# Old Separations on New Resins and New Separations on Old Resins

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# Rapid Separations Designed for Automation
## Soil 100mg, Water 10mL

| Separation Options | Systems |
| --- | --- |
| Actinides (Th, U, Np, Pu, Am) | TEVA/TRU |
| Sr, Tc (Th, U, Pu, Am) | WBEC/UTEVA/Crown-DGA |
| Sr, Tc (Np, Pu, Am) | WBEC/UTEVA/Crown-DGA |

WBEC = Weak Base EC Resin

# Weak Base EC Resin

40% alamine-336 (tertiary amine) on inert support

$(C_8H_{17})_3N$            27%
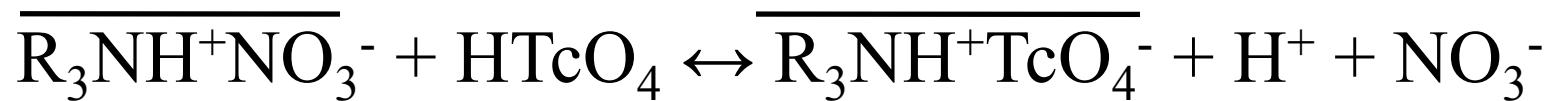
$(C_{10}H_{21})(C_8H_{17})_2N$       47%

$(C_{10}H_{21})_2(C_8H_{17})N$       27%
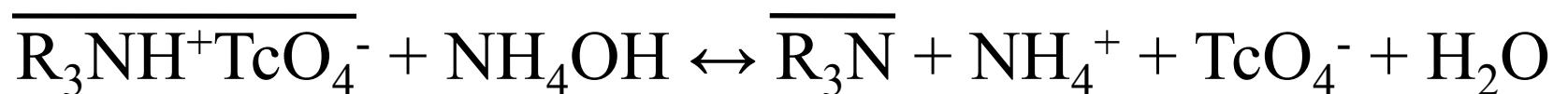
$(C_{10}H_{21})_3N$            2.4%

# Equilibria for Pertechnetate on Weak Base EC Resin

## Extraction:

$$\overline{R_3NH^+NO_3^-} + HTcO_4 \leftrightarrow \overline{R_3NH^+TcO_4^-} + H^+ + NO_3^-$$

## Stripping:

$$\overline{R_3NH^+TcO_4^-} + NH_4OH \leftrightarrow \overline{R_3N} + NH_4^+ + TcO_4^- + H_2O$$

**k' on Weak Base EC Resin**
100-150 um, 22(1)°C, 1 hr equilibration

Tc(VII)
Pu(IV)
Np(IV)
Th(IV)

k'

k' U(VI) < 2 for
0.05 - 2.0 M HNO$_3$

[HNO$_3$], M

**k' on Weak Base EC Resin**
50-100 um, 22(1)°C, 1 hr equilibration

Tc(VII)
Th(IV)
U(VI)
Np(IV)
Pu(IV)

k'

[HCl], M
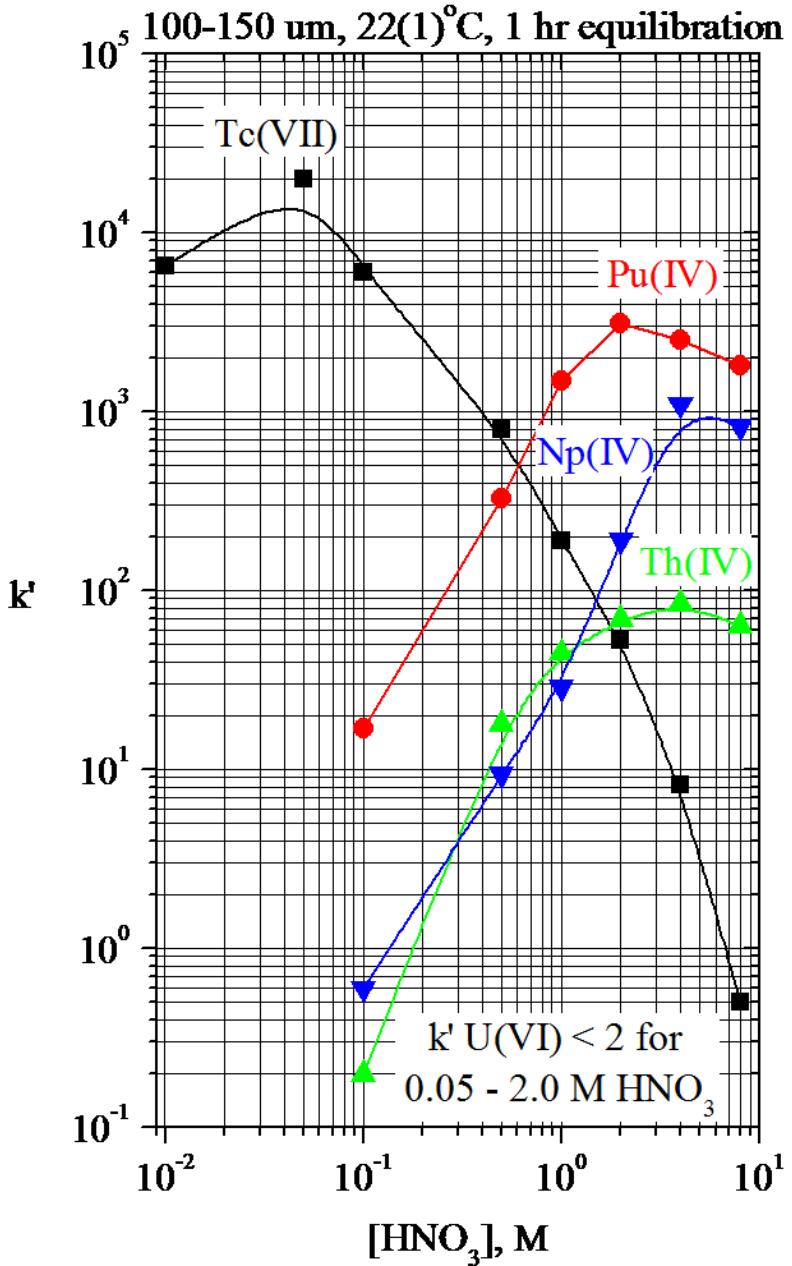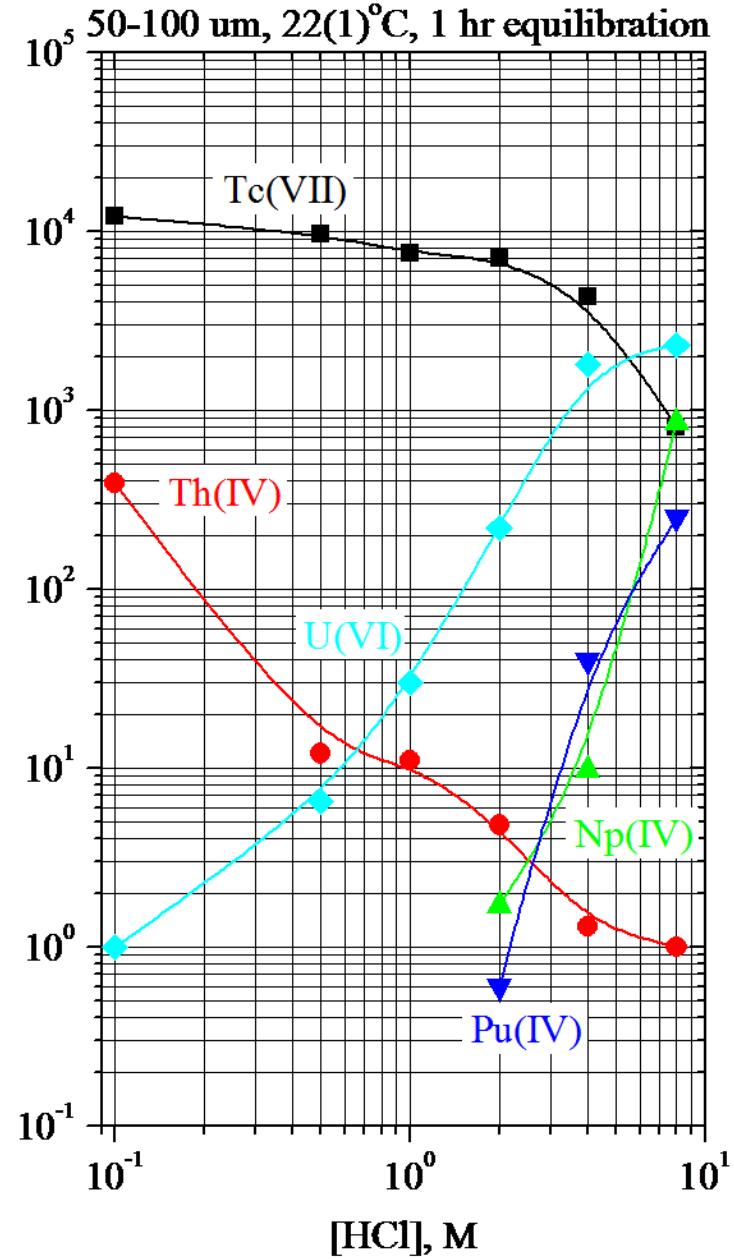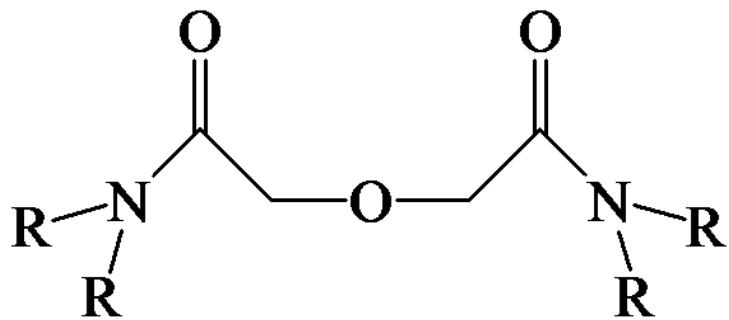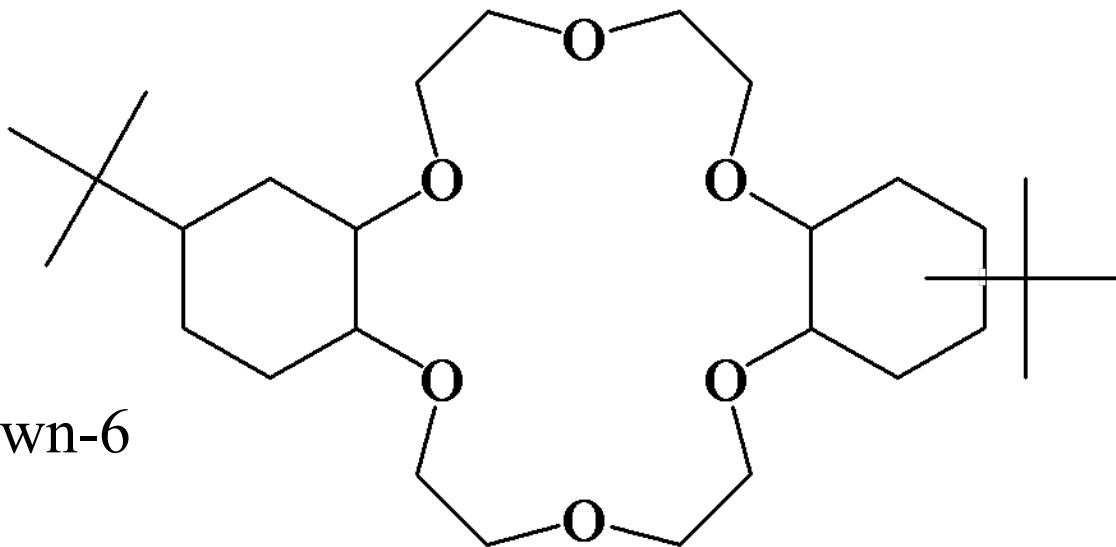
# Crown/DGA Resin



TODGA (R = *n*-octyl)
Ln(III), An(III) (IV) (VI)
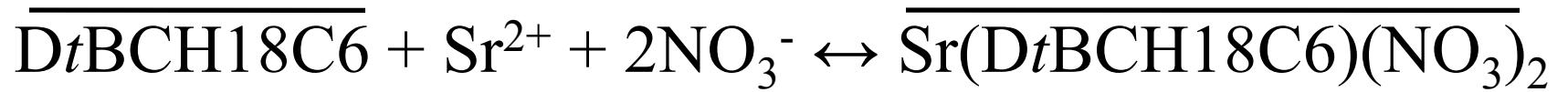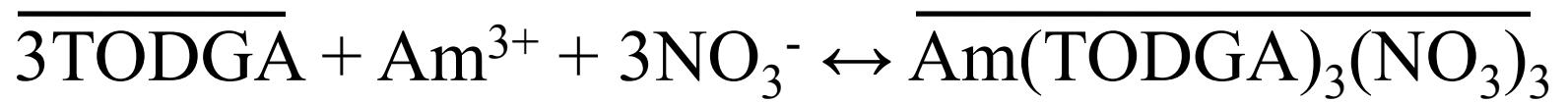
D*t*BCH18-crown-6 present at the same loading as Sr Resin

TODGA replaces 1-octanol as diluent for the crown ether.
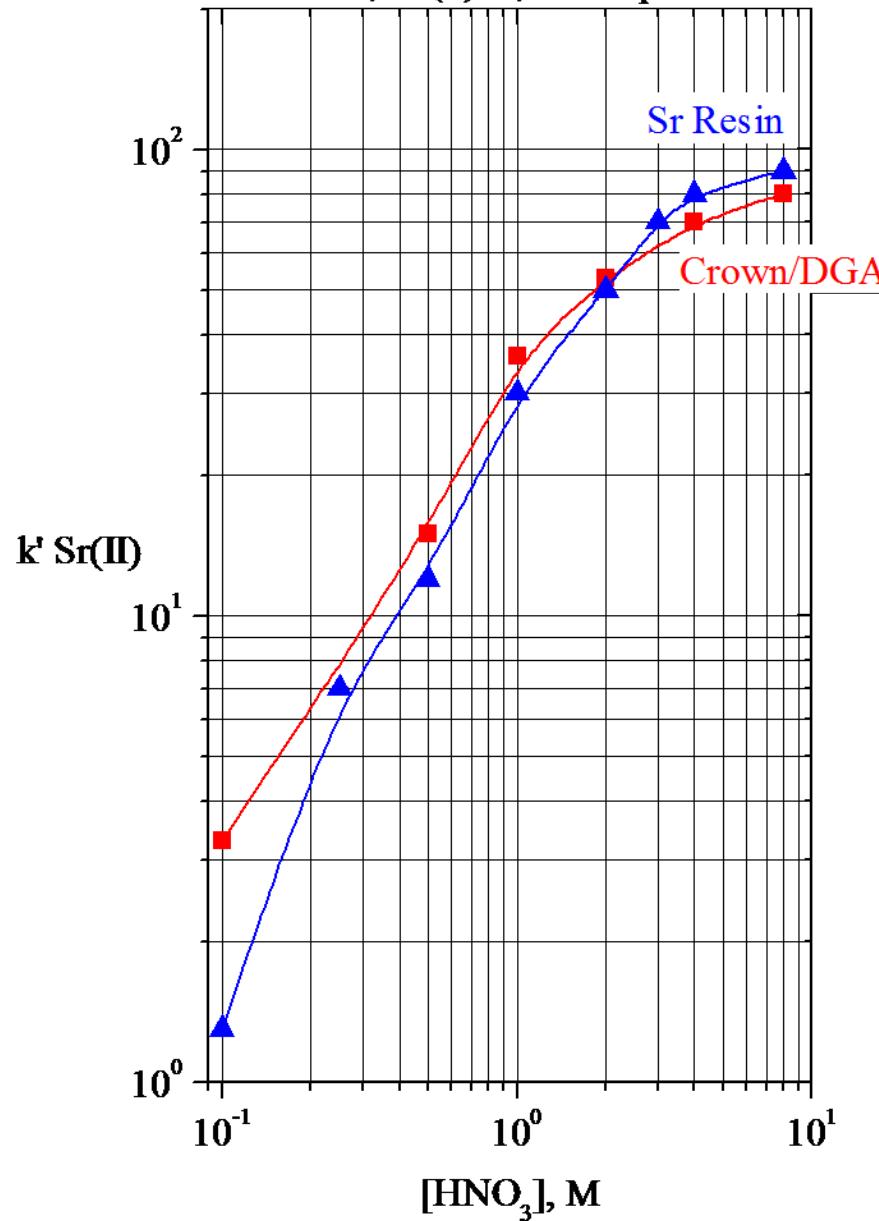


D*t*BCH18-crown-6
Sr(II)

# Equilibria for Extraction of Sr(II) and Am(III)

$$\overline{3\text{TODGA}} + \text{Am}^{3+} + 3\text{NO}_3^- \leftrightarrow \overline{\text{Am}(\text{TODGA})_3(\text{NO}_3)_3}$$

$$\overline{\text{D}t\text{BCH18C6}} + \text{Sr}^{2+} + 2\text{NO}_3^- \leftrightarrow \overline{\text{Sr}(\text{D}t\text{BCH18C6})(\text{NO}_3)_2}$$
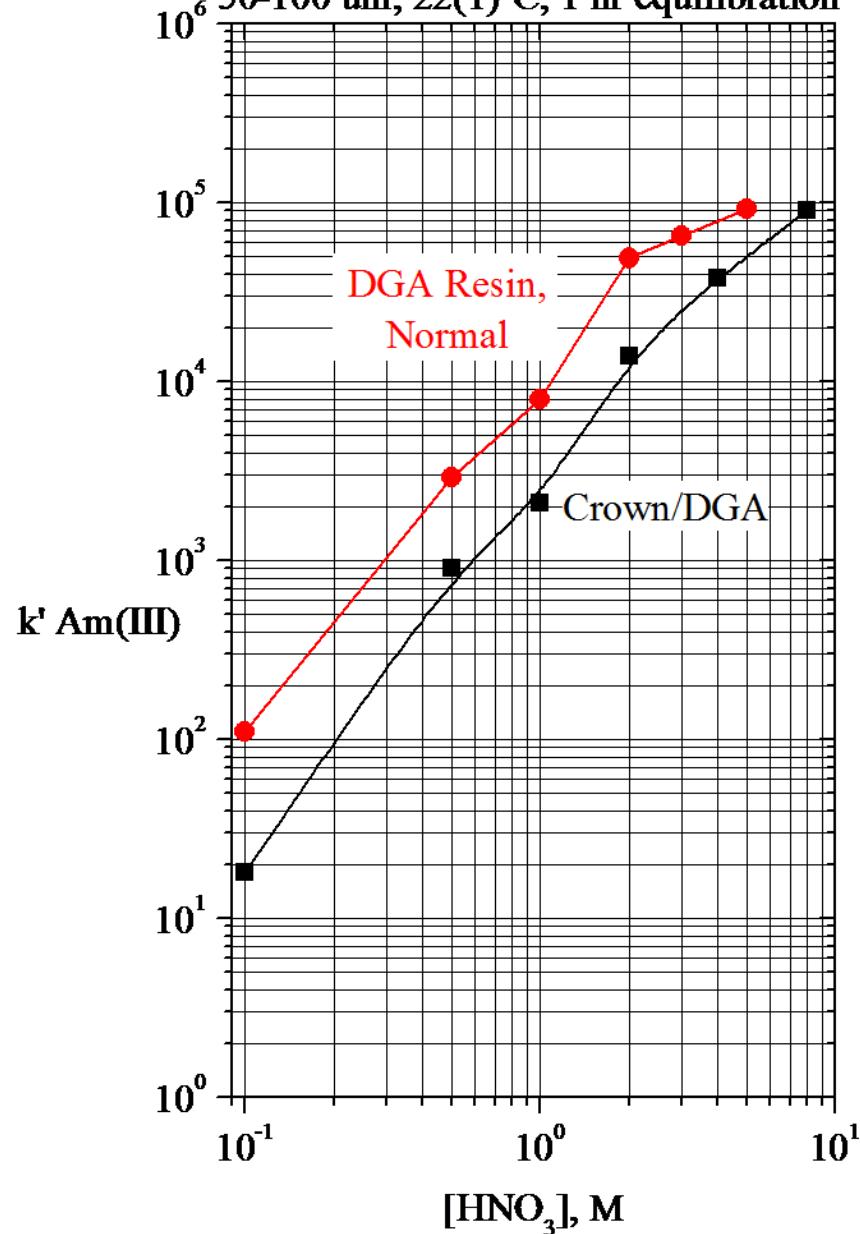
**k' Sr(II) on Sr and Crown/DGA Resins**

50-100 um, 22(1)°C, 1 hr equilibration

Sr Resin

Crown/DGA

k' Sr(II)

$[HNO_3]$, M

**k' Am(III) on DGA and Crown/DGA Resin**

50-100 um, 22(1)$^{o}$C, 1 hr equilibration

DGA Resin, Normal

Crown/DGA

k' Am(III)

[HNO$_3$], M
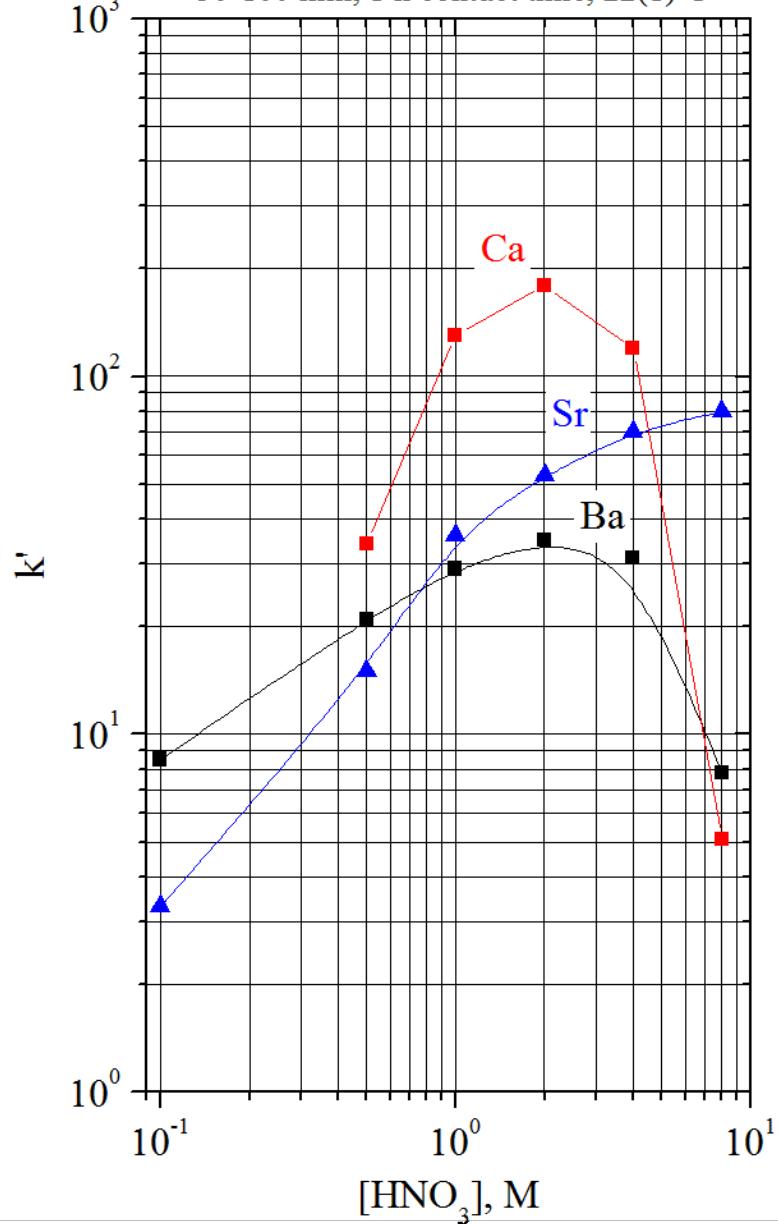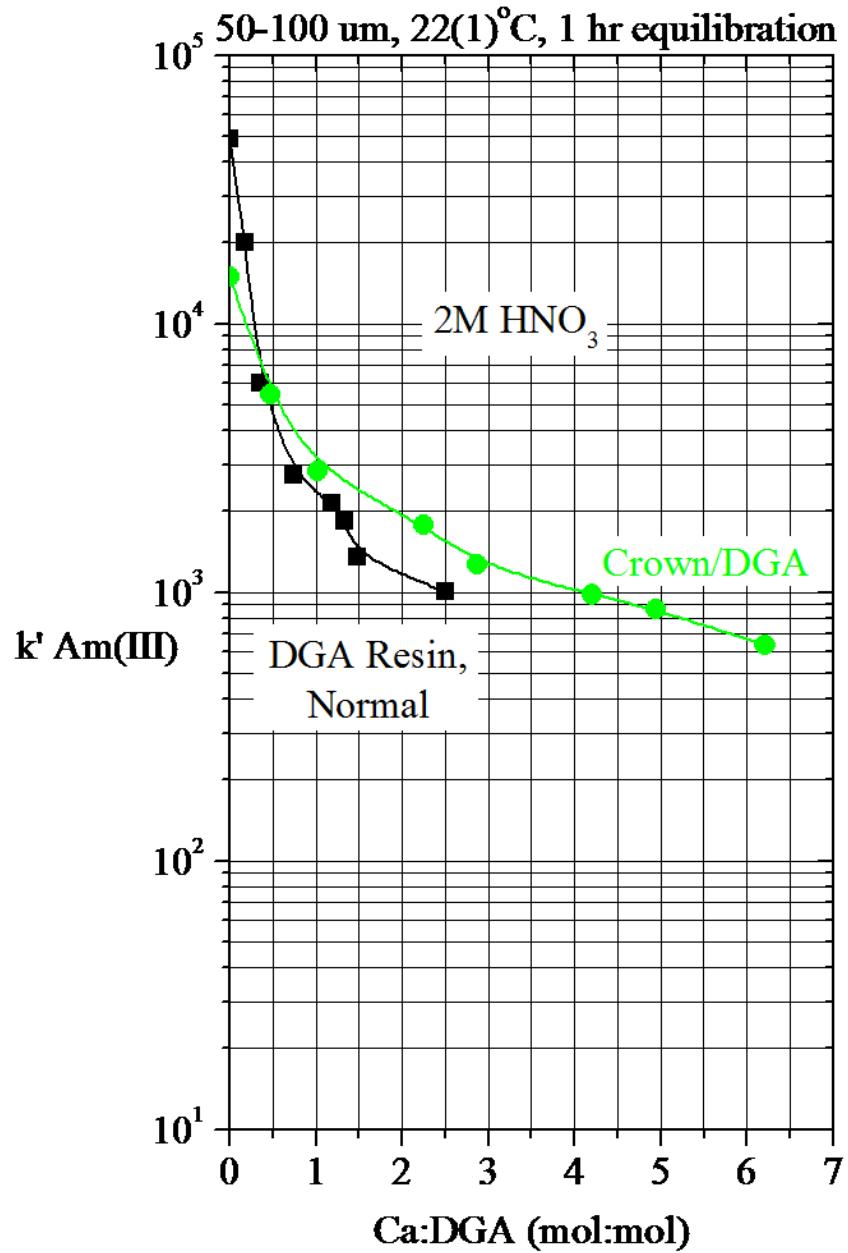
**k' on Crown/DGA Resin vs. HNO$_3$**
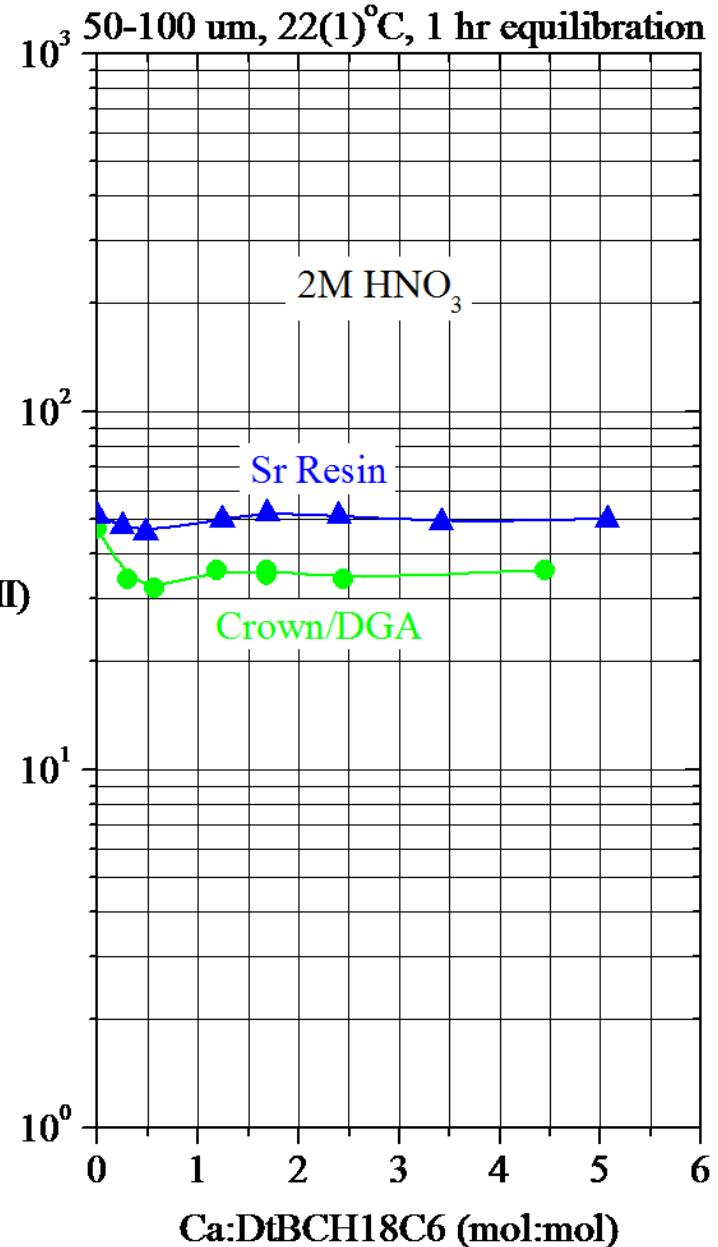
50-100 mm, 1 h contact time, 22(1)$^\circ$C

**k' Am(III) on DGA and Crown/DGA Resin**

50-100 um, 22(1)°C, 1 hr equilibration

2M HNO$_3$

Crown/DGA

DGA Resin, Normal

k' Am(III)

Ca:DGA (mol:mol)

**k' Sr(II) on Sr and Crown/DGA Resin**

50-100 um, 22(1)°C, 1 hr equilibration

2M HNO$_3$

Sr Resin

Crown/DGA

k' Sr(II)

Ca:DtBCH18C6 (mol:mol)

Soil Leachate or Water Sample

$\downarrow$ acidify to 2M $HNO_3$

Weak Base EC → Th, Pu, Tc

$\downarrow$

UTEVA → Th, U

$\downarrow$

Crown-DGA → Sr, Am

$\downarrow$
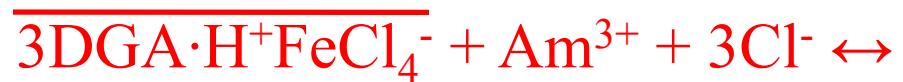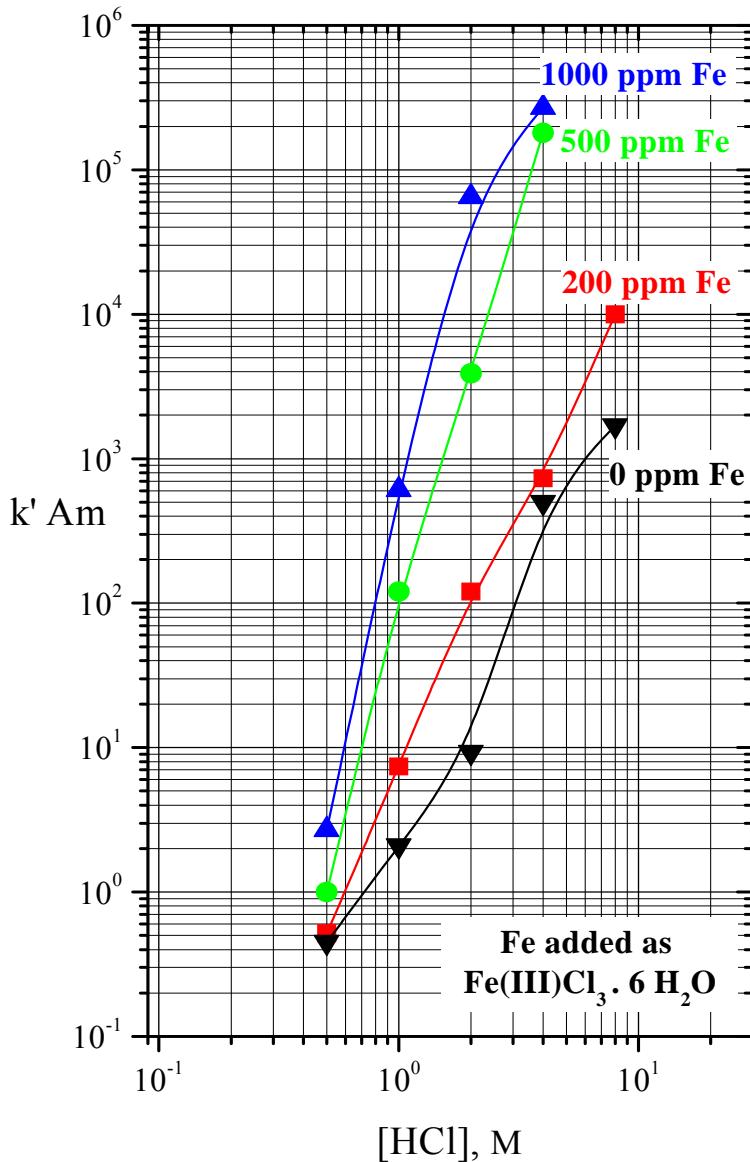
Waste
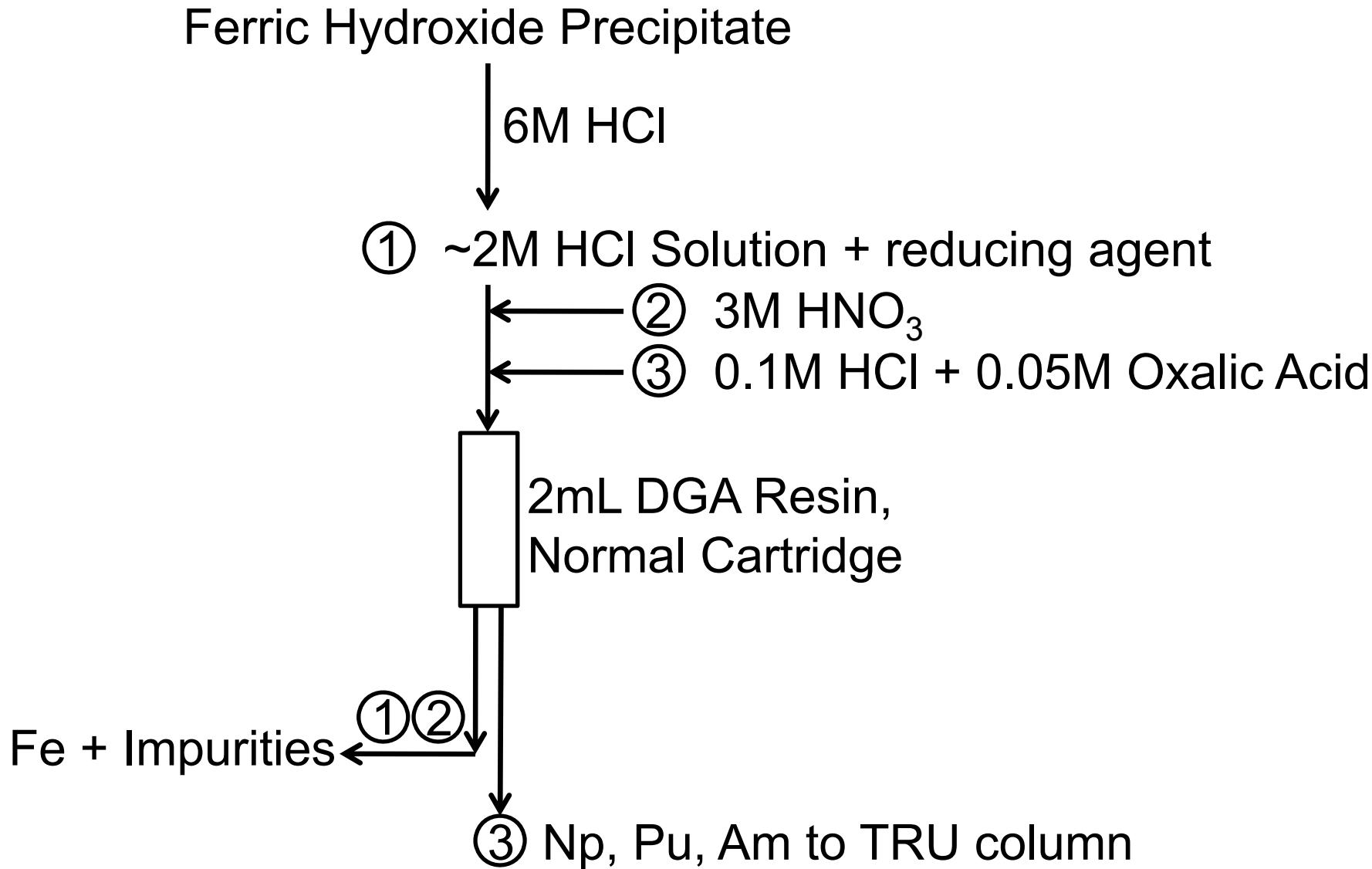
# Separation of Tc, Pu, Th, U, Am and Sr using 2 mL Cartridges (Weak Base EC/UTEVA/Crown-DGA)

|  |  |  | % | | | | | |
| Fraction | Solution | BV | Tc | Pu | U | Th | Sr | Am |
|---|---|---|---|---|---|---|---|---|
| Load | 2 M HNO3/0.1 M NaNO2 | 5 | 4.8 | 0.4 | 0.2 | 0.3 | 0.4 | 0.2 |
|  |  | 5 | 2.1 | 0.1 | 0.1 | 0.2 | 0.4 | 0.2 |
| Rinse | 2 M HNO3 | 5 | 0.0 | 0.0 | 0.1 | 0.3 | 0.6 | 0.2 |
|  |  | 5 | 0.0 | 0.0 | 0.1 | 0.3 | 0.6 | 0.0 |
| Th Strip | 6 M HCl | 6 | 0.2 | 0.0 | 0.1 | 30.1 | 0.0 | 0.1 |
|  |  | 6 | 0.2 | 0.0 | 0.1 | 40.0 | 0.0 | 0.2 |
| Pu Strip | 1 M HCl | 6 | 0.1 | 98.4 | 0.3 | 1.2 | 0.1 | 0.6 |
|  |  | 6 | 0.1 | 99.0 | 0.2 | 3.1 | 0.1 | 1.6 |
| Tc Strip | 1 M NH4OH | 6 | 94.1 | 0.2 | 0.3 | 0.0 | 0.1 | 0.0 |
|  |  | 6 | 96.8 | 0.2 | 0.3 | 0.0 | 0.1 | 0.0 |
| U Strip | 1 M HCl | 6 | 0.4 | 0.5 | 98.6 | 66.7 | 0.0 | 0.2 |
|  |  | 6 | 0.5 | 0.3 | 98.8 | 54.1 | 0.1 | 0.5 |
| Sr Strip | 4 M HCl | 6 | 0.0 | 0.0 | 0.2 | 0.2 | 97.9 | 0.0 |
|  |  | 6 | 0.0 | 0.0 | 0.2 | 0.2 | 97.8 | 0.0 |
| Am Strip | 1 M HCl | 6 | 0.0 | 0.2 | 0.1 | 0.2 | 0.9 | 98.4 |
|  |  | 6 | 0.1 | 0.2 | 0.1 | 0.1 | 0.9 | 97.3 |
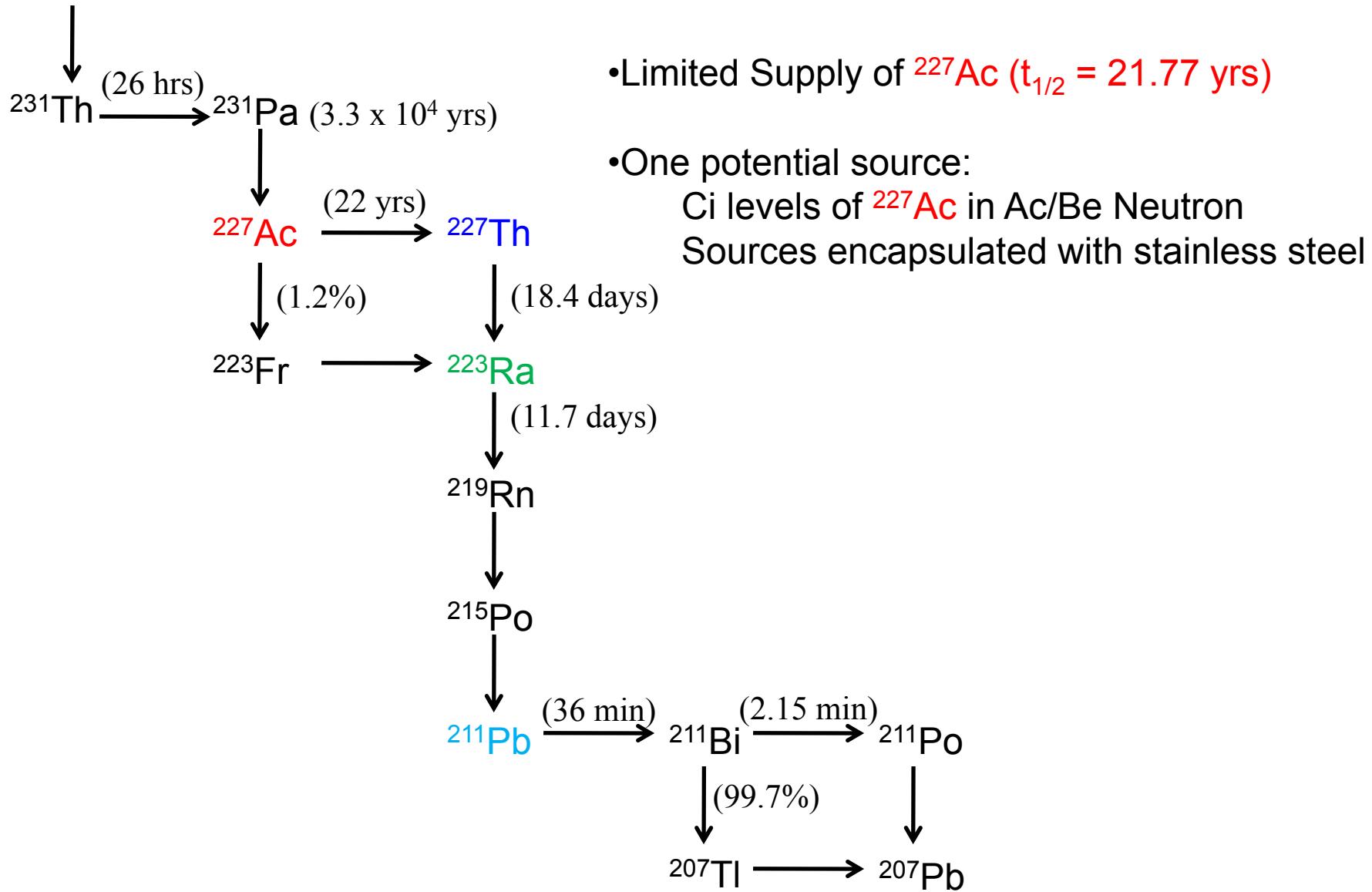
# DGA·FeCl$_3$ Resin / HCl System



**1000 ppm Fe**

**500 ppm Fe**

**200 ppm Fe**

**0 ppm Fe**

k' Am

Fe added as
Fe(III)Cl$_3$ · 6 H$_2$O

[HCl], M

$$\overline{DGA} + FeCl_3 + HCl \leftrightarrow \overline{DGA \cdot H^+FeCl_4^-}$$

$$\overline{3DGA \cdot H^+FeCl_4^-} + Am^{3+} + 3Cl^- \leftrightarrow$$

$$\overline{[(DGA)_3Am]^{3+} ([FeCl_4]^-)_3} + 3HCl$$
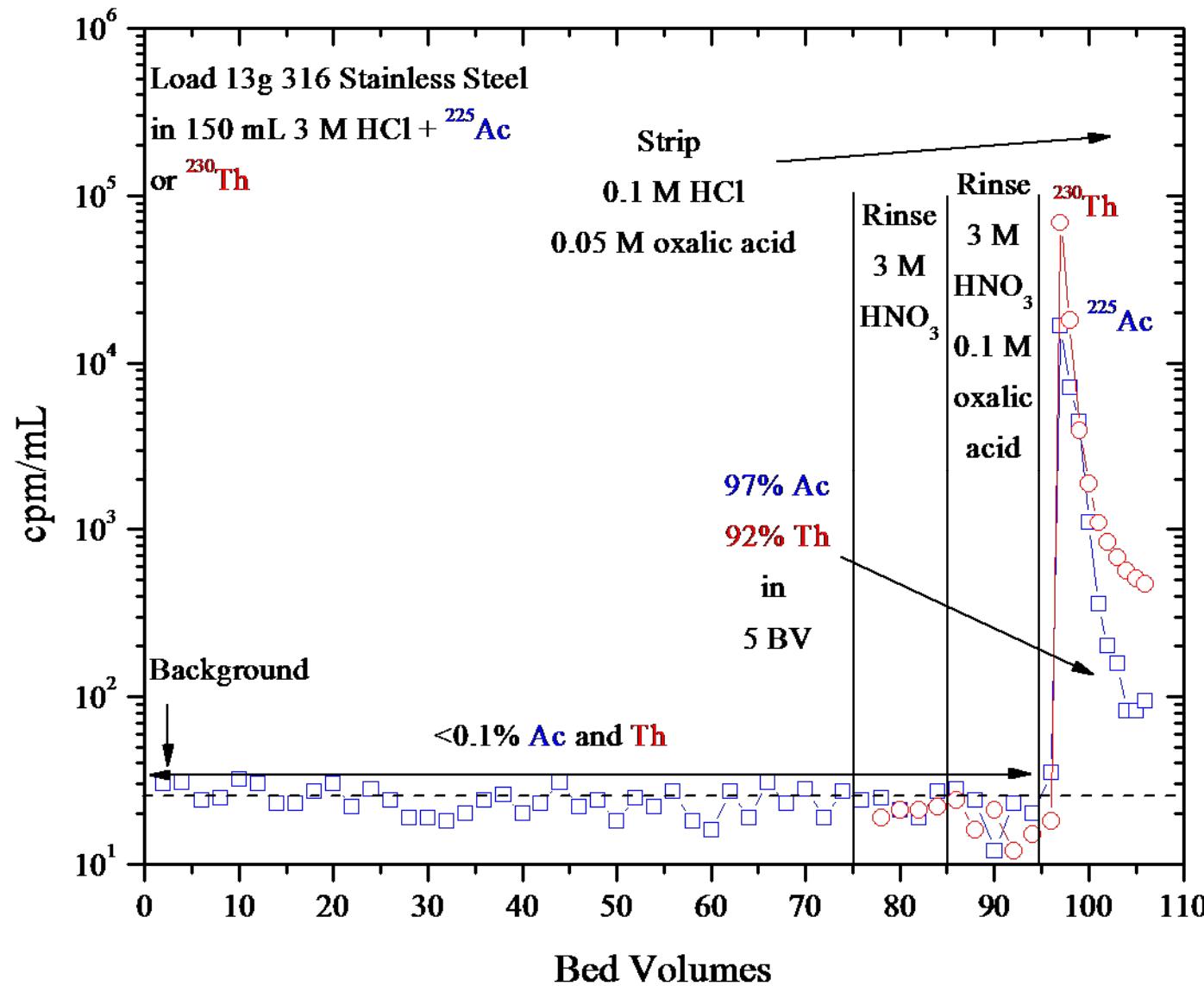
# Recovery of Np, Pu and Am from Ferric Hydroxide Precipitate

Ferric Hydroxide Precipitate

↓ 6M HCl

① ~2M HCl Solution + reducing agent

← ② 3M $HNO_3$

← ③ 0.1M HCl + 0.05M Oxalic Acid

2mL DGA Resin,
Normal Cartridge

①② Fe + Impurities

③ Np, Pu, Am to TRU column

# Recovery of $^{227}$Ac

$^{235}$U (7.1 x 10$^8$ yrs)

$^{231}$Th $\xrightarrow{\text{(26 hrs)}}$ $^{231}$Pa (3.3 x 10$^4$ yrs)

$^{227}$Ac $\xrightarrow{\text{(22 yrs)}}$ $^{227}$Th

$^{227}$Ac $\xrightarrow{\text{(1.2\%)}}$ $^{223}$Fr $\longrightarrow$ $^{223}$Ra

$^{227}$Th $\xrightarrow{\text{(18.4 days)}}$ $^{223}$Ra

$^{223}$Ra $\xrightarrow{\text{(11.7 days)}}$ $^{219}$Rn

$^{219}$Rn $\longrightarrow$ $^{215}$Po

$^{215}$Po $\longrightarrow$ $^{211}$Pb

$^{211}$Pb $\xrightarrow{\text{(36 min)}}$ $^{211}$Bi $\xrightarrow{\text{(2.15 min)}}$ $^{211}$Po

$^{211}$Bi $\xrightarrow{\text{(99.7\%)}}$ $^{207}$Tl $\longrightarrow$ $^{207}$Pb

$^{211}$Po $\longrightarrow$ $^{207}$Pb

- Limited Supply of $^{227}$Ac ($t_{1/2}$ = 21.77 yrs)

- One potential source:
  Ci levels of $^{227}$Ac in Ac/Be Neutron Sources encapsulated with stainless steel

# Ac/Th in HCl on 2mL DGA Resin, Normal cartridge



Load 13g 316 Stainless Steel
in 150 mL 3 M HCl + $^{225}$Ac
or $^{230}$Th

Strip

0.1 M HCl

0.05 M oxalic acid

Rinse 3 M HNO$_3$

Rinse 3 M HNO$_3$ 0.1 M oxalic acid

$^{230}$Th

$^{225}$Ac

97% Ac
92% Th
in
5 BV

Background

<0.1% Ac and Th

cpm/mL

Bed Volumes

Load Rinse Strip

Before Use | After Load | After Rinse

Prefilter
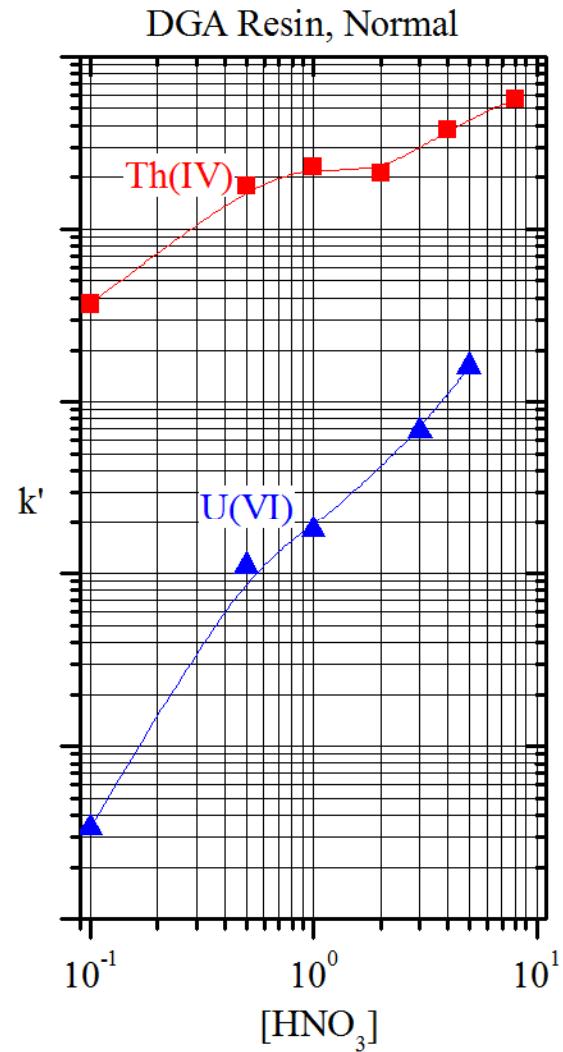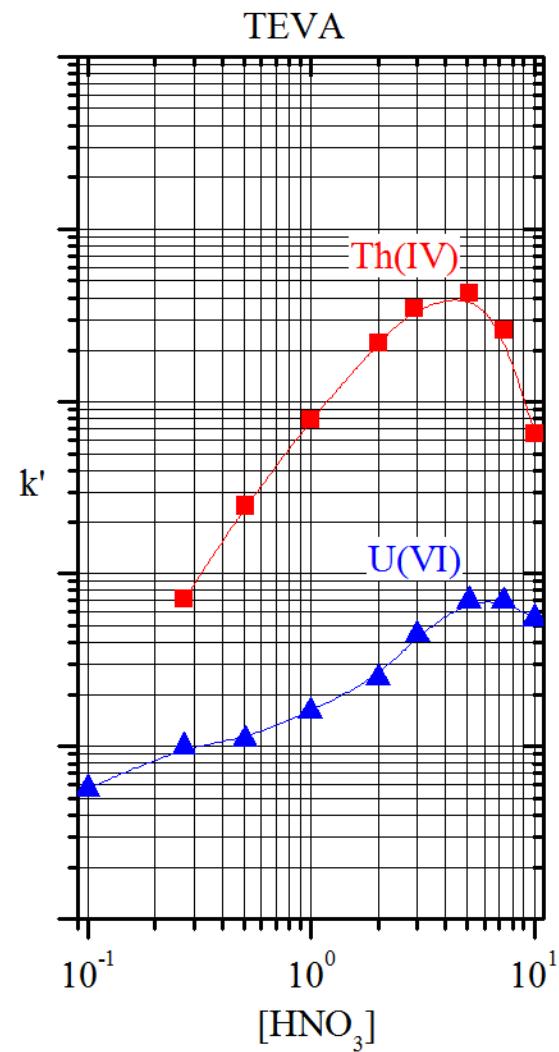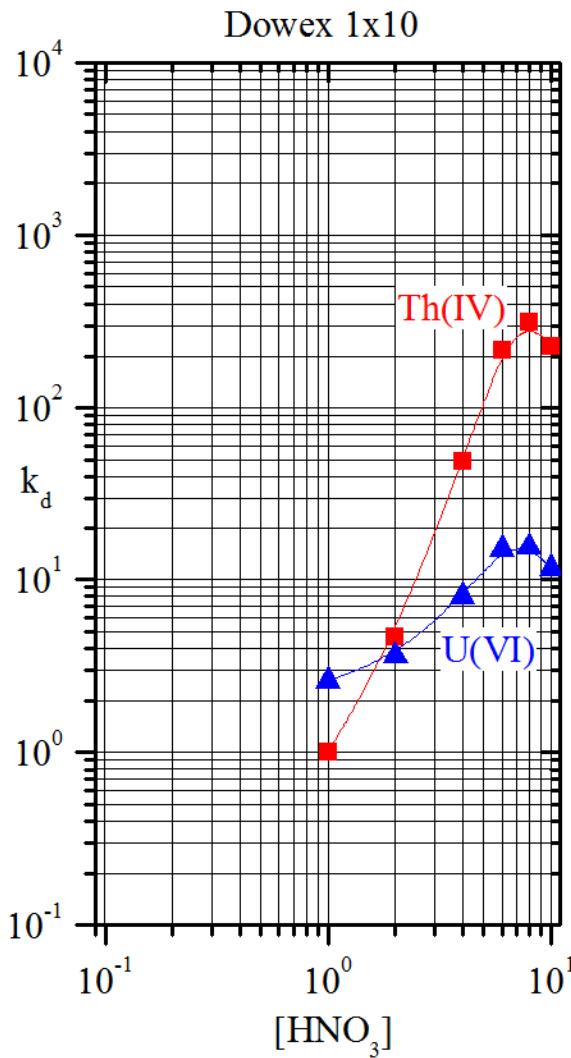
DGA

# Recovery of Trace Th from Bulk U

- Applications:

    - $^{229}$Th (1.4 kg of $^{233}$U contains 171 mg (37 mCi) of $^{229}$Th

    - $^{234}$Th (50 g of $^{238}$U contains 17 $\mu$Ci of $^{234}$Th

# Recovery of Trace Th from Bulk U

# cpm Th-227 vs. Bed Volumes of Eluate
## 35 mL column of DGA Resin (12.6cm x 1.9cm), 100-150 μm, 18mL/min, 22(1)°C



Load 2 liters of 2M $HNO_3$ +50g U + Th-227

$^{227}$Th

Strip
1.0 M

Rinse
1.0 M

Acetic

$HNO_3$

Acid

Gravity flow ~4mL/min

overpressure applied to reach ~18mL/min

Total processing time 2.5 hrs

U breakthrough at ~3.5 Bed Volumes

>99% Th
0.5% U

**cpm** (y-axis)

**Bed Volumes** (x-axis)