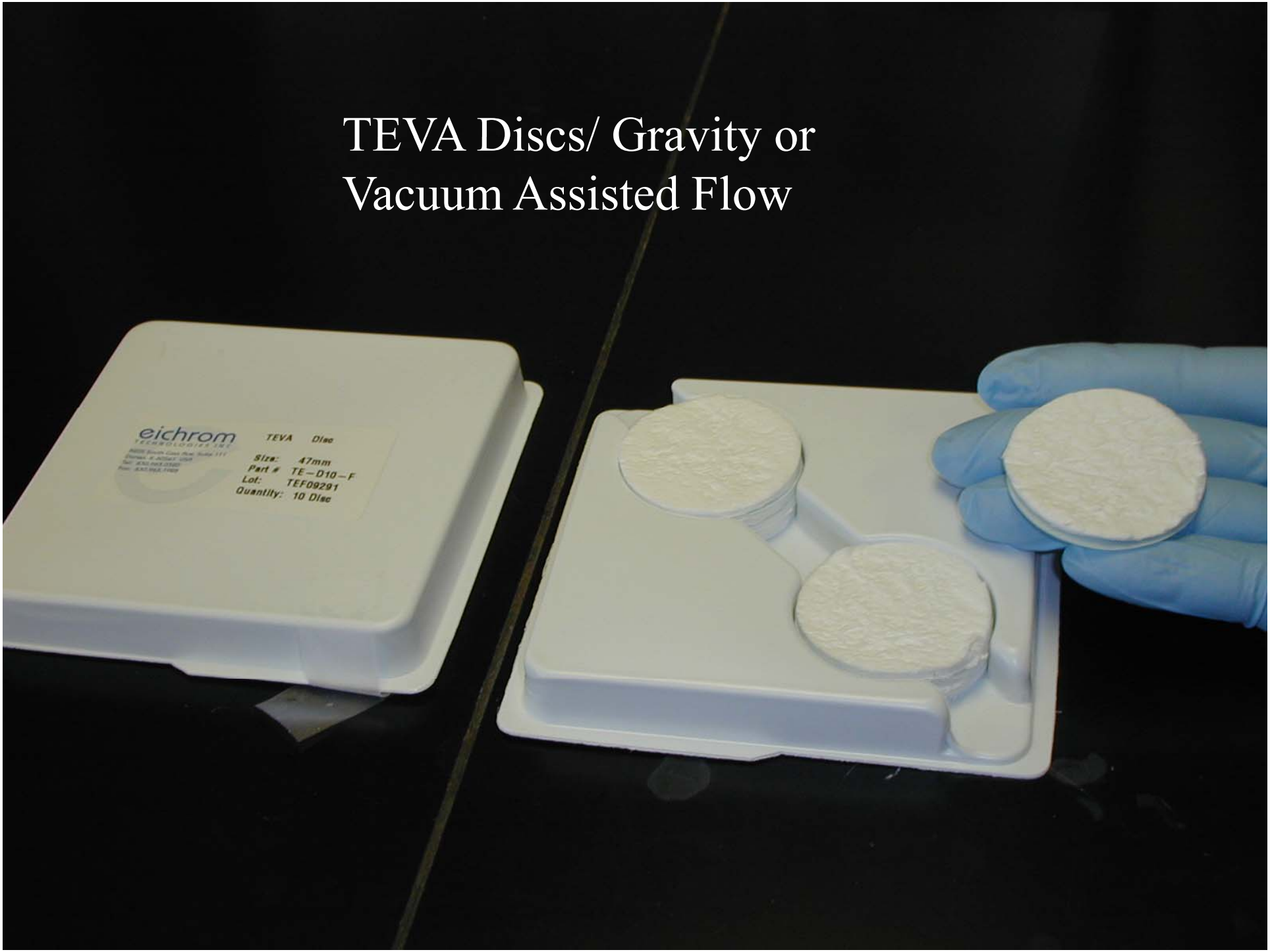
Column Format / Gravity Flow

Gravity Flow vs. Vacuum Assisted


TEVA Discs/ Gravity or
Vacuum Assisted Flow
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TEVA Disc
Size: 47mm
Part # TE-D10-F
Lot: TEF09291
Quantity: 10 Disc

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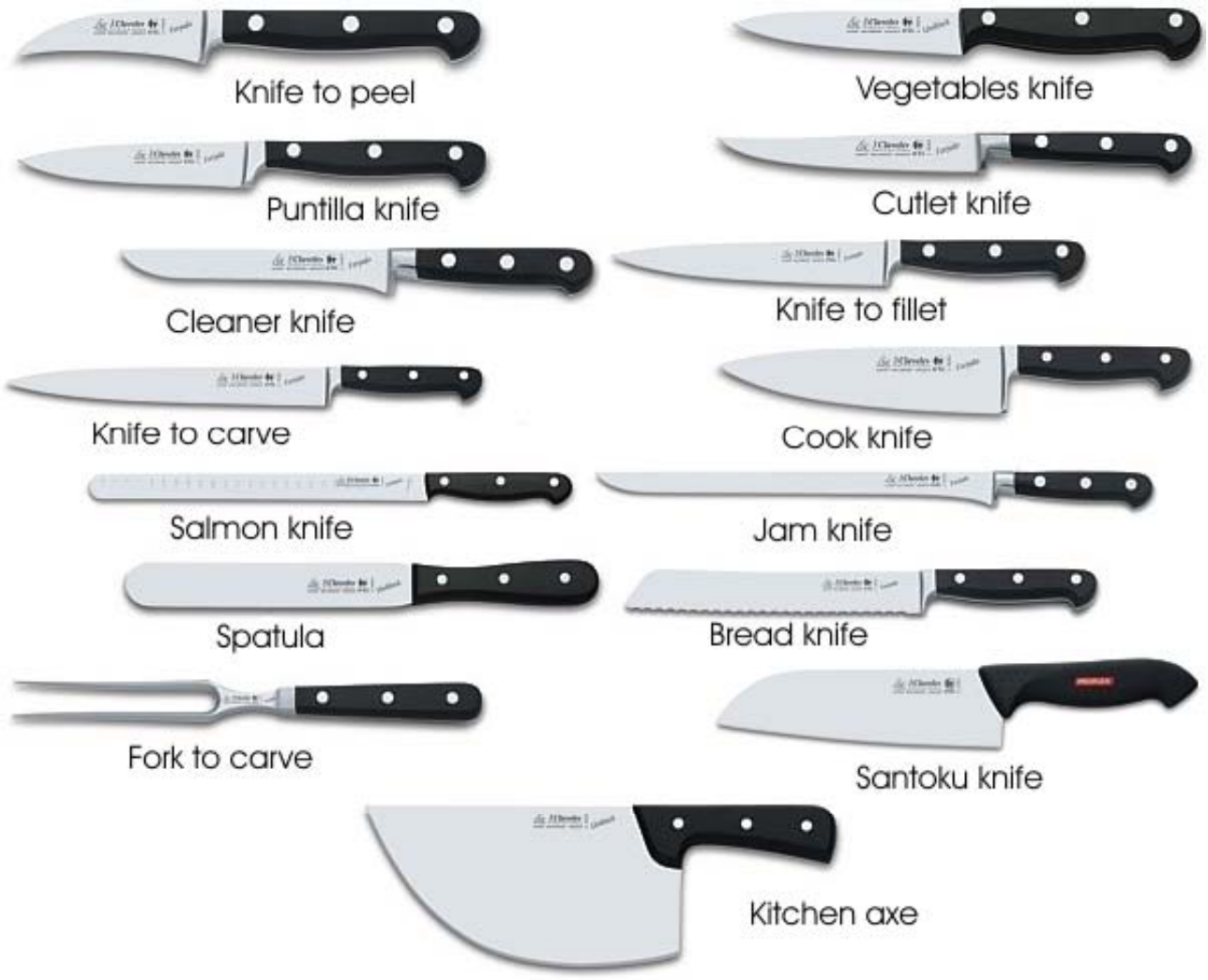
Selecting the right utensil for the job



Our Products

Eichrom commercialized its breakthrough chemical separation techniques in the 1990s. Today, accredited laboratories and regulatory agencies worldwide trust Eichrom's line of analytical-chemistry products, all developed through the expertise of our team of dedicated chemists.

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		^3H	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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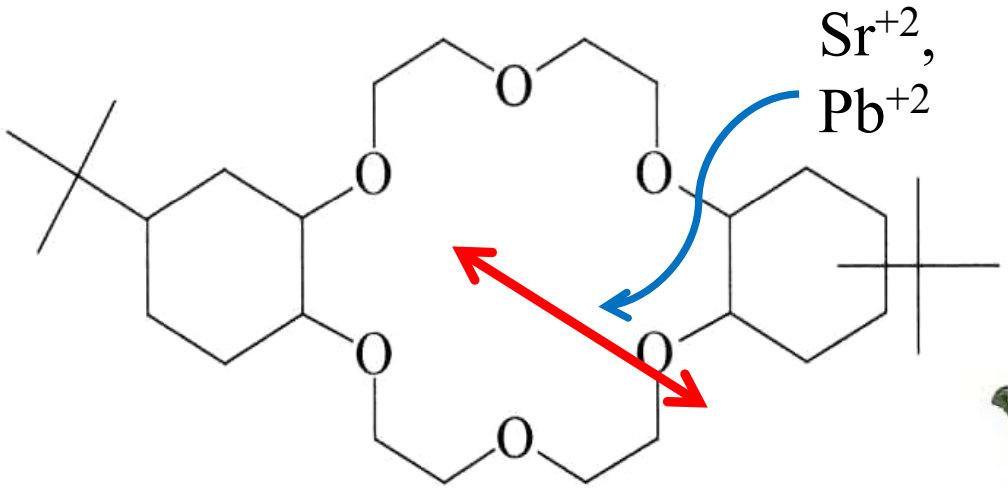
Sr Resin

di-t-butylcyclohexano 18-crown-6



Diluent: 1-octanol

Ionic
Recognition,
size and charge

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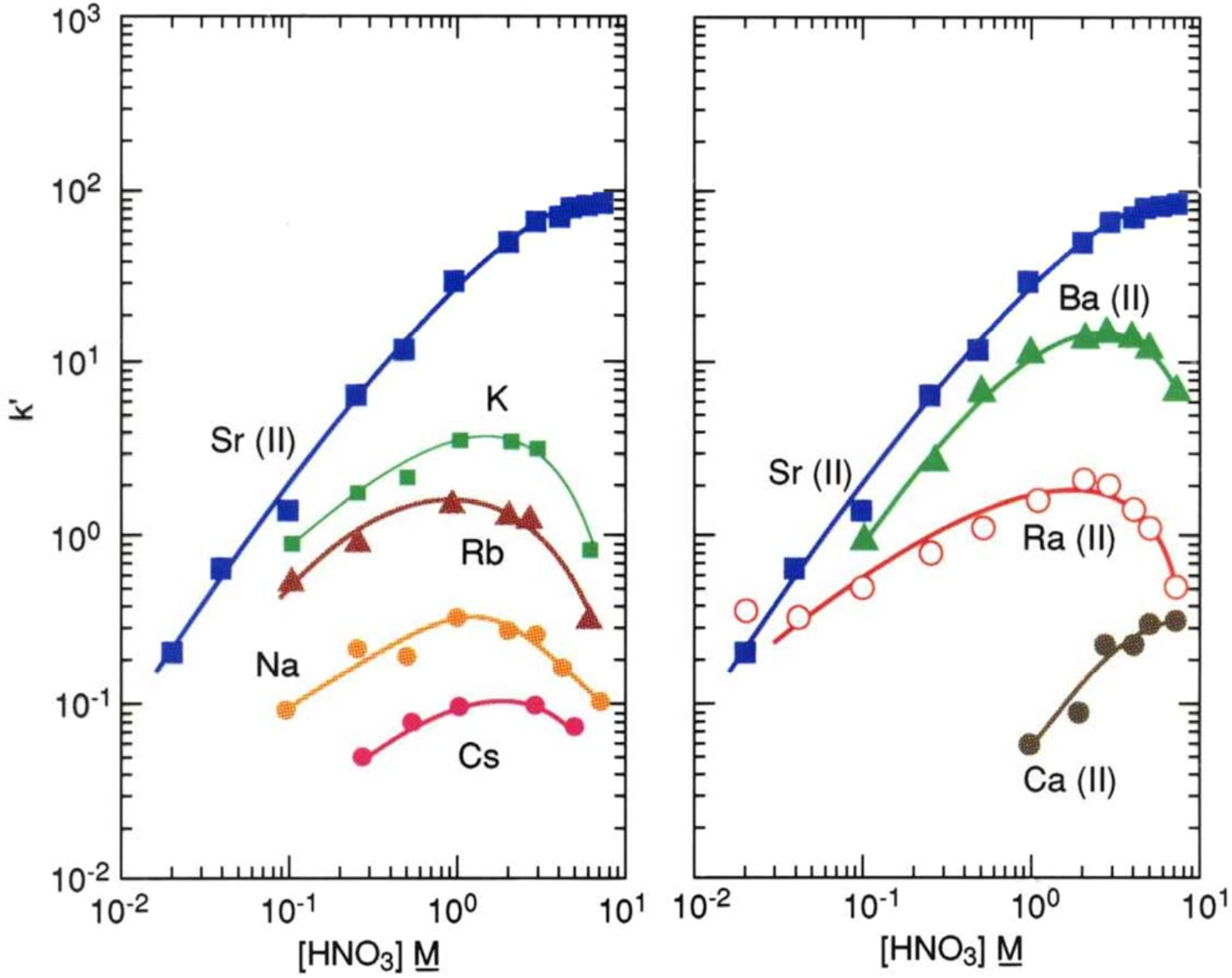
Acid dependency of k' for various ions at 23-25°C.
Sr Resin



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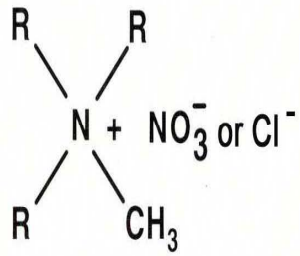
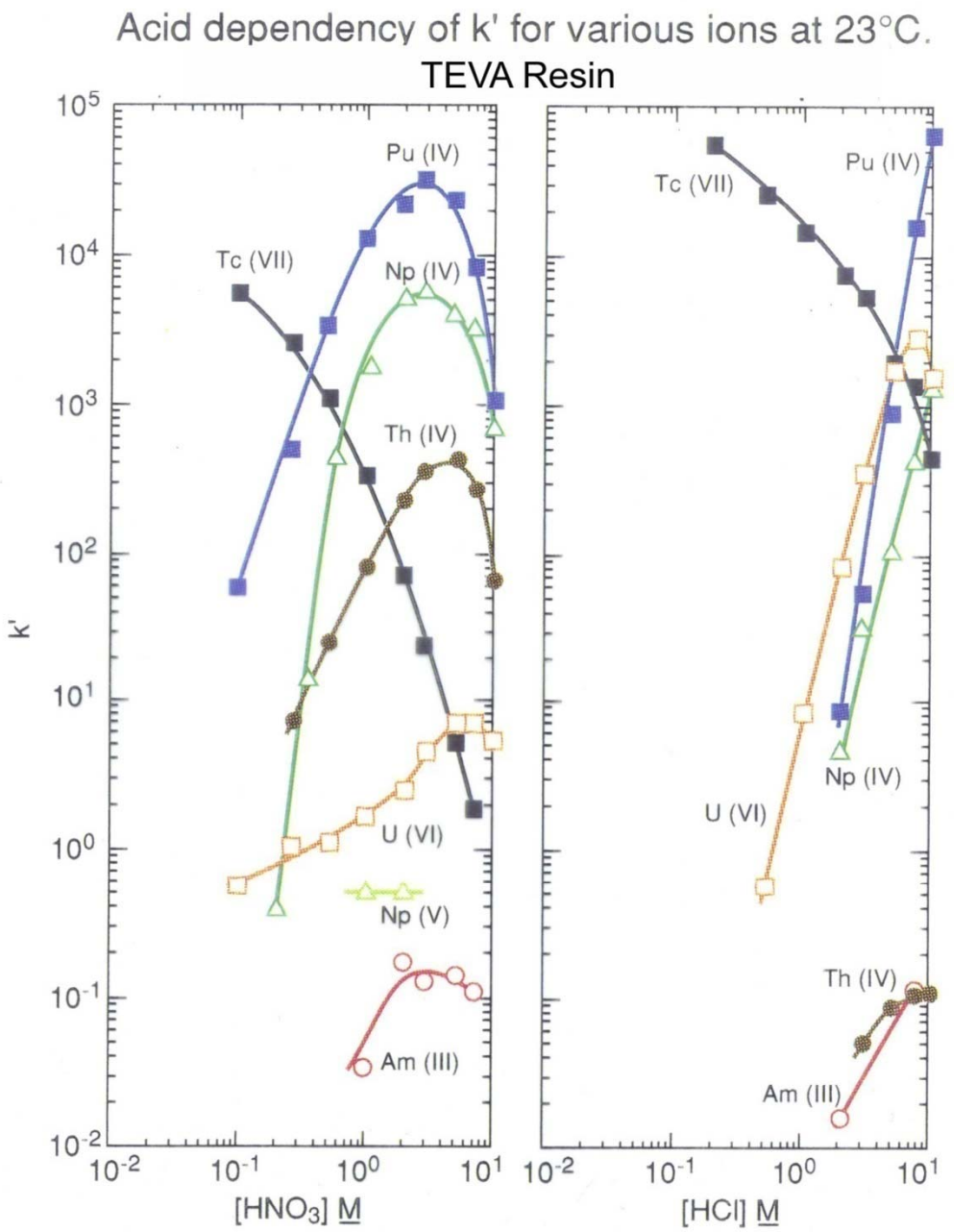
Anionic Extractant
TEVA Resin

Trialkylmethylammonium Nitrate or Chloride



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



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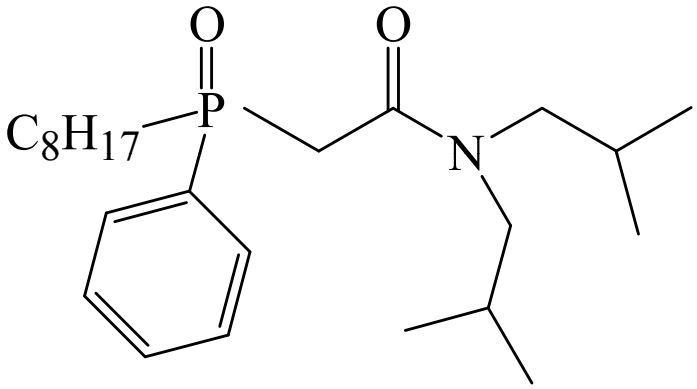
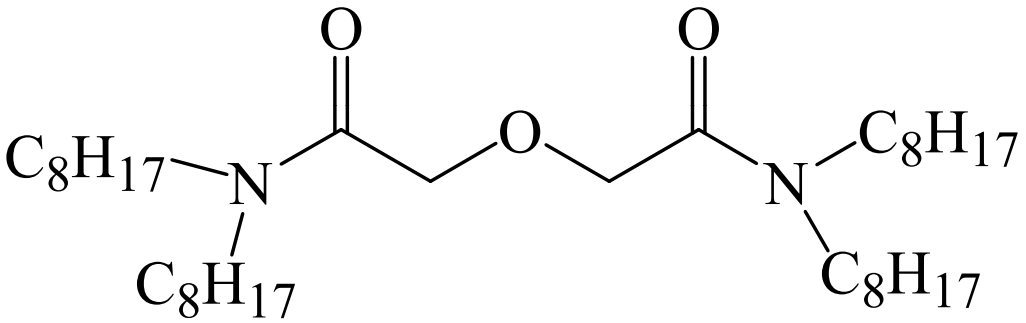
TRU Resin: Neutral Extractant

DGA Resin: Neutral extractant/ ionic recognition



TRU (CMPO)

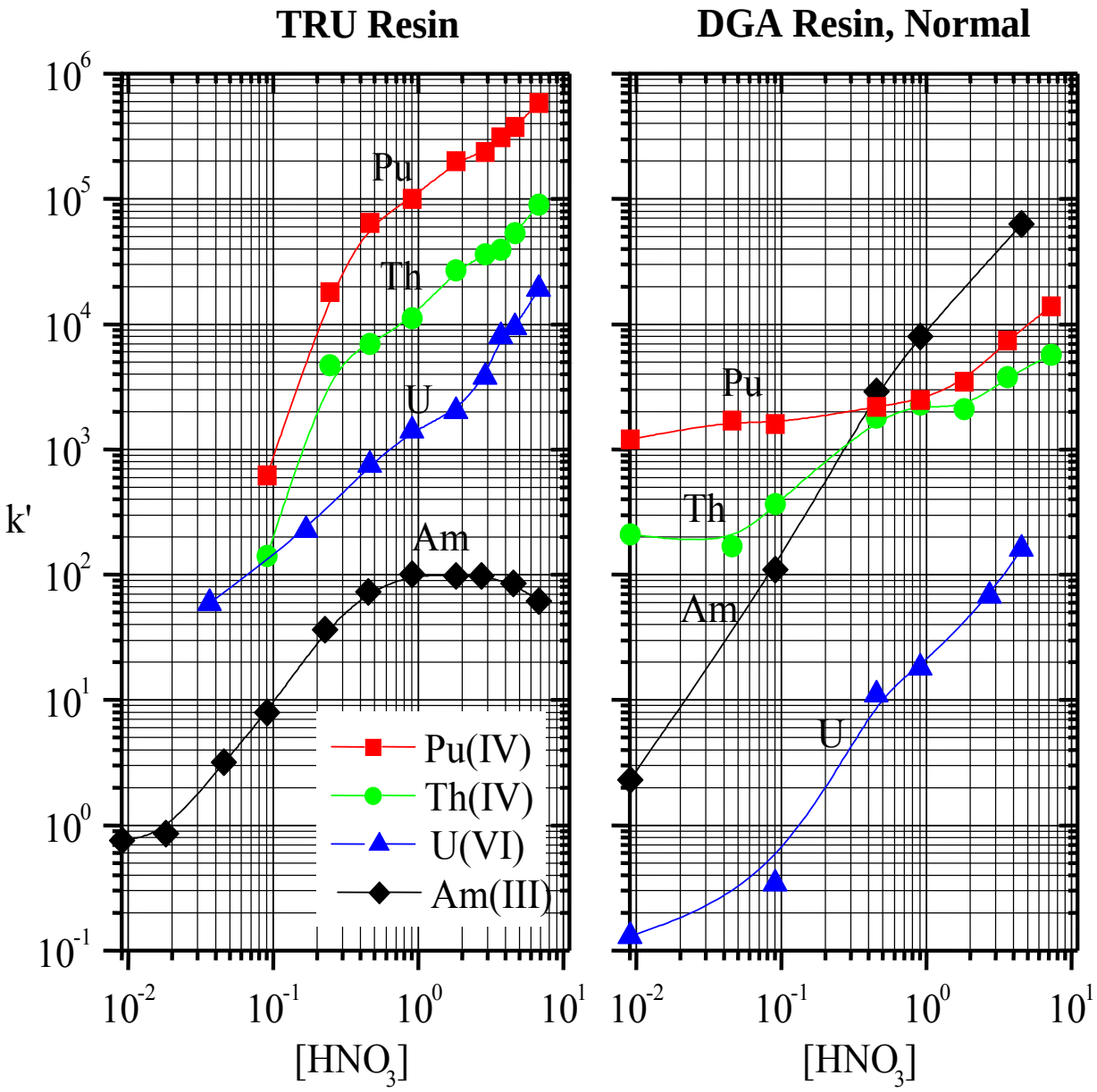


DGA

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

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

Actinides on TRU vs DGA out of HNO_3



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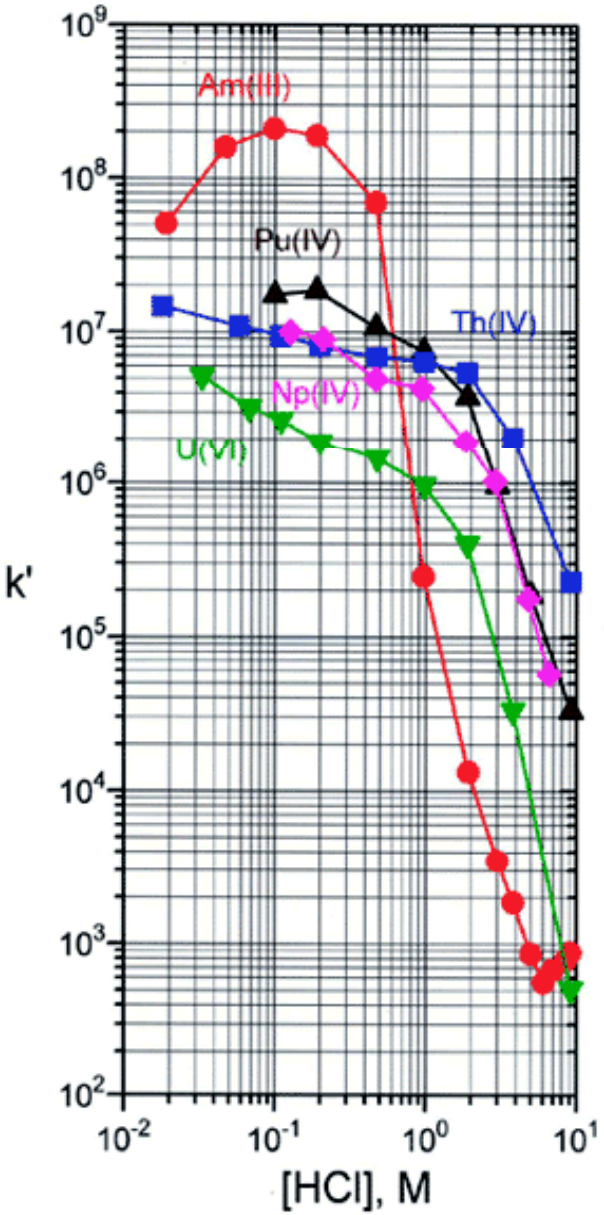
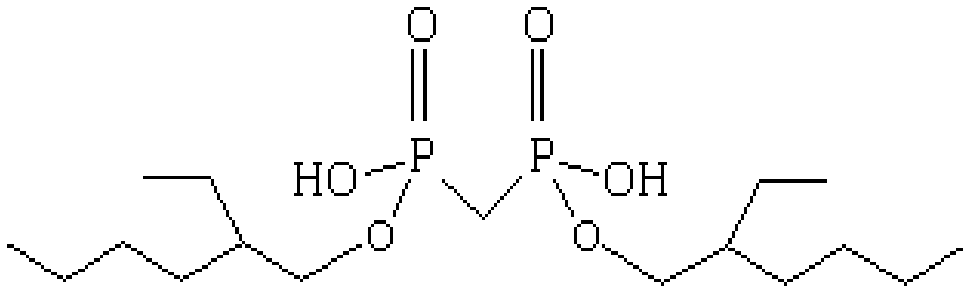


Actinide Resin uptake of various actinides with DIPEX® extractant (Liquid Chelating Exchanger)



Data developed at Argonne National Laboratory, USA

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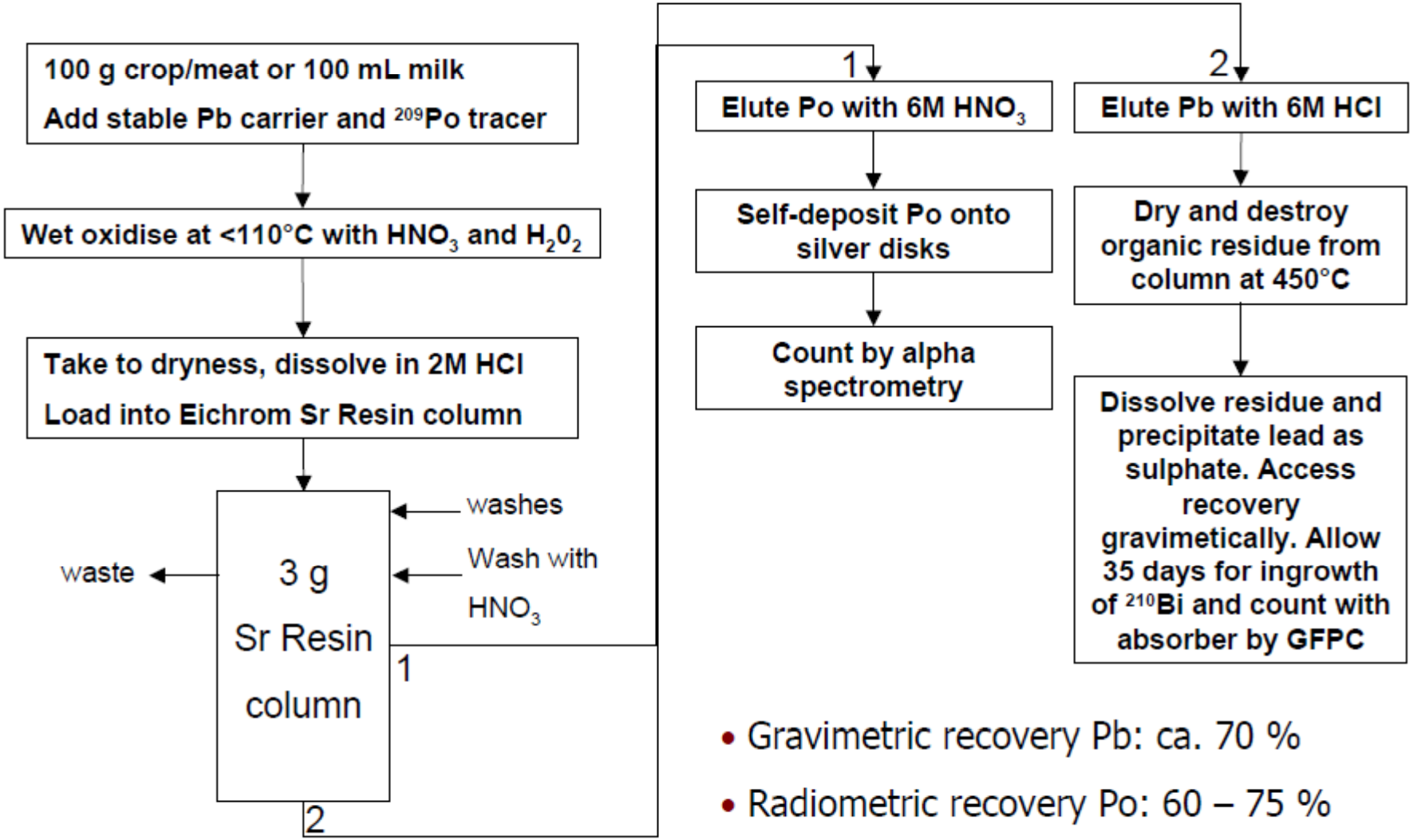
Pb and Po in milk, crop and animal samples (Dell)



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

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)

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

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:
  - 15 mL of 8M HNO3
  - 5 ml 3M HNO3-0.05M oxalic acid
  - 7 ml 8M HNO3
- Sr Elution: 13 ml 0.05M HNO3

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

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Your separation resin drawer!

Hows

Versatility

Results

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¿ Questions ?