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Radiochemistry Webinars
Nuclear Materials Analysis–Chemical Methods

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Meet the Presenter…

Dr. Brian Powell

Dr. Brian A. Powell is an Associate Professor in the Department of Environmental Engineering and Earth Sciences at Clemson University and holds the Fjeld Professorship in Nuclear Environmental Engineering and Science. His research focuses on understanding and prediction of the physical, chemical, and biological processes which govern the mobility of radionuclides in natural and engineered systems. He previously held postdoctoral appointments at the Lawrence Livermore National Laboratory and the Lawrence Berkeley National Laboratory. Dr. Powell earned a B.S. in Chemistry from the University of Montevallo and M.S. and Ph.D. in Environmental Engineering and Science from Clemson University. Dr. Powell is the winner of the 2014 South Carolina Governor's Young Researcher Award for Excellence in Scientific Research and the 2011 Clemson University Sigma Xi Young Investigator of the Year. He also serves on the Radiation Safety Committee of the USEPA Scientific Advisory Board and is a member of the National Council on Radiation Protection, Program Activity Committee 5: Environmental Radiation and Radioactive Waste Issues. Dr. Powell has published over 50 refereed journal publications, 16 research reports, and made over 100 technical presentations on these topical areas. He has conducted sponsored research in a wide range of projects dealing with topics of nuclear forensics, evaluation of nanoparticle behavior, sorption and environmental transport of plutonium, development of radiation detection and radiation detection laboratory courses, iodine, radium, strontium geochemistry in wetland and subsurface sediments, radionuclide geochemistry of saltstone and solid waste performance assessments at the Savannah River Site, measurement of thermodynamic parameters supporting advanced fuel cycle chemistry, and related topics. These research projects have received over $13.9M in funding from the National Science Foundation, the Department of Energy, the Nuclear Regulatory Commission, the Department of Homeland Security, the National Nuclear Security Agency, and Savannah River Nuclear Services (through the South Carolina Universities Education and Research Foundation). The knowledge gained from this work can be used to evaluate risk posed by subsurface contamination, to design remediation strategies for contaminated sites, and to facilitate the use of safe disposal practices.

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CLEMSON UNIVERSITY

Nuclear Materials Analysis- Chemical Methods

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U.S. Department of Energy Carlsbad Field Office

TRAINING AND EDUCATION SUBCOMMITTEE

Scope

- Goal is to use chemical processes to isolate an isotope of interest from a complex sample matrix.
- Need careful laboratory work and procedures based on known and reliable chemistry to produce pure samples for analysis
  - Note these methods are not unique to nuclear forensics. Rather they are widely applied.
- Radioanalytical methods are generally applied to aqueous liquids so assumption in todays lecture is that sample dissolution will have already occurred
  - A good overview of sample preparation and dissolution was given by Prof. Amy Hixon in the April 21, 2016 webinar "*Sample Matrices and Collection, Sample Preparation*"
    - https://www.icln.org/webinars/sample-matrices-and-collection-sample-preparation/
  - A presentation on Analytical chemistry of uranium and plutonium was given by Prof. Ralf Sudowe on October 11, 2012
    - https://www.icln.org/webinars/analytical-chemistry-of-uranium-and-plutonium/

Relevant chapters

- *Nuclear Forensics Analysis* by Kenton J. Moody, Ian D. Hutcheon, and Patrick C. Grant
  - Chapter 4: Chemistry and Nuclear Forensic Science
  - Chapter 8: Collateral Forensic Indicators
  - Chapter 10: Radiochemical Procedures

Other Good Resources

- MARLAP
  - MARLAP Chapter 12: Laboratory Sample Preparation
  - MARLAP Chapter 13: Sample Dissolution
  - MARLAP Chapter 14: Separation Techniques
- Radiochemistry Monographs
  - http://library.lanl.gov/radiochemistry/elements.htm
- Review texts
  - Chemistry of the Actinide and Transactinide Elements, http://www.springer.com/chemistry/inorganic+chemistry/book/978-94-007-0210-3
  - Chemistry of Plutonium, J. Cleveland, 1979
    - Only used texts available

Outline

- Introduction
- Sample considerations
- Use of tracers
- Solvent Extraction
- Ion Exchange
- Extraction Chromatography

Chemical separations and analysis in nuclear forensics

Table 2. Classes of Techniques Applied to Nuclear Forensics

Class of Techniques	Examples	Applications
Bulk analysis	X-ray fluorescence (XRF) and X-ray diffraction (XRD)	Characterize the elemental and isotopic composition of the bulk material
	Inductively coupled plasma mass spectrometry (ICPMS)	Detect and quantify trace constituents
	Gamma spectrometry	
Imaging	Optical microscopy	Determine sample homogeneity or heterogeneity
	Scanning electron microscopy	Assess material morphology and microstructure
Microanalysis	Secondary ion mass spectrometry (SIMS)	Quantitatively or semiquantitatively characterize the individual constituents of the bulk material
	X-ray microanalysis	Particle analysis
		Analyze thin layers or coatings

Keegan et al., *Anal. Chem.* 2016, 88, 1496−1505

Schwantes et al., *Anal. Chem.* 2009, 81, 1297−1306.

Sample matrices

- Samples may vary in composition, size, physical form, and purity
  - Soil, sediment
  - Biota
  - Water
  - Gas
  - Solids (anthropogenic metallic or metal oxide solids)
  - With or without traditional forensics evidence present
- This presentation will cover radionuclide separation procedures required when analyzing complex, heterogeneous samples
- Procedures are generally applicable to aqueous liquids

Considerations of sample matrix and processing

- Potentials for sample loss during processing
  - Volatilization
  - Reactions between sample and container
  - Losses due to precipitation/dust deposition
- Contamination and cross contamination
- Cleaning of labware
- Complete dissolution of a solid sample
- Loss of secular equilibrium during radiochemical separation

Carriers and Tracers

Carriers and Tracers

- Carriers and tracers are frequently added before sample manipulation to subject them to the same chemical treatment as the target analyte
- Many separations are seeking 10^{-15} to 10^{-10} molar concentrations of ions
  - Example ^{210}Po 500 dpm = 5E-14 g
  - Common analytical techniques cannot be used: spectroscopy, gravimetric analysis, electrochemistry, etc.
  - Such trace concentration can be drastically effected by macroscopic constituents
- Solution is to add:
  - Carrier: macroscopic stable isotope
  - Tracer: microscopic radioisotope
  - Note: the carrier or tracer isotopes must be different that the one you are looking for (unless you are using the method of standard additions)

Tracers

- Tracers are used to determine chemical yield of a radionuclide of interest during physical/chemical separations
- Generally prefer isotopic tracer (i.e. the same element but a different isotope) but in some cases this is not possible: ^{133}Ba frequently used as a tracer for ^{226}Ra/^{228}Ra separations
- Generally tracer should be at microscopic mass concentrations and not add "mass" of the analyte of interest to the system
- Since tracer isotope will behave similar to isotope of interest, percent recovery of tracer can be used as chemical yield for isotope of interest
- Example with ^{242}Pu or ^{238}Pu tracer when doing analysis for ^{239}Pu
  - Add ^{238}Pu to sample at a few times the expected ^{239}Pu concentration
  - Perform radiochemical separation of Pu
  - Quantify the mass/activity of ^{238}Pu and ^{239}Pu
  - Assume ^{239}Pu and ^{238}Pu behave similarly

$$\text{Chemical Yield}=Y=\frac{\text{mass/activity of } ^{238}\text{Pu recovered}}{\text{mass/activity of } ^{238}\text{Pu added}}$$

$$[^{239}\text{Pu}]\text{sample}=\frac{[^{239}\text{Pu}]\text{measured}}{Y}$$

Carriers

- Based on the concept that separations are more easily accomplished when performed on a macroscale
- Add carrier to raise the chemical concentration of an analyte
  - Example stable Sr carrier for ^{90}Sr precipitation
  - Stable Sr: ^{84}Sr, ^{86}Sr, ^{87}Sr, ^{88}Sr
  - Same number of protons and electrons so will behave chemically similar (i.e. chemical phenomena such as precipitation, complexation, and redox chemistry will apply equally to all isotopes on this scale)
  - If 99.95% of stable Sr precipitates as $SrSO_4(s)$ then 99.95% of ^{90}Sr will precipitate as well
- Therefore, a carrier can be used to increase the effective chemical concentration of a radionuclide and be used as a chemical yield indicator (gravimetrically)
  - Example: added 10mg Sr and recovered 9.5 mg => Chemical yield is 95%

Hold-back carrier

- Carrier that is added to improve separation of one radionuclide over another at low concentrations
- Regular carrier: separate radionuclide of interest from solution
- Hold-back carrier: keep interfering radionuclide in solution while radionuclide of interest is precipitated.
- Think complexation!

Method of Standard Additions

- Typically employed when a complex matrix is encountered and the influence of other ions on the separation or measurement is unknown
- Generally when a calibration curve is used, the calibration standards are prepared from pure solutions
- When the sample may be present in an unpure solutions, the calibration standards may not be valid
- Method of standard additions is essentially generating a calibration curve with spiked samples
- Run analysis with unspiked sample then run analysis of several samples with various concentrations of the analyte of interest spiked into each sample.
- Generally want samples spanning multiples of 3x to 5x the expected concentrations

Example: expect 5 dpm ^{239}Pu	
Sample	Spiked ^{239}Pu (dpm)
A	0
B	15
C	25
D	75

- Note: This is typically done without a tracer and it is assumed that the chemical yield is consistent for all samples. A tracer can be used to gain accuracy

Solvent Extraction (i.e. liquid-liquid extraction)

Solvent extraction

- Solvent extraction = the process of selectively removing a solute from a liquid mixture with a solvent. Separation is based on unequal distribution of a solute between two immiscible solvents
  - i.e. aqueous and organic solvents
  - $[An]_{aqueous} \neq [An]_{organic}$
- Ions (particularly highly charged actinides) are strongly hydrated and will likely remain in polar aqueous phases
- Extractants can be added to complex the solute and generate a species which will extract into the organic phase
- Generally lipophilic complexants with O, N, S donor atoms used as extractants

Solvent Extraction Procedures

- Mix organic and aqueous phases to form a fine dispersion of each solvent
- Then separate into two distinct layers
- Once equilibrium is achieved, the concentration of solute in one phase is directly related to the concentration in the other phase by a distribution coefficient (K_d):

  $$K_d = [M]_{organic}/[M]_{aqueous}$$ (unitless number)

- Example: Assume equal volumes are used for an extraction and a K_d of 60 is determined:
  - 60x is in the organic phase
  - 1/61x is in the aqueous phase
  - With increasing K_d, more solute will be detected in the organic phase

Distribution Ratios

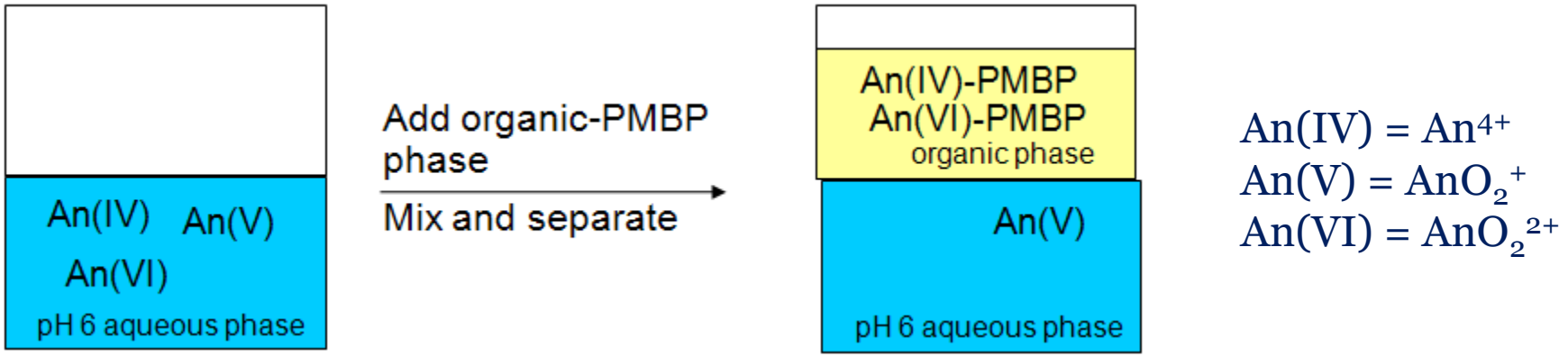
- Solvent extractions are repeated extractions to quantitatively extract a solute from a liquid
- K_d are useful terms but do not contain additional speciation information
- Consider the dimerization reaction: $2[A]_{org} \Leftrightarrow [A_2]_{org}$
  - Dimerization constant K_{dimer}
- Distribution ratio is an alternative form on the K_d which can account for specific species of interest

$$D_{o/a} = \frac{[A]_{organic} + 2[A_2]_{organic}}{[A]_{aqueous}} \qquad D_{o/a} = 1 + 2K_{\text{dimer}}[A]_{organic}$$

- Can observe changes in $D_{o/a}$ in terms of changes in chemical speciation
- Extraction factor (E_f) accounts for volumes as:

$$E_f = D_{o/a} \frac{\text{volume of solvent phase}}{\text{volume of aqueous phase}}$$

Solvent Extraction



- Example: cation extraction
  - Want high K_d for M^{x+}
  - If K_d of $D_{o/a}$ ~1, may need multiple extractions
  - Solubility of M^{x+} in organic phase should be high
  - Want $\rho_{organic}$ and $\rho_{aqueous}$ to be very different to promote disengagement
  - If too close an emulsion may form

Extraction Classes

- Ion Pair Forming Extractants (or Liquid Anion or Cation Exchangers)
- Micellar Extractants
- Solvating Extractants
- Synergistic Extractants

- Each based on different chemical processes
- High dielectric constant of water supports presence of charged ionic species as discrete molecules
- Low polarity of organic solutions demands close contact between cations and anions => solutes are expected to be discrete electroneutral species

Acidic Extractants

- Liquid ion exchangers, chelating agents, micellar systems
- Exchange a number of monovalent ions (H^+) equivalent to the formal charge of the extracted cation
- Liquid/liquid cation exchangers/chelators
  - $M^{x+}(aq) + nHL_{org} \Leftrightarrow ML_{n,org} + {}^{x-n}H^+$
- Micellar extractants
  - $M^{x+}(aq) + (HL)_{n,org} \Leftrightarrow MH_{n-x}L_{n,org} + {}^{x-n}H^+$
- Implies that extraction of metals into organic phases favors low acidity
- Metal ion can be stripped at high acidity

- Example: HDEHP, bis(2-ethylhexylphosphonic acid)
- Two P-O-C alkyl ester bonds which are subject to radiolytic instability
- Make phosphonic (RO)P(O)OH group into phosphinic $R_2P(O)OH$ to increase radiolytic stability
- Greater basicity of functional group => stronger metal ion binding

Solvating Extractant Systems

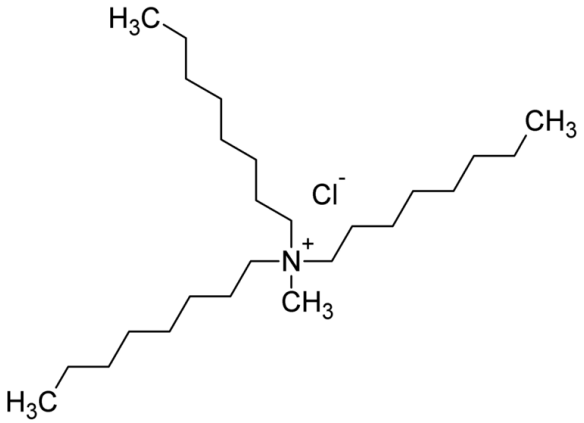
$$M^{n+}(aq) + {}^{n}X^{-}aq + nS_{org} \Leftrightarrow MX_nS_{n,org}$$

- Tributyl phosphate is one of the most important solvating extractants for U and Pu purification
  - Basis of PUREX process (Plutonium and Uranium Recovery by Extraction)
  - Extracts U and Pu and leaves Np, Am, Cm, fission products behind
  - $Pu^{4+} + 4NO_3^- + 2TBP \Leftrightarrow Pu(NO_3)_4(TBP)_2$
  - $UO_2^{2+} + 2NO_3^- + 2TBP \Leftrightarrow UO_2(NO_3)_2(TBP)_2$
- Current efforts are to include another extractant to recover minor actinides to reduce toxicity of waste
  - CMPO (octyl(phenyl)-N, N-dibutyl carbamoylmethyl phosphine oxide) - TRUEX
  - DIAMEX (Diamide Extraction)
  - Diglycolamides (N,N,N′,N′-tetraoctyl *diglycolamide* (TODGA))

Ion-Pair Formation Systems

$$M^{n+} + nX^-(aq) + A^+X^-(org) \Leftrightarrow MX_{n+1}A_{org}$$

- Tertiary amines $R_3NH^+X^-$ and quarternary amines $R_4N^+X^-$
- Chemistry impacted by salt and acid concentration
- Example: Aliquat 336, tri($C_{8\text{-}10}$ alkyl)methylammonium nitrate



Solvent Extraction Reagents

Multiple References, See Reference Sheet

Reagent	Conditions	An(III)	An(IV)	An(V)	An(VI)
TTA, $C_8H_5O_2F_3S$ Thenoyltrifluoroacetone	pH 0	Aqu	Org	Aqu	Aqu
	pH 4.5	Org	Org	Aqu	Org
HDEHP, $[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2PO_2H$ bis(2-ethylhexyl)phosphoric acid	pH 0	Aqu	Org	Aqu	Org
	pH 4.5	Org	Org	Aqu	Org
PMBP, $C_{17}H_{14}N_2O_2$ 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone	pH 0	Aqu	Org	Aqu	Aqu
	pH 4.5	Org	Org	Aqu	Org
DBM, $C_{15}H_{12}O_2$, 1,2-Diphenyl-1,2-propanedione	pH 5.0-5.5	Aqu	Org	Aqu	Org
	pH 8	Org	Aqu	Aqu	Org

Solvent Extraction Flow-sheet: Neutral pH

Satio and Choppin, Analytical Chem., 1983, 55, 2454-2457

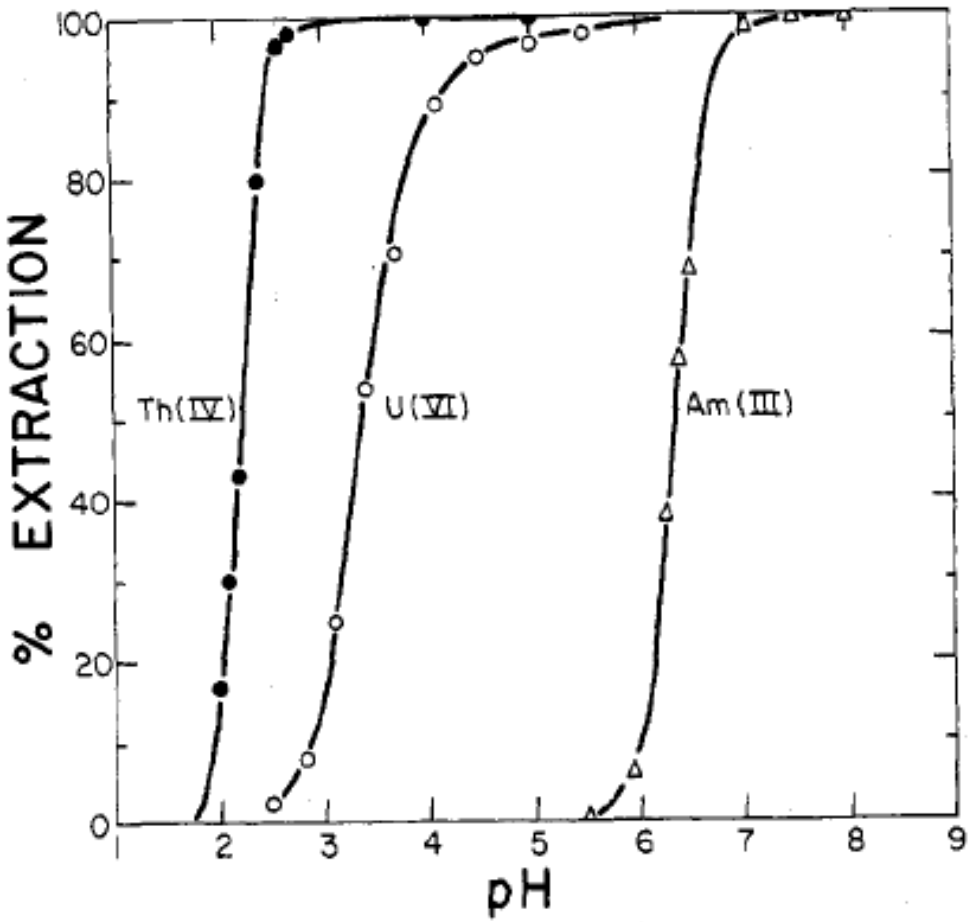


Figure 1. pH dependence of extraction: [DBM] = 0.2 M in benzene; aqueous phase; 0.7 M NaCl ionic strength; no buffer for Th(IV), 0.01 M acetate for U(VI), and 0.05 M imidazole or hydroxylamine for Am-(III); 1:1 volume ratio.

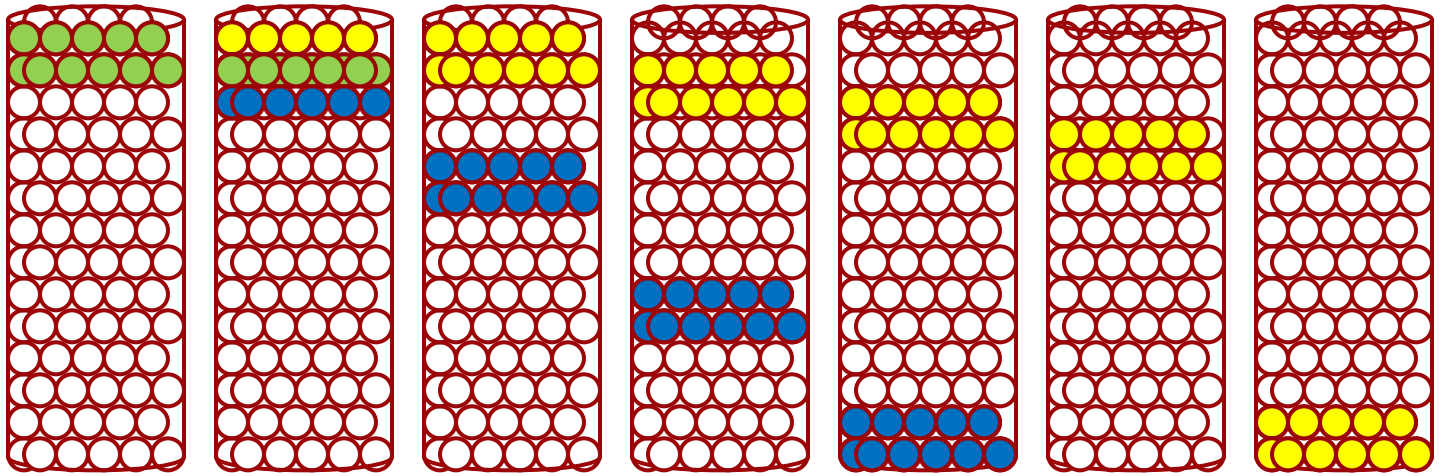
Solvent Extraction Advantages and Disadvantages

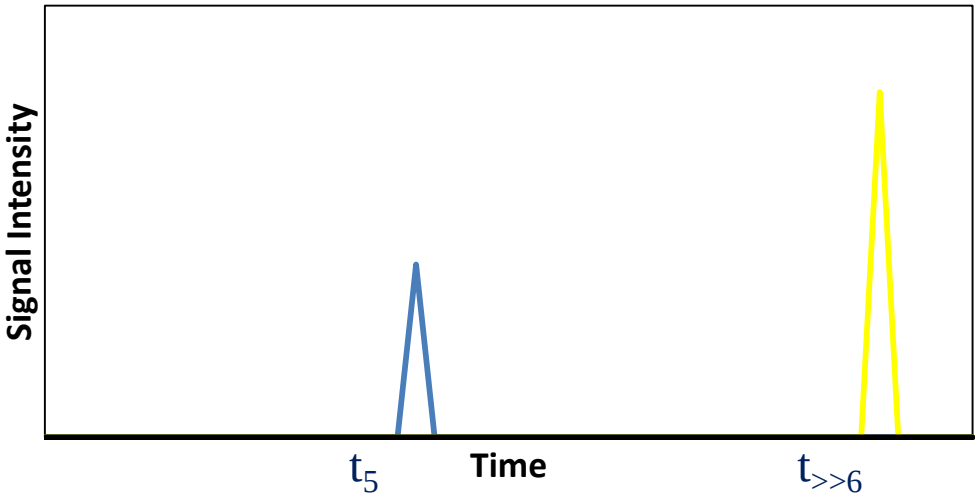
- Advantages
  - Separate large amounts of material
  - Rapid separation
  - Very selective
  - Simple equipment required
  - Distribution coefficients often independent of concentration down to trace levels
- Disadvantages
  - Flammable solvents
  - Emulsions interfere
  - Can be effected by small impurities or changes in chemical form during extraction
  - Multiple extractions may be required
  - Colloidal species cannot be extracted

Ion Exchange and Extraction Chromatography

Chromatography Column Dynamics

Chromatography = separation process based on unequal distribution of substances between a mobile phase and a stationary phase





$=R^-H^+ + A^+ \Leftrightarrow =R^-A^+ + H^+$

$=R^-H^+ + B^+ \Leftrightarrow =R^-B^+ + H^+$

=A

=B

$K_d = C_s/C_a$

C_s = analyte conc per gram of resin

C_a = analyte conc in solution

Same as K_d in sorption reaction

Separation factor (a)

$a = K_{d,A}/K_{d,B}$

Overview

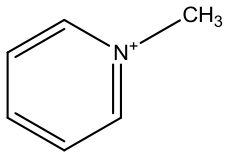
- Ion exchange/ion chromatography = based on reversible exchange between a mobile liquid phase and a solid stationary phase
- Ion exchange
  - Solid ionic phase interacts with metal ion of opposite charge
  - Resin competes with ion solvent interactions (hydration and complexation) through ion-dipole interactions and hydrogen bonding
  - Resin is insoluble but permeable inert polymeric matrix containing fixed charge groups (exchange sites) associated with mobile counter ions of opposite charge

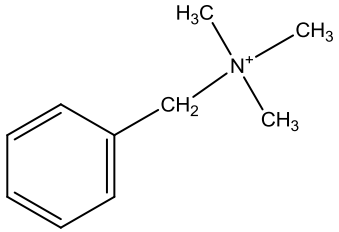
Resin Properties

- Anion exchange
  - $R^+A^- + B^- \Leftrightarrow R^+B^- + A^-$
- Cation exchange
  - $N^-X^+ + Y^+ \Leftrightarrow N^-Y^+ + X^+$
- Ideal IX resin properties
  - Hydrophilic structure
  - Reproducible form
  - Effective IX capacity
  - Rapid exchange rate
  - Chemical stability
  - Physical stability
- Resins are commonly prepared by copolymerization and functionalization of styrene and divinylbenzene

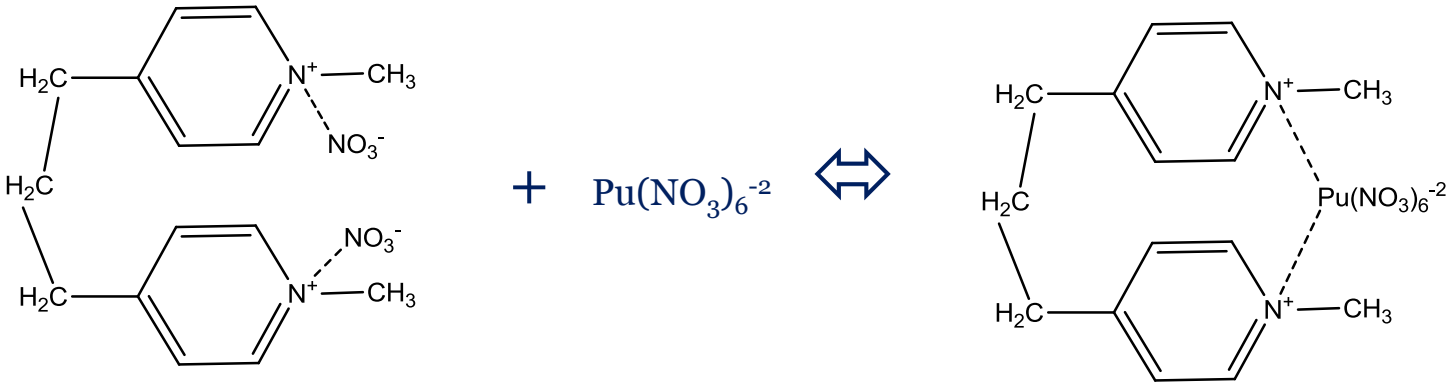
Properties of Resins

- Natural resins: zeolites, hair, soils
- Synthetics:
  - functionalized organic polymers
  - Acid or base groups
    - Amines, phenols, carboxylic acids, sulfamic acid
  - Typical cation exchange
    - Sulfonate, RSO_3^-
    - Carboxylate, $RCOO^-$
  - Typical anion exchange
    - Quaternary amines, RNH_3^+



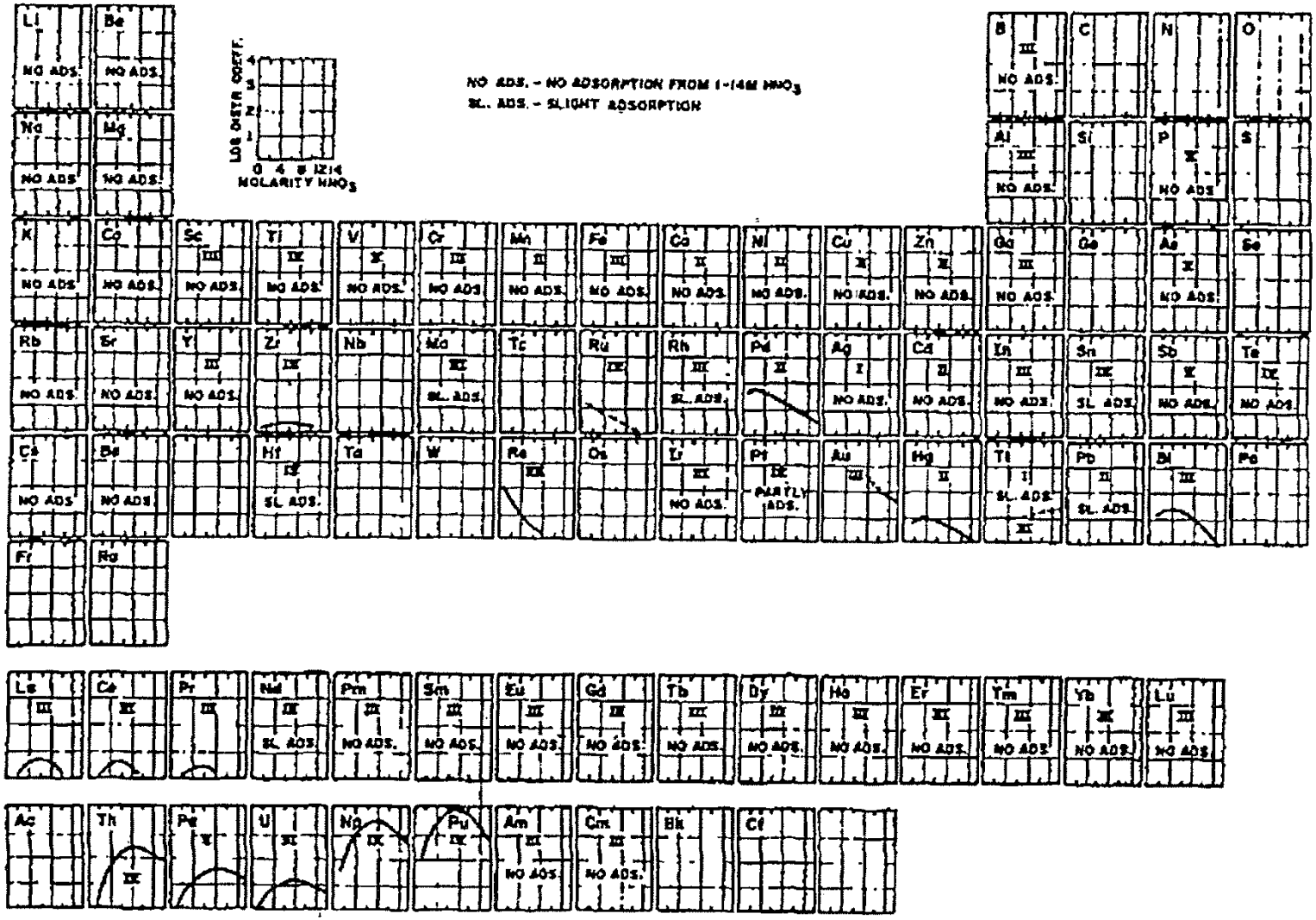


Anion exchange processes



Anion Exchange Distribution Coefficients in HNO_3

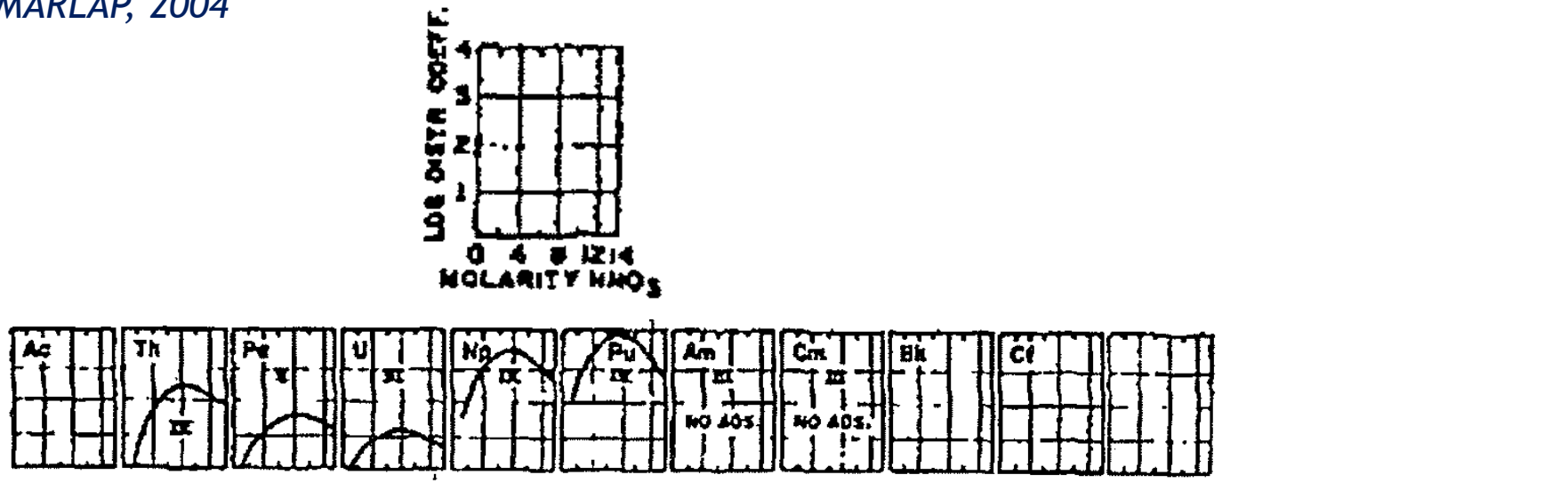
MARLAP, 2004



Distribution of elements from nitric acid onto strong-base anion exchange resin.

Anion Exchange Distribution Coefficients in HNO_3

MARLAP, 2004

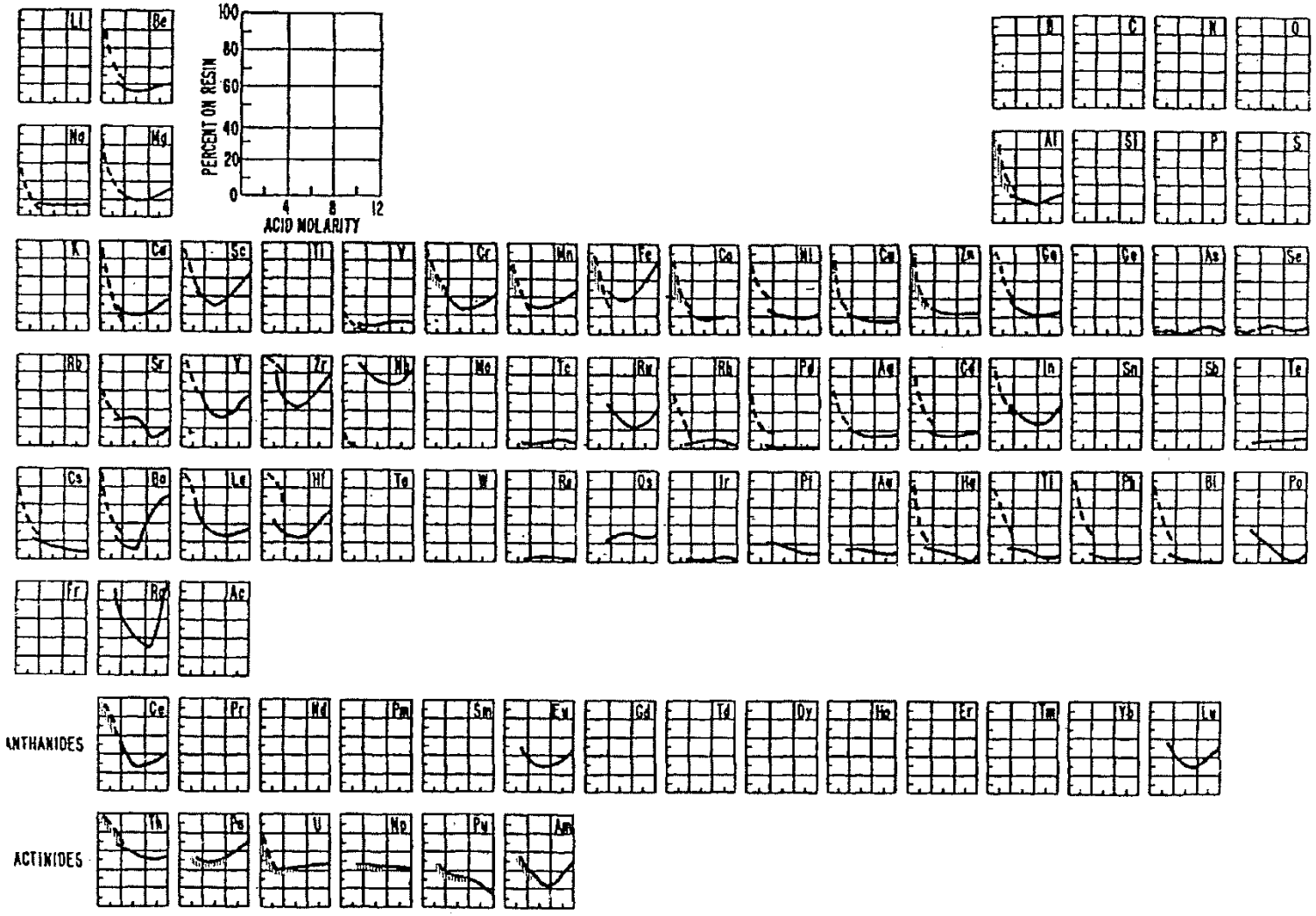


Distribution of elements from nitric acid onto strong-base anion exchange resin.

- Extraction of tetravalent and hexavalent actinides tends to increase with increasing [HNO_3] up to approximately 8 M then decrease.
- The increase is due to formation of anionic nitrate complexes such as hexanitrato Pu(IV) ($Pu(NO_3)_6^{-2}$)
- In concentrated acids, competition from high NO_3^- concentrations hinder removal of Pu(IV)

Cation Exchange Distribution Coefficients in HNO_3

MARLAP, 2004



Sorption of elements by 50 x8 cation-exchange resin from nitric acid (acid volume/resin weight = 10)

Physical Properties – Size and Form

- Particle size
  - Size based on mesh screen particles can pass through
    - 40-300 mm (40-50 mesh)
    - ~300 mm (50 mesh)
    - ~150 mm (100 mesh)
  - Larger particle size = faster flow rate
  - Decreasing particle size decreases time required to reach equilibrium but also decreases flow rate
- Physical form
  - Smooth spherical beads
  - Macroporous resins, created during polymerization
  - Pore size varies but can be up to 700 m2/g
- Cross-linking: degree of linkage between polymer layers
  - High Crosslinking = more mechanical strength, less swelling, hard/brittle resins
  - Low Crosslinking = considerable swelling, gelatinous resins, faster kinetics

Chemical Properties

- Reaction has equivalency, i.e. progresses stoichiometrically
  - $Ca^{2+} + 2R^{-}H^{+} \Leftrightarrow (2R^{2-})Ca^{2+} + 2H^{+}$
- Capacity: the number of sites per mass of resin (specified as dry weight or wet weight)
  - Example: Dowex 50 x 8 has 5.1 meq/g_{dry}
- Selectivity for counter ion
  - If solution contains a counter ion different from the original, a different equilibrium may be reached
  - Hence, the need for "washing" resins
  - The form of the resin will depend on the concentration of counter ions
    - Ex: $RSO_3^{-}Na^{+} + K^{+} + Cl^{-} \Leftrightarrow RSO_3^{-}K^{+} + Na^{+} + Cl^{-}$

General Resin Selectivity

- In dilute solutions, resin will show preference for ions of higher charge
- Higher polarizability and lower degree of solvation (favored by low charge and large size) the more strongly an ion will be adsorbed
- Selectivity increases with increases in atomic number within same periodic group
- Tetravalent actinides are generally sorbed much stronger than most metal ions
- As cross linking increases, resins become more selective towards ions of different sizes

Element	Formal Charge	K_d
Pu	4	978
La	3	1.4
U	2	3.9
Bi	2	3.8
Fe,Al,Ni,Co	3	~0
Cu, Zn, Sr, Sn	2	~0
Cs, Ba, Na, Li	1	~0

$$K_d = [M]_{resin}/[M]_{aqu}$$

Types of Resins

- Strong Cation Exchange ($R\text{-}SO_3^-$ as Na^+ or H^+ form)
  - Absorbs cations from weak acid solution
  - Elute cations from strong acid solutions
  - Not selective for Pu
  - $3(R\text{-}SO_3H) + Pu^{3+} \Leftrightarrow (R\text{-}SO_3)_3Pu + 3H^+$
- Strong Base Anion Exchange ($(R\text{-}N(CH_3)_3^+$
  - Takes advantage of formation of strong anionic complexes in strong acid solutions (i.e. $Pu(NO_3)_6^{-2}$, $Th(NO_3)_6^{-2}$)
  - Can be eluted by weak acids, possibly with the addition of a reducing agent
  - Normally run in HNO_3

$$2(R\text{-}N(CH_3)NO_3) + Pu(NO_3)_6^{-2} \Leftrightarrow (R\text{-}N(CH_3))_2Pu(NO_3)_6 + 2\ NO_3^-$$

Example: lanthanide separation using cation exchange and α-hydroxyisobutyrate (α-HIBA)

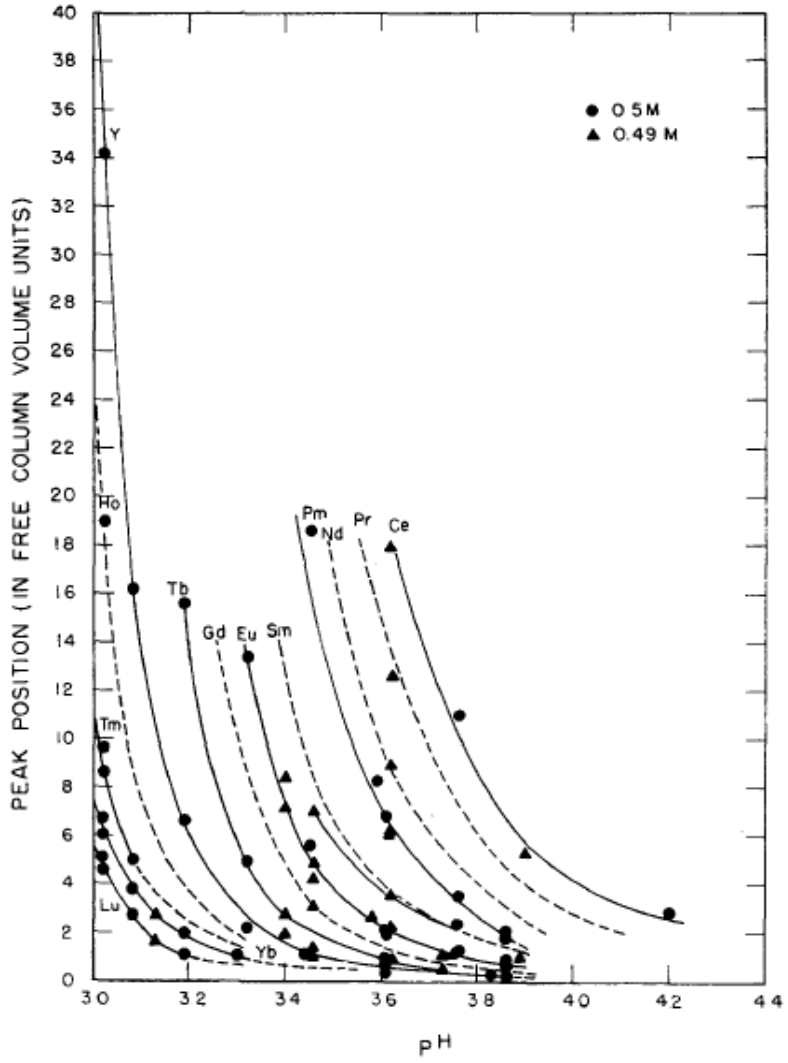


FIG. 1.

Smith and Hoffman, *Journal of Inorganic and Nuclear Chemistry*, 1956, 3, (3-4), 243-247.

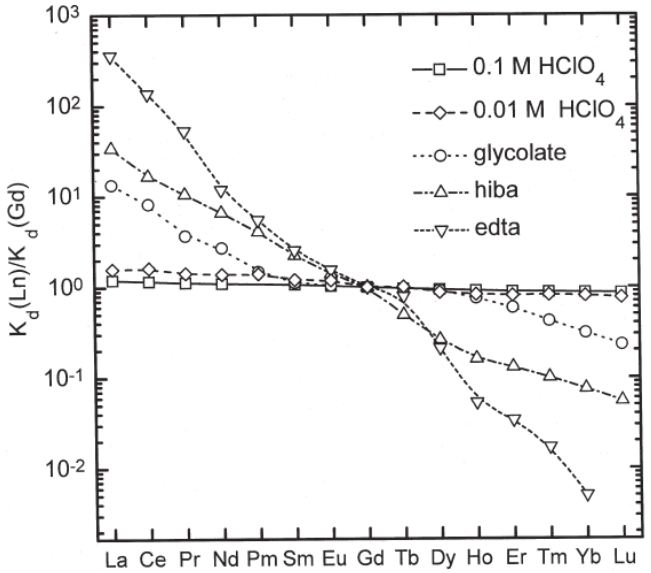


Figure 2. Comparison of the relative distribution of lanthanides onto Dowex 50 cation exchange resin from various aqueous media.

Nash and Jensen, *Separation Science and Technology* **2001,** *36*, (5-6), 1257-1282

Example: lanthanide separation using cation exchange and α-hydroxyisobutyrate (α-HIBA)

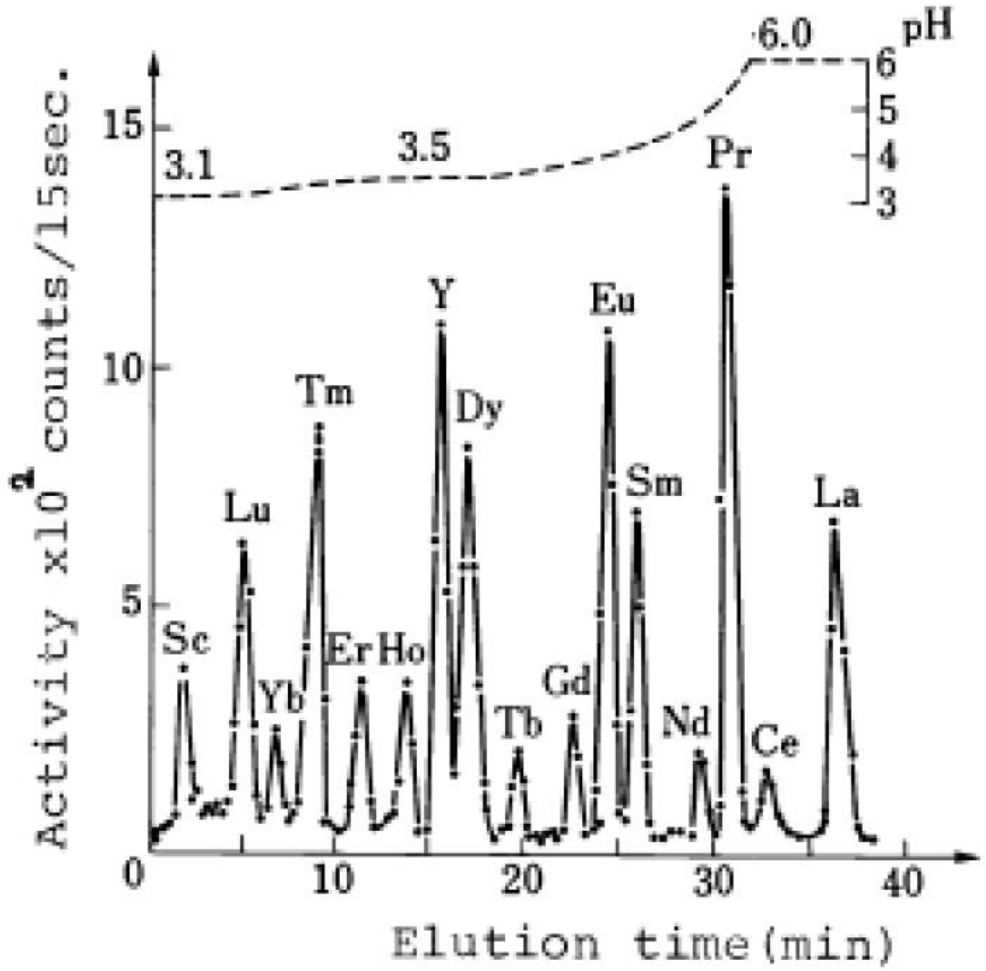
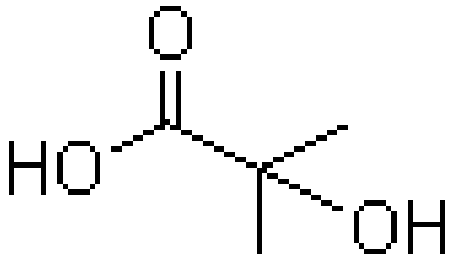


Fig.13. Separation of rare earth elements.(Ref.24)

Elements:Rare earth elements.Ion exchange resin:TSK LS-212 high performance ion exchange resin. Column:75mmX0.5mm(ID).Flow rate: 8 μl/min..Temperature:Room temperature.Eluent:0.4M Ammonium hydroxyisobutyrate(pH 3.1-6.0) (gradient elution).



Example: Actinide separation using HIBA and cation exchange

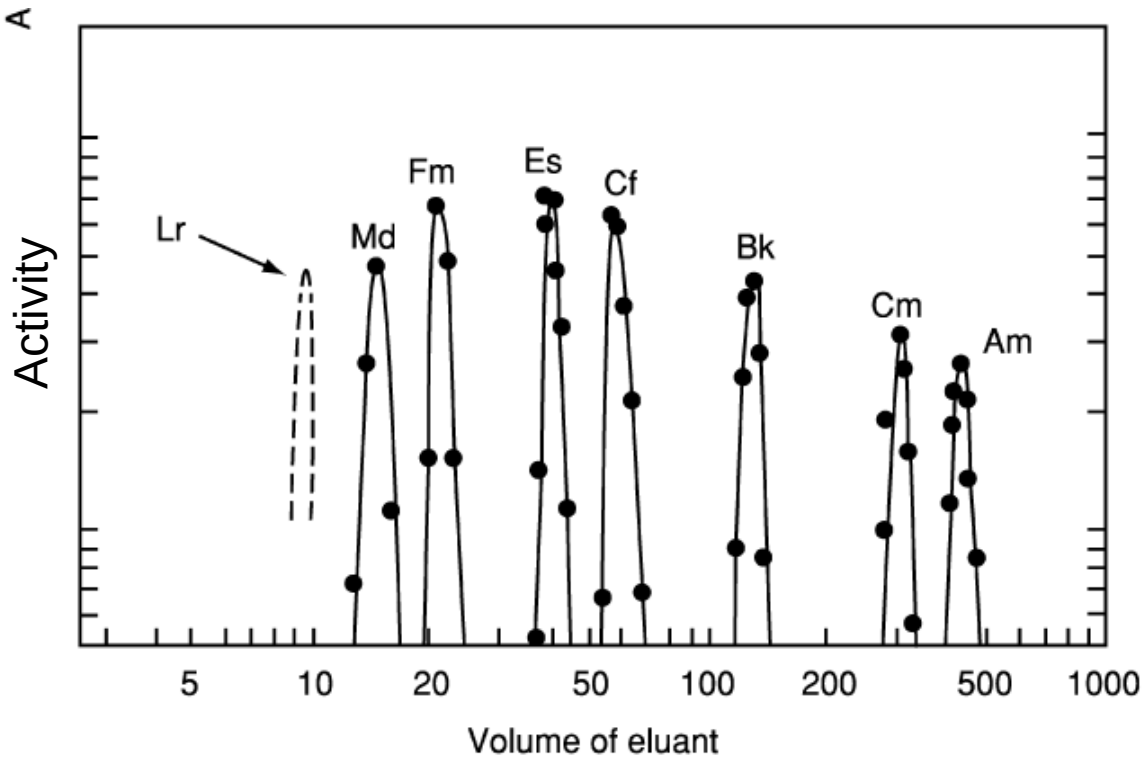
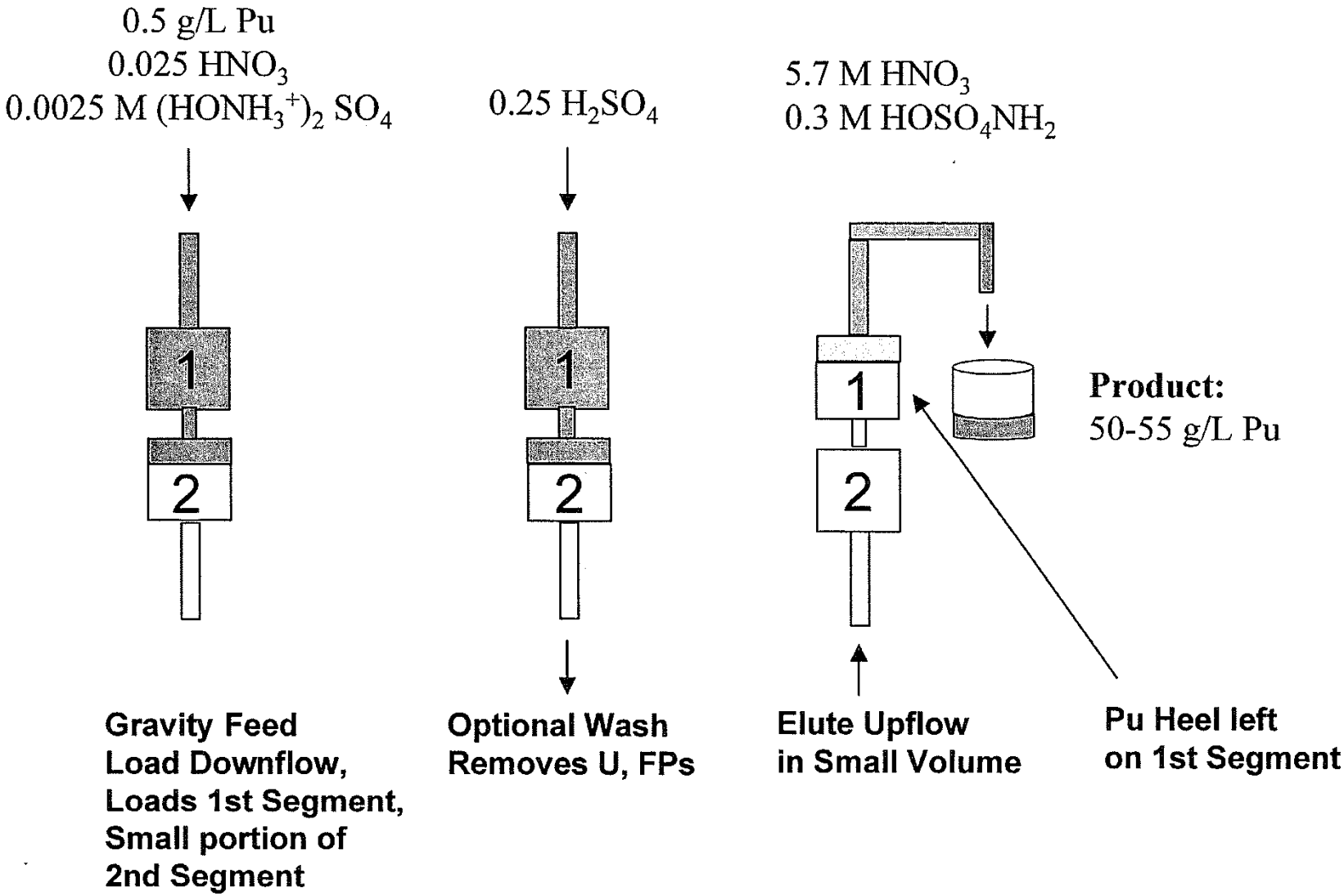


Fig. 13.1 *Elution of homologous trivalent actinides and lanthanides from a Dowex 50 cation-exchange resin column at 87°C with ammonium α-hydroxyisobutyrate as eluant. The broken curve for element 103 (Lr) is an estimate based on its predicted radius.*

Figure: Silva, R. J., Fermium, Mendelevium, Nobelium, and Lawrencium. In *The Chemistry of the Actinide and Transactinide Elements*, Morss, L. R.; Edelstein, N. M.; Fuger, J., Eds. Springer: Netherlands, 2006; p 3442.
Figure based on data from Choppin et al., J. Inorg. Nulc. Chem., 1956, 2, 66-68.

FB-Line Cation Flowsheet at SRNL –

Images Courtesy of Bill Crooks, LANL

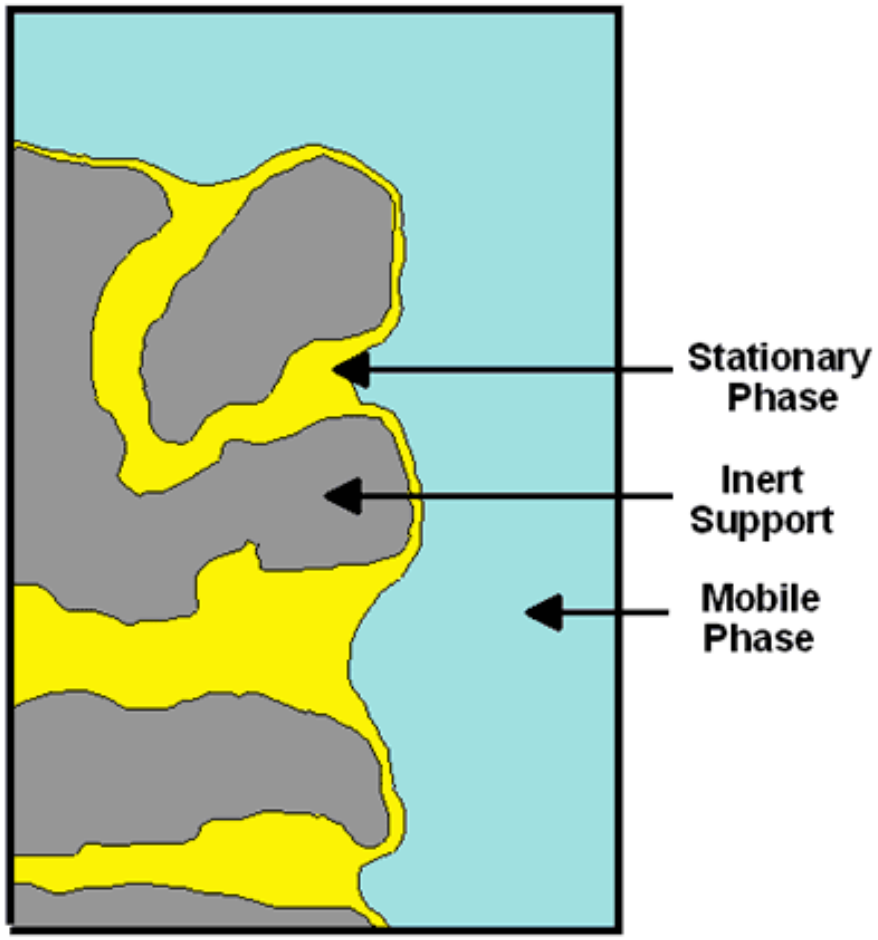


Extraction Chromatography

- Extraction Chromatography = “Solvent extraction on a bead”
- Separation based on unequal distribution (i.e. partitioning) of substances between two immiscible phases
- Combines selectivity of liquid-liquid extraction with ease of an ion exchange resin
- Becoming more desireable than LL extraction because it is generally faster, generates less waste, and is more efficient

- Liquid-Liquid Extraction -Advantages
  - Rapid, selective extraction
  - Wide scope of applications
  - Simple equipment
  - Coefficients independent of concentration
- Liquid-Liquid Extraction – Disadvantages
  - Cumbersome for large samples
  - Toxic/flammable solvents
  - Multiple extractions required in many cases
  - Emulsions and third phase formation common

Extraction Chromatography



$$k' = D \bullet \frac{v_s}{v_m} \qquad D_w = \frac{A_o - A_s}{A_s} \bullet \frac{mL}{g}$$

- D = volume distribution ratio, ratio of concentration on solid versus aqueous phase
- D_w = weight distribution ratio
- A_o-A_s = activity sorbed onto known weight of resin
- A_s = activity in known volume initially
- mL = volume of aqueous phase
- g = mass of resin
- k' = capacity factor, number of free volumes to peak maximum

- Therefore, if k' is high, you can concentrate greater volumes of sample
- Analogous to a retardation factor

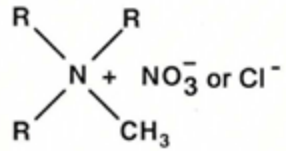
http://www.eichrom.com/eichrom/products/extraction.aspx

Acid Dependency of TEVA Resin Extraction

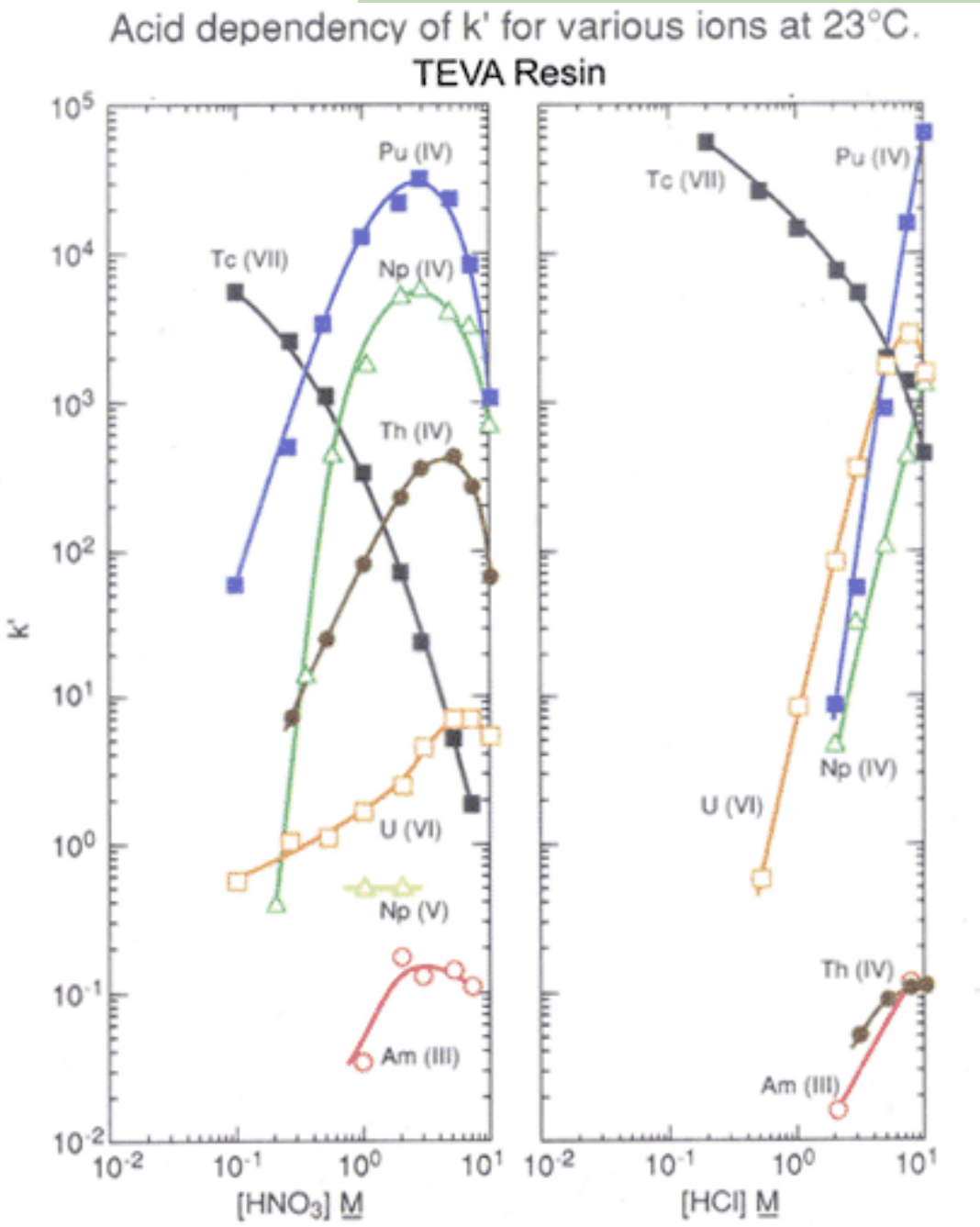
Figures from www.eichrom.com

Figure 1

Trialkyl, methylammonium nitrate (or chloride)



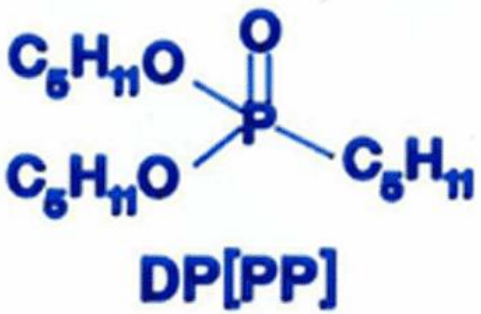
R = C_8H_{17} and $C_{10}H_{21}$



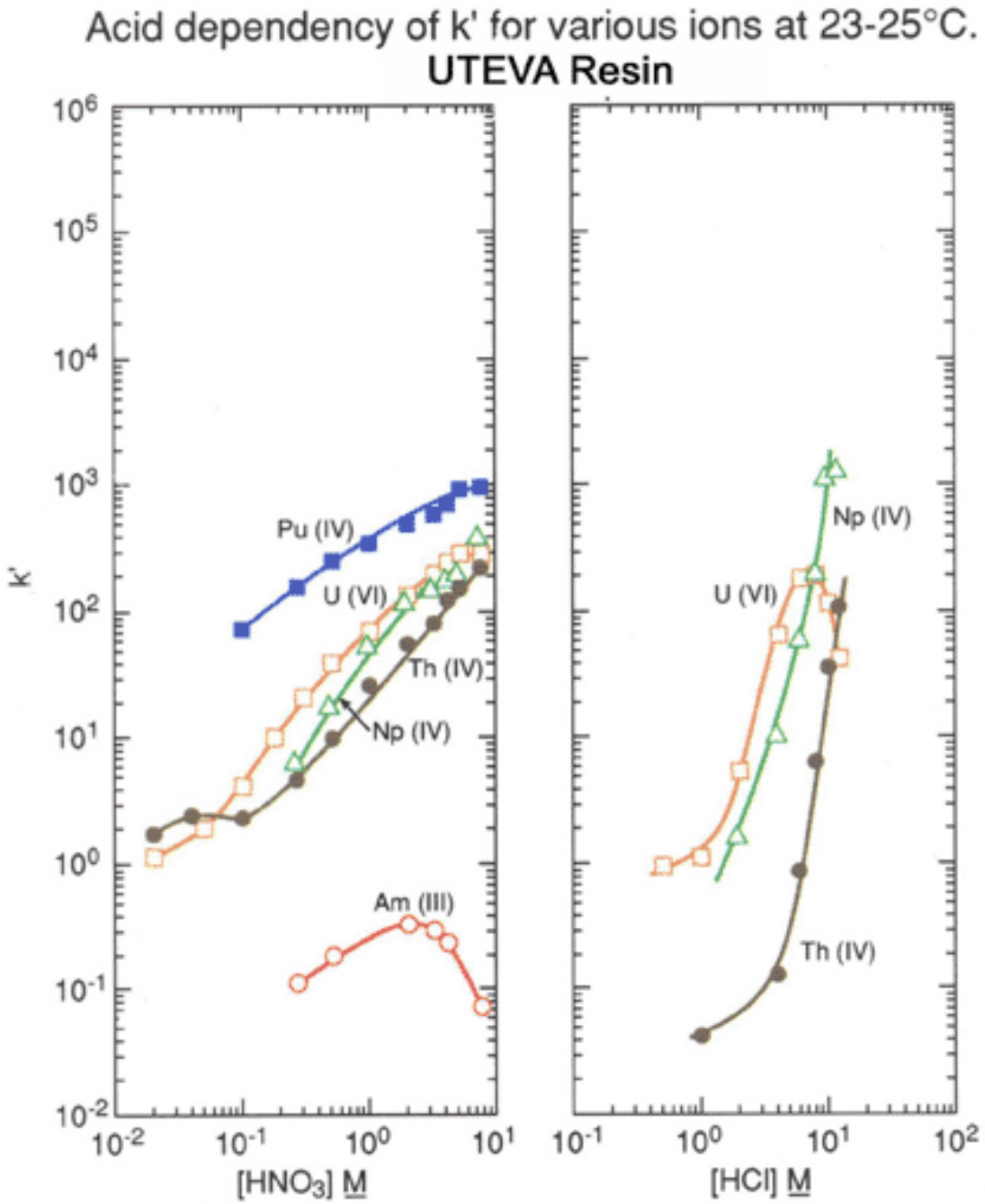
Acid Dependency of U/TEVA Resin Extraction

Figures from www.eichrom.com

Figure 1



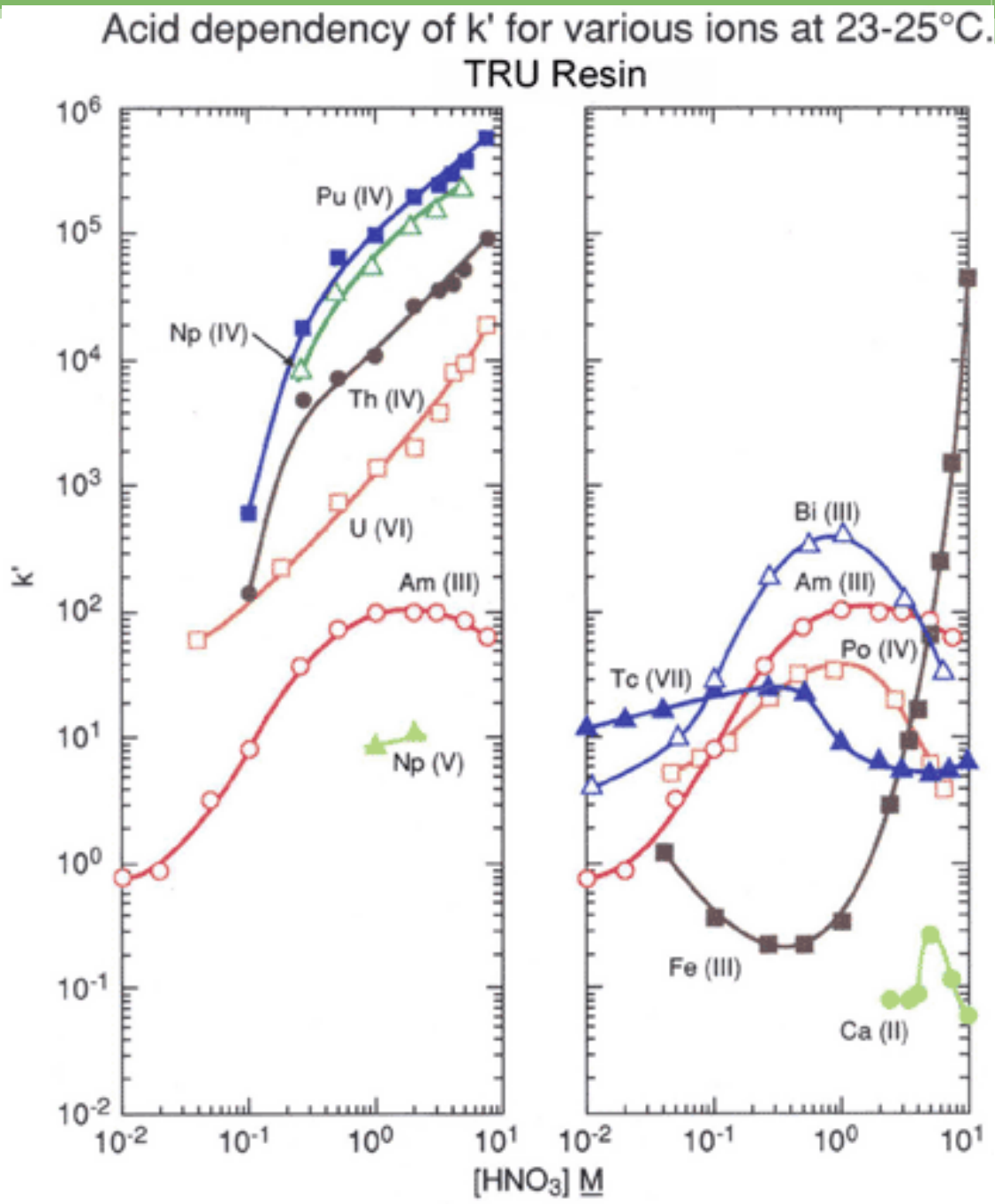
Dipentyl, pentylphosphonate
(or Diamyl, amylphosphonate – DAAP)



Acid Dependency of TRU Resin Extraction

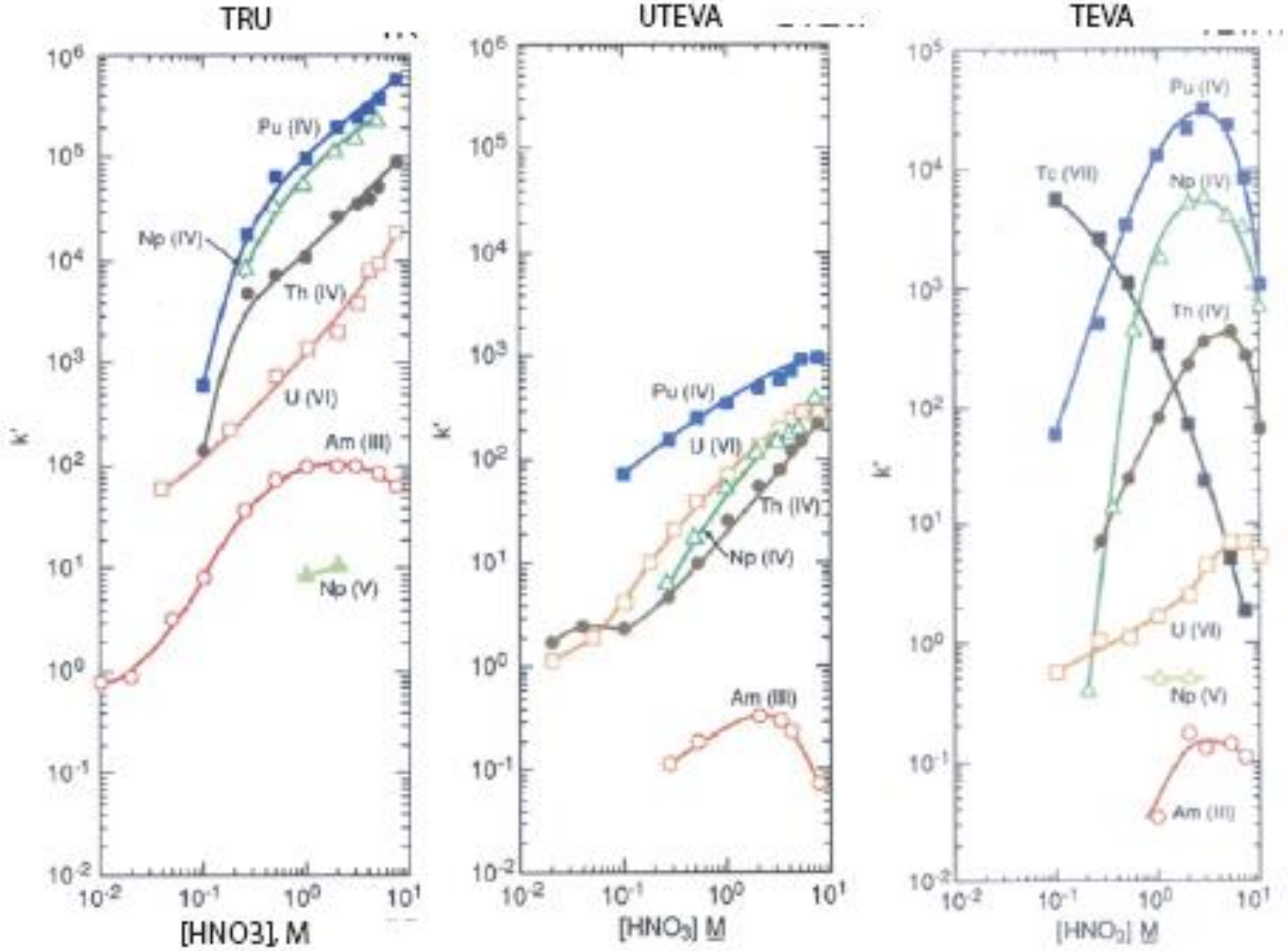
Figures from www.eichrom.com

Figure 1



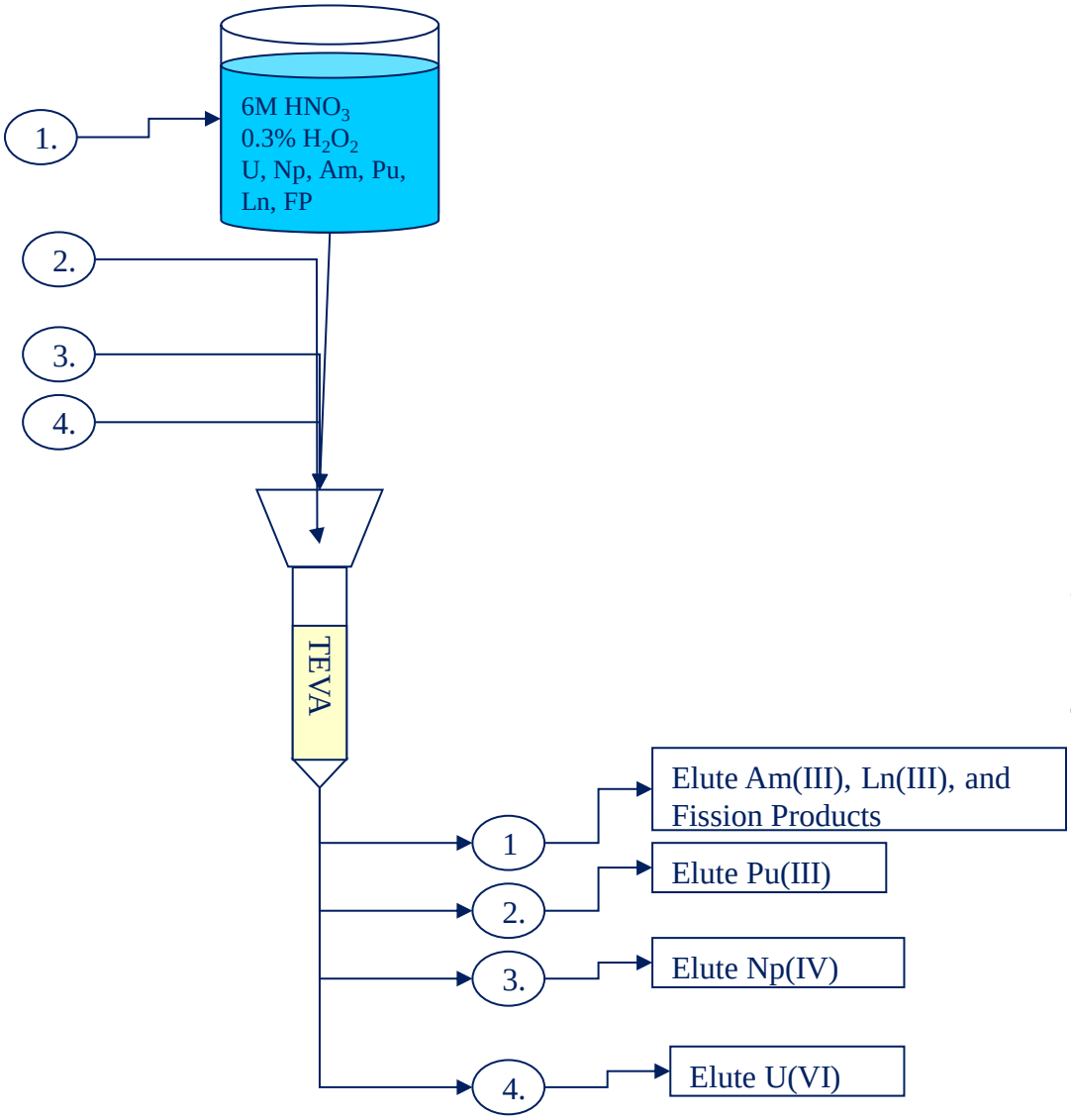
Comparison of Eichrom Resins

Figures from www.eichrom.com



Sample Extraction Scheme

Morgenstern et al., Radiochim. Acta, 90, 81-85, 2002



1. Load Solution: 6M HNO_3, 0.3% H_2O_2
2. 2 M HNO_3, 2 x 10^{-3} M Ascorbic acid, 2 x 10^{-3} M hydroxylamine-hydrochloride
3. 2 M HNO_3, 0.1 M $H_2C_2O_4$ (oxalic acid)
4. 7.0 x 10^{-3} M $(NH_4)C_2O_4$ (ammonium oxalate)

Pu, Np, U, Am, Cm, Th Separation

Maxwell, J. Radioanal. Nucl. Chem., 275, 497-502, 2008

100-200 g soil sample.
Add Tracers (Pu242 or Pu236, Am243).
Heat to 550 ℃

↓

Acid leach (75-100 ml con. HNO_3 + 25 ml HCl). Heat to dryness on hot plate. Rinse with conc. HNO_3, 4M HCl. Centrifuge, filter, evaporate. Ash with conc. HNO_3.

↓

Fuse in Zr crucible 20 min. (20-25 g NaOH - 600 ℃).
Hydroxide precipitation (7 mg Ce carrier, $TiCl_3$, Ba).
Cerium fluoride matrix removal (2 mg Ce, HCl/HF, H_2O_2)

↓

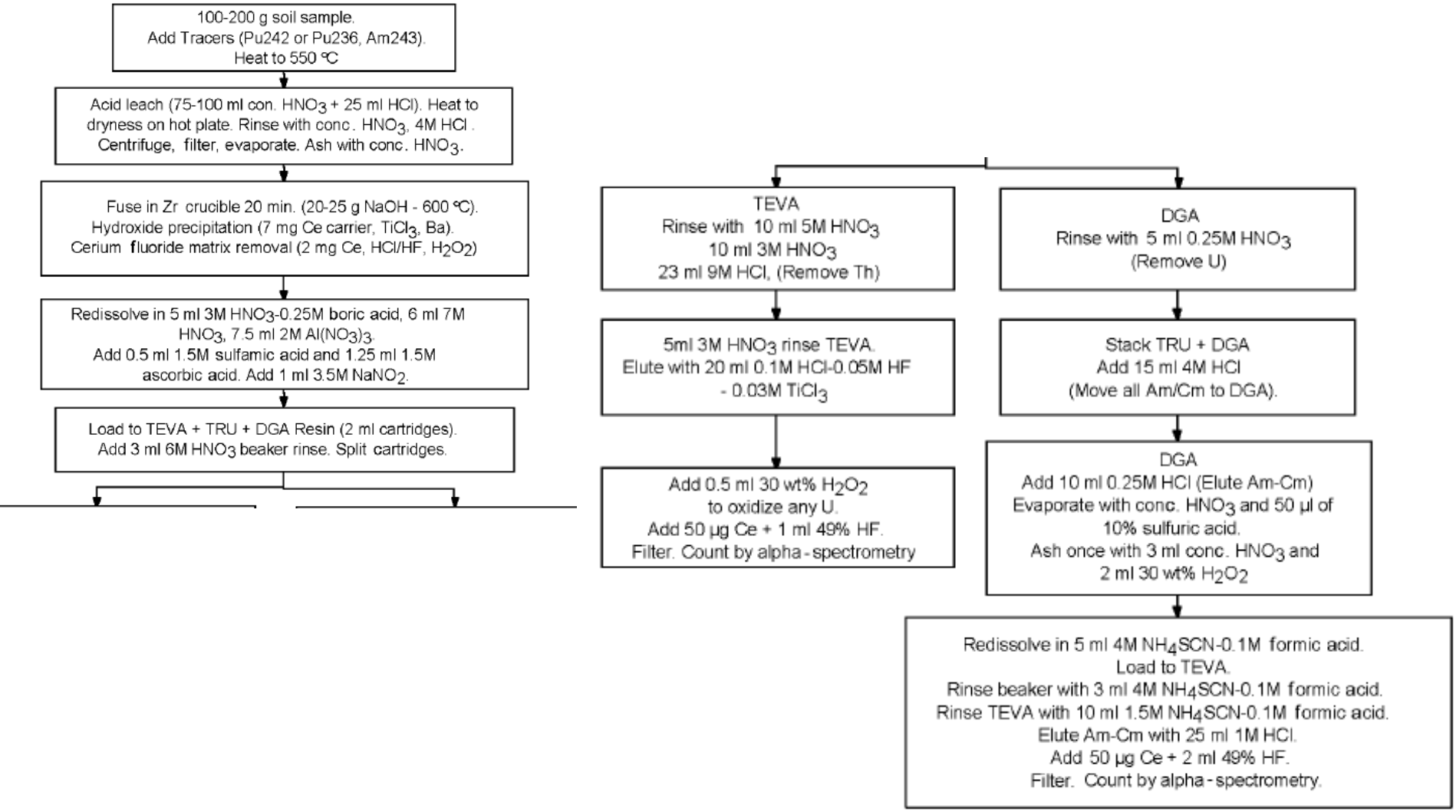
Redissolve in 5 ml 3M HNO_3-0.25M boric acid, 6 ml 7M HNO_3, 7.5 ml 2M $Al(NO_3)_3$.
Add 0.5 ml 1.5M sulfamic acid and 1.25 ml 1.5M ascorbic acid. Add 1 ml 3.5M $NaNO_2$.

↓

Load to TEVA + TRU + DGA Resin (2 ml cartridges).
Add 3 ml 6M HNO_3 beaker rinse. Split cartridges.

Pu, Np, U, Am, Cm, Th Separation

Maxwell, J. Radioanal. Nucl. Chem., 275, 497-502, 2008



MARLAP Table 14.6

TABLE 14.6 — Radioanalytical methods employing extraction chromatography (1)

Analyte	Ligand	Method Citations
Ni-59/63	dimethylglyoxime	Aqueous samples (DOE, 1997)
Sr-89/90	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in n-octanol	Biological, Environmental, and Nuclear Waste (Horwitz et al., 1991 and 1992a); Water (ASTM, D5811-95; DOE, 1997, Method RP500); Urine (Dietz and Horwitz, 1992; Alvarez and Navarro, 1996); Milk (Jeter and Grob, 1994); Geological Materials (Pin and Bassin, 1992)
Sr-90	octyl(phenyl)-*N,N*-diisobutyl-carbamoylmethylphosphine oxide (CMPO) in tributyl phosphate	Brines (Bunzl et al., 1996)
Y-90	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in n-octanol	Medical applications (Dietz and Horwitz, 1992)
Tc-99	Aliquat-336N	Low-level radioactive waste (Banavali, 1995); Water (Sullivan et al., 1993; DOE, 1997, Method RP550)
Pb-210	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in isodecanol	Water (DOE, 1997, Method RP280); Geological materials (Horwitz et al., 1994; Woittiez and Kroon, 1995); complex metal ores (Gale, 1996)
Ra-228	CMPO in tributyl phosphate or HDEHP impregnated in Amberlite XAD-7	Natural waters (Burnett et al., 1995); Volcanic rocks (Chabaux, 1994)
Rare earths	diamyl,amylphosphonate	Actinide-containing matrices (Carney, 1995)
	CMPO in tributyl phosphate and HDEHP impregnated in Amberlite XAD-7	Sequential separation of light rare earths, U, and Th in geological materials (Pin et al., 1996)
	CMPO in tributyl phosphate and 4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in n-octanol	Concomitant separation of Sr, Sm, and Nd in silicate samples (Pin et al., 1994)
Actinides	CMPO in tributyl phosphate	Air filters (Berne, 1995); Waters (Berne, 1995); Group-screening (DOE, 1997, Method RP725); Urine (Horwitz et al., 1990; Nguyen et al., 1996); Acidic media (Horwitz, 1993; DOE, 1997); Soil and sludge (Smith et al., 1995; Kaye et al., 1995); Environmental (Bunzl and Kracke, 1994)
	diamyl,amylphosphonate	Acidic media (Horwitz et al., 1992b)
	tri-*n*-octylphosphine oxide [TOPO] and HDEHP	Environmental and industrial samples (Testa et al., 1995)

(1) This list is representative of the methods found in the literature. It is not complete, nor does it imply preference over methods not listed.

Some useful resources for methodology

- EPA NAREL, *Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events*, EPA 402-R-10-001, 2010, www.epa.gov/narel
- Environmental Measurements Laboratory, HASL-300 Procedures Manual, https://www.orau.org/ptp/PTP%20Library/library/DOE/eml/hasl300/HASL300TOC.htm
- MARLAP, *Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)*, NUREG-1576, EPA 402-B-04-001A, NTIS PB2004-105421, 2004 https://www.epa.gov/radiation/multi-agency-radiological-laboratory-analytical-protocols-manual-marlap

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- Morgenstern et al., *Radiochim. Acta, 2002, 90, 81-85*
- Moody, K. J.; Grant, P. K.; Hutcheon, I. D., *Nuclear Forensic Analysis*. CRC Press: 2005.
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- Nash and Jensen, *Separation Science and Technology* **2001,** *36*, (5-6), 1257-1282

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NAMP website: www.wipp.energy.gov/namp