

DGA Resin: Update on Properties and Applications

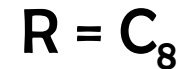
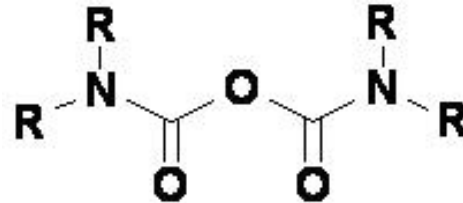
Bratislava – 10th November 2006

Outline

- General information on DGA
- Actinide/Am separation
- Actinides in large soil samples
- Ra/Ac separation
- Sr/Y separation
- Conclusions

DGA Resins

Extractant:



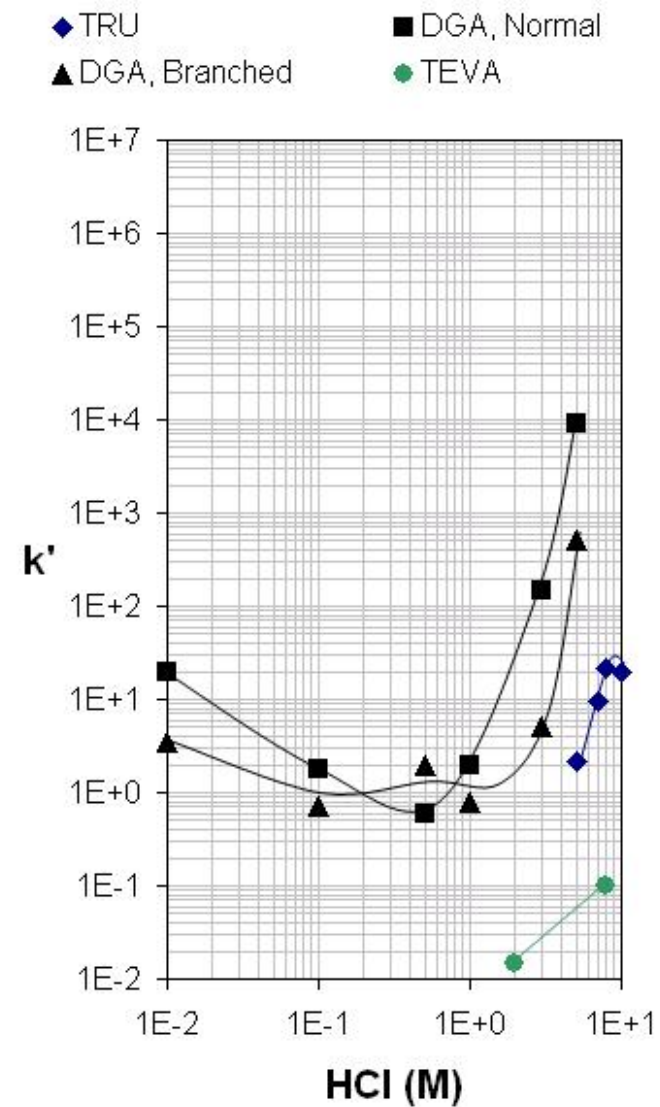
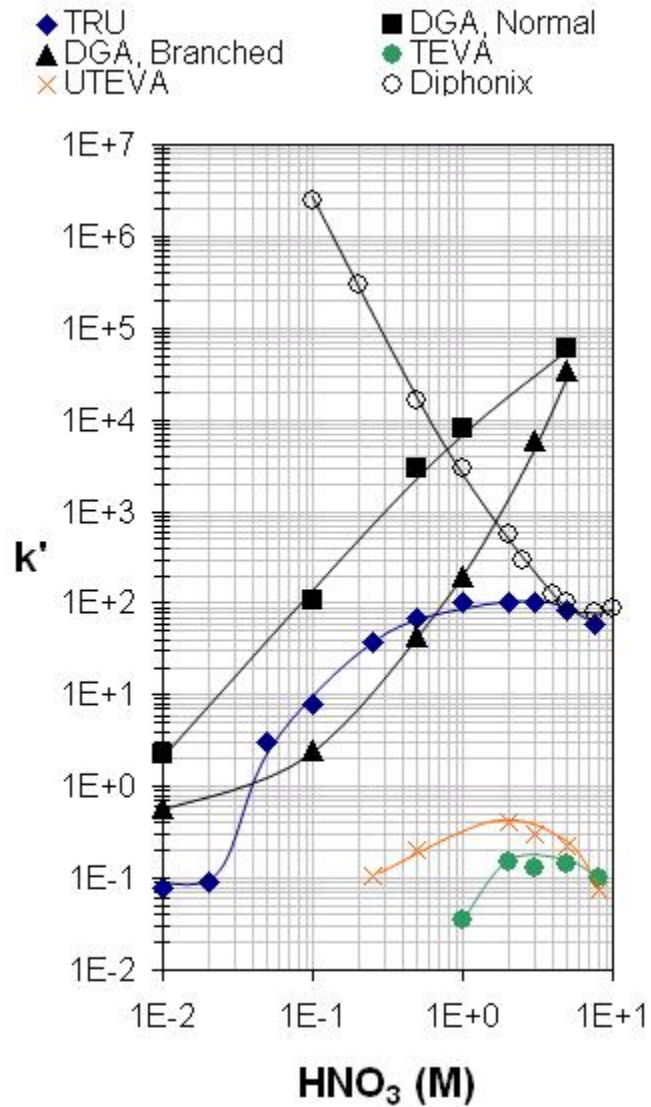
Extraction Equilibria:



with $X = NO_3^{-}$ or Cl^{-}

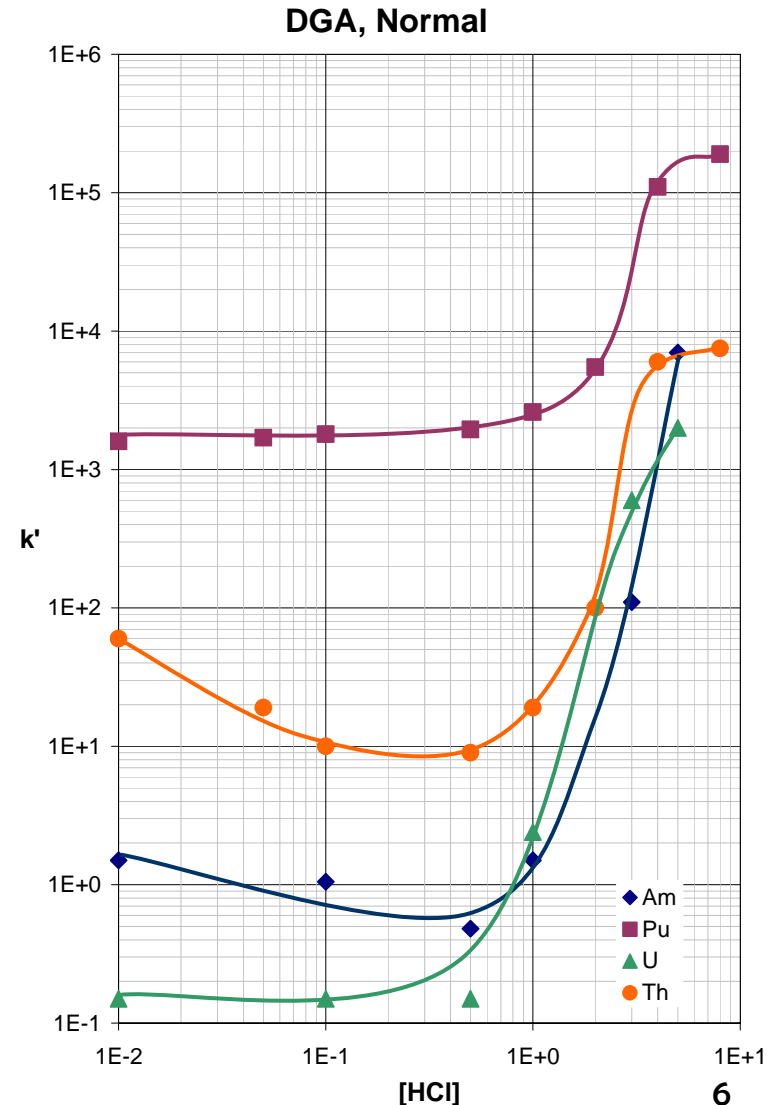
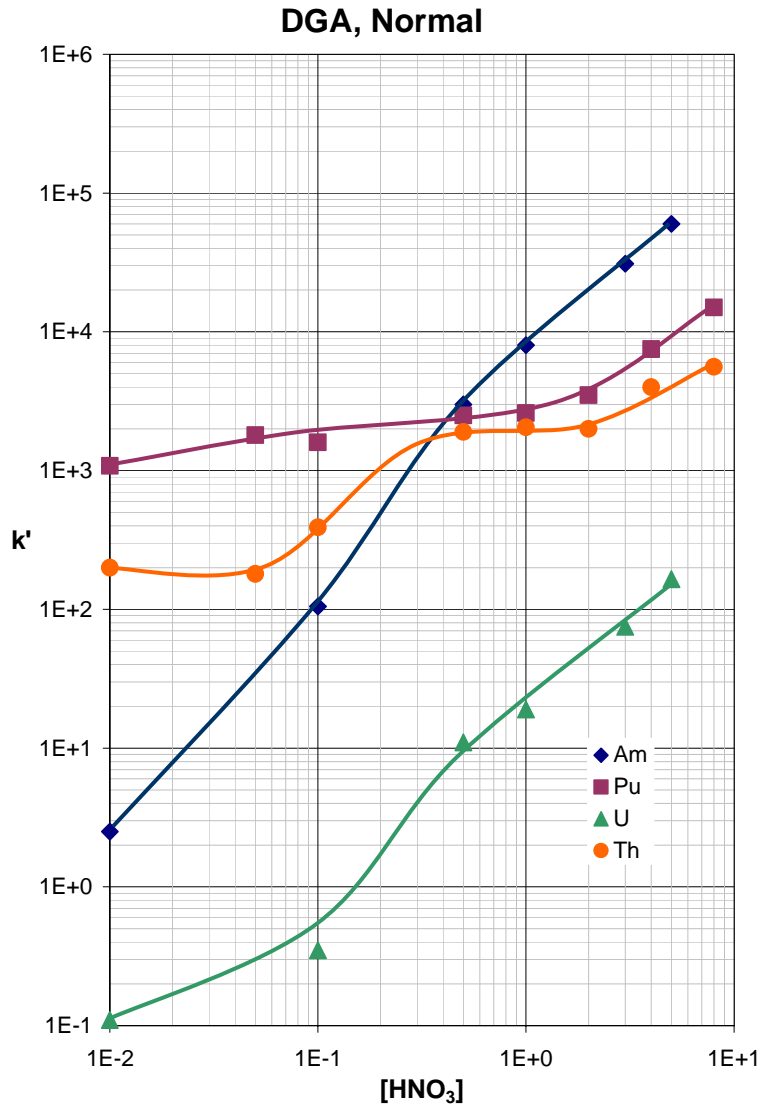
- DGA, Normal (*N,N,N',N'*-tetra-*n*-octyldiglycolamide)
 - Generally used
- DGA, Branched (*N,N,N',N'*-tetrakis-2-ethylhexyldiglycolamide)

Comparison of $k'_{(Am)}$ values on various Eichrom Resins

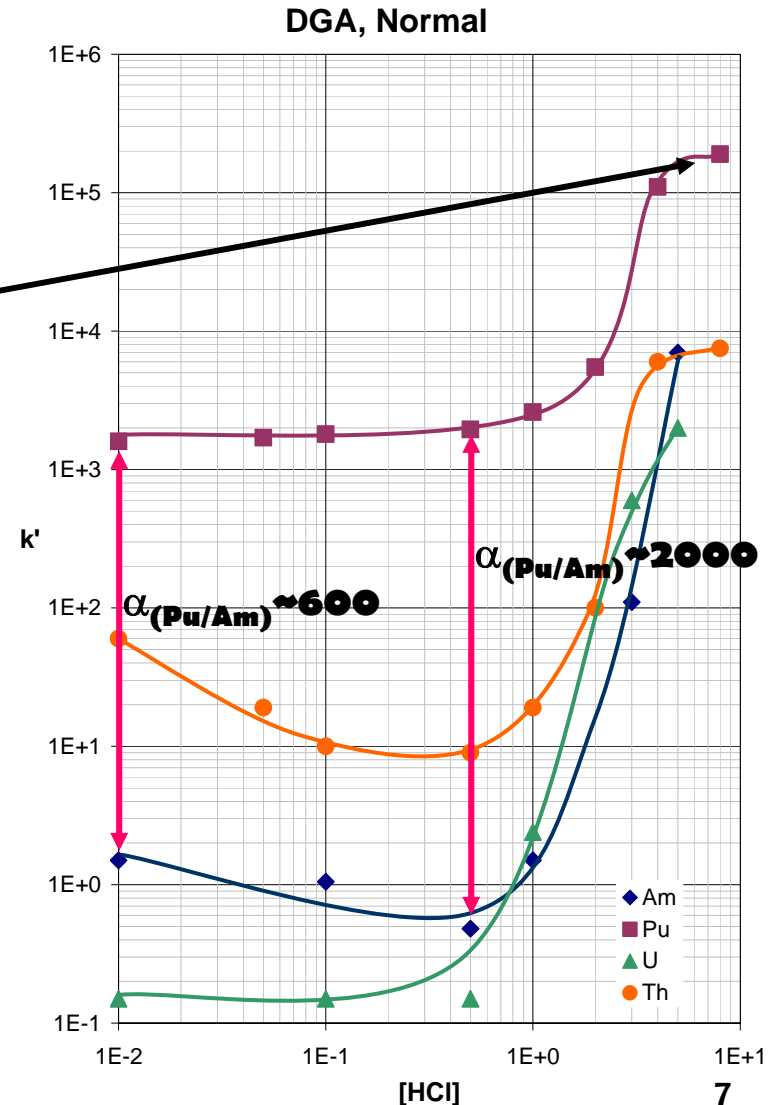
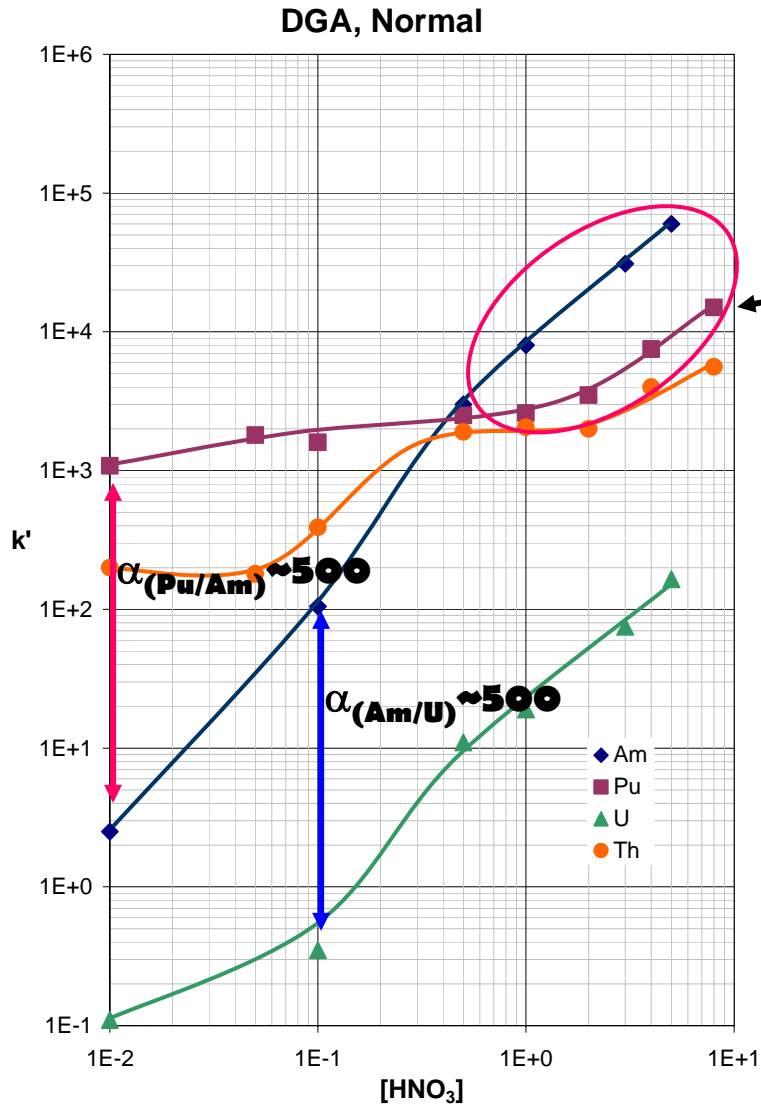


- Very favourable retention of Am on DGA compared to other Eichrom Resins (e.g. TRU):
 - Am fixed at high concentrations of HNO_3 or HCl ($k'_{\text{HNO}_3} \cong 2-5 \cdot 10^4$ and $k'_{\text{HCl}} \cong 500-10^4$)
 - Am stripped by either 0.01 M HNO_3 or 0.1-1M HCl ($k' \cong 1$)

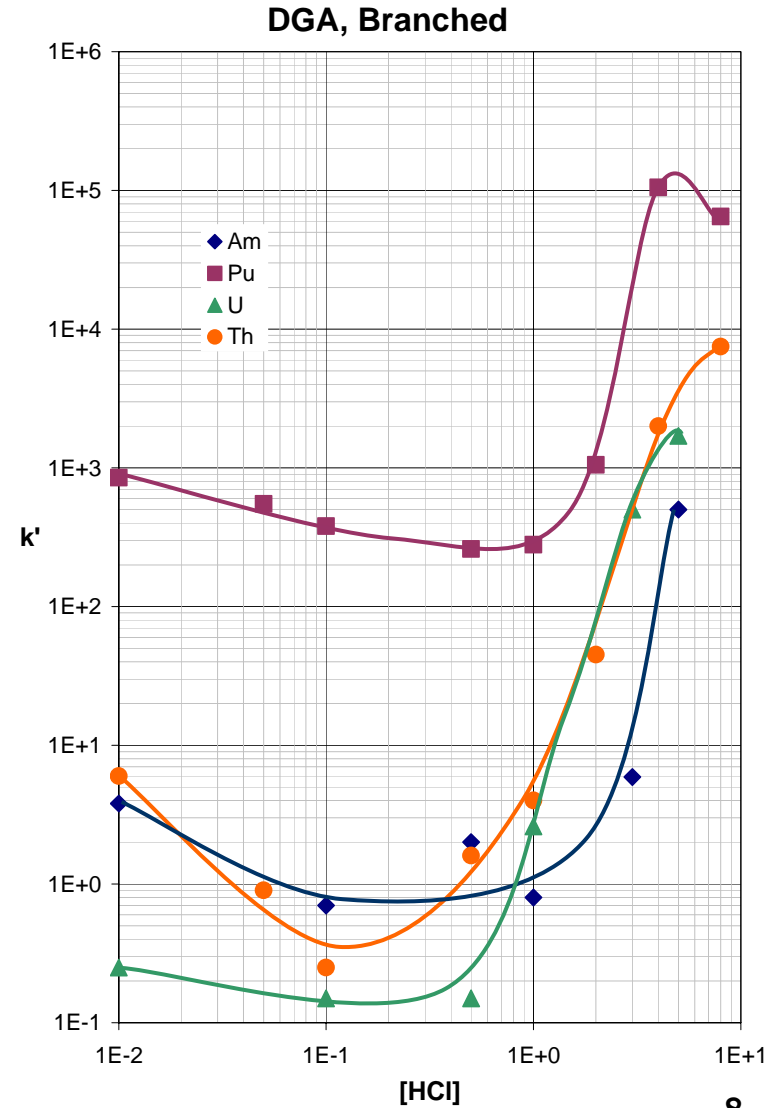
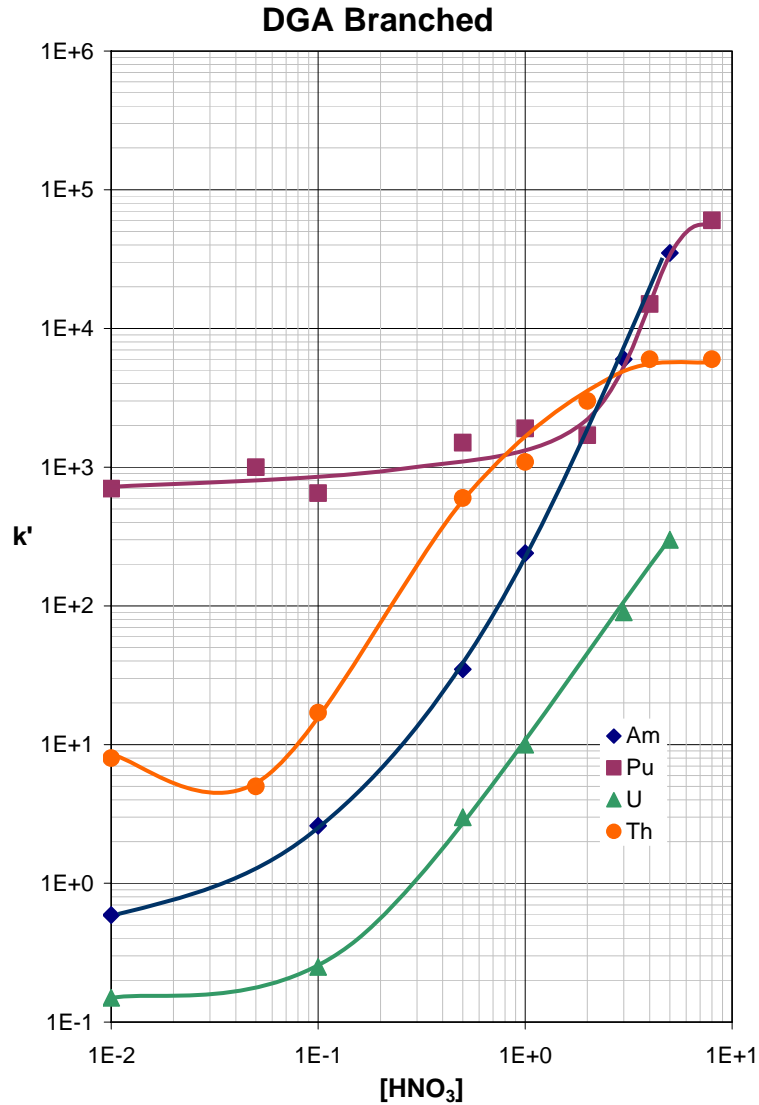
Acid dependency of k' for Am, Pu, U and Th in HNO_3 and HCl on DGA, Normal



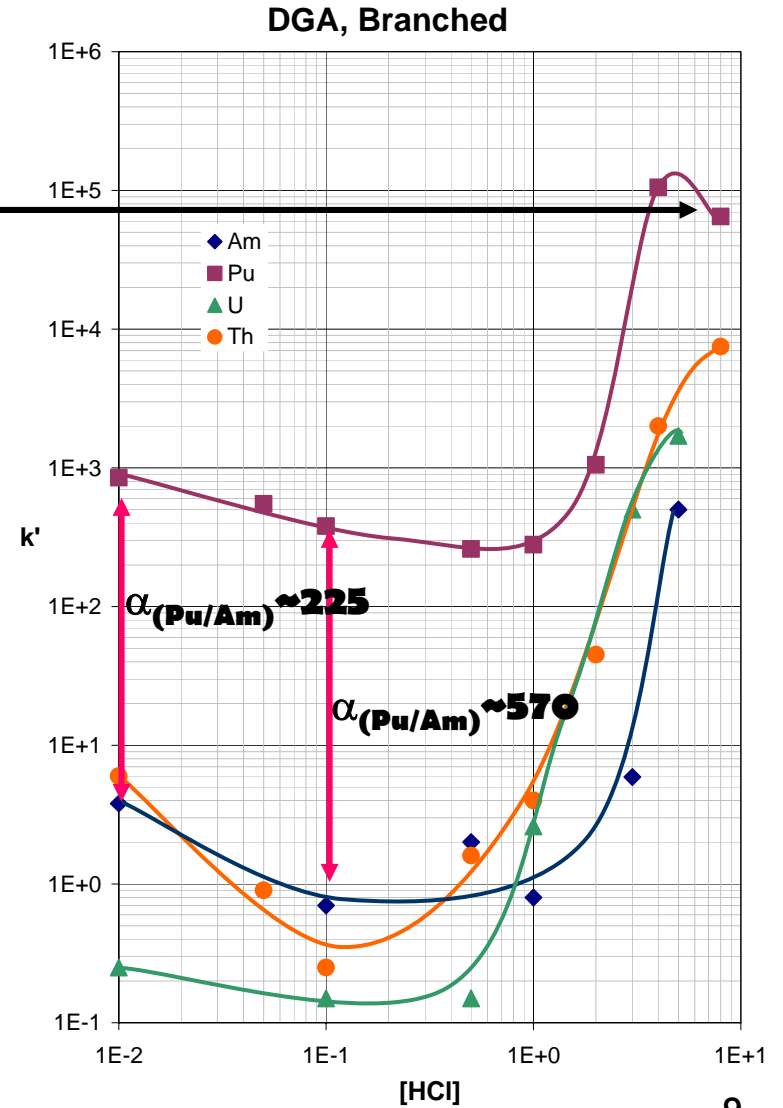
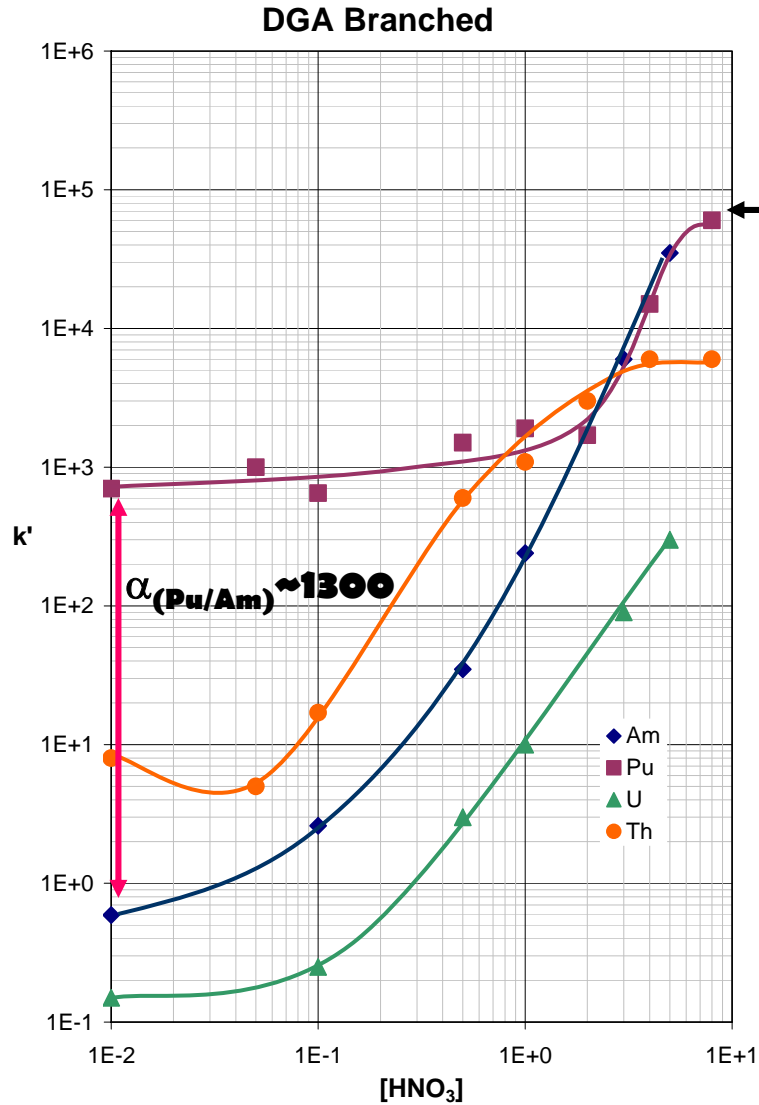
Acid dependency of k' for Am, Pu, U and Th in HNO_3 and HCl on DGA, Normal



Acid dependency of k' for Am, Pu, U and Th in HNO_3 and HCl on DGA, Branched



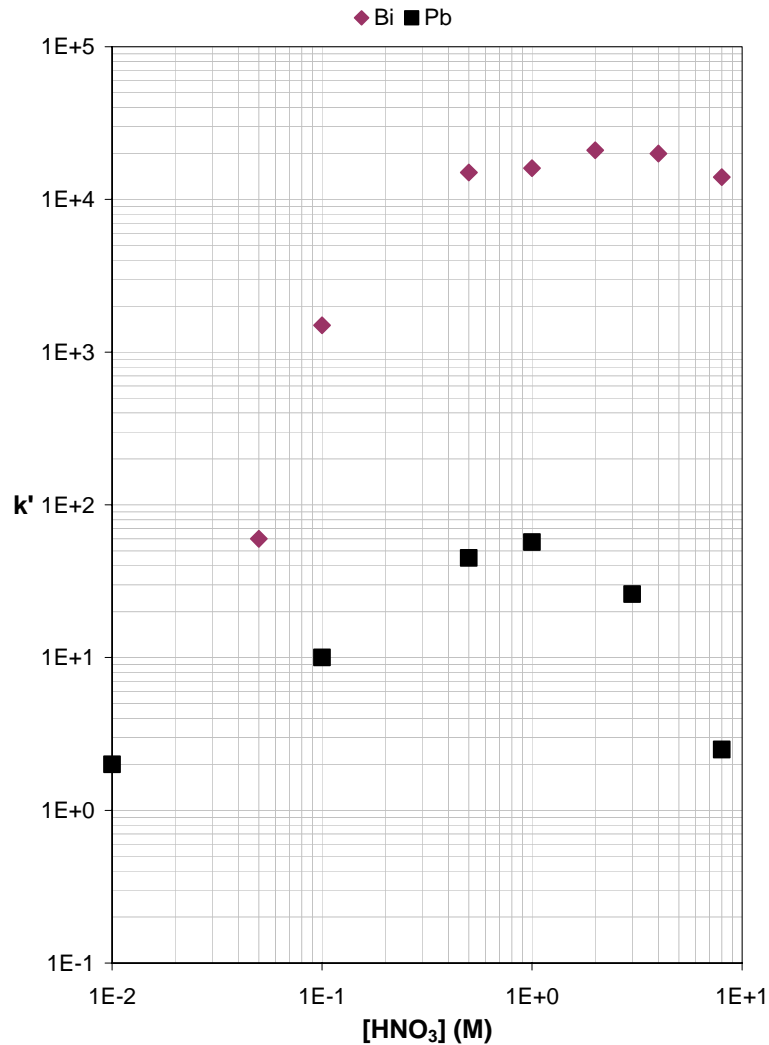
Acid dependency of k' for Am, Pu, U and Th in HNO_3 and HCl on DGA, Branched



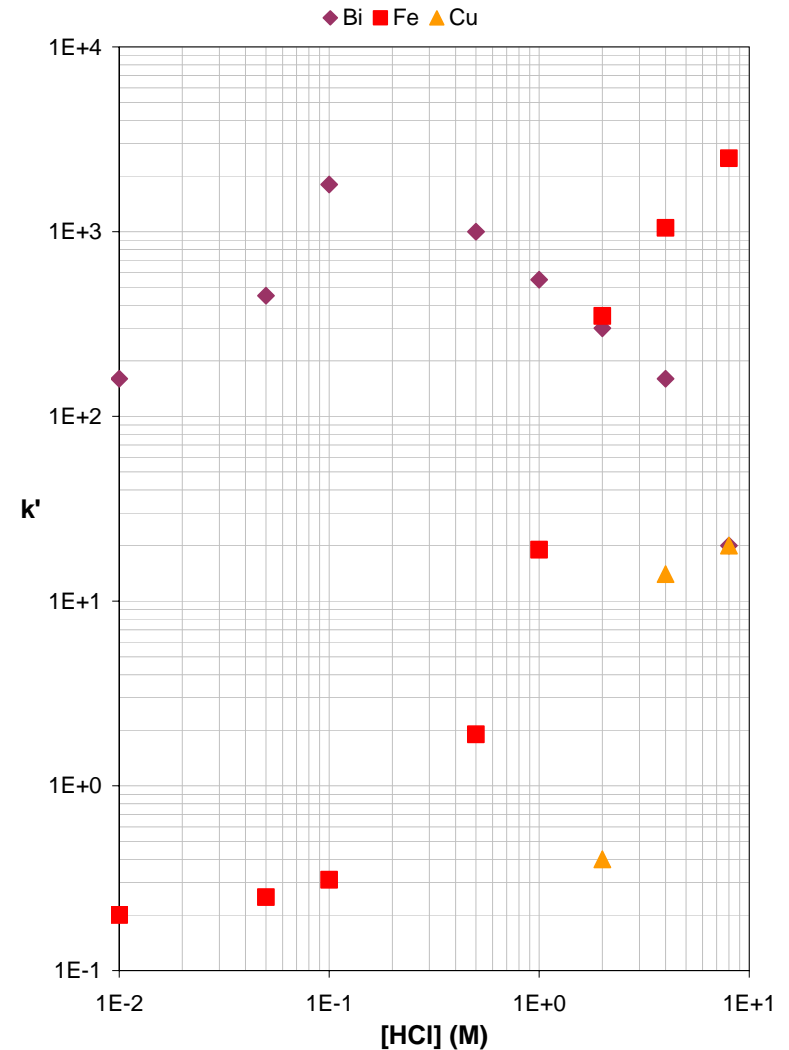
Americium Separation

- Selective separation from Pu with either 0.01M HNO₃ or 0.5M HCl on DGA Resins in principle possible
 - $k'_{\text{Pu}} \cong 10^3\text{-}10^5$
- Selective separation Am/U on DGA,Normal:
 - Stripping U with 0.25 M HNO₃
 - Stripping Am with 0.25 M HCl
- $k'_{\text{DGA,Branched}}$ smaller than $k'_{\text{DGA,Normal}}$

Interferents

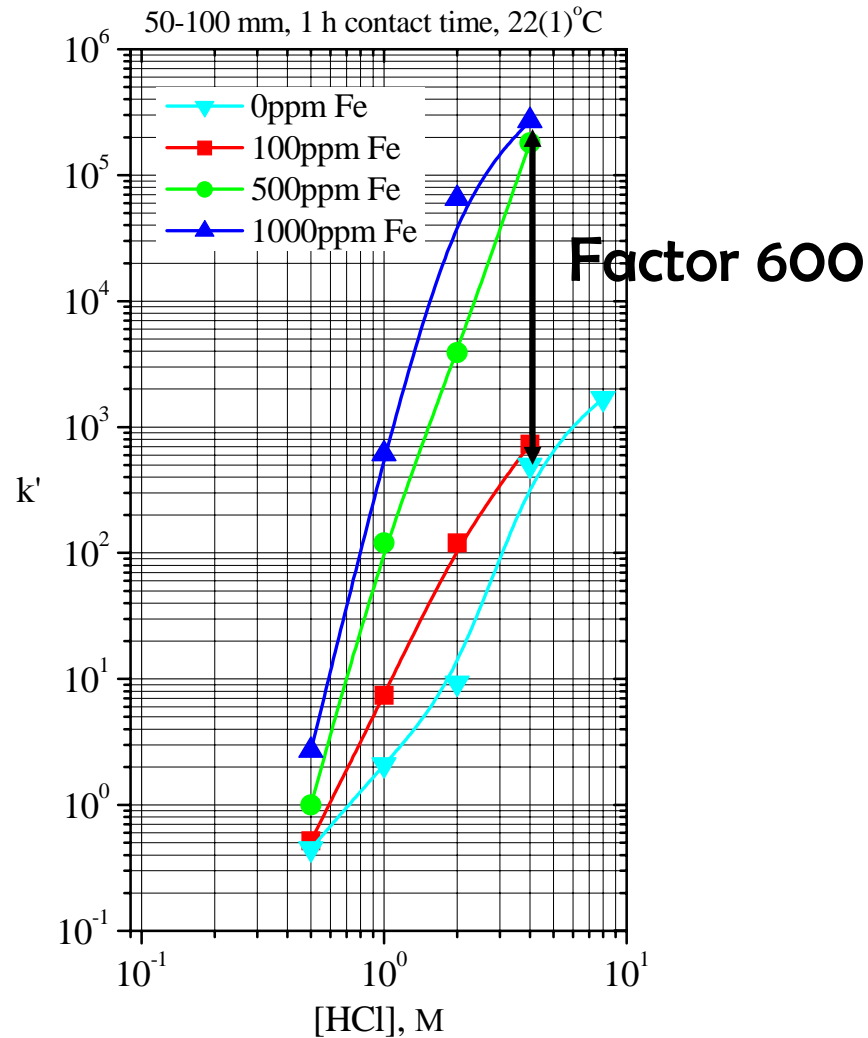


k' for V(V), Ti(IV), Al(III), Fe(III),
Co(II), Cu(II), Ni(II), Zn(II) < 2 for all [HNO₃]

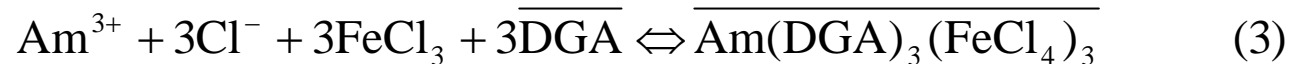


k' for Ti(IV), Al(III), Co(II), Ni(II),
Pb(II), Zn(II) < 2 for all [HCl]

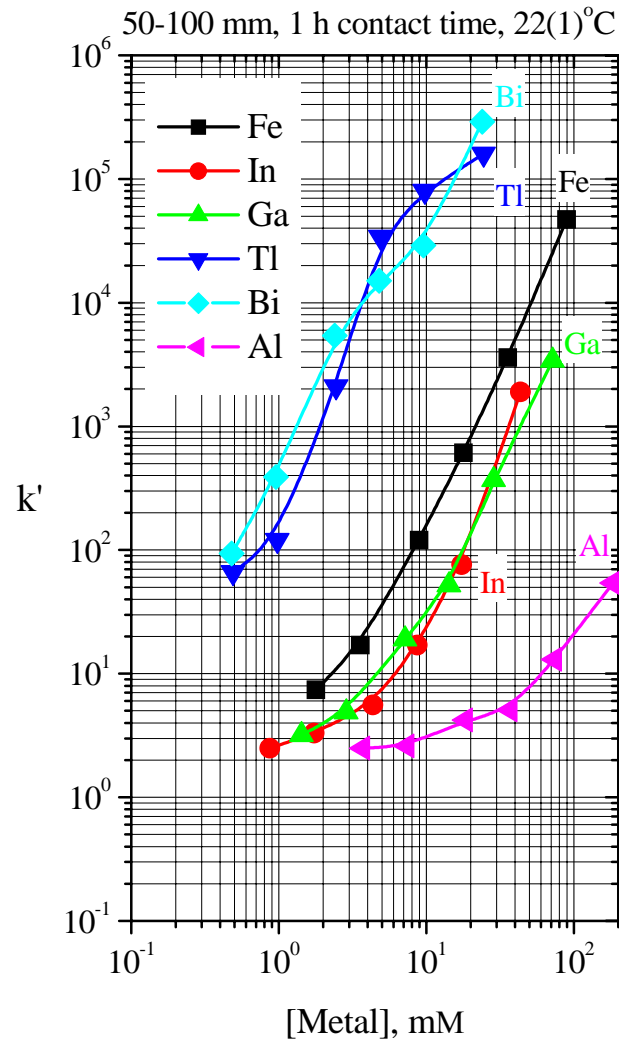
Particular case Am(III) in presence of Fe(III) in HCl on DGA, Normal



Equilibria for the synergistic extraction of Am(III) from HCl + FeCl₃



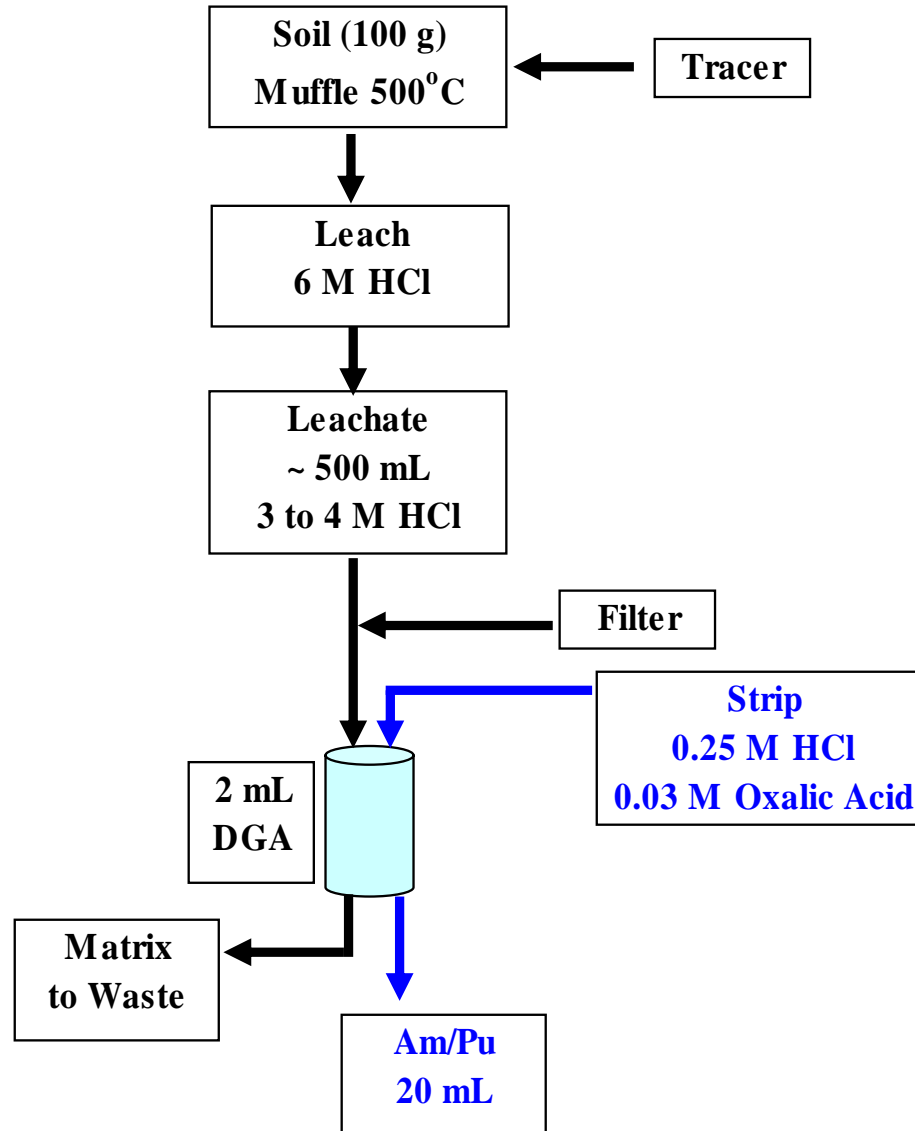
k' for Am(III) on DGA,N from 1 M HCl + M(III)



Application to environmental samples

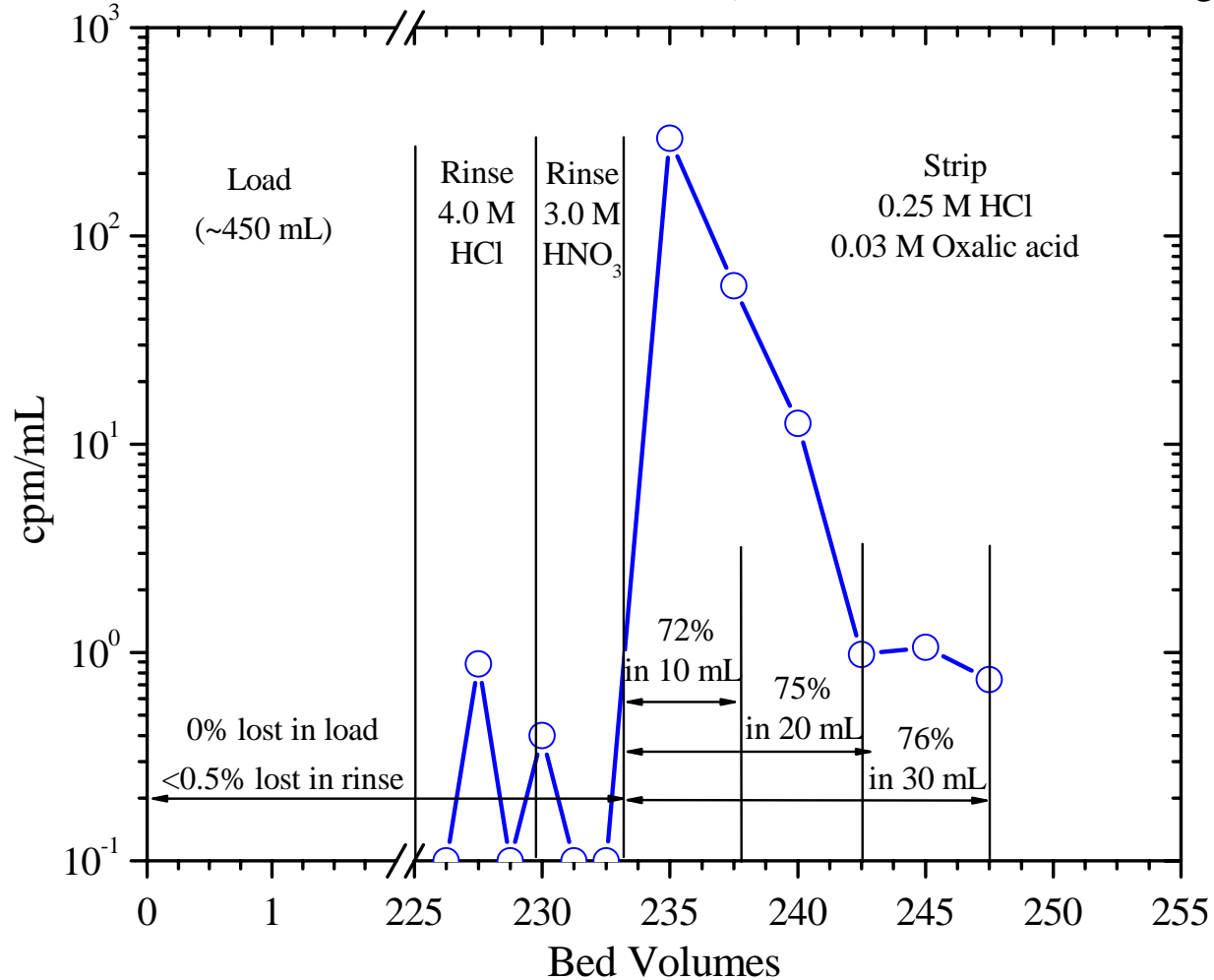
- Method for analysis of Am, Pu (and Np) in large soil samples (SRS)
- Applied to 100 – 200 g samples leached with HNO_3 and HCl
 - Rapid separation method using cartridges and vacuum box
- Also applicable to other difficult matrices

Flowchart for the Preconcentration of Am and Pu from 100 g of Soil



Elution of Am and Pu from 100 g Soil Leach on DGA Resin

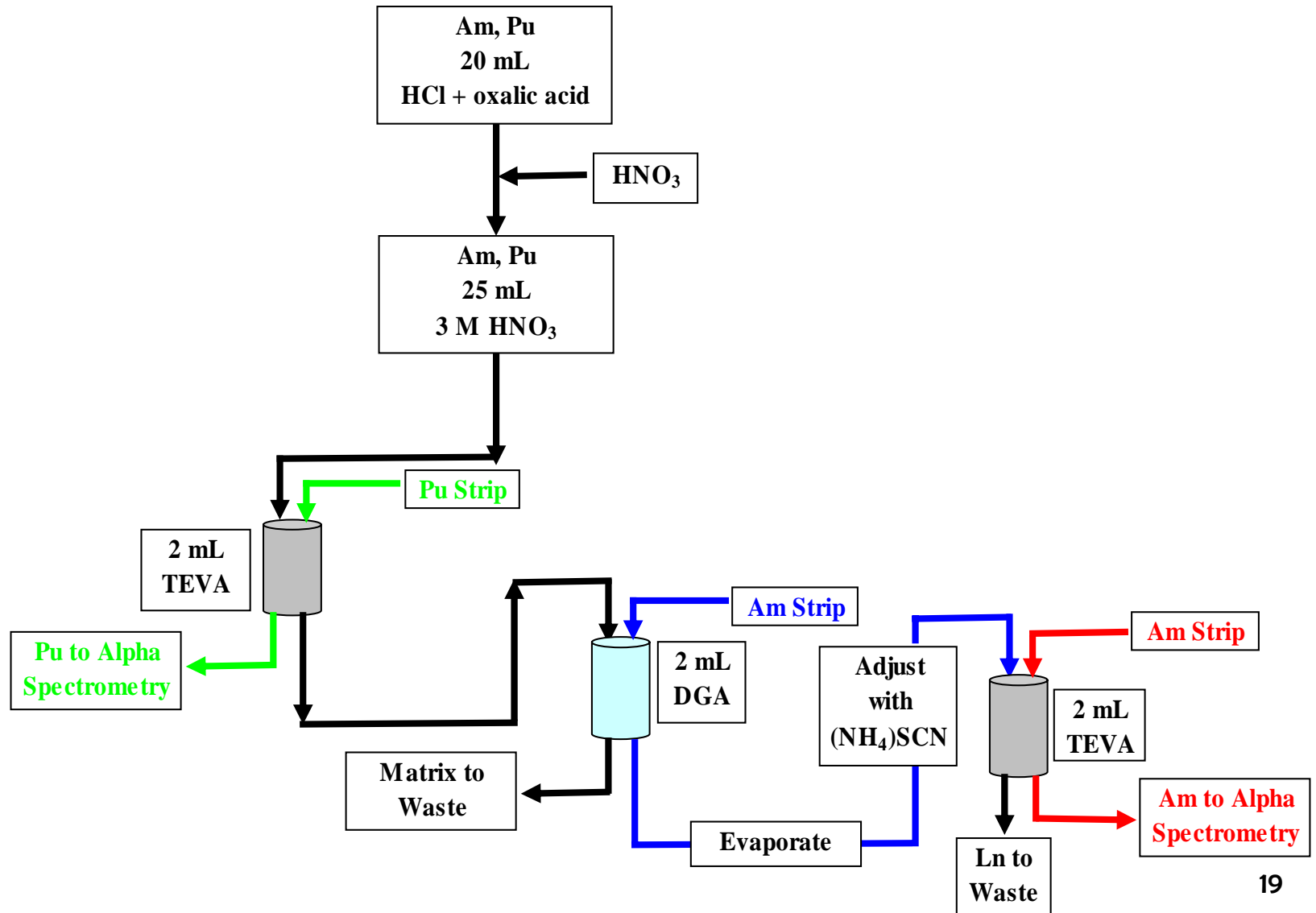
2.0 mL column of DGA Resin (50-100 μm), 1.5 cm i.d. x 1 cm length



**Fraction of Major and Minor Constituents
Removed from Am/Pu Fraction**

Major Constituents	Fraction Removed
Al	3×10^4
Ca	3×10^1
Fe	4×10^4
Mg	6×10^4
P	$>10^2$
Lanthanides	
La-Nd	~ 2
Sm-Eu	negligible
Minor Constituents	
Ba, Cu, Mn, Na	$>10^2$
Ni, Pb, Si	$>10^2$

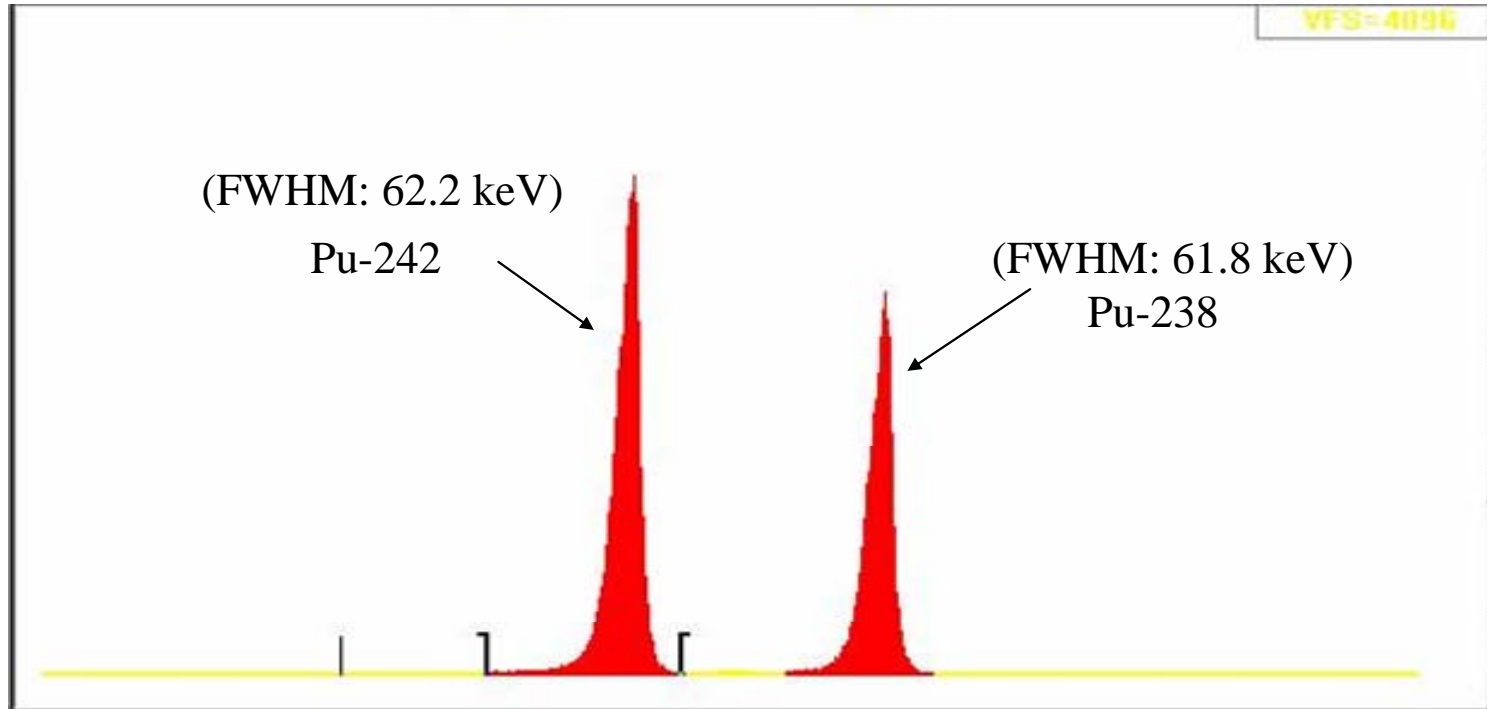
Flowchart for the Separation of Pu and Am from Preconcentrate



Results of Rapid Soil Method (100 g Soil)

Isotope	MAPEP-04		MAPEP-05	
	Found (Bq/kg)	Reported (Bq/kg)	Found (Bq/kg)	Reported (Bq/kg)
^{238}Pu	31.2	35.4	59.0	60.8
^{241}Am	68.4	69.0	107	94.0
Results based on : 50 to 60% recovery of ^{243}Am 40 to 65% recovery of ^{242}Pu				

Pu fraction: 100 g MAPEP-05-MaS14 Soil Sample



MARKER INFO

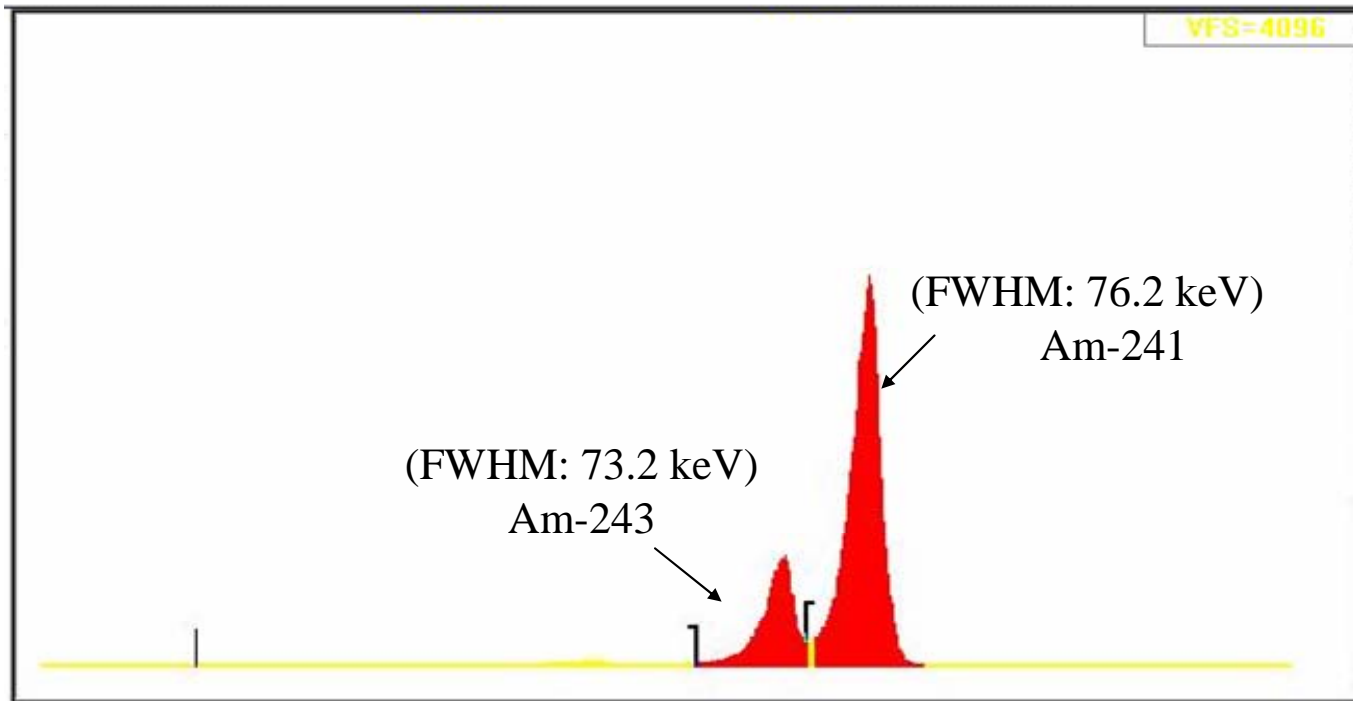
Next

Prev

Left Marker: 334 : 4506.9 keV
 Right Marker: 476 : 4977.6 keV
 Centroid: 434 : 4838.2 keV
 Area: 68144 ± 0.38%

FWHM, FWTM: 62.218, 135.141 keV
 Gaussian Ratio: 1.191
 ROI Type: 1
 Integral: 68144

Am fraction: 100 g MAPEP-05-MaS14 Soil Sample



MARKER INFO

Next

Prev

Left Marker: 540 : 5034.4 keV

Right Marker: 627 : 5305.6 keV

Centroid: 602 : 5228.9 keV

Area: 20266 ± 0.70%

FWHM, FWTM: 73.213, 164.473 keV

Gaussian Ratio: 1.232

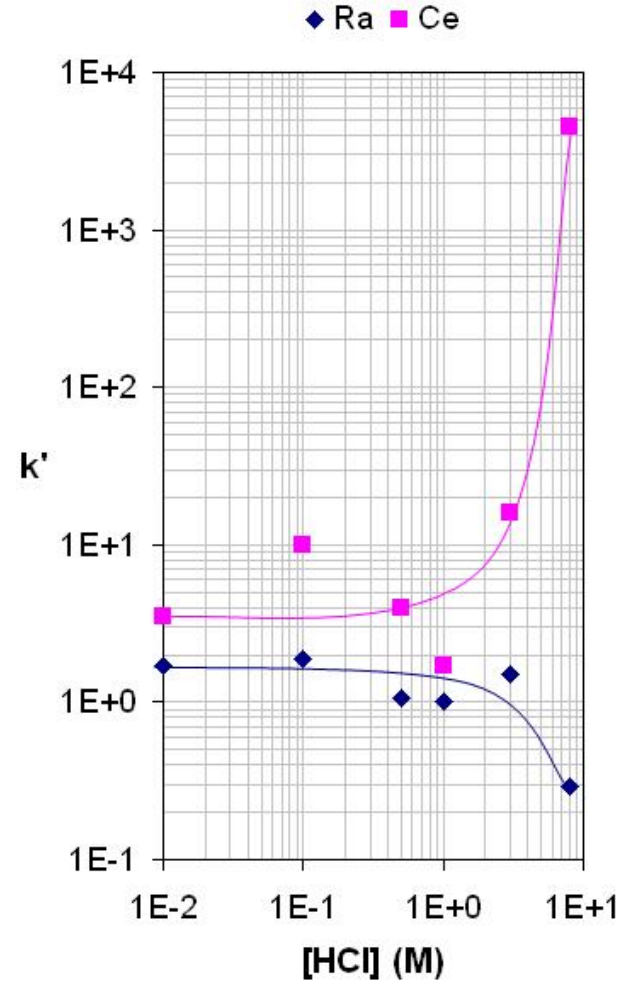
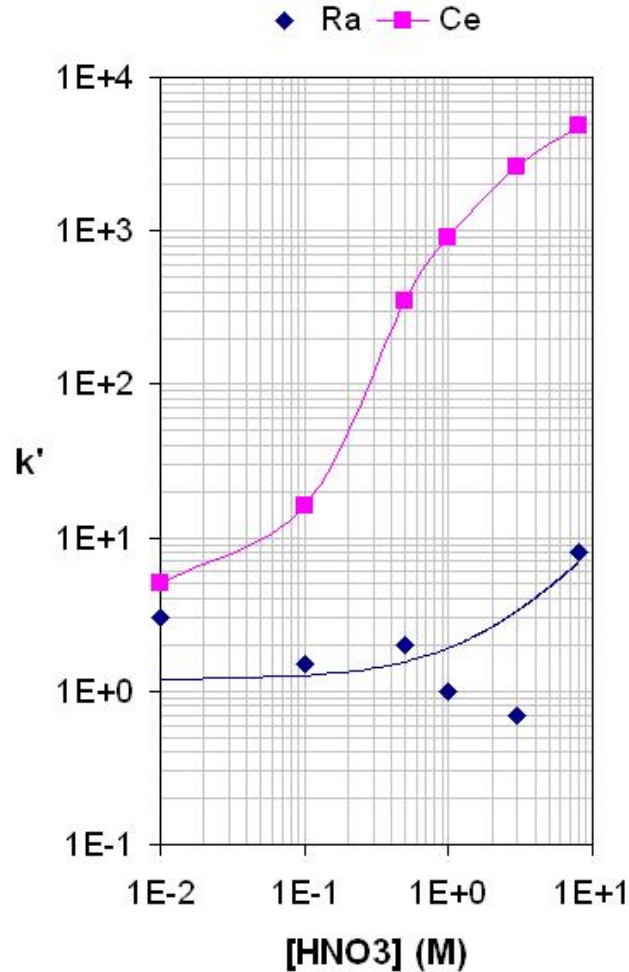
ROI Type: 1

Integral: 20266

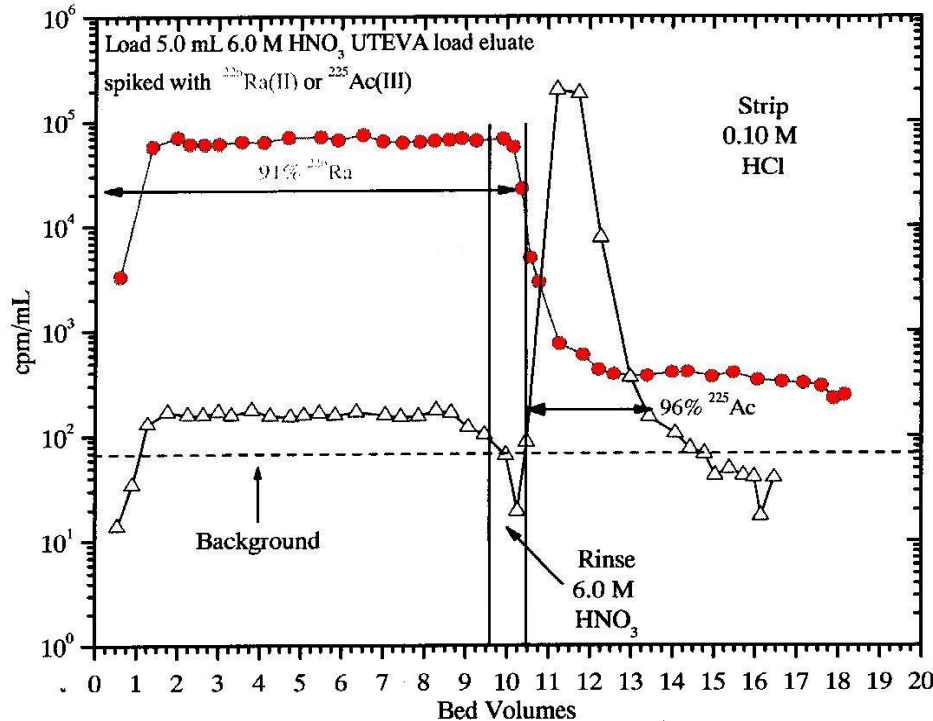
Radium/Actinium separation

- Nuclear medicine
- Determination of ^{226}Ra and ^{228}Ra in environmental samples
 - Chemical yield: ^{133}Ba (γ -spec.)
 - Measurement of ^{226}Ra *via* α -spec after micro-precipitation
 - Measurement of ^{228}Ra *via* ^{228}Ac (GPC)
- Actinium: La and Ce used as homologues

Radium/Actinium separation



Results obtained on DGA, Normal (50-100 μ m)



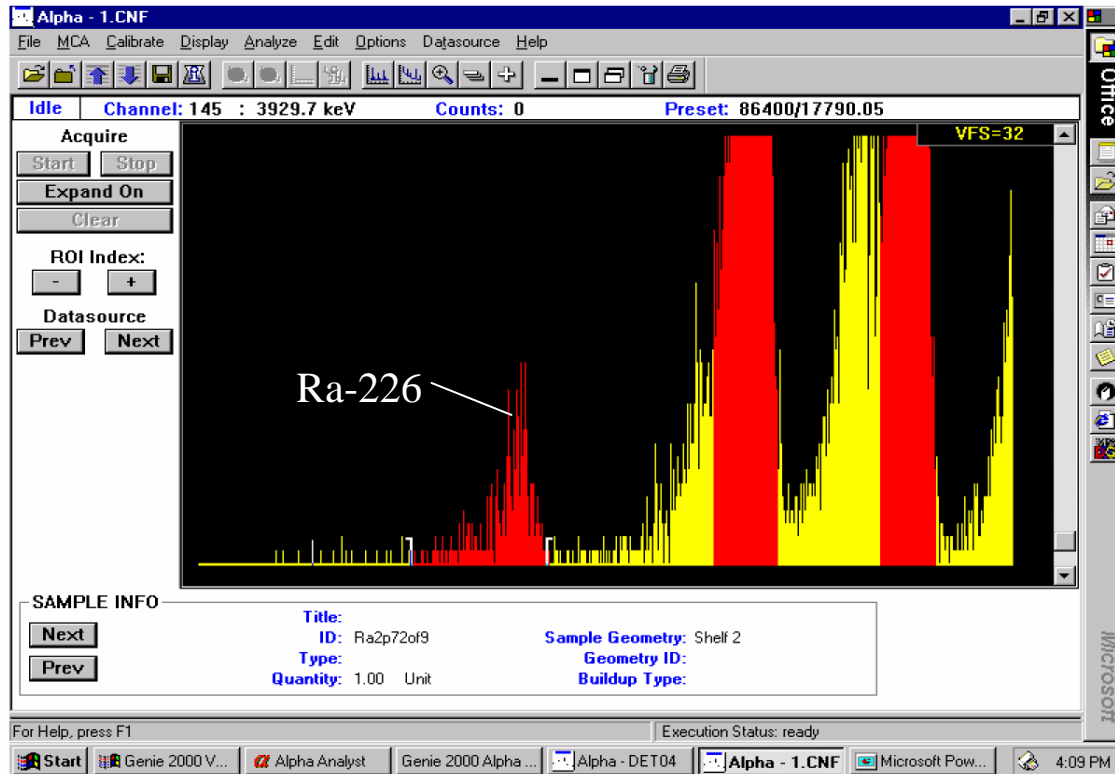
Separation of Ac(III) and Ra(II) on TODGA resin (50-100 μm) with 6.0 M HNO₃ and 0.1 M HCl, 0.5 mL bed volume, flow rate equals 2 mL/min load/rinse, 1 mL/min strip, 22(1)°C.

- Application in Ac-225 separation for Bi-213 production
- DGA on Silica

- New draft method using MnO_2 and DGA
- Water samples
- Advantages:
 - High sample throughput
 - Via GPC and α -spec
 - No need to wait for ^{226}Ra to equilibrate
 - Only one aliquot for both Ra isotopes (0,5 – 1 L)
 - Detection limits
 - Ra-226: ca. 1 mBq.L⁻¹,
 - Ra-228: ca. 10 – 40 mBq.L⁻¹
 - over night counting
- Disadvantage:
 - No internal standard for Ac

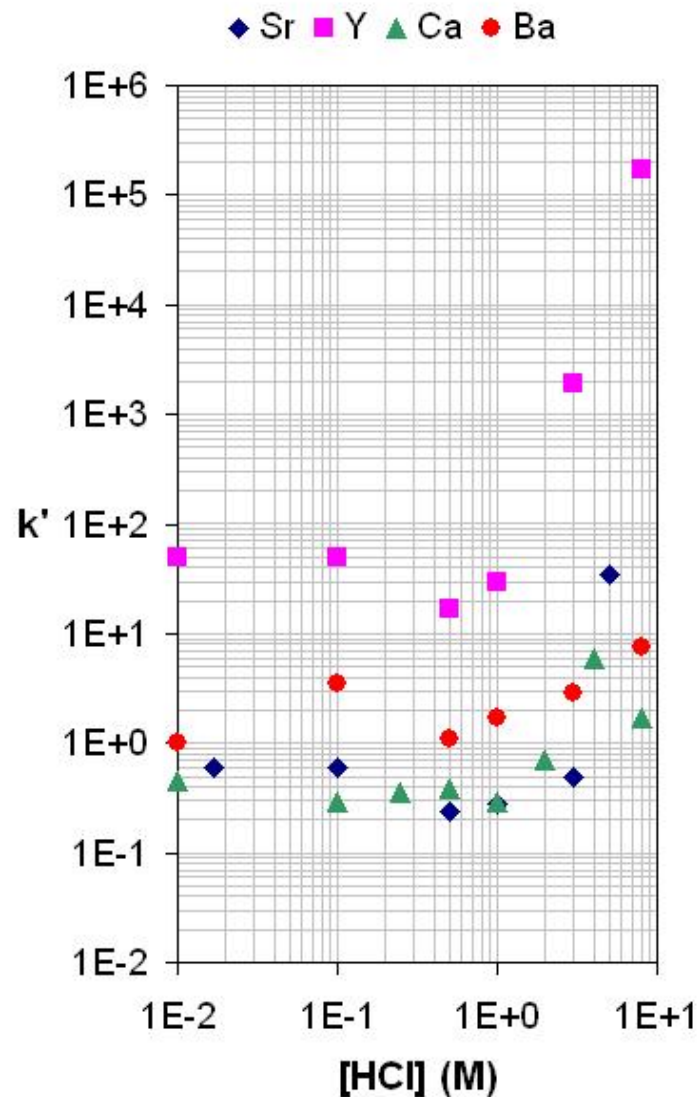
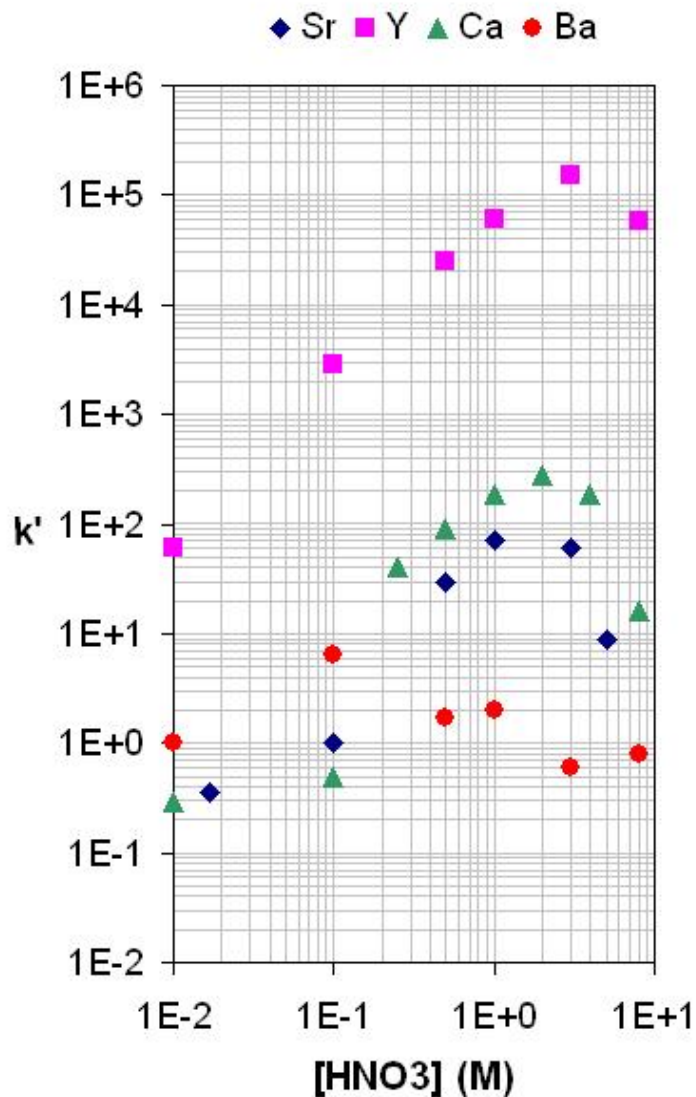
- MnO_2 resin used for preconcentration
 - Column mode (batch mode also possible)
 - 1 L aliquotes, flow rate $15 \text{ mL}\cdot\text{min}^{-1}$, 1 g MnO_2 Resin
- ^{133}Ba for extraction yield determination
- Ba/Ra elution with 5M HCl / 1,5% H_2O_2
- Sample stored > 30 h for Ac-228 ingrowth
- Load onto DGA cartridge
- Rinse with 5M HCl
 - Ba and Ra pass during load and rinse
 - Other alpha emitters and Ac are retained

- Ac selectively eluted with 2M HCl
- Microprecipitation with CeF_3 and GP counting
- Good Decontamination factors for potential interferents
 - $^{90}\text{Sr}/^{90}\text{Y}$ and $^{210}\text{Pb}/^{210}\text{Bi}/^{210}\text{Po} > 1000$
 - U and Th > 300
- Yield for ^{133}Ba and ^{228}Ac in the order of 80%
- Sample load and rinse combined for ^{226}Ra determination
 - Source preparation for α -spectrometry *via* microprecipitation (BaSO_4)
 - yield determination *via* γ -spectrometry

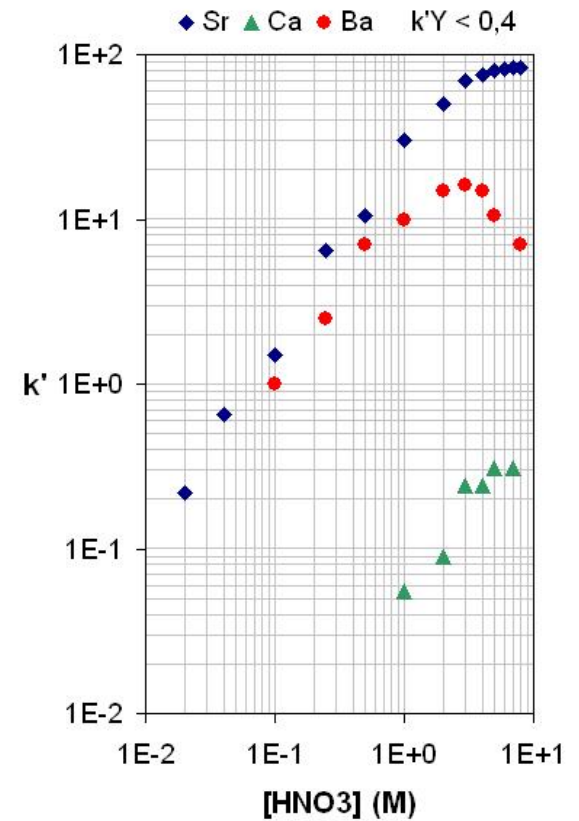
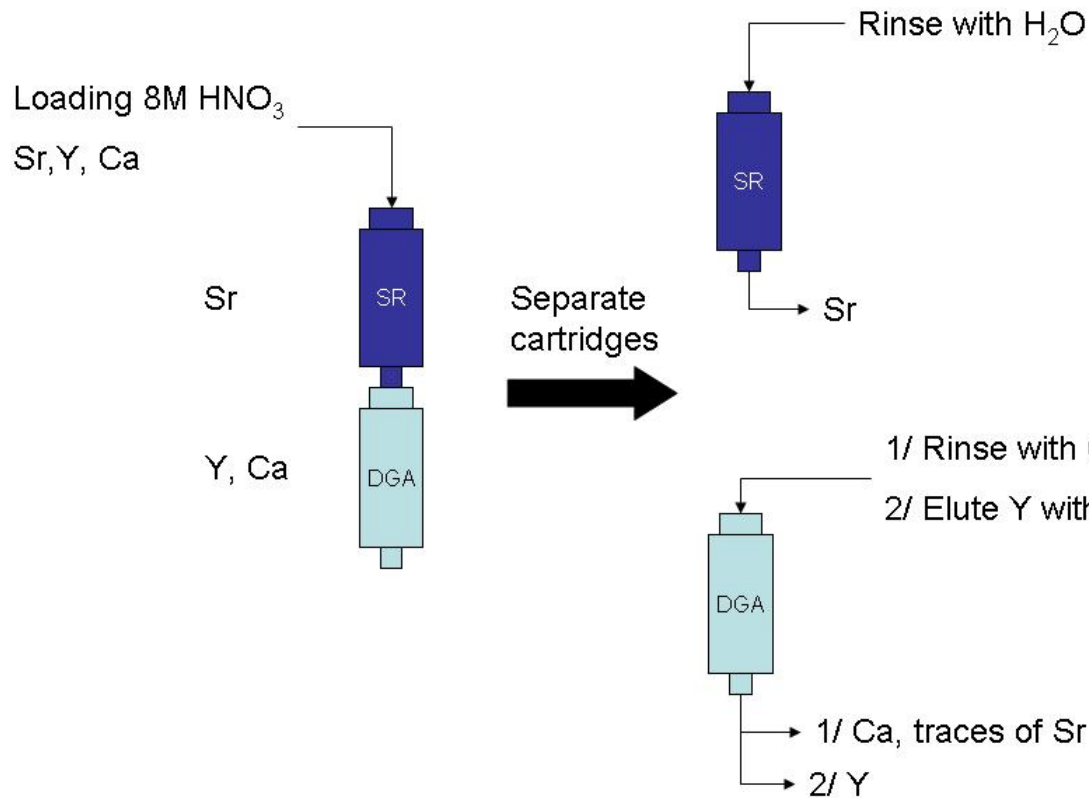


- ^{226}Ra spectrum of a tap water sample (500 mL) after separation and microprecipitation with BaSO_4 (^{133}Ba as yield monitor)
- No interference from ^{226}Ra daughters after ingrowth

Strontium/Yttrium separation



- **Sr/Ca: no separation, Sr/Ba separation possible**
- **Separation of Y from Sr/Ca**
- **Stripping of Y with 0.5 M HCl**
- **Potential applications:**
 - Preparation of high purity Y and Sr by combining Sr and DGA Resins (Nuclear medicine)
 - Direct analysis of ^{89}Sr and ^{90}Y *via* Cerenkov counting using 2 columns method



Sr Resin

Conclusion

Applications for DGA Resin

- Am determination in difficult matrices
- Preconcentration of Actinides from soil leachates
- Ra/Ac separation
 - ^{225}Ac for nuclear medicine
 - In combination with MnO_2 : Ra-226/8 determination
- Y/Sr separation
 - Use in combination with Sr resin
 - Nuclear Medicine (^{90}Y production)
 - Environmental analysis

Bibliography

- Horwitz E.P., Thakkar A., McAlister D.R.; *10th International Symposium on Environmental Radiochemical Analysis, September 2006*
- Horwitz E.P., McAlister D.R., Bond A.H., Barrans R.E. Jr.; *Solvent Extraction & Ion Exchange, Vol. 23, p. 319-344(2005)*
(Eichrom ref #HP104)