Separation of Mock Used Fuel and Mock Glass Debris using Eichrom Resins

Radiobioassy and Radiochemical Measurement Conference

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October 28, 2014

LA-UR -14-28270

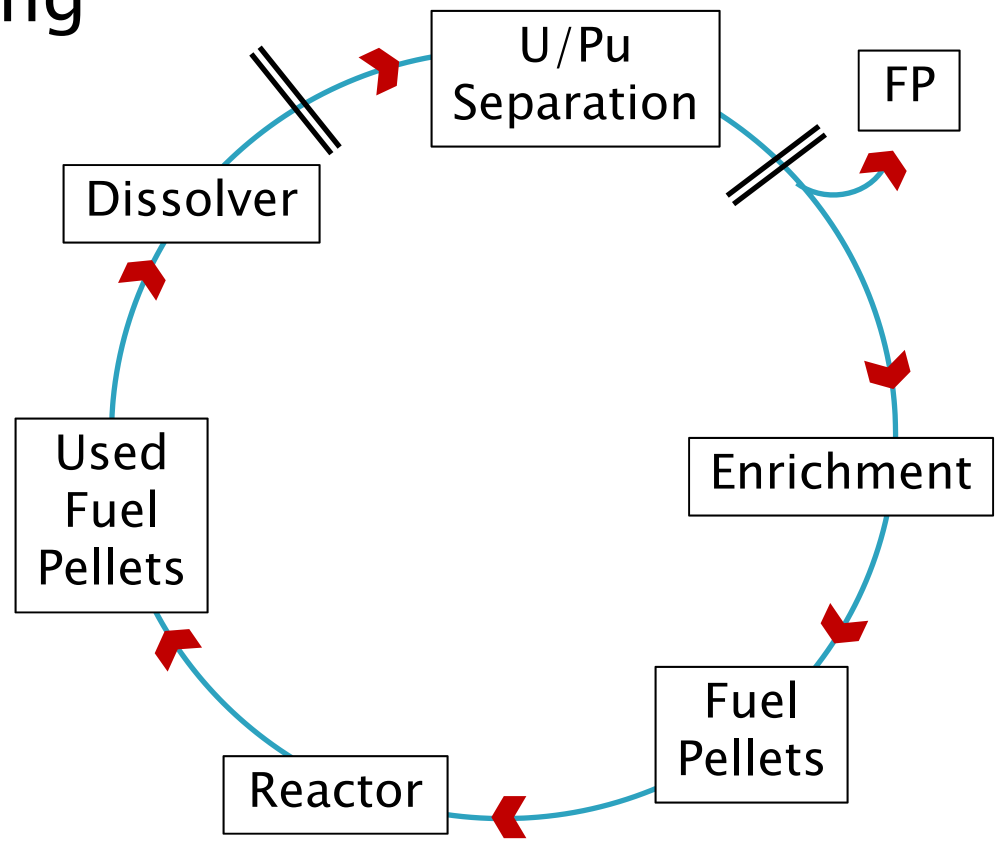
Mock Used Fuel

Safeguards

- Material Accountancy (IAEA)
  - Special Nuclear Material: Pu-239, U-233, and U-235
  - Near Real Time Accountancy (NRTA)
  - Homogenous Samples
  - Batch Data
    - "Source data may include, for example, … element concentration, isotopic ratios, relationship between volume and manometer readings and relationship between plutonium produced and power generated"

Material Accountancy of Used Fuel

- Spent Fuel Reprocessing Streams
  - Spent Fuel Composition
  - PUREX process
  - Possible contaminants



Safeguard Analytical Methods for the Nuclear Fuel Cycle

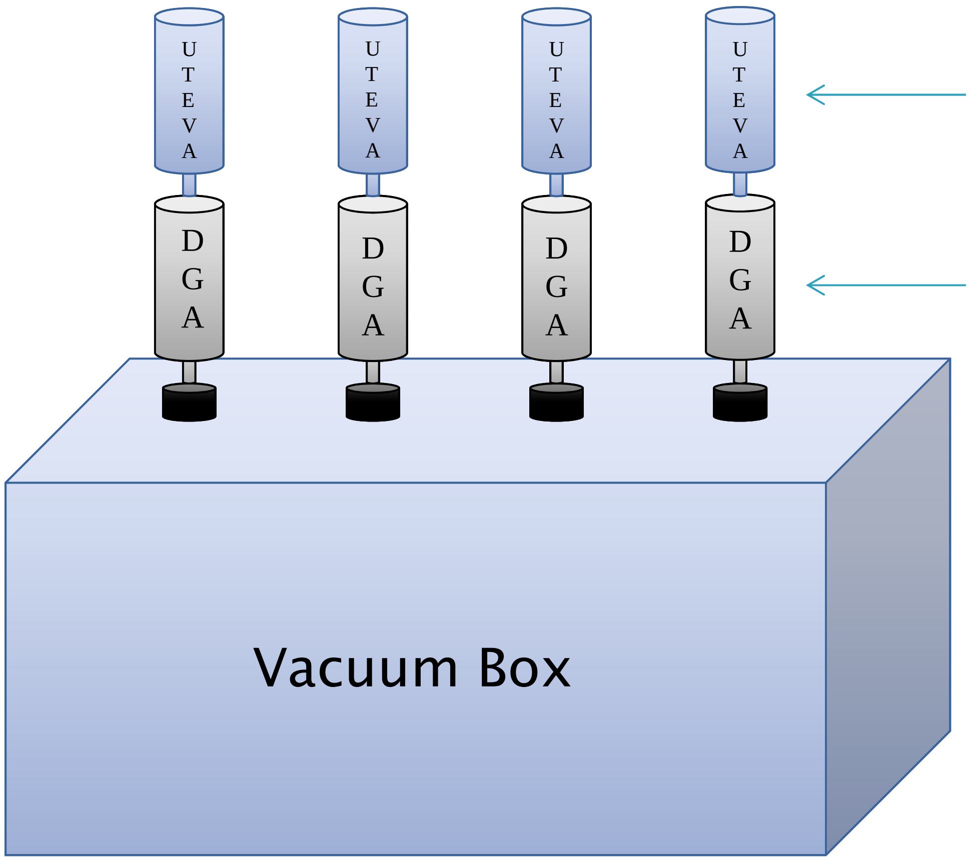
Current Method

- Hybrid K-Edge (HKED)
  - XRF and KED
  - Very accurate
  - Only detects concentration

Proposed Method

- Inductively Coupled Plasma – Mass Spectrometer (ICP-MS)
  - Very accurate
  - Detects concentration of isotopes
  - Numerous isobaric overlaps for actinides
  - Need chemistry of samples prior to analysis

Automated Elution Scheme



Scheme 1

Elute Sr/U(VI)
Add strip
U(IV)

Elute Am Pu(IV)
Add strip
then Am(III)
Pu(III)

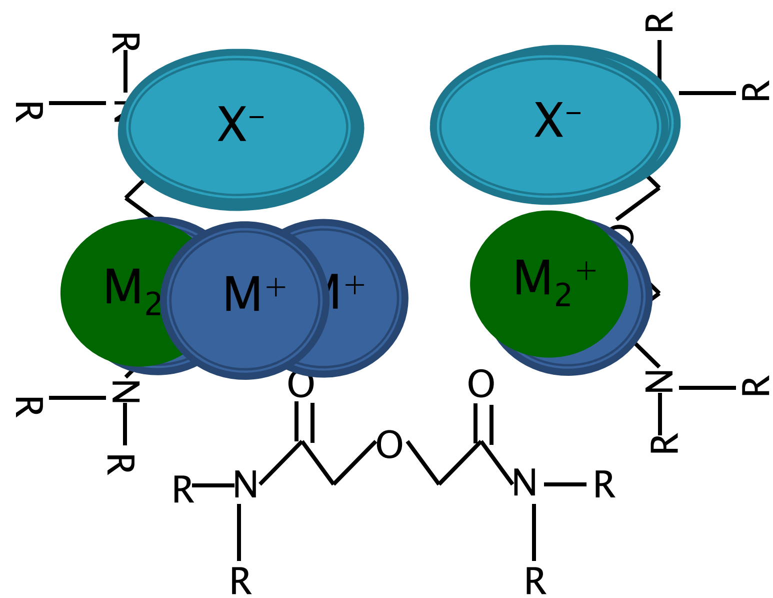
Scheme 2

Elute Pu(III)
Add strip
and strip
Uranium and
U(IV)
Plutonium

Elute Am(III)
Add strip
Americium

Component Effects on Adsorption

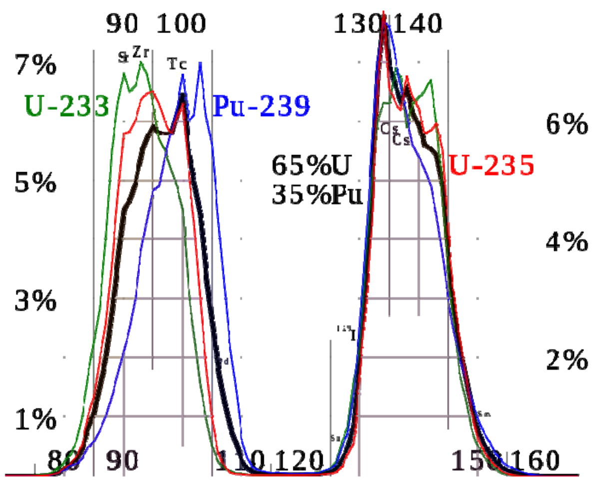
- Synergistic Effect
  - The combined species has a higher affinity than the individual species
- Antagonistic Effect
  - The combined species has a lower affinity than the individual species
- Competition Effect
  - The additional component competes with another metal for adsorption sites, lowering the number of available sites



Used Fuel Components

ORIGIN calculation for mass percentages are based on:

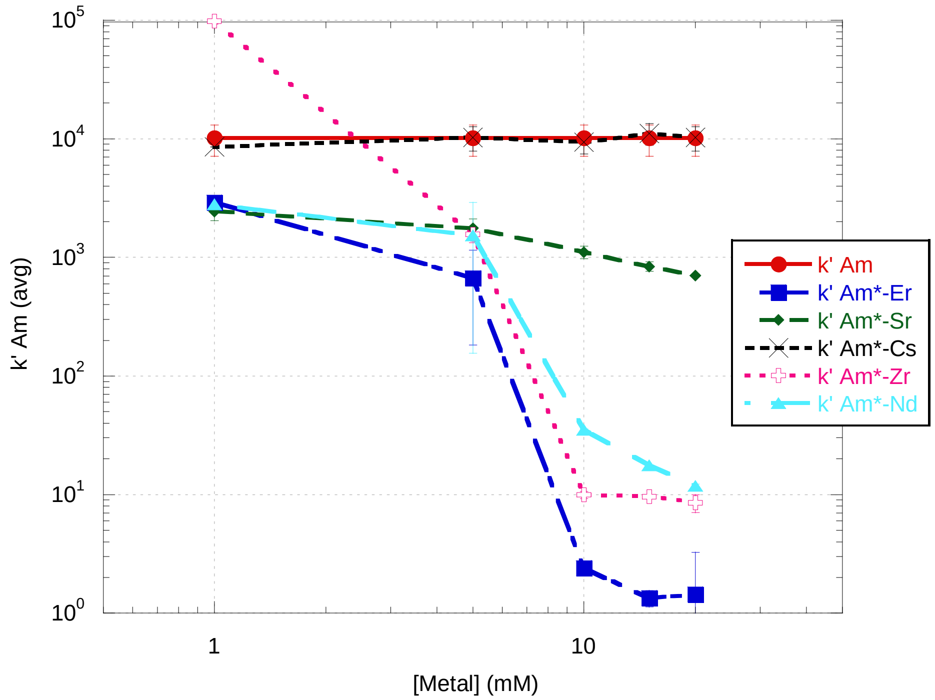
1. 30 MWd/kg M burnup
2. 10 year cool down period
3. 2.9% initial ^{235}U enrichment

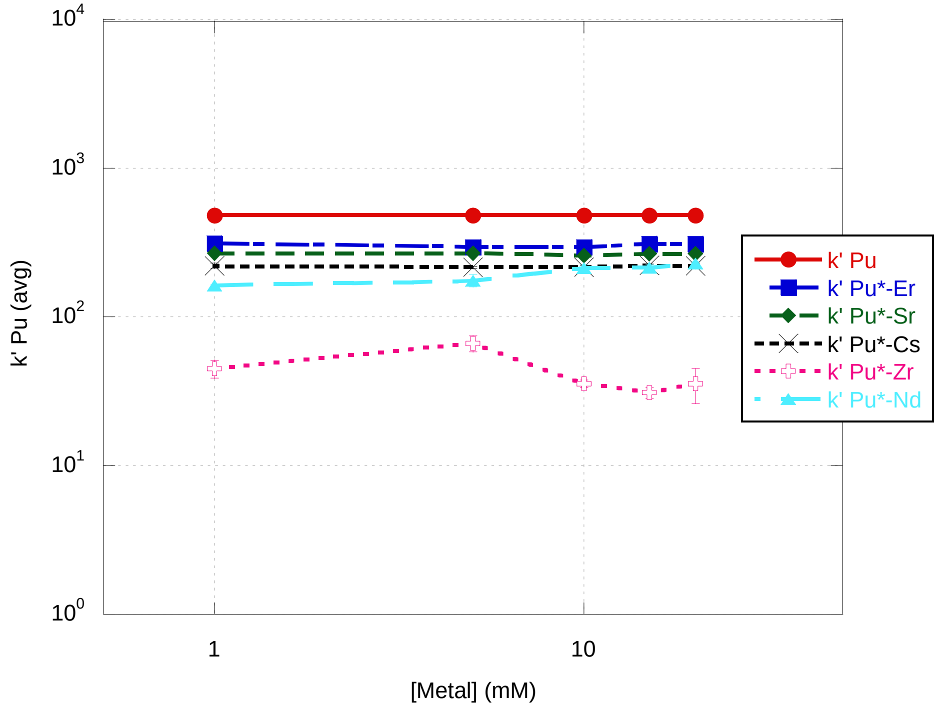


Ranked by Mass		
Rank	Element	Percent
1	U	98.43
2	Pu	0.85
3	Nd	0.13
4	Cs	0.13
5	Ce	0.1
6	Tc	0.07
7	Zr	0.07
8	Am	0.06
9	Np	0.04
10	Sr	0.04
11	Rb	0.02
12	Sm	0.02
13	I	0.02
14	Cm	0.01
15	Sn	<0.00

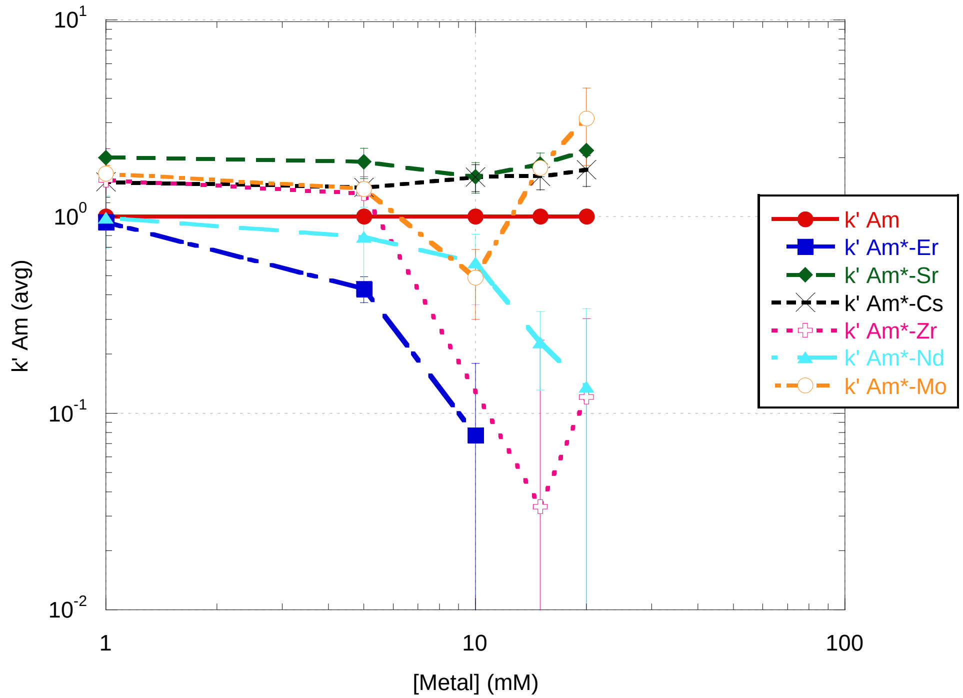
Characterization of Am and Pu Adsorption to DGA Resin in 1M HNO_3 and HCl

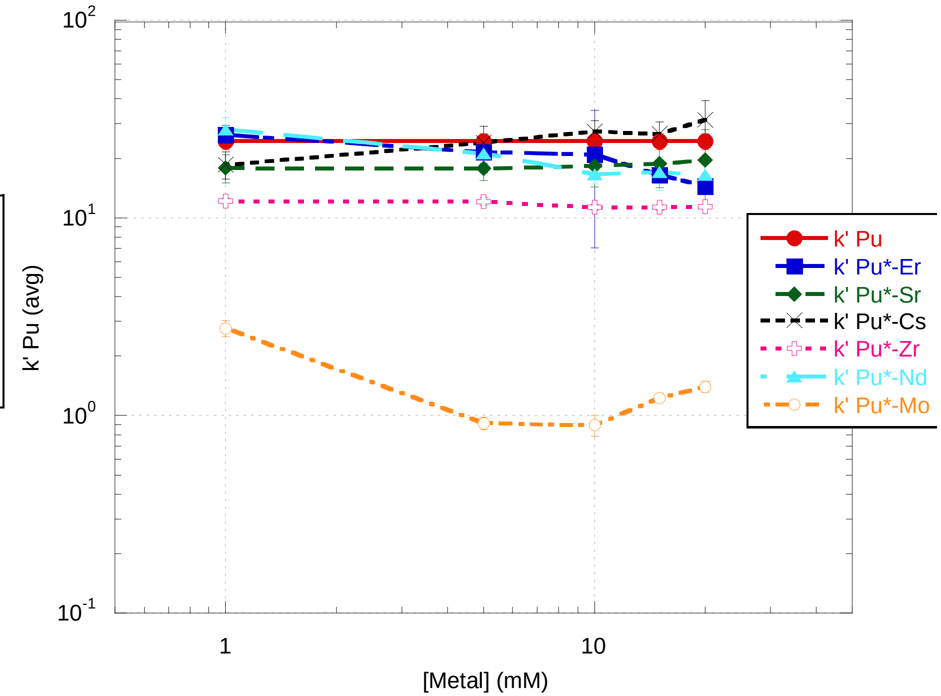
Component Effects on Am and Pu Adsorption to DGA Resin in 1M HNO_3



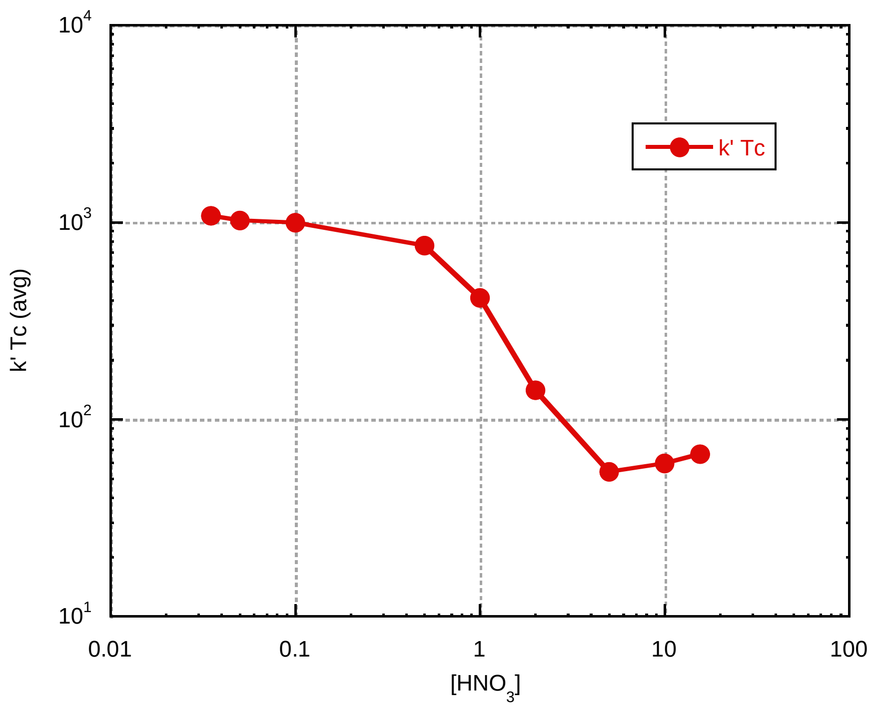


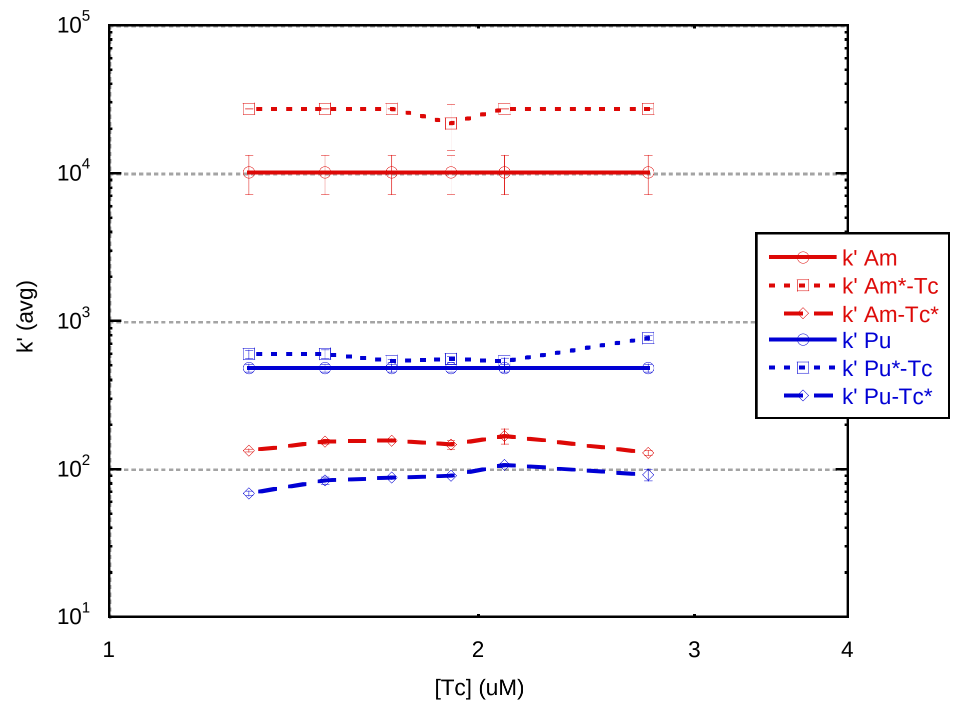
Component Effects on Am and Pu Adsorption to DGA Resin in 1M HCl



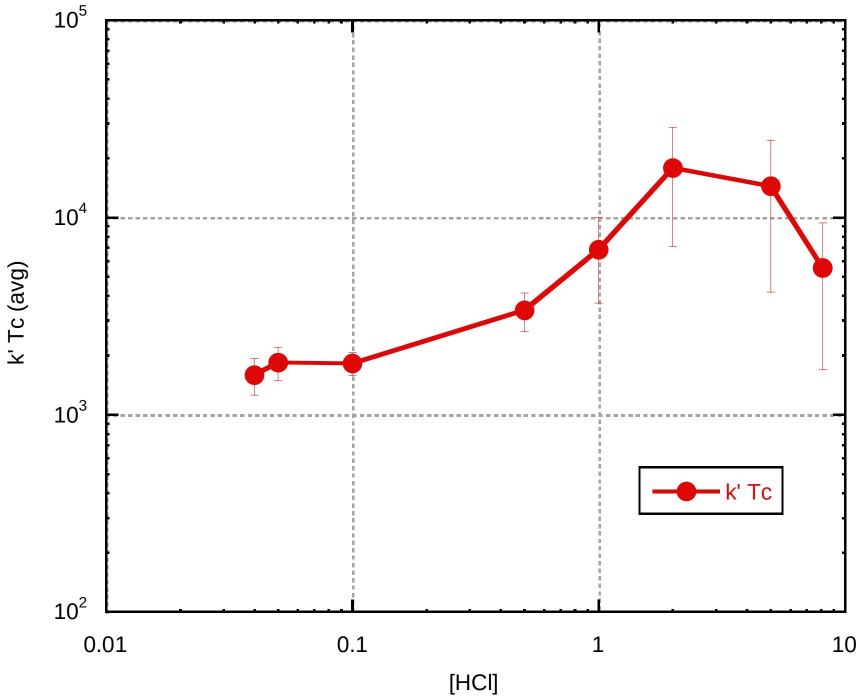


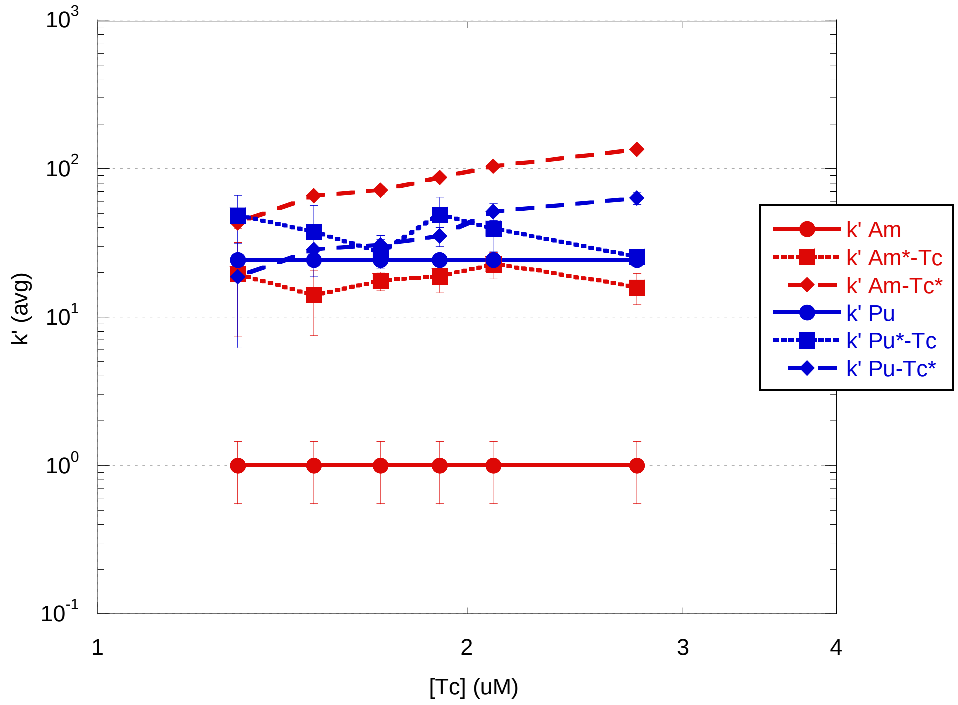
Technetium Characteristics on DGA in 1M HNO_3





Technetium Characteristics on DGA in 1M HCl



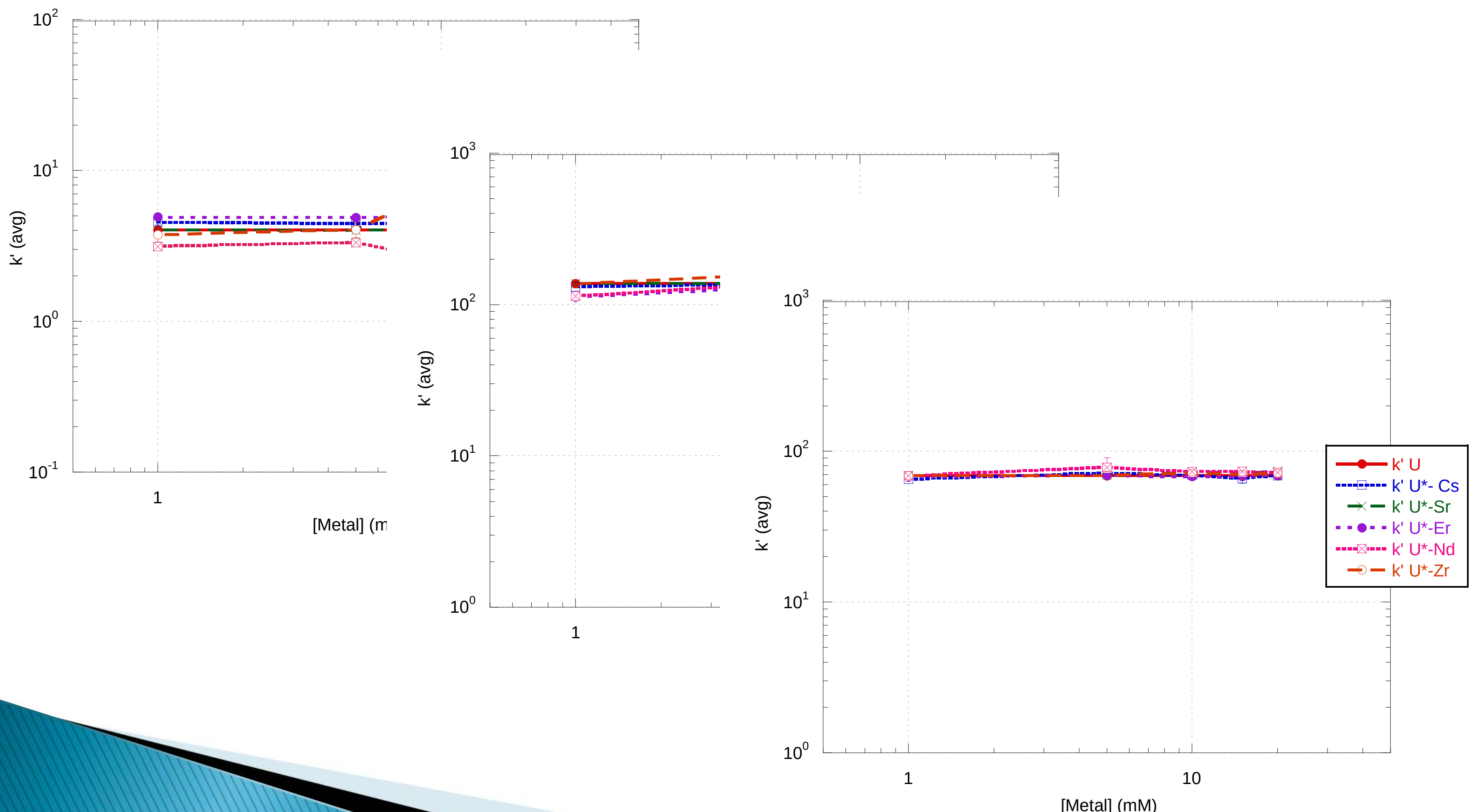


Conclusions on Am, Pu Adsorption to DGA Resin

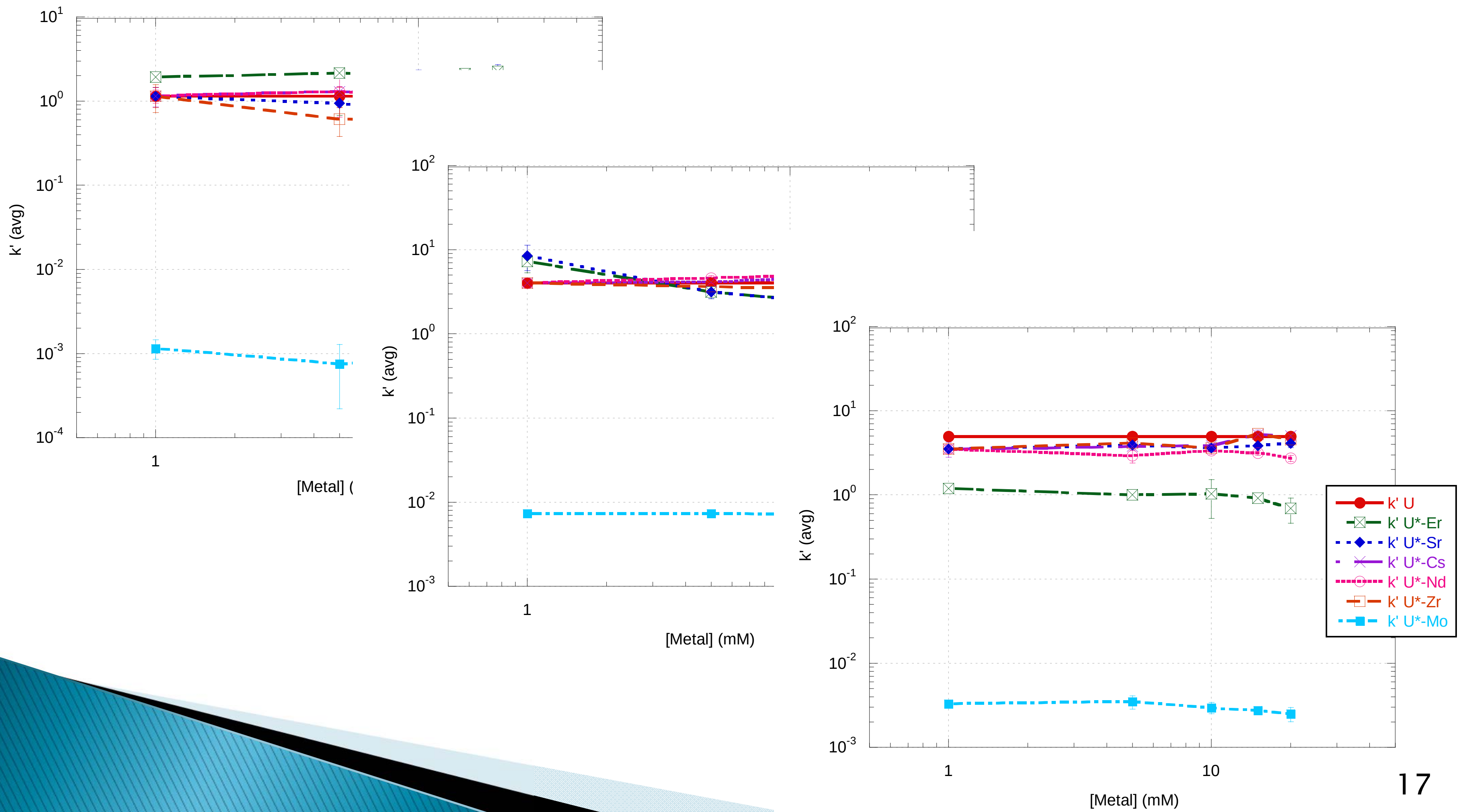
- 5M HNO_3 loading phase seems highly viable since Am and Pu adsorption in 1M HNO_3 is not considerably affected
  - Lanthanides and trivalent actinides are expected to be found in similar elution fractions
- Working capacity of the resin must be determined for DGA based on all trivalent metals
- TcO_4^- shows a synergistic effect on Am adsorption in 1M HCl acid

Characterization of Am, Pu and U Adsorption to UTEVA Resin in 1M HNO_3 and HCl

Component Effects on Am, Pu and U Adsorption to UTEVA Resin in 1M HNO_3



Component Effects on Am, Pu and U Adsorption to UTEVA Resin in 1M HCl



Conclusions on Am, Pu, and U Adsorption to UTEVA Resin

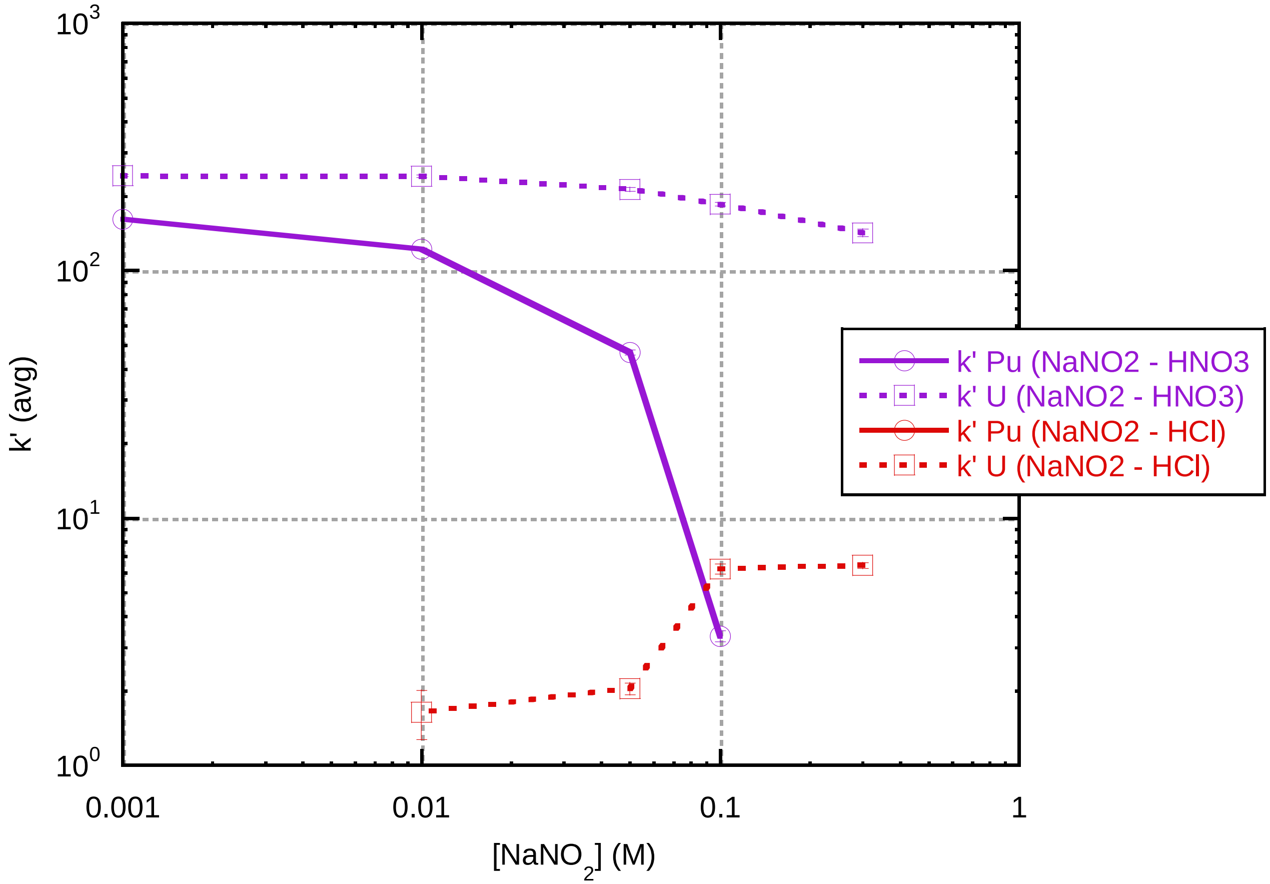
- No affects seen from additional components in 1M HNO_3
  - Loading characteristics should remain unchanged for used fuel
- Molybdenum antagonistic effects most likely due to the formation of complex oxyanions
- Overall, UTEVA very selective to tetra- and hexavalent metals

Investigation of Varying Matrices

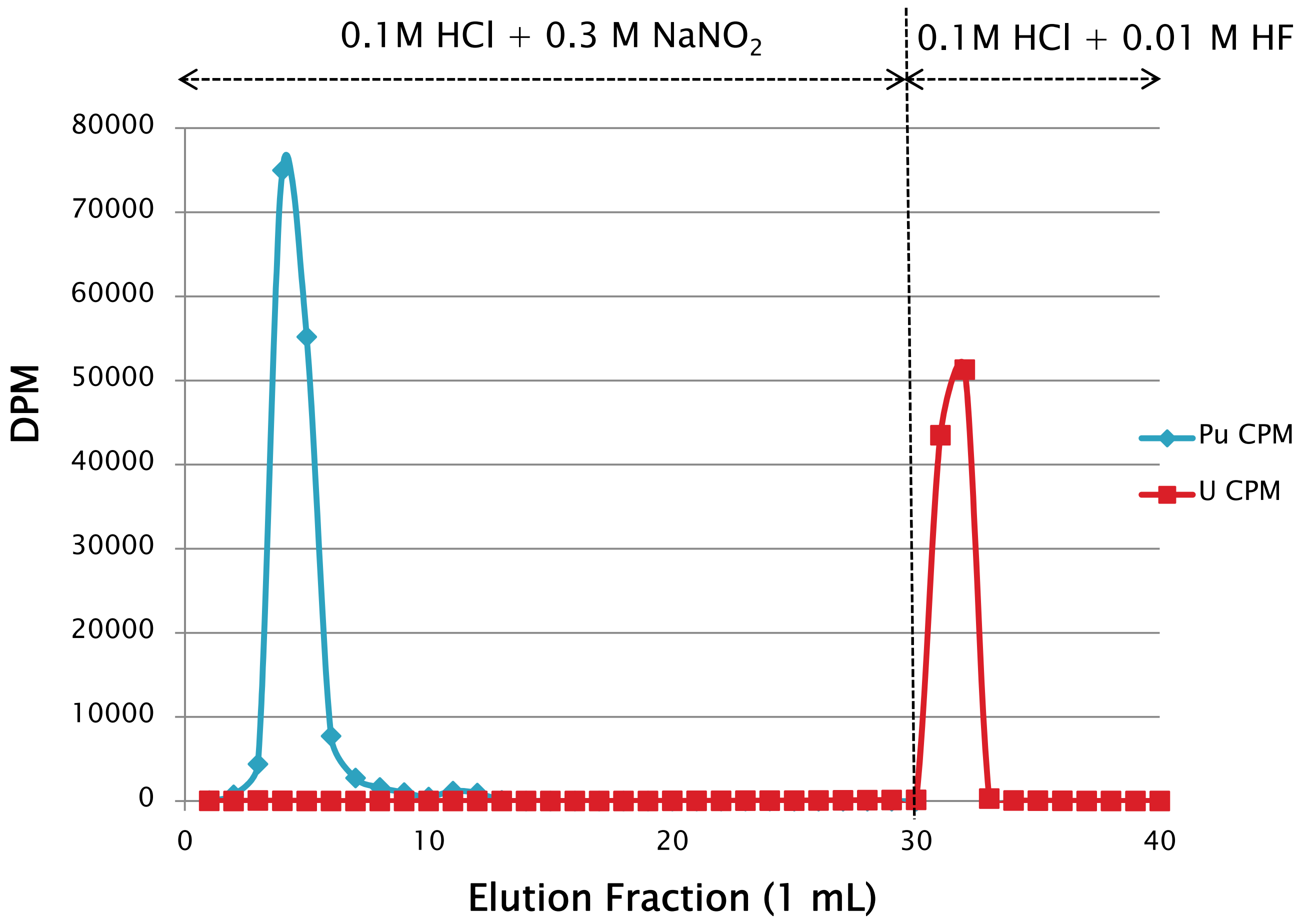
Summary of Varying Matrices Studied

Matrix Constituents	Concentrations (M)	DGA	UTEVA
HNO_3	0.035, 0.05, 0.5, 1.0, 5.0, 10.0, 10.57	Am, Cm, Pu	Am, Cm, Pu, U
HCl	0.035, 0.05, 0.1, 0.5, 2.0, 5.0, 8.1	Am, Cm, Pu	Am, Cm, Pu, U
H_2SO_4	0.25, 0.5, 0.7, 1, 2, 3, 4	Am, Cm, Pu	
HI	0.001, 0.007, 0.015, 0.1, 0.145	Am, Cm, Pu	
HBr	0.001, 0.007, 0.015, 0.1, 0.145	Am, Cm, Pu	
$NaSO_4$ + 1M HNO_3	0.1, 0.5, 1.0, 1.5, 2.0	Am, Cm, Pu	
$NaSO_4$ + 1M HCl	0.1, 0.5, 1.0, 1.5, 2.0	Am, Cm, Pu	
NaBr + 1M HNO_3	0.01, 0.1, 0.5, 1.0, 4.0	Am, Cm, Pu	
NaBr + 1M HCl	0.01, 0.1, 0.5, 1.0, 4.0	Am, Cm, Pu	
$NaNO_2$ + 1M HNO_3	0.001, 0.01, 0.05, 0.1, 0.5	Am, Cm, Pu	Am, Pu, U
$NaNO_2$ + 1M HCl	0.001, 0.01, 0.05, 0.1, 0.6	Am, Cm, Pu	Am, Pu, U
Ascorbic Acid + 1M HNO_3	0.001, 0.01, 0.05, 0.1, 0.3	Am, Cm, Pu	Am, Pu, U
Ascorbic Acid + 1M HCl	0.001, 0.01, 0.05, 0.1, 0.3	Am, Cm, Pu	Am, Pu, U
Oxalic Acid + 1M HNO_3	0.001, 0.01, 0.05, 0.1, 0.3	Am, Cm, Pu	Am, Pu, U
Oxalic Acid + 1M HCl	0.001, 0.01, 0.05, 0.1, 0.3	Am, Cm, Pu	Am, Pu, U

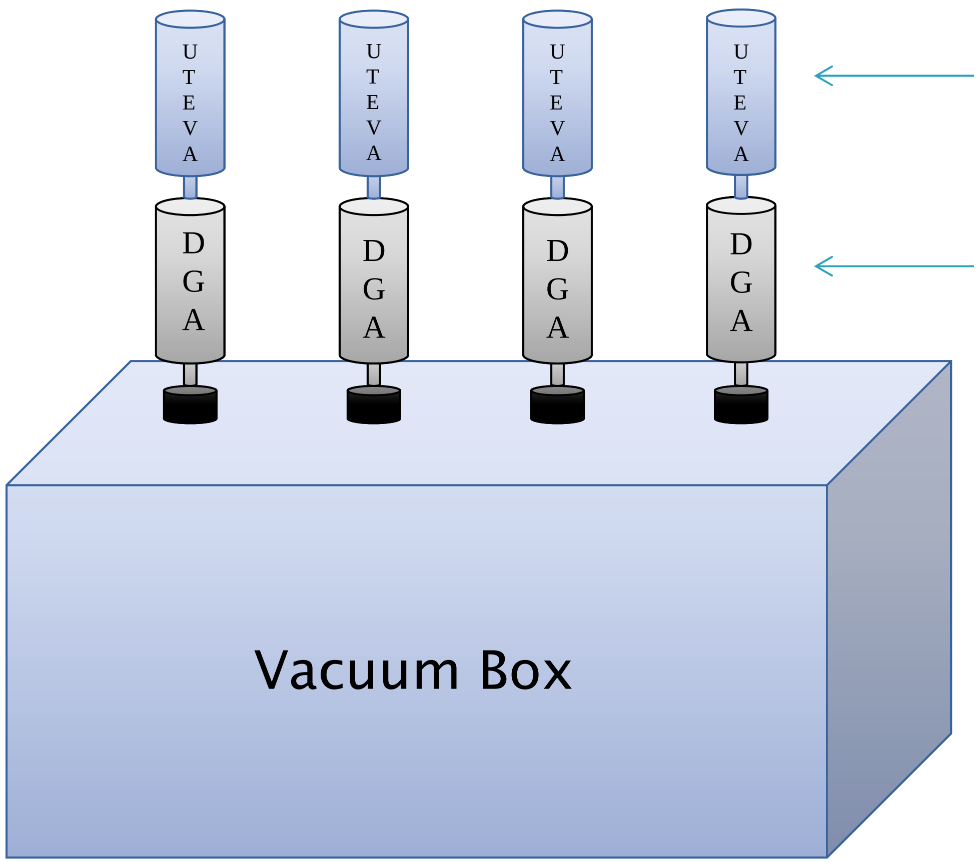
Pu, and U Adsorption to UTEVA in $NaNO_2$



Pu and U separation on UTEVA



Conclusions from Elution Profile Characterizations



Scheme 2

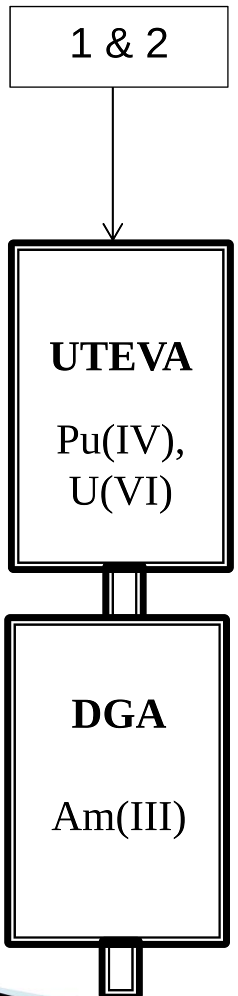
Adsorb Pu(III) and strip Pu(IV)

Elute Uranium and Plutonium

Adsorb Am(III)

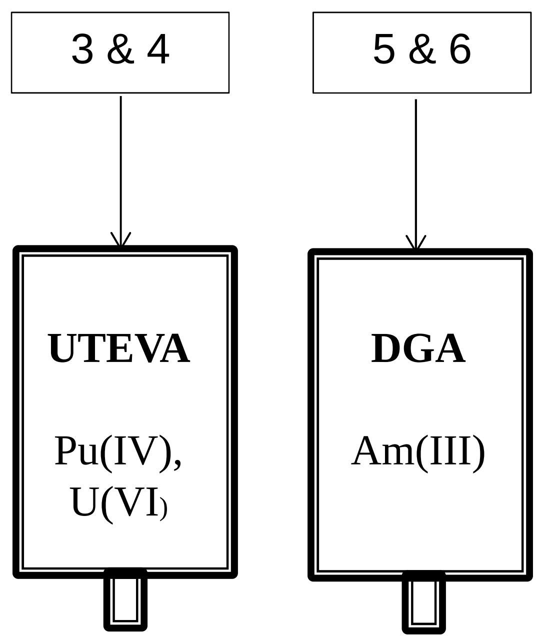
Elute Americium

Proposed Used Fuel Separation



1) Load used fuel onto joined columns using 5M HNO_3.

2) Rinse columns with 5M HNO_3, Pu and U are retained on UTEVA and Am elutes through to DGA



3) Pu(III) Elution:
0.1 M HCl + 0.3M $NaNO_2$

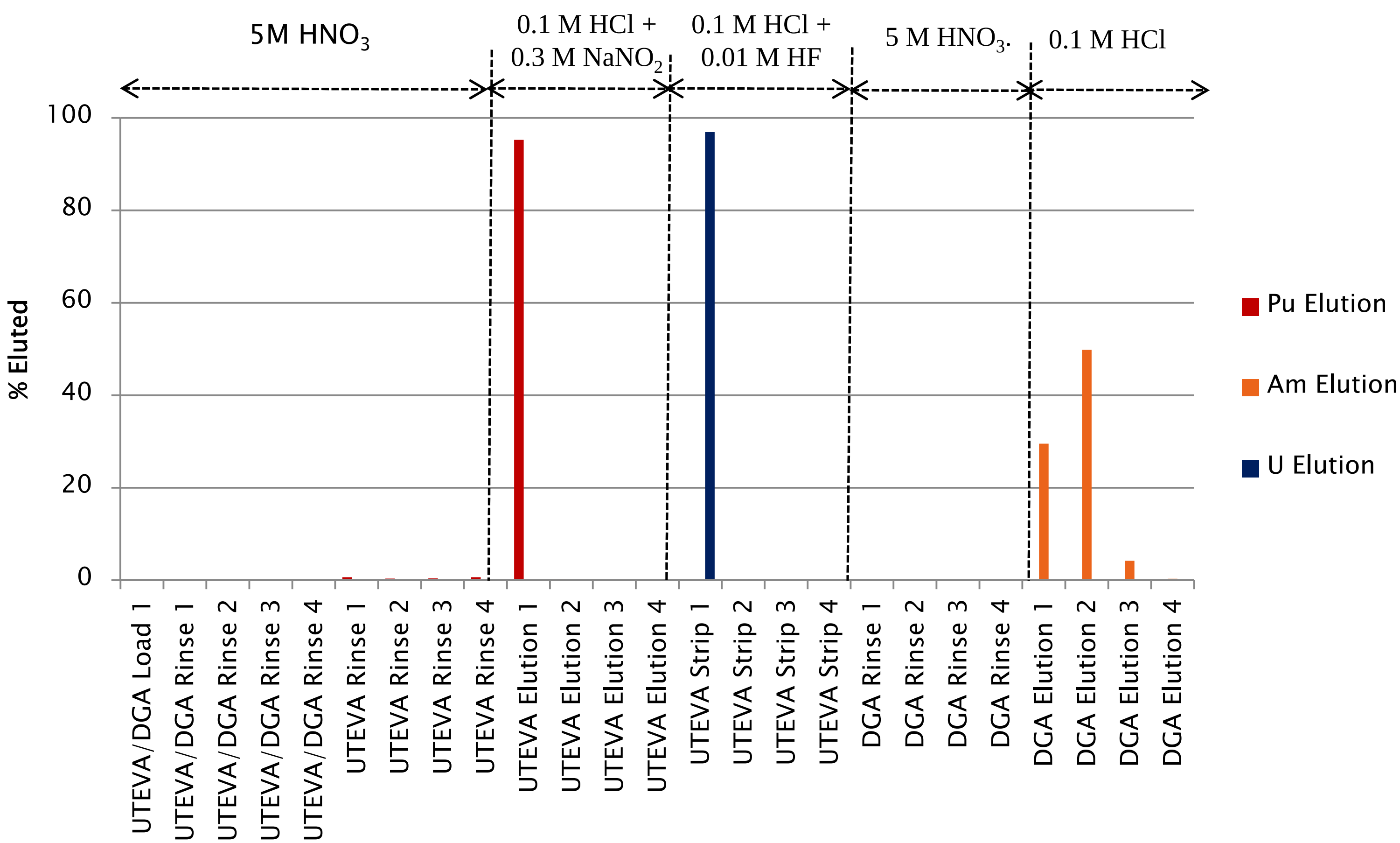
4) U(IV) Elution:
0.1 M HCl + 0.01 M HF

5) Am(III) Elution:
0.1 M HCl.

6) Strip:
0.1 M HCl + 0.01 M HF

Vacuum Box Separations

Actinide Separation on Vacuum Box



2mL prepacked cartridges,
5mL fractions

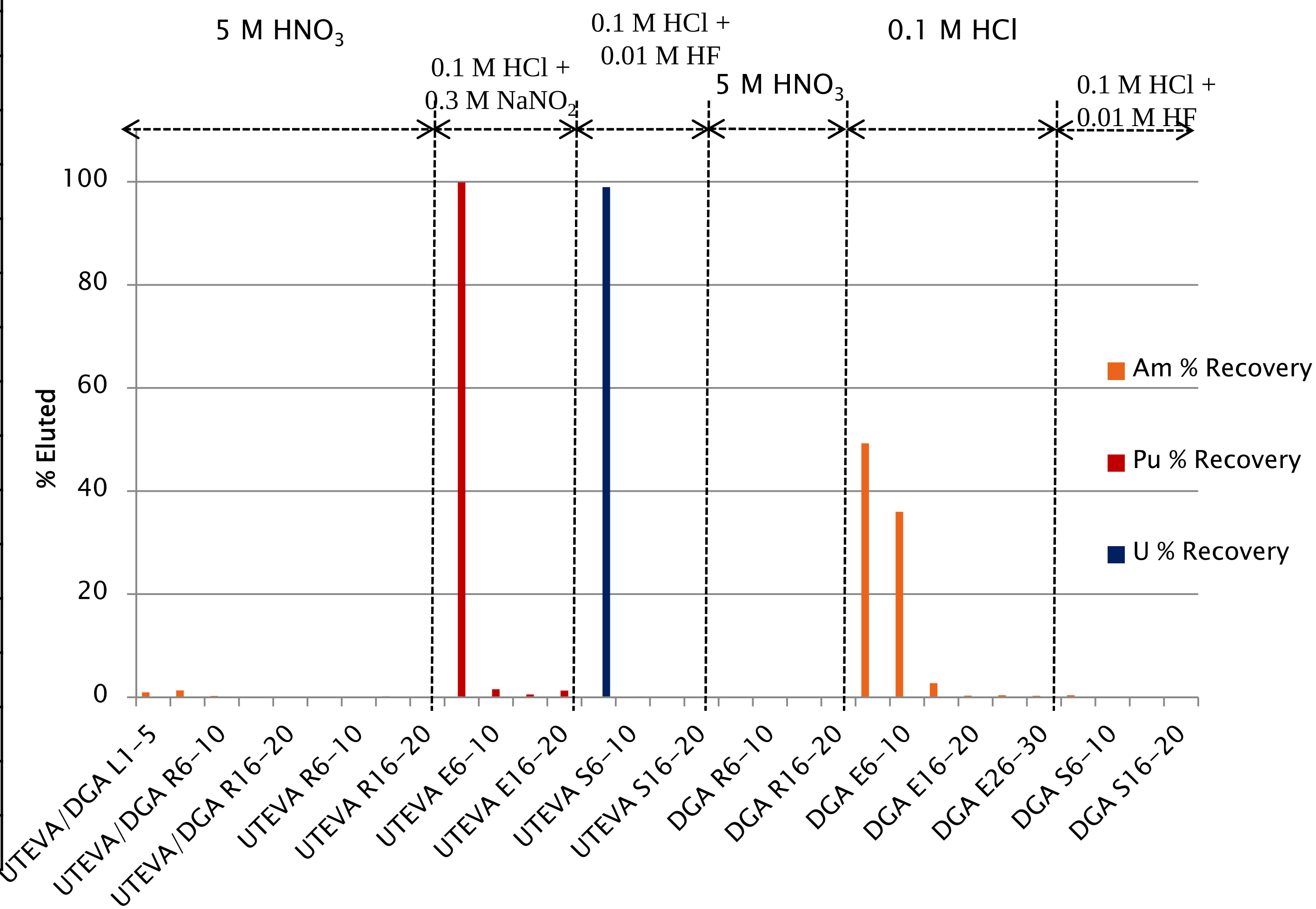
Actinide Separation Conclusion

- Pu and U had sharp elution peaks
- Am had broad elution from DGA resin
  - Most likely due to the elevated flow rates
- Further broadening expected for mock used fuel separation

	% Recovery	**STD**
Am-241	95.01	14.04
Pu-239	95.54	0.06
U-233	97.29	0.68

Rapid Mock Used Fuel Separation

Ranked by Mass		
Rank	Element	Percent
1	U	98.43
2	Pu	0.85
3	Nd	0.13
4	Cs	0.13
5	Ce	0.1
6	Tc	0.07
7	Zr	0.07
8	Am	0.06
9	Np	0.04
10	Sr	0.04
11	Rb	0.02
12	Sm	0.02
13	I	0.02
14	Cm	0.01
15	Sn	<0.00



Conclusions

- Overall, recoveries were still high but had large deviations
- Some additional broadening in Pu elution
- Am elution characteristics varied
  - Most likely due to the addition of Tc-99

	% Recovery	STD
Am-241	92.68	39.60
Pu-239	99.18	1.65
U-233	103.29	5.27

Overall Conclusions

- UTEVA worked great
- Scheme 2 is viable and promising
- Replace DGA possibly with another extraction chromatography resin
  - TRU

Melt Glass Bead Separation

Mock Melt Glass

- Mixture of glass and cement to represent melt glass and urban debris
- Typically a 2 gram sample
- Long digestion process

Material	Main Compounds
Glass	SiO_2, Na_2O, CaO, MgO, Al_2O_3
Cement	CaO, SiO_2, Al_2O_3, Fe_2O_3, $CaSO_4 \bullet H_2O$

Expected Activation Products

Element	Isotope	Natural Abundance (%)[135]	Neutron Cross Section (barns)[136]*	(n,p) Product	Product $T_{1/2}$ (unless noted otherwise)
Titanium	48	73.72	0.05927	^{48}Sc	43.67 h
	46	8.25	0.2893	^{46}Sc	83.79 d
	47	7.44	0.14503	^{47}Sc	3.349 d
	49	5.41	0.0512	^{49}Sc	57.18 m
	50	5.18	0.0113	^{50}Sc	102.50 m
Iron	56	91.75	0.11436	^{56}Mn	2.58 h
	54	5.8	0.33447	^{54}Mn	312.12 d
	57	2.12	0.05705	^{57}Mn	85.40 s
Nickel	58	68.07	0.36358	^{58}Co	70.86 d
	60	26.22	0.1456	^{60}Co	1925.28 d
	62	3.63	0.03117	^{62}Co	1.50 m
	61	1.14	0.09473	^{61}Co	1.65 h
Gold**	197	100	0.00188	^{197}Pt	19.89 h
	196	n/a	0.0056	$^{196}Pt_{(stable)}$	^{196}Au, 6.17 d
	195	n/a	0.003083	$^{195}Pt_{(stable)}$	^{195}Au, 186.09 d

*14.1 MeV neutron energy, for n,p reactions

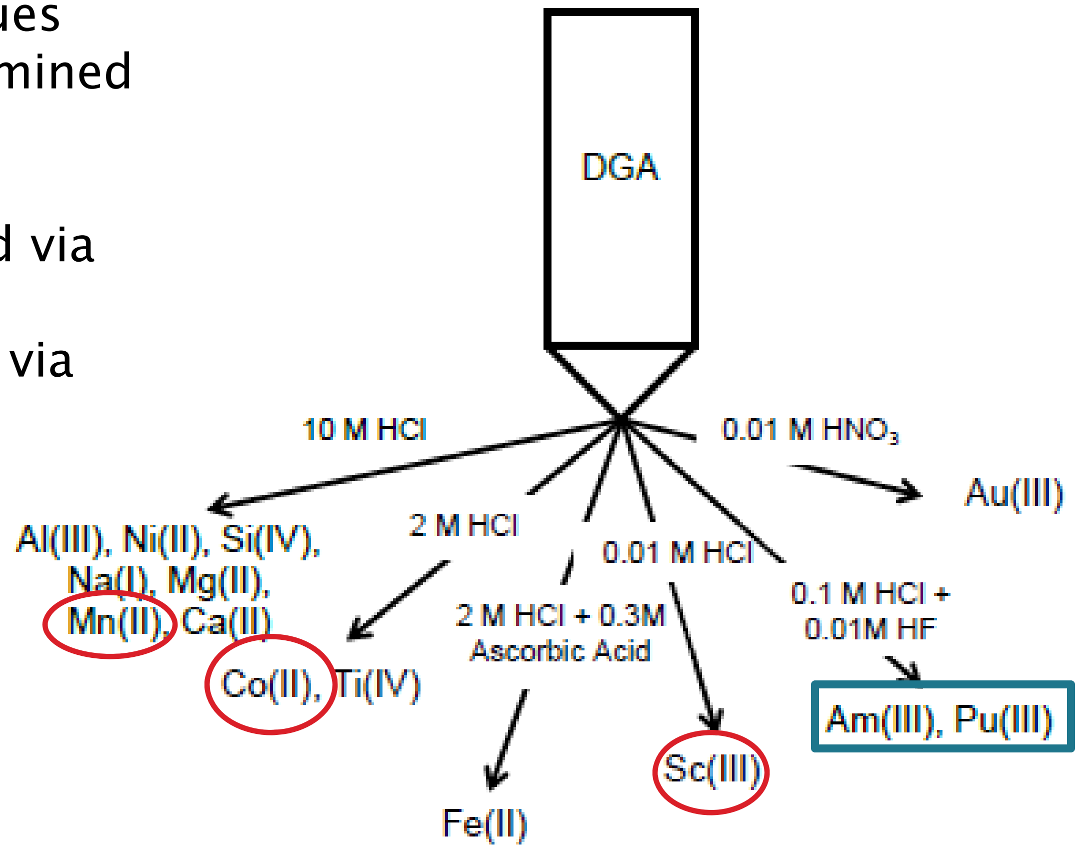
**^{197}Au, elastic scattering σ=2.6354b and n,2n σ=2.1323b

^{196}Au, inl=0.193b and n,2n=1.975578b

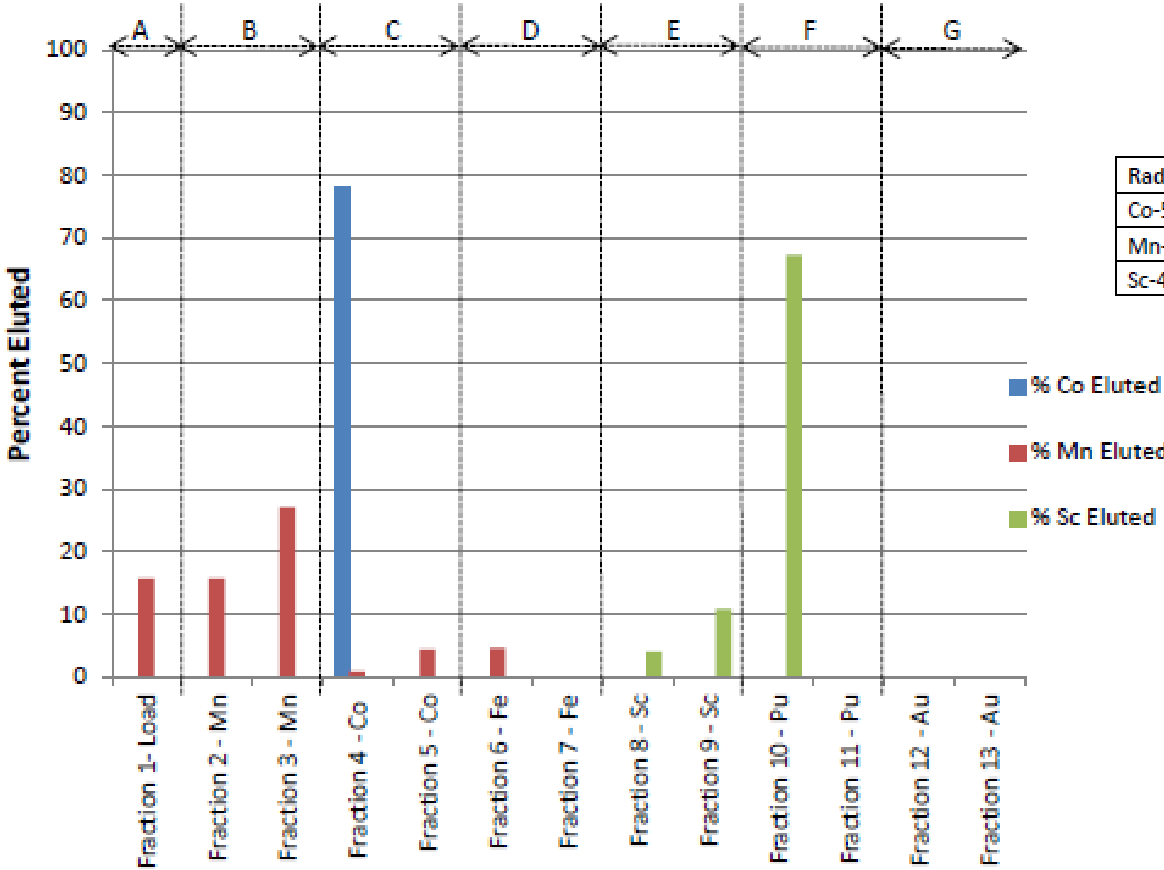
^{195}Au, n-2n=0.8849b or n,p=0.003083b

Proposed Separation Scheme

- Based on literature k' values and experimentally determined k' values
- 10 mL DGA column
- Circled elements analyzed via gamma spectroscopy
- Stable elements analyzed via ICP-AES



Elution Profile for Detectable Activation Products



Radionuclide	% Recovery
Co-57	78.05
Mn-54	68.70
Sc-46	82.25

Figure 112. Glass/Cement Bead Separation Co, Mn, and Sc Elute Profiles
All fractions are in 25 mL volumes. Mobile phases are as follows: A: 11 M HCl, B: 10 M HCl, C: 2 M HCl, D: 2 M HCl + 0.3 M Ascorbic Acid, E: 0.1 M HCl, F: 0.1 M HCl + 0.01 M HF, G: 0.01 M HNO_3

Elution Profile for all Components

	Al (%)	Au (%)	Ca (%)	Fe (%)	Mg (%)	Na (%)	Ni (%)	Ti (%)	Mn-54 (%)	Co-60 (%)	Sc-46 (%)
Fraction 1: Load	72.8	0	99.4	0	82.5	33.4	82.3	13.4	14	0	0
Fraction 2: 11 M HCl	0.0	0	0.6	0	0.0	20.5	0.0	0.0	16	0	0
Fraction 3: 11 M HCl	27.2	0	0.0	0	17.5	32.9	17.7	19.8	28	0	0
Fraction 4: 2 M HCl	0.0	0	0.0	0	0.0	13.2	0	66.8	1	78.1	0
Fraction 5: 2 M HCl	0.0	0	0.0	0	0.0	0.0	0	0	4	0	0
Fraction 6: 2 M HCl + 0.3 M Ascorbic Acid	0.0	0	0.0	52.4	0.0	0.0	0	0	5	0	0
Fraction 7: 2 M HCl + 0.3 M Ascorbic Acid	0.0	0	0.0	6.5	0.0	0.0	0	0	0	0	0
Fraction 8: 0.1 M HCl	0.0	0	0.0	41.0	0.0	0.0	0	0	0	0	4
Fraction 9: 0.1 M HCl	0.0	0	0.0	0	0.0	0.0	0	0	0	0	11
Fraction 10: 0.1 M HCl + 0.01 M HF	0.0	0	0.0	0	0.0	0.0	0	0	0	0	67
Fraction 11: 0.1 M HCl + 0.01 M HF	0.0	0	0.0	0	0.0	0.0	0	0	0	0	0
Fraction 12: 0.01 M HNO3	0.0	0	0.0	0	0.0	0.0	0	0	0	0	0
Fraction 13: 0.01 M HNO3	0.0	0	0.0	0	0.0	0.0	0	0	0	0	0

Foils are highlighted in green

Glass Components highlighted in purple

Activation Products highlighted in pink

Conclusions

- More work is needed refine larger constituents in the glass bead
  - Include more rinsing
- Investigate each activation products individual elution profile in the complex sample matrices
- Optimize column size and elution volumes

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Acknowledgements

Thesis Committee/UNLV Radiochemistry: Ralf Sudowe, Rebecca Springs, Evelyn Bond, Ken Czerwinski, Gary Cerefice, Patricia Paviet, Julie Bertoia, Trevor Lowe, Mary Turner, and everyone in the Radiochemistry group

Any Questions?