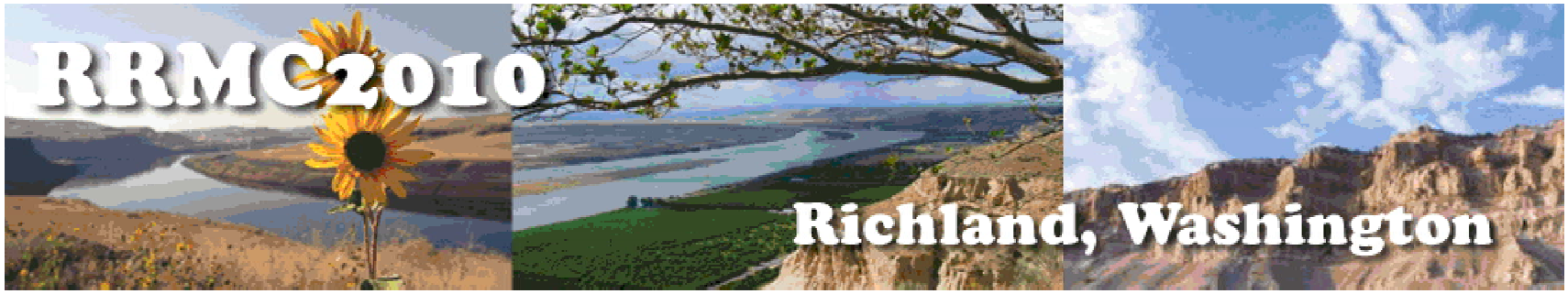
Rapid Methods for the Isolation of Actinides Sr, Tc and Po from Raw Urine (Are you using the right aqueous phase chemistry?)

Daniel R. McAlister and E. Philip Horwitz
PG Research Foundation, Inc.



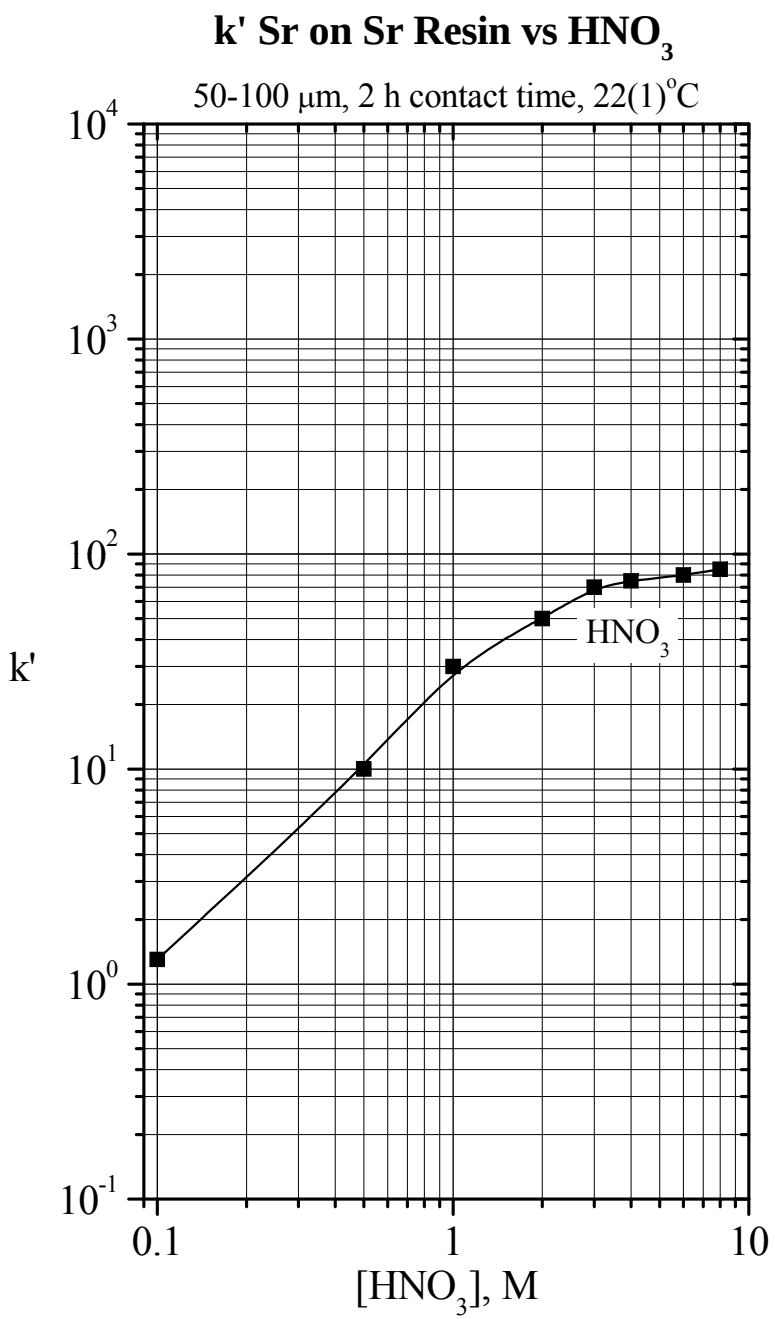
eichrom
expertise. collaboration. results.

PGRF
REALIZING THE FUTURE

Aqueous Phase Chemistry

- Separations with Eichrom Resins Typically employ mineral acids (HCl, HNO_3) in the aqueous phase.

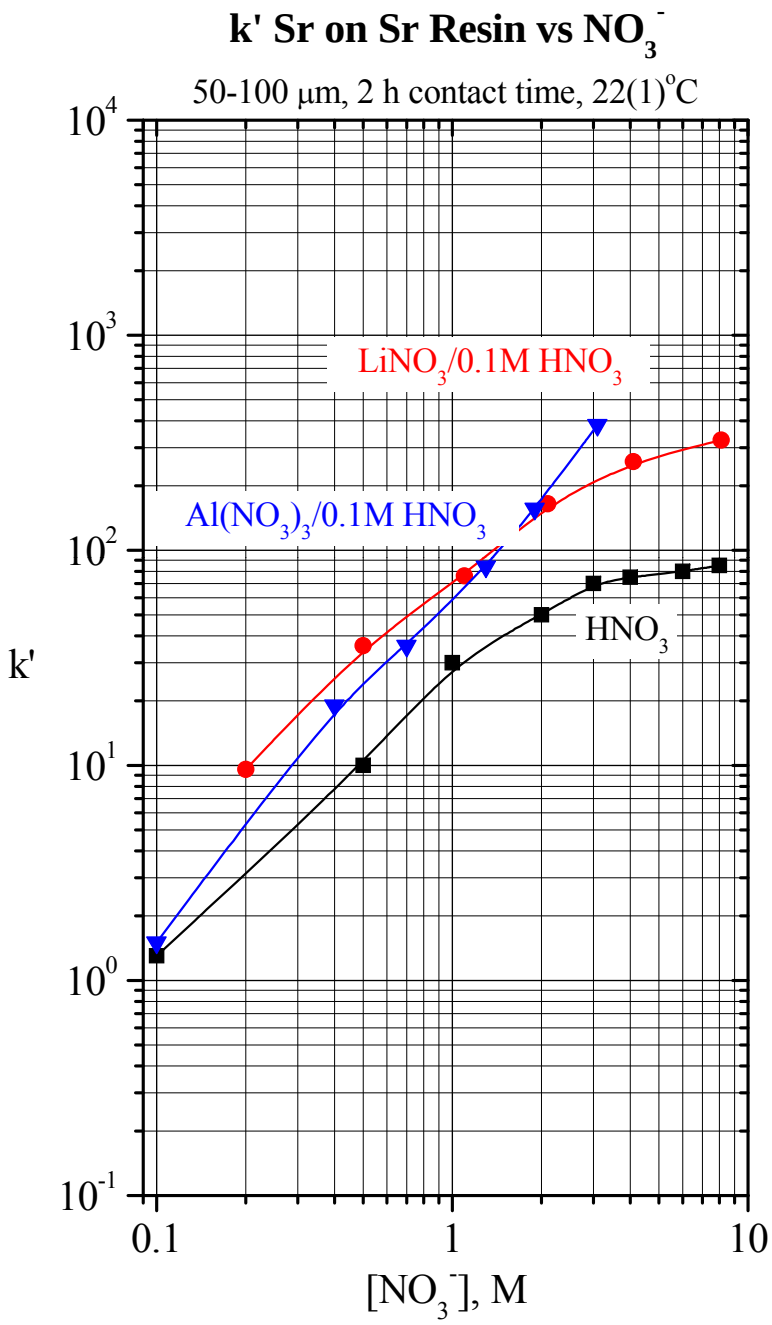
- However, in some applications other aqueous matrices may offer advantages:
  - $Al(NO_3)_3/AlCl_3$ in place of HNO_3/HCl for complex matrices (urine, soil)
  - NH_4Cl in place of HCl (when employing reducing agents)

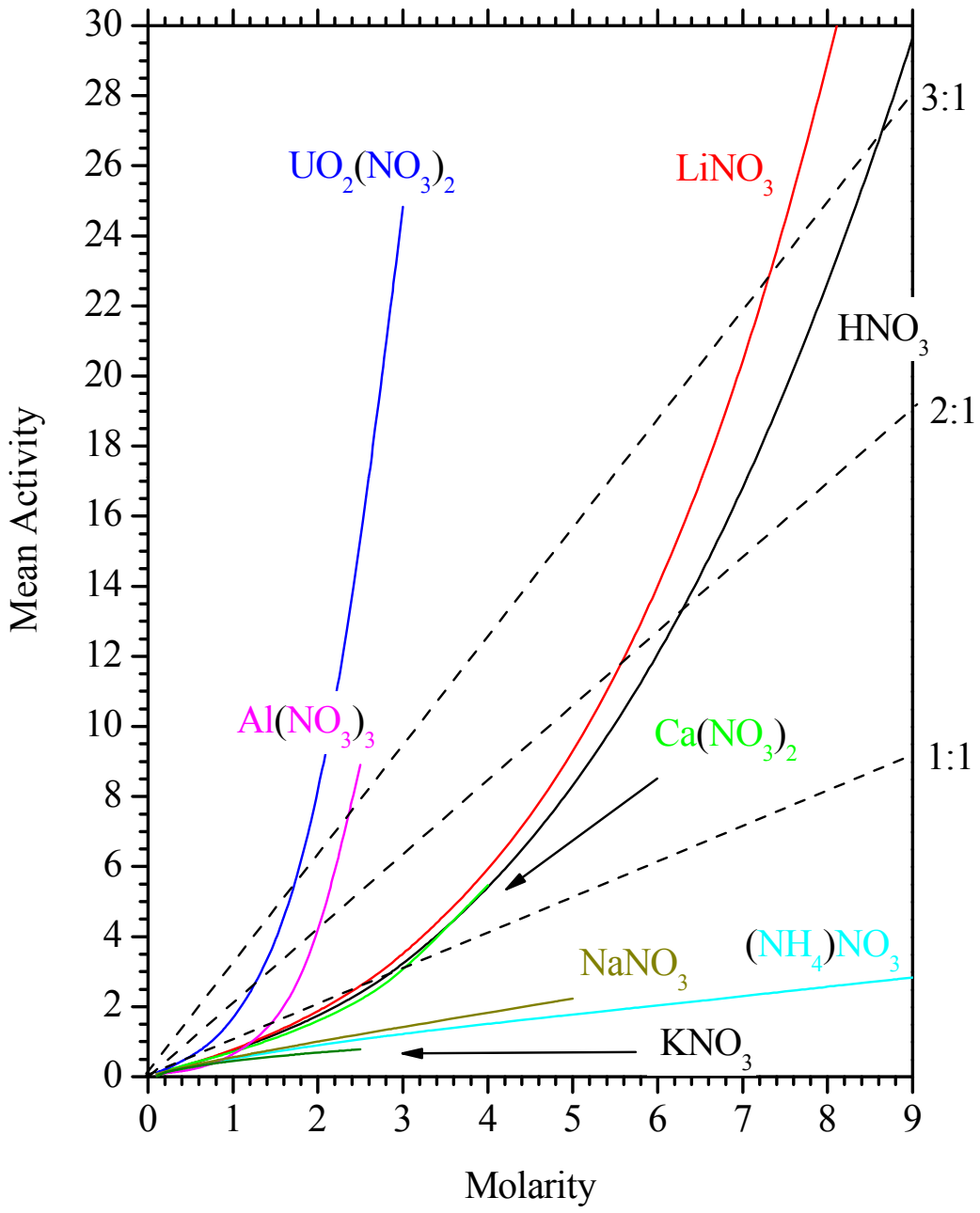

k' Sr on Sr Resin vs HNO3
50-100 μm, 2 h contact time, 22(1)°C
10^4
10^3
10^2
10^1
10^0
10^-1
k'
HNO3
0.1
1
10
[HNO3], M

Extraction of Metal Ions

$$\overline{\text{D}t\text{BCH18C6}} + \text{Sr}^{2+} + 2\text{NO}_3^- \leftrightarrow \overline{\text{Sr}(\text{D}t\text{BCH18C6})(\text{NO}_3)_2}$$

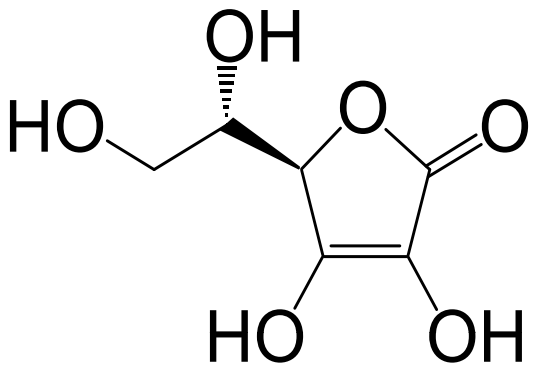
$$\overline{\text{D}t\text{BCH18C6}} + \text{H}_3\text{O}^+ + \text{NO}_3^- \leftrightarrow \overline{(\text{D}t\text{BCH18C6})(\text{H}_3\text{O}^+)(\text{NO}_3^-)}$$


k' Sr on Sr Resin vs NO3-
50-100 μm, 2 h contact time, 22(1)°C
LiNO3/0.1M HNO3
Al(NO3)3/0.1M HNO3
HNO3
k'
[NO3-], M
10^4
10^3
10^2
10^1
10^0
10^-1
0.1
1
10

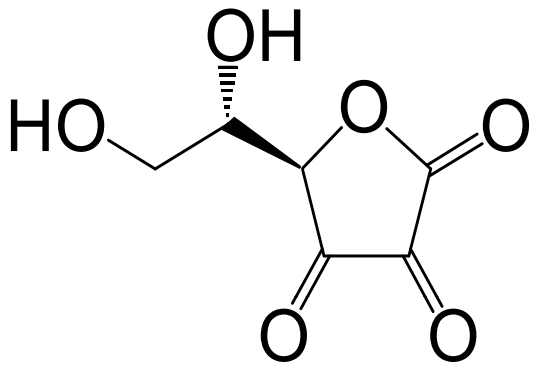

Mean Activity
Molarity
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0
1
2
3
4
5
6
7
8
9
UO2(NO3)2
LiNO3
HNO3
Al(NO3)3
Ca(NO3)2
NaNO3
(NH4)NO3
KNO3
3:1
2:1
1:1

Reduction/Oxidation Chemistry

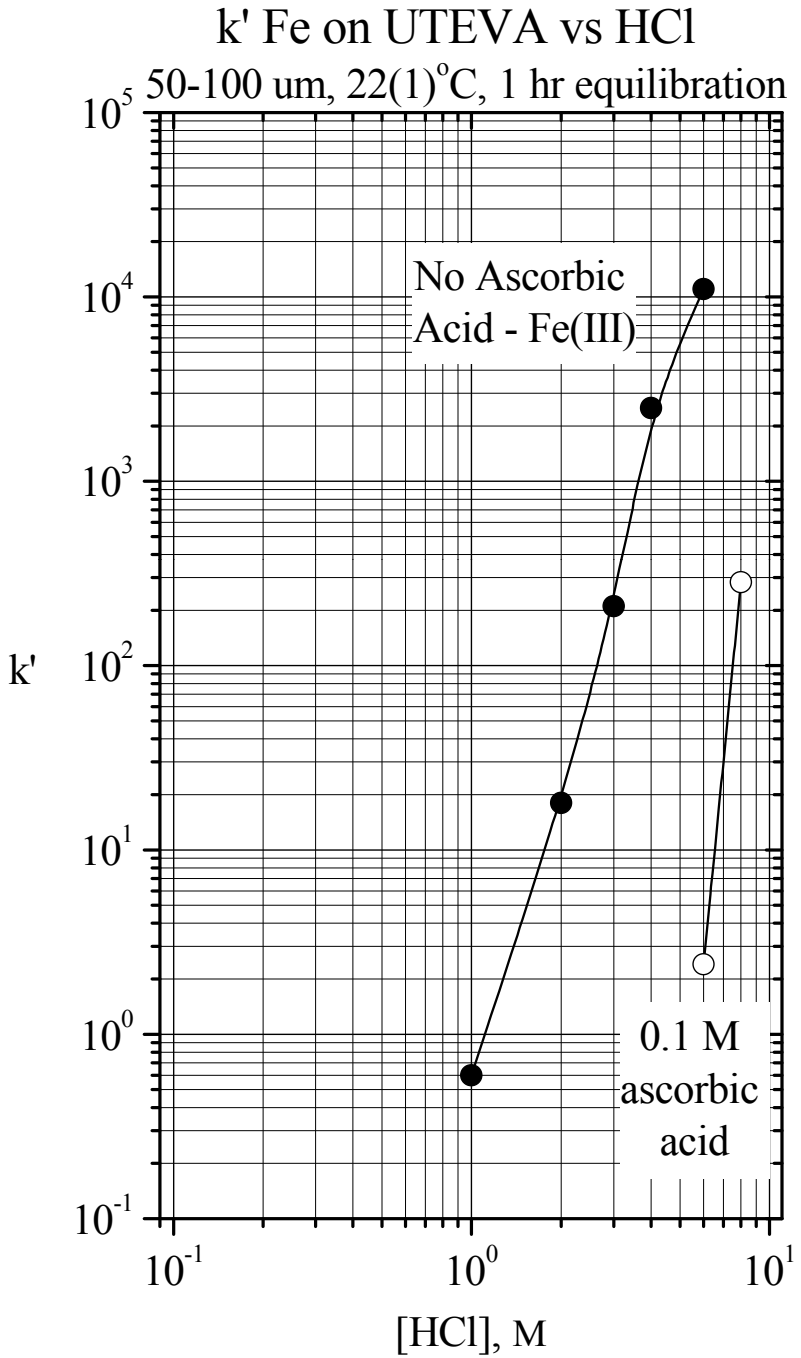
Reduction of Metal Ions with Ascorbic Acid

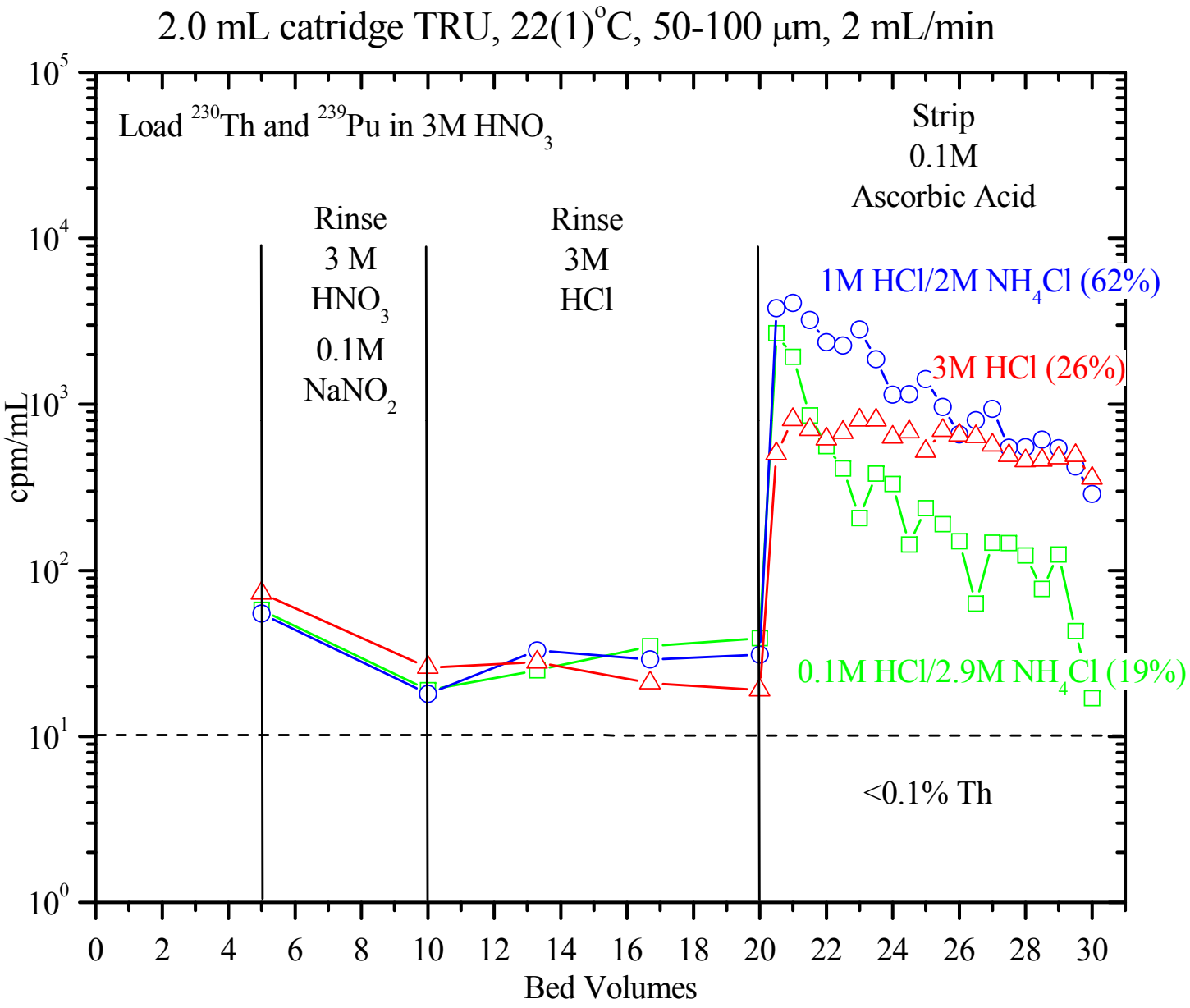


$$+ 2Fe(III) \leftrightarrow 2Fe(II) + 2H^{+} +$$



High Concentrations of H^{+} Inhibit Reduction by Ascorbic Acid


k' Fe on UTEVA vs HCl
50-100 um, 22(1)°C, 1 hr equilibration
No Ascorbic Acid - Fe(III)
0.1 M ascorbic acid
k'
[HCl], M
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
10^-1
10^0
10^1


2.0 mL catridge TRU, 22(1)°C, 50-100 μm, 2 mL/min
Load 230Th and 239Pu in 3M HNO3
Rinse
3 M
HNO3
0.1M
NaNO2
Rinse
3M
HCl
Strip
0.1M
Ascorbic Acid
1M HCl/2M NH4Cl (62%)
3M HCl (26%)
0.1M HCl/2.9M NH4Cl (19%)
<0.1% Th
cpm/mL
Bed Volumes
10^5
10^4
10^3
10^2
10^1
10^0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

Hydrolysis and Metal Ions

$$Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+$$

$$Fe(OH)^{2+} + H_2O \leftrightarrow Fe(OH)_2^{+} + H^+$$

$$2Fe^{3+} + 2H_2O \leftrightarrow Fe_2(OH)_2^{4+} + 2H^+$$

$$3Fe^{3+} + 4H_2O \leftrightarrow Fe_3(OH)_4^{5+} + 4H^+$$

In some cases, hydrolysis and/or potential for extraction by acidic impurities prevent complete replacement of Acid.

Application to Urine Analysis

Rapid methods for single actinides

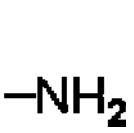
5-20 mL urine

Simplified methods to facilitate processing of large numbers of samples

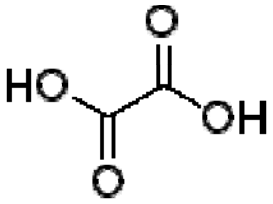
Challenging Matrix

1) Volume: 600- 2500 ml/24 hrs. Average: 1,200 ml.
2) Specific gravity: 1.003 - 1.030
3) Reaction: Acidic (pH: 4.7 - 7.5) Average pH: 6.0
4) Total solids: 30 - 70 g/liter.

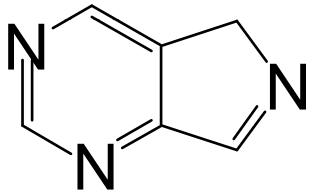
Na^+ (3-4g)
K^+ (1-2g)
Ca^{2+} (0.1-0.3g)
PO_4^{3-} (1-2g)
SO_4^{2-} (1-4g)
Mg (40-200mg)
NH_4^+ (0.3-1g)
I (50-250mg)
Cl^- (9-16g)



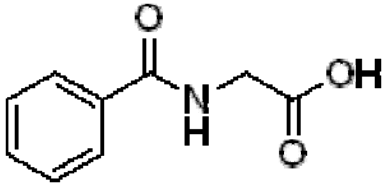
Urea (25-30g)



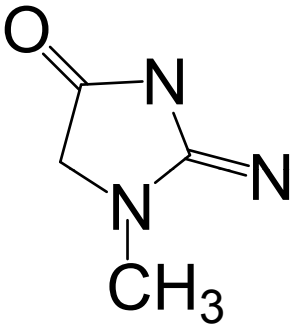
Oxalic acid (15-20mg)



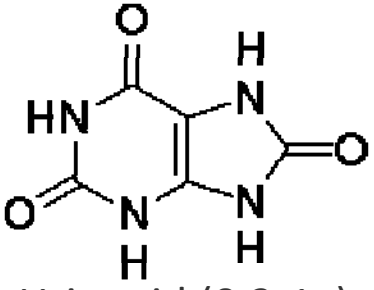
Purine Bases (7-10mg)



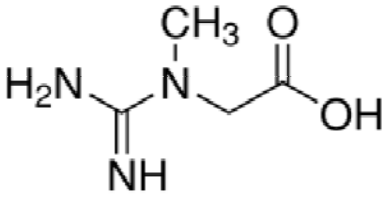
Hippuric acid (0.1-1g)



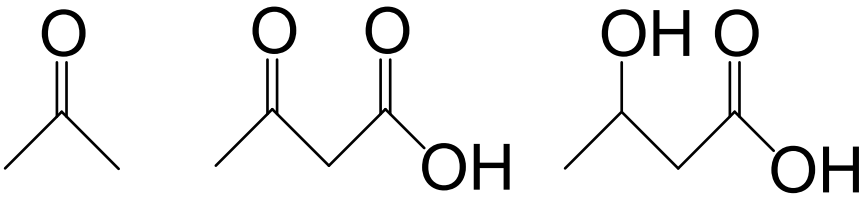
Creatinine (1-2g)



Uric acid (0.3-1g)

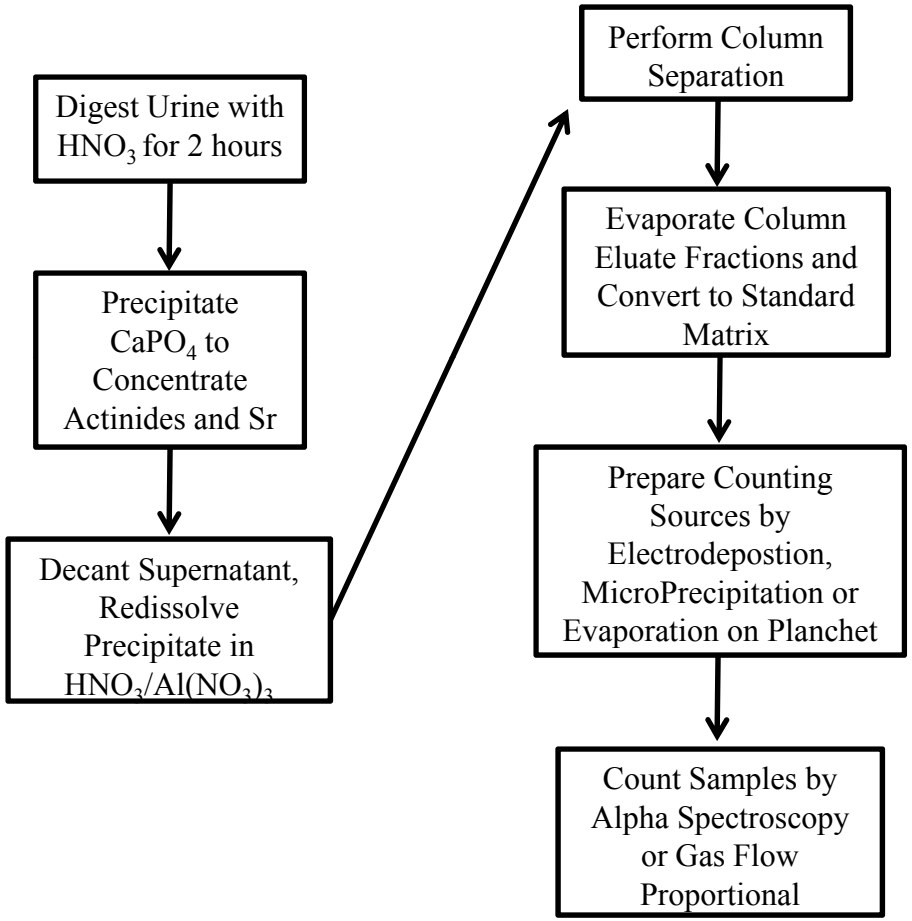


Creatine (1-2g)



Ketone Bodies (3-15mg)

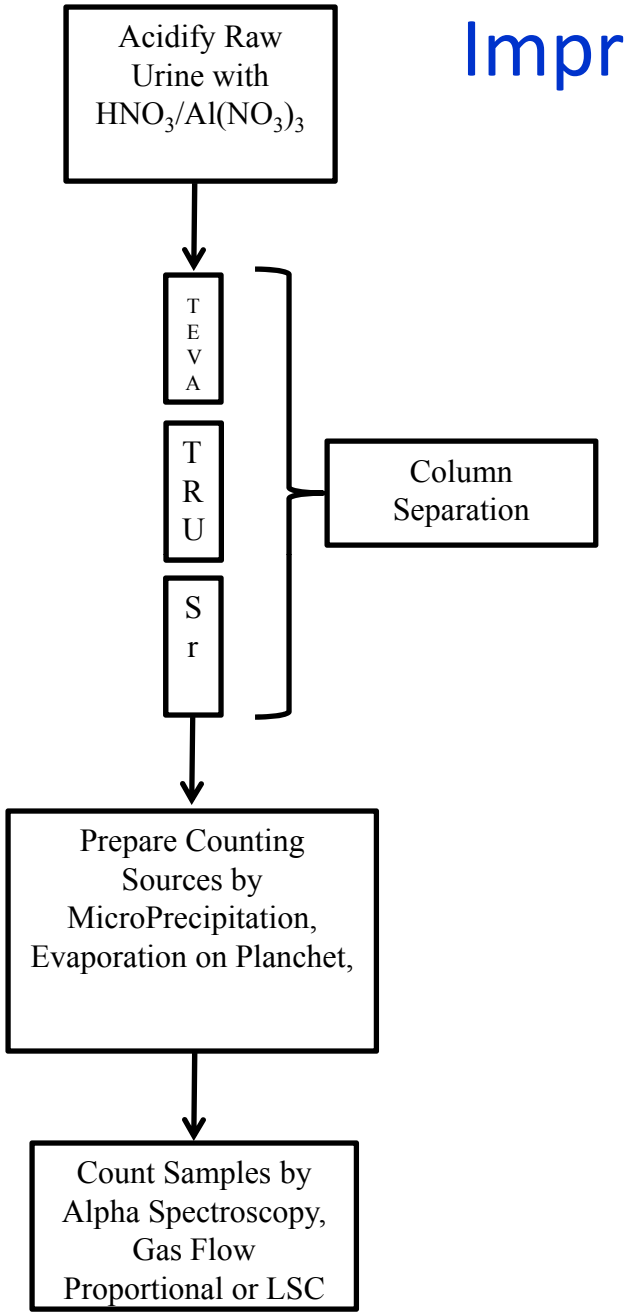
Classic Method



Multiple Evaporations/ Digestions

Precipitation

24-48 hour turnaround times



Improved Method

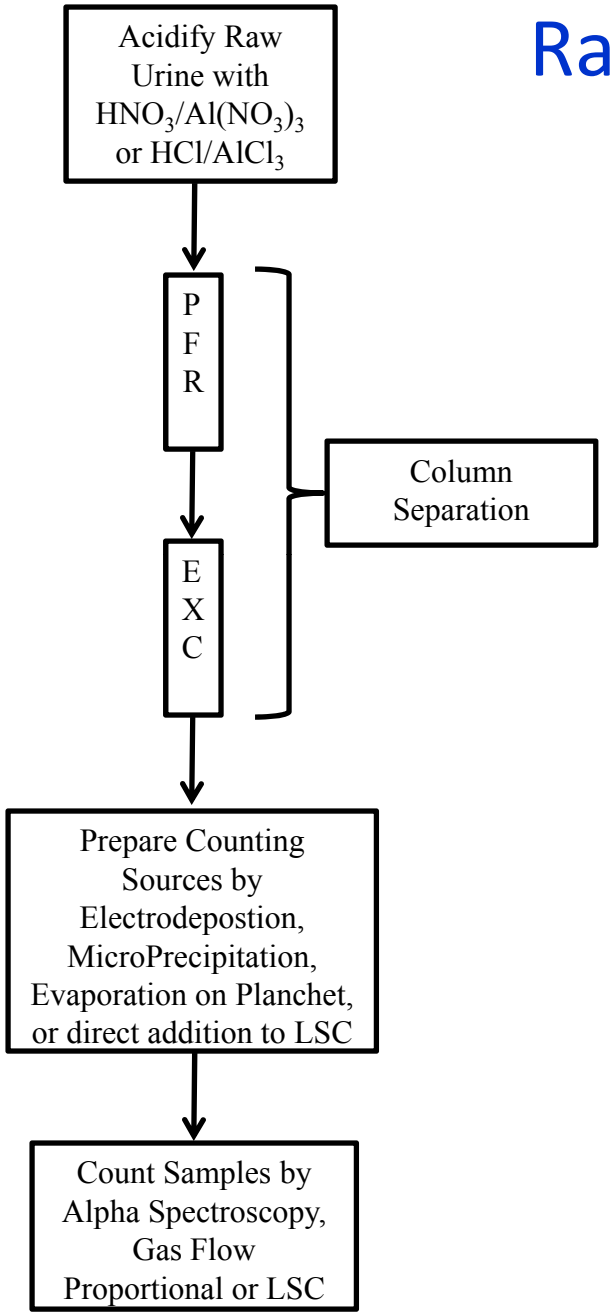
Maxwell SL, Culligan BK. New column separation method for emergency urine samples. J Radioanal Nucl Chem 279: 105-111; 2009.

Am/Cm, Pu, U, Sr in Urine

4-5 hour turnaround times

Results within -11% to 5% of NIST Values

Rapid Method



Expand to include Am/Cm, Th, U, Pu, Tc, Sr, Po

Provide options for multiple or single element methods

Provide measurement options

-LSC for most rapid

-alpha for most information

Sample Preparation

Acidify Raw Urine with $HNO_3/Al(NO_3)_3$ or $HCl/AlCl_3$

Acidify to reduce complexing power of phosphate, sulfate, and complexing organics + limit hydrolysis

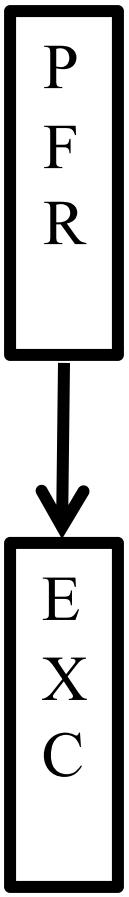
$Al(NO_3)_3$ or $AlCl_3$ salting out agents + bind to complexing agents

Al-salts bind less to neutral extractants than HNO_3 or HCl, so k' values higher in many cases

50% Urine, 50% Acid/Al-salt stock
40mL total volume

No Pu/Np oxidation state fixation
TRU will retain Pu(III) or Pu(IV)

Column Separation



Stacked 2mL cartridges connected by luer connections

Prefilter Resin to remove organics and color (For LSC applications)

Single EXC resin for single element

Multiple EXC for An + Sr/Tc

Po done separately from Cl^- matrix

Conditions

Table 1. Method Summary for Rapid Urine Analysis

Analyte	Column 1[a]	Column 2[b]	Load[c]	Rinse 1	Rinse 2	Strip	Measurement Technique
Sr	Prefilter	Sr Resin	0.5M $Al(NO_3)_3$ 0.5M HNO_3	10 mL 8.0M HNO_3	20 mL 3.0M HNO_3 + 0.05M NH_4-Bioxalate	10 mL 0.05M HNO_3	LSC[d]
Tc	Prefilter	Weak Base	0.5M $Al(NO_3)_3$ 0.1M HNO_3	10 mL 0.1M HCl	20 mL 0.1M + NH_4-Bioxalate	10 mL 1.0M NH_4OH	LSC
Th	Prefilter	TRU	0.5M $Al(NO_3)_3$ 0.5M HNO_3	10 mL 3.0M HNO_3 + 0.1M $NaNO_2$	20 mL 4M HCl	10 mL 4M HCl + 0.05M HF	Alpha Spectroscopy or LSC
U	Prefilter	UTEVA	0.5M $Al(NO_3)_3$ 0.5M HNO_3	10 mL 3.0M HNO_3	20 mL 6M HCl + 0.05M HF	10 mL 1M HCl	Alpha Spectroscopy or LSC
Pu	Prefilter	TRU	0.5M $Al(NO_3)_3$ 0.5M HNO_3	10 mL 3.0M HNO_3 + 0.1M $NaNO_2$	25 mL 4M HCl + 0.1M HF	10 mL 1M HCl + 0.05M HF	Alpha Spectroscopy or LSC
Am	Prefilter	TRU	0.5M $Al(NO_3)_3$ 0.5M HNO_3	20 mL 3.0M HNO_3 + 0.1M $NaNO_2$	N/A	10 mL 4M HCl	Alpha Spectroscopy or LSC
Po	Prefilter	Sr Resin	0.5M $AlCl_3$ 2.0M HCl	10 mL 0.1M HCl	20 mL 8M HCl	10 mL 0.2M Ammonium Bioxalate	Alpha Spectroscopy or LSC

[a]2 mL cartridge 100-150 µm

[b]2mL cartridge 50-100 µm

[c]40 mL, 50% raw urine

[d]Liquid Scintillation Counting

Load Conditions

Analyte	Column 1[a]	Column 2[b]	Load[c]
Sr	Prefilter	Sr Resin	0.5M $Al(NO_3)_3$ 0.5M HNO_3
Tc	Prefilter	Weak Base	0.5M $Al(NO_3)_3$ 0.1M HNO_3
Th	Prefilter	TRU	0.5M $Al(NO_3)_3$ 0.5M HNO_3
U	Prefilter	UTEVA	0.5M $Al(NO_3)_3$ 0.5M HNO_3
Pu	Prefilter	TRU	0.5M $Al(NO_3)_3$ 0.5M HNO_3
Am	Prefilter	TRU	0.5M $Al(NO_3)_3$ 0.5M HNO_3
Po	Prefilter	Sr Resin	0.5M $AlCl_3$ 2.0M HCl

Stripping Conditions/Measurement

Analyte	Strip	Measurement Technique
Sr	10 mL 0.05M HNO_3	LSC[d]
Tc	10 mL 1.0M NH_4OH	LSC
Th	10 mL 4M HCl + 0.05M HF	Alpha Spectroscopy or LSC
U	10 mL 1M HCl	Alpha Spectroscopy or LSC
Pu	10 mL 1M HCl + 0.05M HF	Alpha Spectroscopy or LSC
Am	10 mL 4M HCl	Alpha Spectroscopy or LSC
Po	10 mL 0.2M Ammonium Bioxalate	Alpha Spectroscopy or LSC

Yield and Impurities

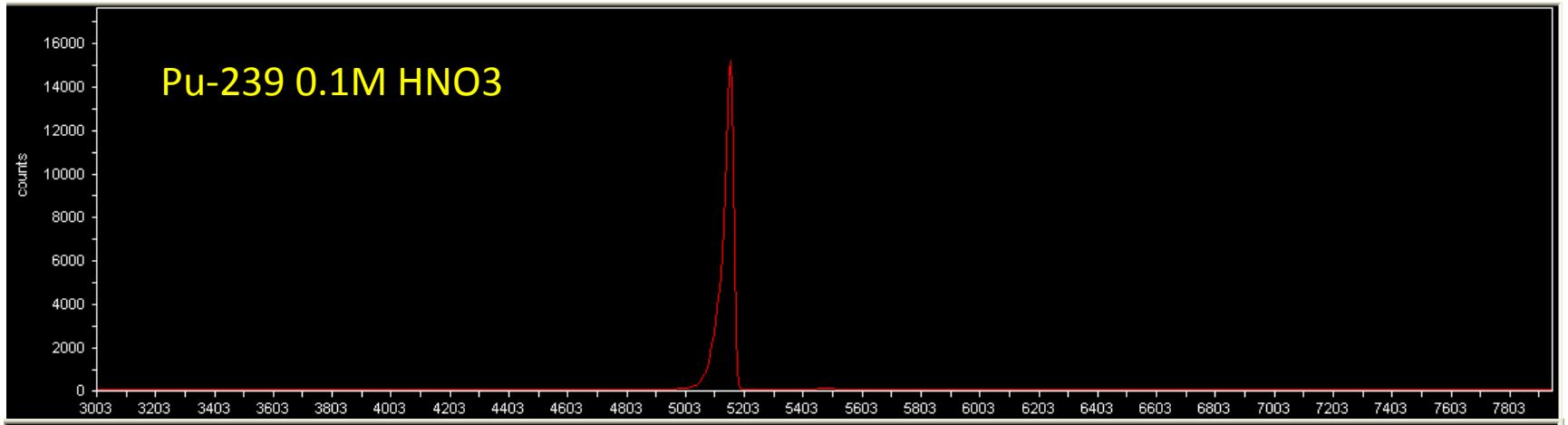
Yield and Key Impurities for Chromatographic Separation

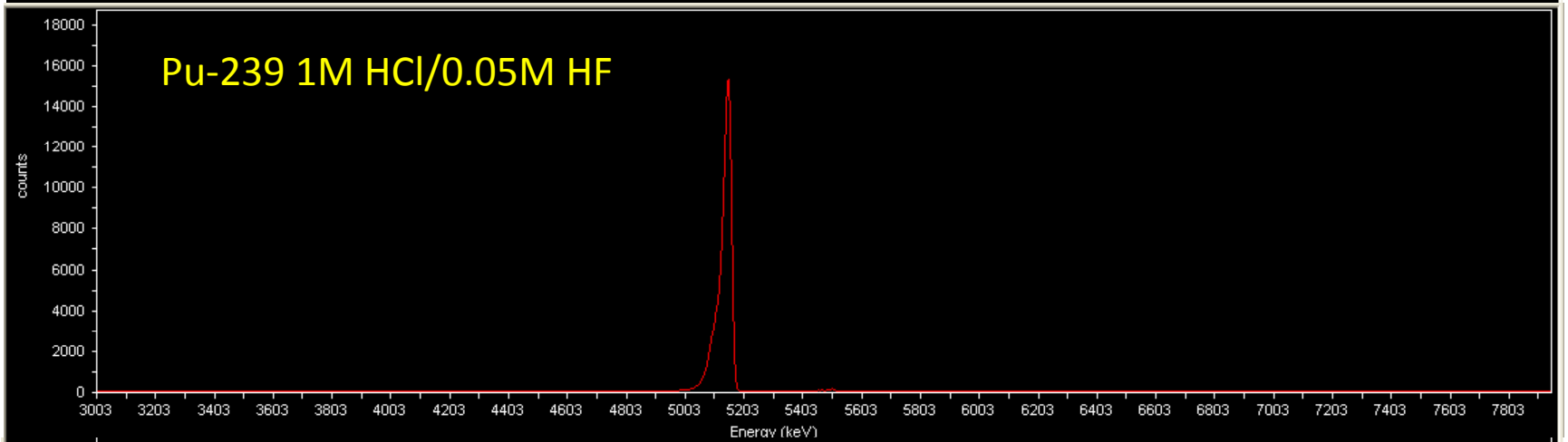
Analyte	Yield %	Key Impurities
Sr-90	95 ± 5	Np (0.8%), Th (0.05%), Pu (0.03%)
Tc-99	83 ± 4	Po (2.0%), Th (1.9%), Np (0.4%), U (0.1%), Pu (0.01%)
Th-230	80 ± 5	Np (11%), Am (0.3%), Pu (0.01%), U (0.004%)
U-233	95 ± 1	Po (0.4%), Th (0.03%), Pu (0.01%)
Pu-239	98 ± 1	Np (45%), Th (4.3%), U (0.05)
Am-241	97 ± 1	Y(<1%), Np (0.8%), Th (0.2%), U (0.2%), Pu (0.008%)
Po-210	85 ± 5	Th (0.6%), Pu (0.01)

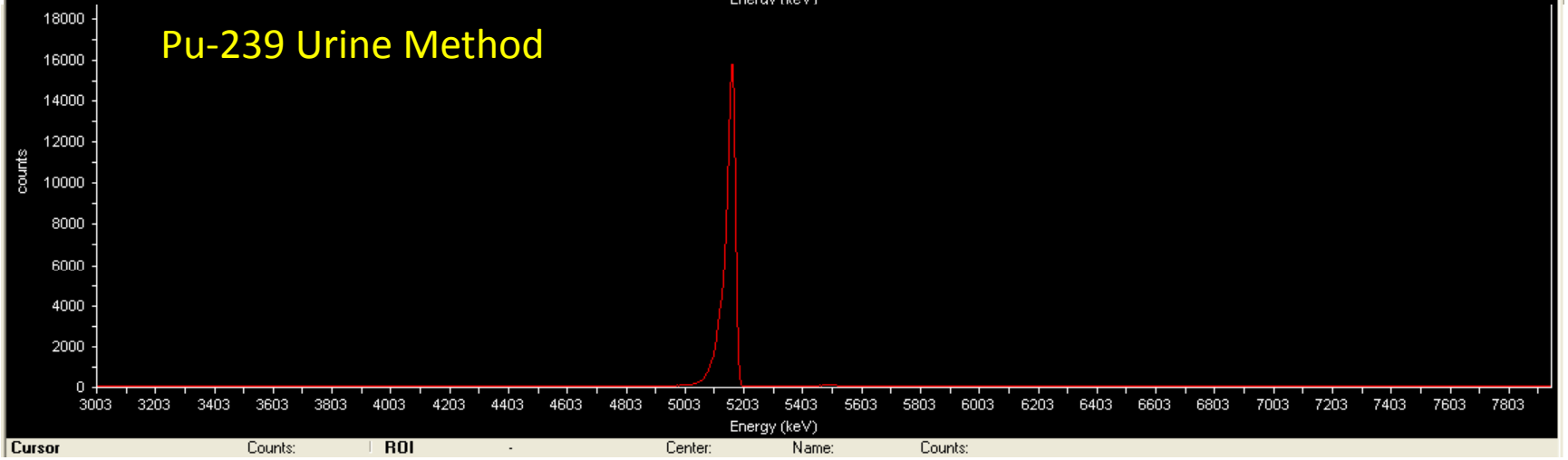
Urine samples spiked with Co-60, Sr-90, Y-90, Tc-99, Cs-137, Pb-210, Po-210
Bi-210, Th-230, U-233, Np-239, Pu-239, Am-241

Alpha Spectroscopy

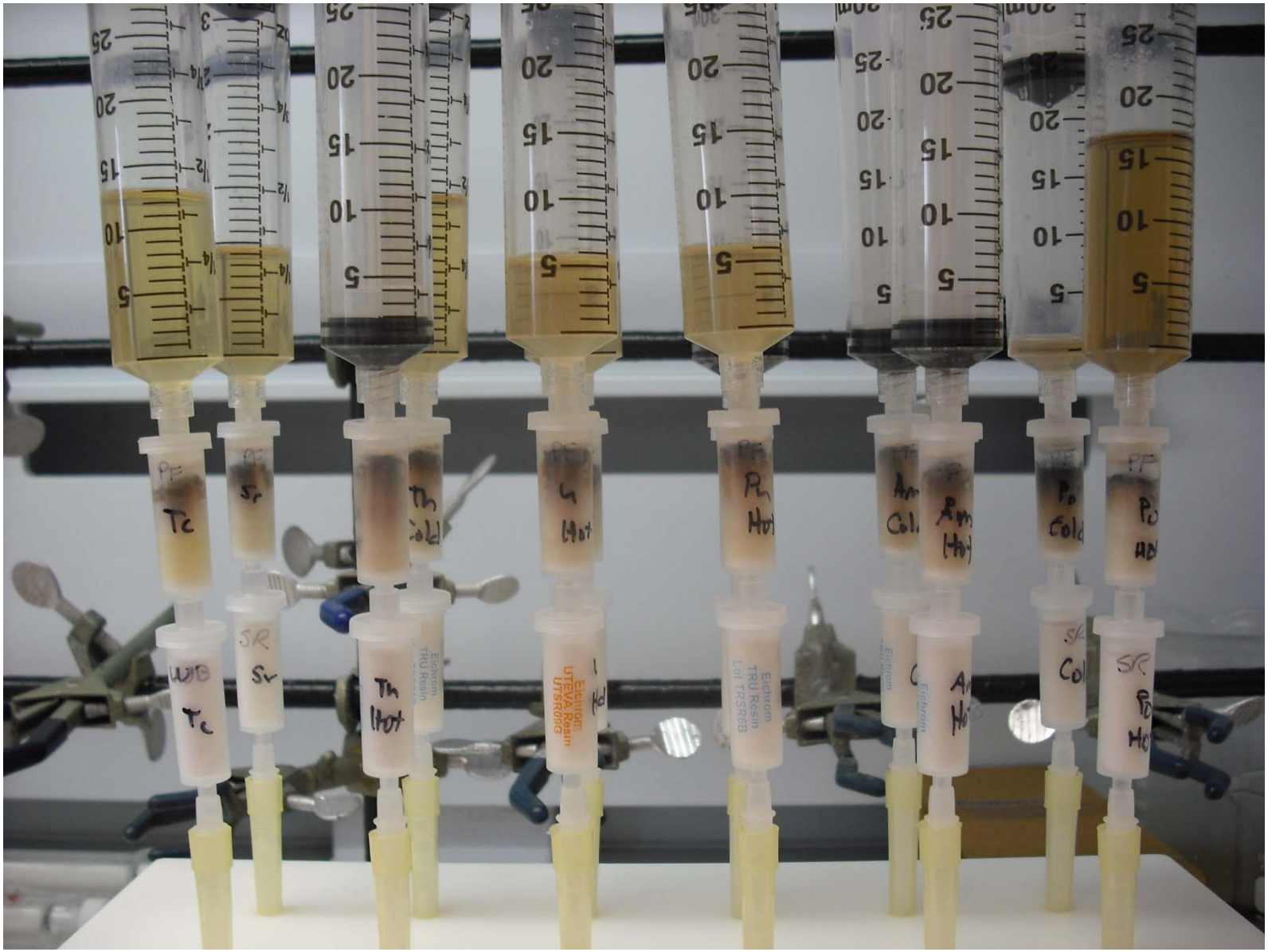
Nuclide	Matrix	meV max	(keV) FWHM	Relative % recovery
Th-230	0.1M HNO_3	4.687	42	
	4M HCl/0.1M HF	4.687	42	101
	Urine Method Strip	4.687	30	96.4
U-233	0.1M HCl	4.824	46	
	1M HCl	4.824	37	100
	Urine Method Strip	4.824	39	106
Pu-239	0.1M HNO_3	5.155	37	
	1M HCl/0.05M HF	5.155	35	106
	Urine Method Strip	5.155	39	95.0
Am-241	0.1M HNO_3	5.486	45	
	4M HCl	5.486	50	92.4
	Urine Method Strip	5.486	58	95.5


Pu-239 0.1M HNO3
counts
16000
14000
12000
10000
8000
6000
4000
2000
0
3003 3203 3403 3603 3803 4003 4203 4403 4603 4803 5003 5203 5403 5603 5803 6003 6203 6403 6603 6803 7003 7203 7403 7603 7803

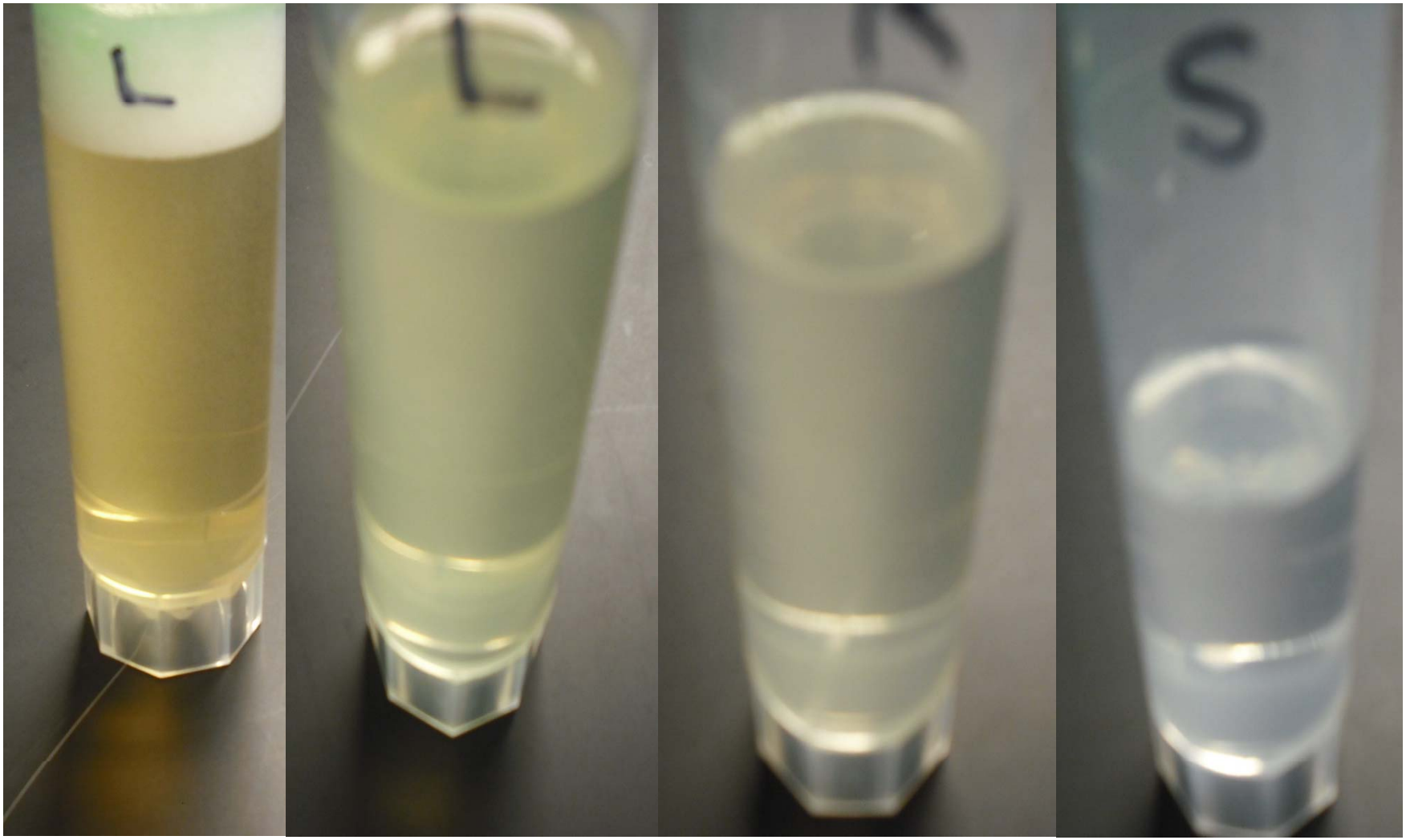

Pu-239 1M HCl/0.05M HF
counts
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
3003 3203 3403 3603 3803 4003 4203 4403 4603 4803 5003 5203 5403 5603 5803 6003 6203 6403 6603 6803 7003 7203 7403 7603 7803
Energy (keV)


Pu-239 Urine Method
counts
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
3003 3203 3403 3603 3803 4003 4203 4403 4603 4803 5003 5203 5403 5603 5803 6003 6203 6403 6603 6803 7003 7203 7403 7603 7803
Energy (keV)
Cursor
Counts:
ROI
-
Center:
Name:
Counts:

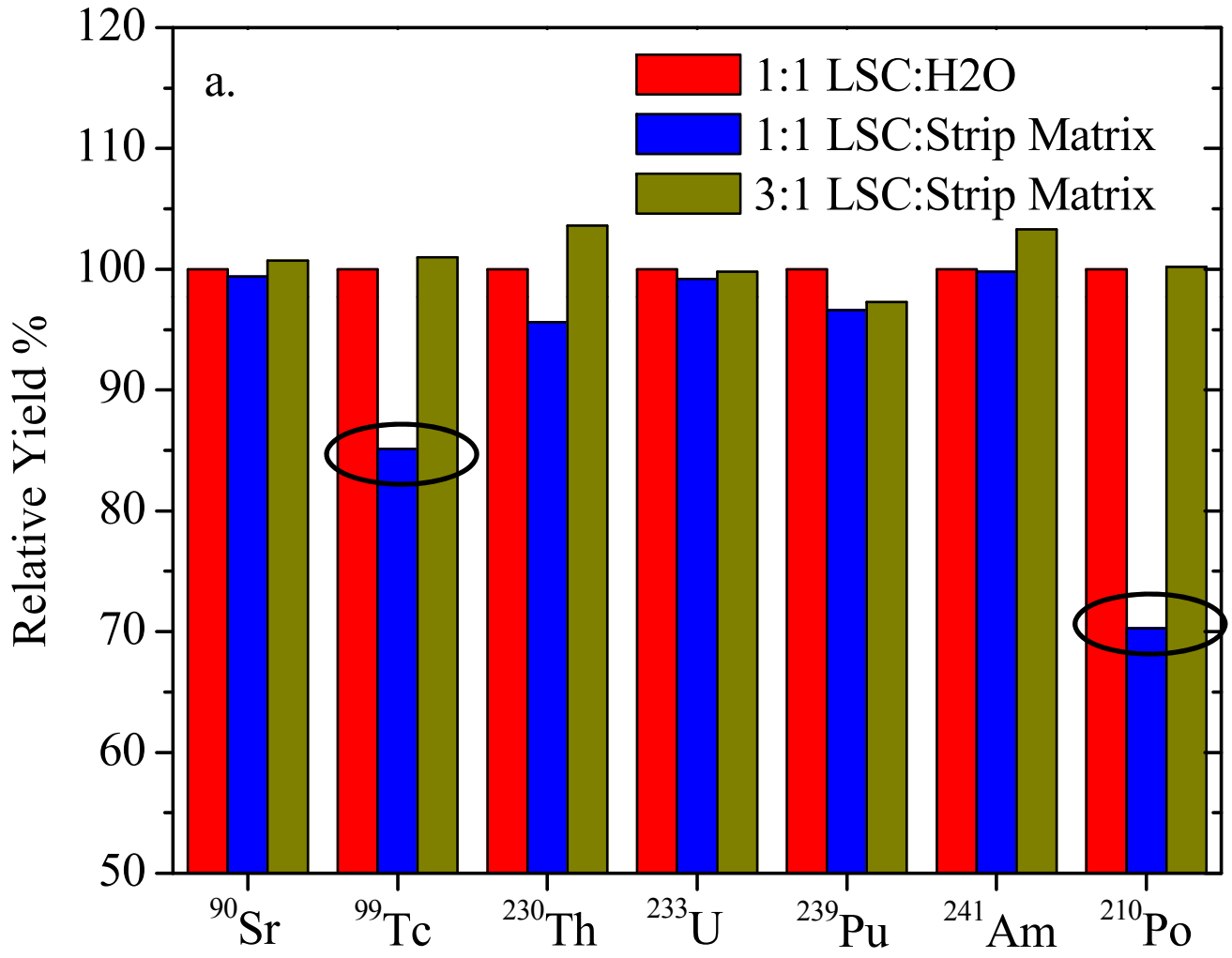
Removal of Color Compounds



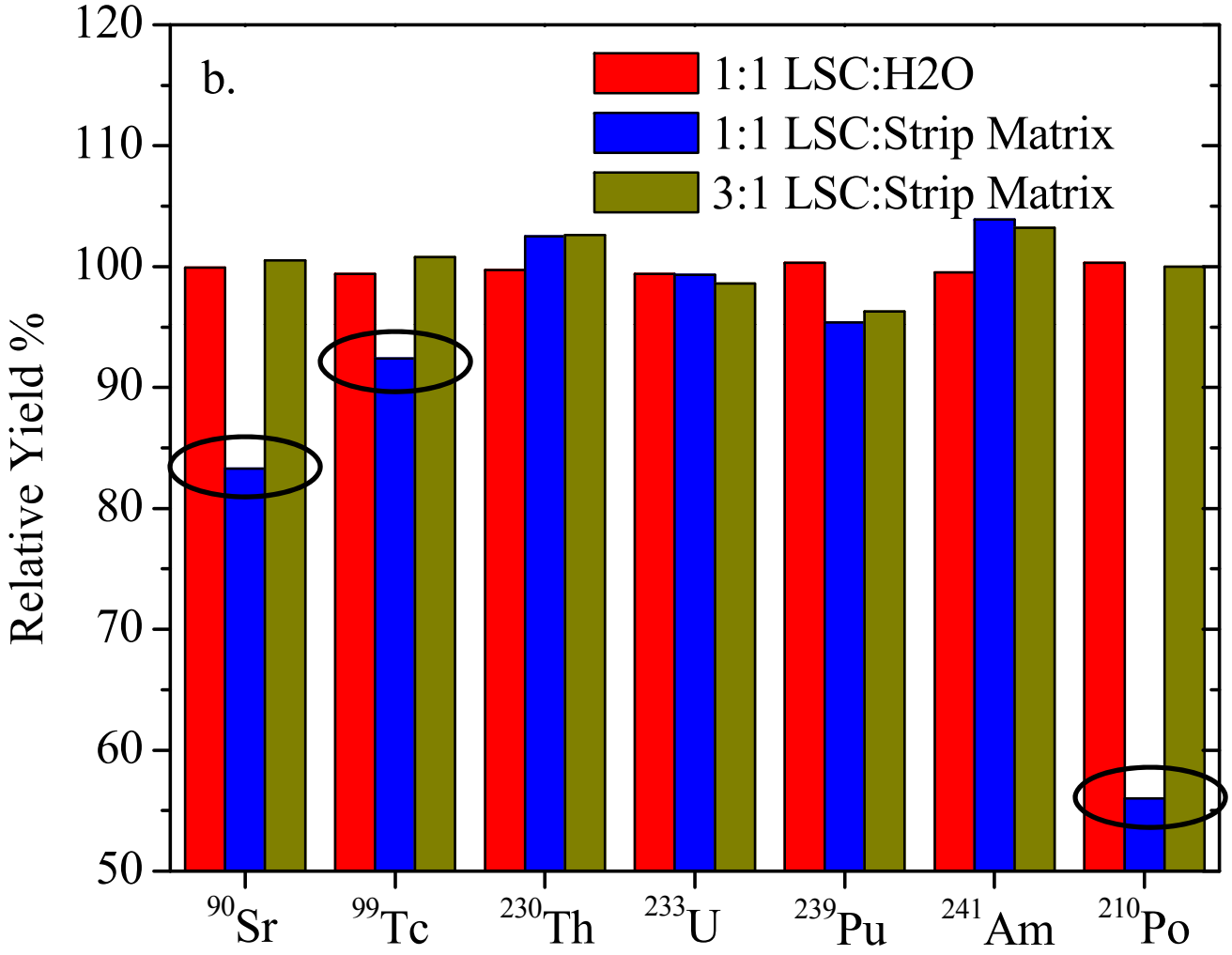
Removal of color compounds



LSC Quenching (Immediate Count)



LSC Quenching (18hrs)



Conclusions

-Application of alternative aqueous chemistries can provide advantages over traditional mineral acids.

-Salting out agents can:

- -provide alternative sources of charge balancing anions
- -tie up complexing agents
- -improve reduction/oxidation reactions
- -mix more effectively with LSC cocktails