New Chromatographic Materials for Determinations of Actinides, Strontium, and Technetium in Environmental, Bioassay, and Nuclear Waste Samples*

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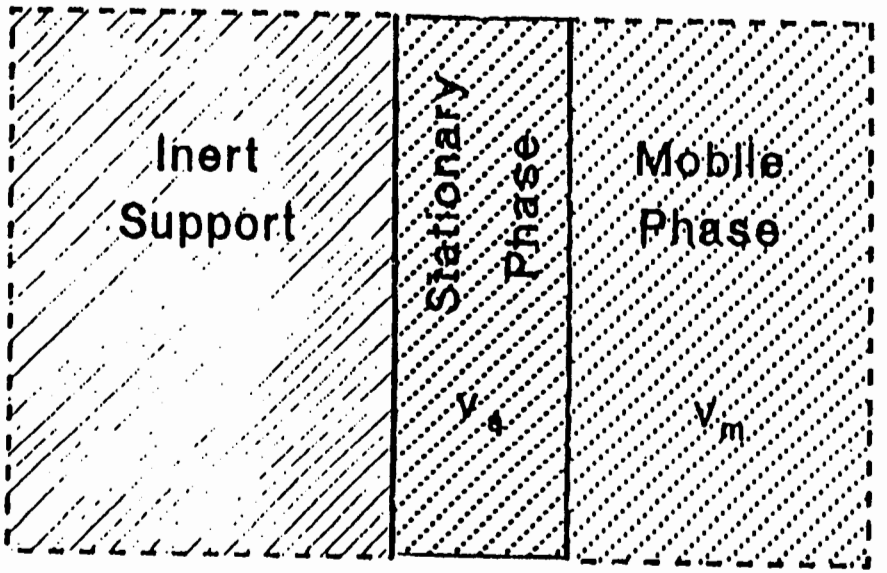
FUNDAMENTALS

FUNDAMENTALS

EXTRACTION CHROMATOGRAPHY



$$k' = D\ v_e/v_m$$

k' = free column volumes to peak maximum

Features of the New Chromatographic Materials

- High specificity
- Room temperature operation
- Gravity flow
- Acid – side loading from a wide range of concentrations
- Minimal waste generation
- Column compatibility for tandem arrangements

Extraction Chromatographic Materials

Currently Available

Material	Specificity
TRU•Spec	Actinides (III, IV, VI), Ln(III)
U/TEVA•Spec	U(VI), Actinides (IV)
TEVA•Spec	Actinides (IV), Tc(VII)
Sr•Spec	Sr

Currently Under Development

Tc•Spec	Tc
Ra•Spec	Ra

Characteristics of Extraction Chromatographic Materials and Columns

Stationary Phase	**Neat Extractant or Extractant – Diluent**
Support	**Amberlite XAD – 7**
Particle Sizes	**50 – 100 μm, 100 – 125 μm**
Extractant Loading	**40 weight percent**
Bed Density	**0.33 to 0.37 g/mL**

Fractional Volumes:

Void	**0.65**
Support	**0.20**
Extractant	**0.15**

Relationship Between SX and LLC

$$k' = D \cdot \frac{V_s}{V_m}$$

where

k' = retention volume

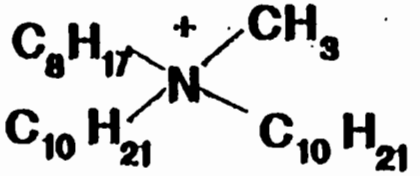
D = distribution ratio

V_s = volume of stationary phase

V_m = volume of mobile phase

TEVA·Spec

Extractant:



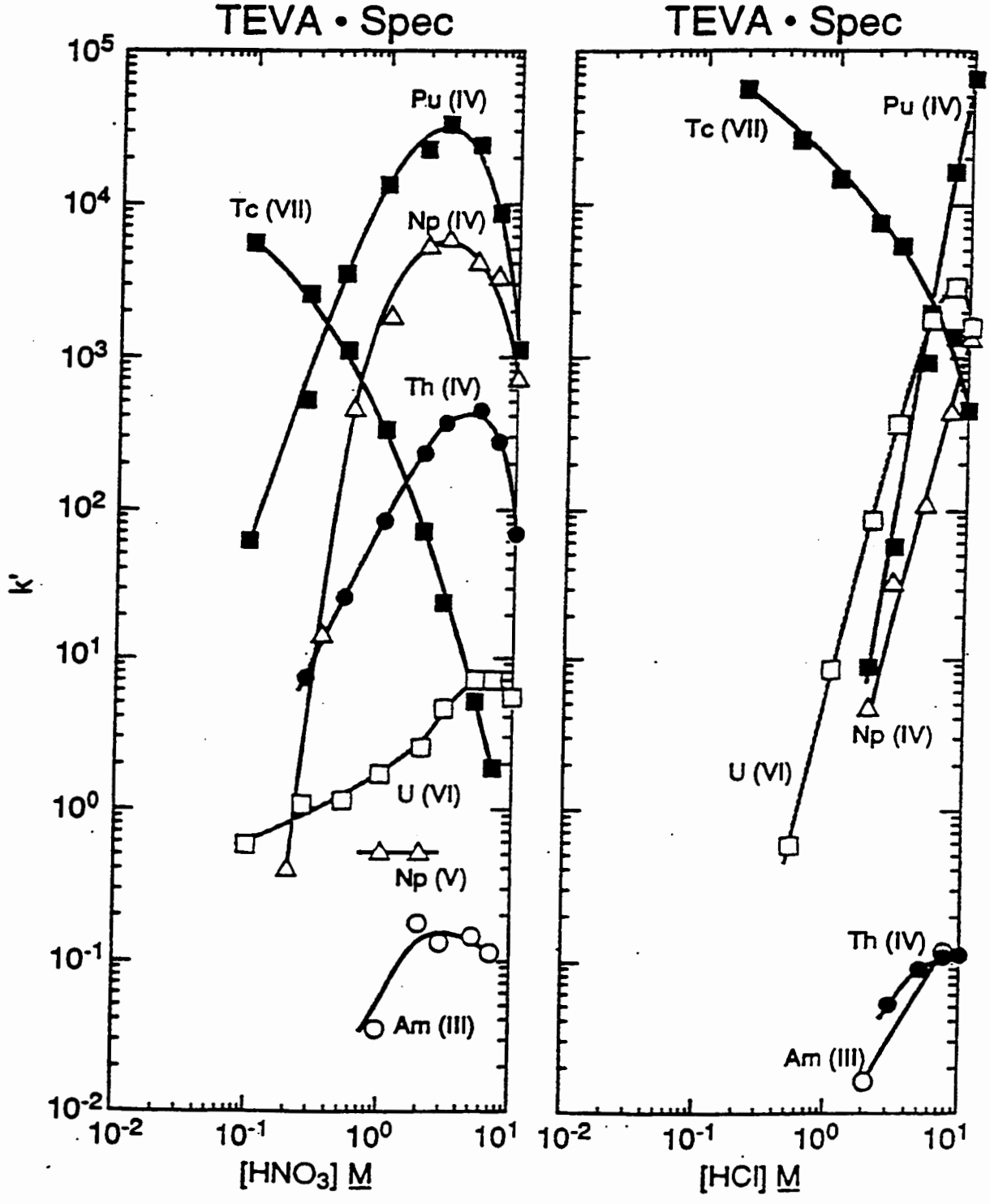
Diluent: None

Extraction Equilibria:

$$Pu^{4+} + 4NO_3^- + \overline{2E \cdot NO_3} \rightleftharpoons E_2^+ \cdot Pu(NO_3)_6^{-2}$$

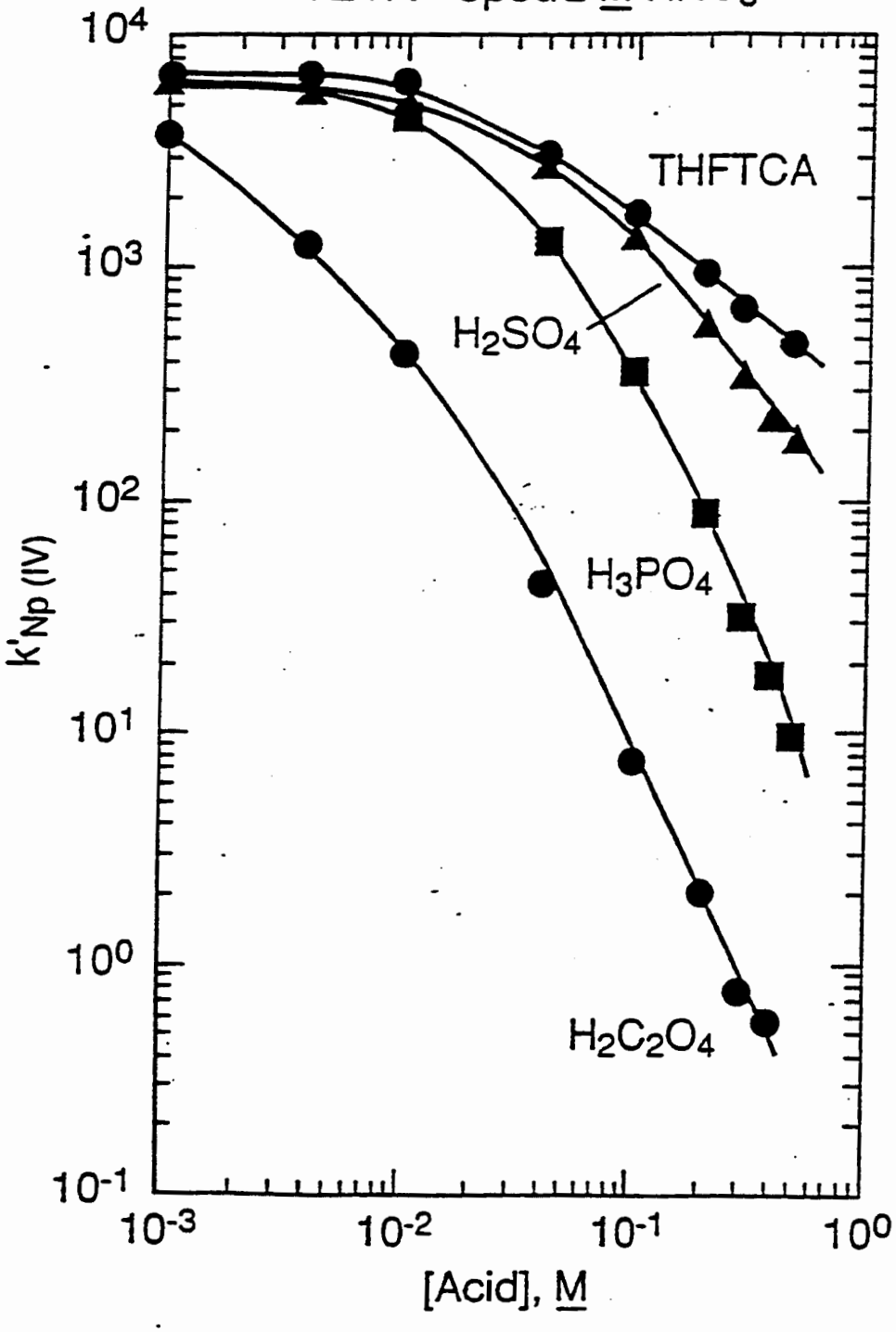
(Th^{4+}, Np^{4+})

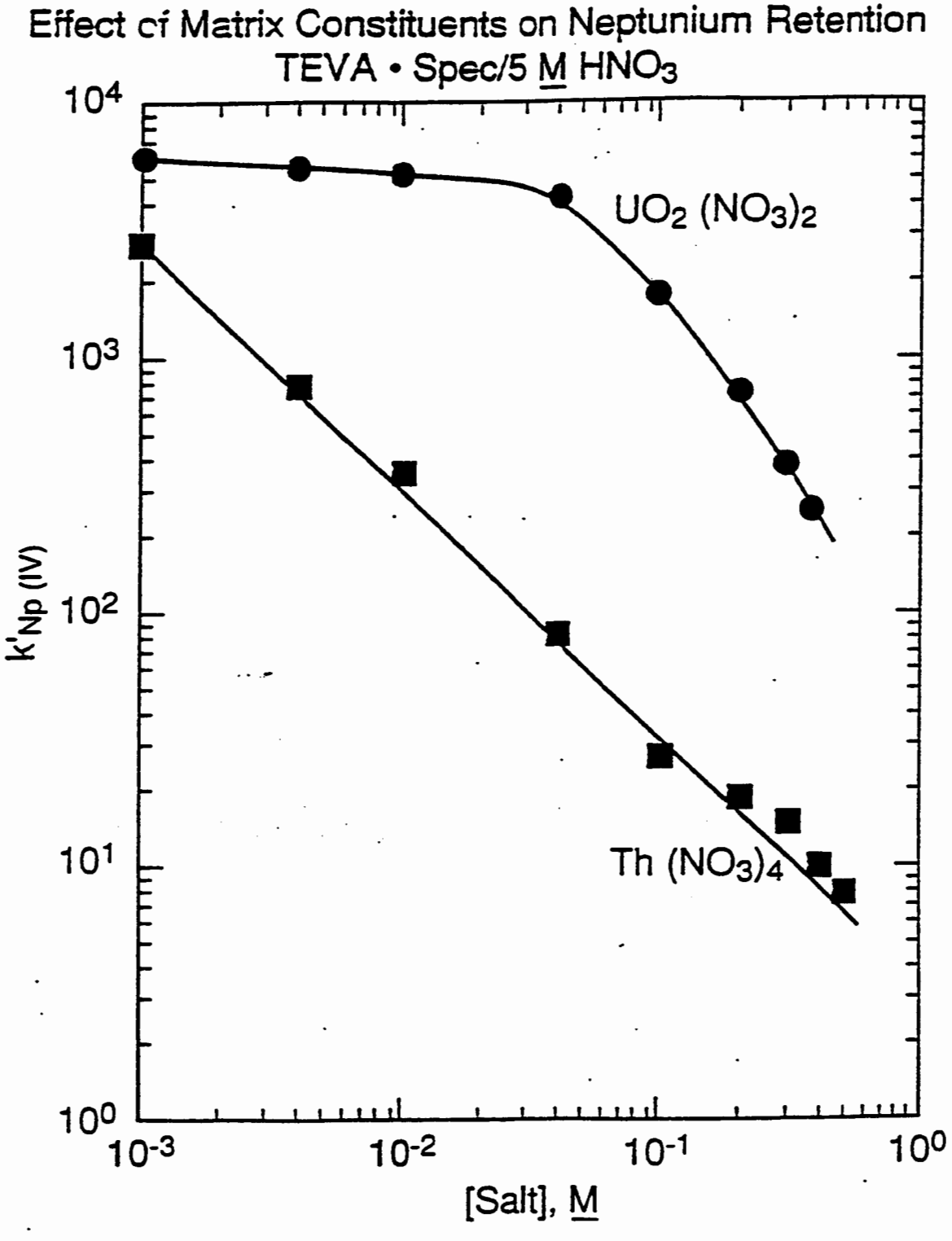
Acid dependency of k' for various ions at 23°C.

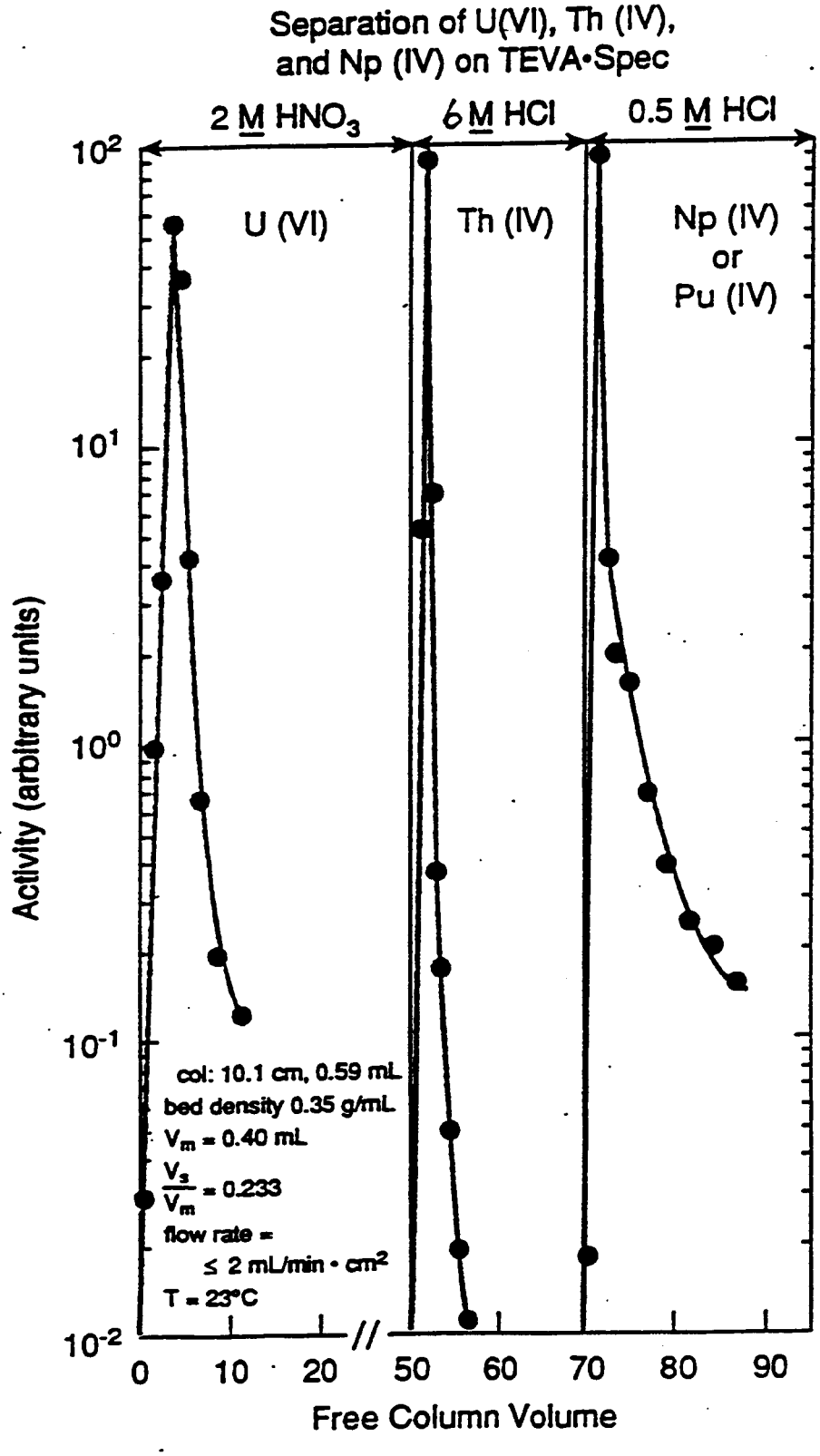


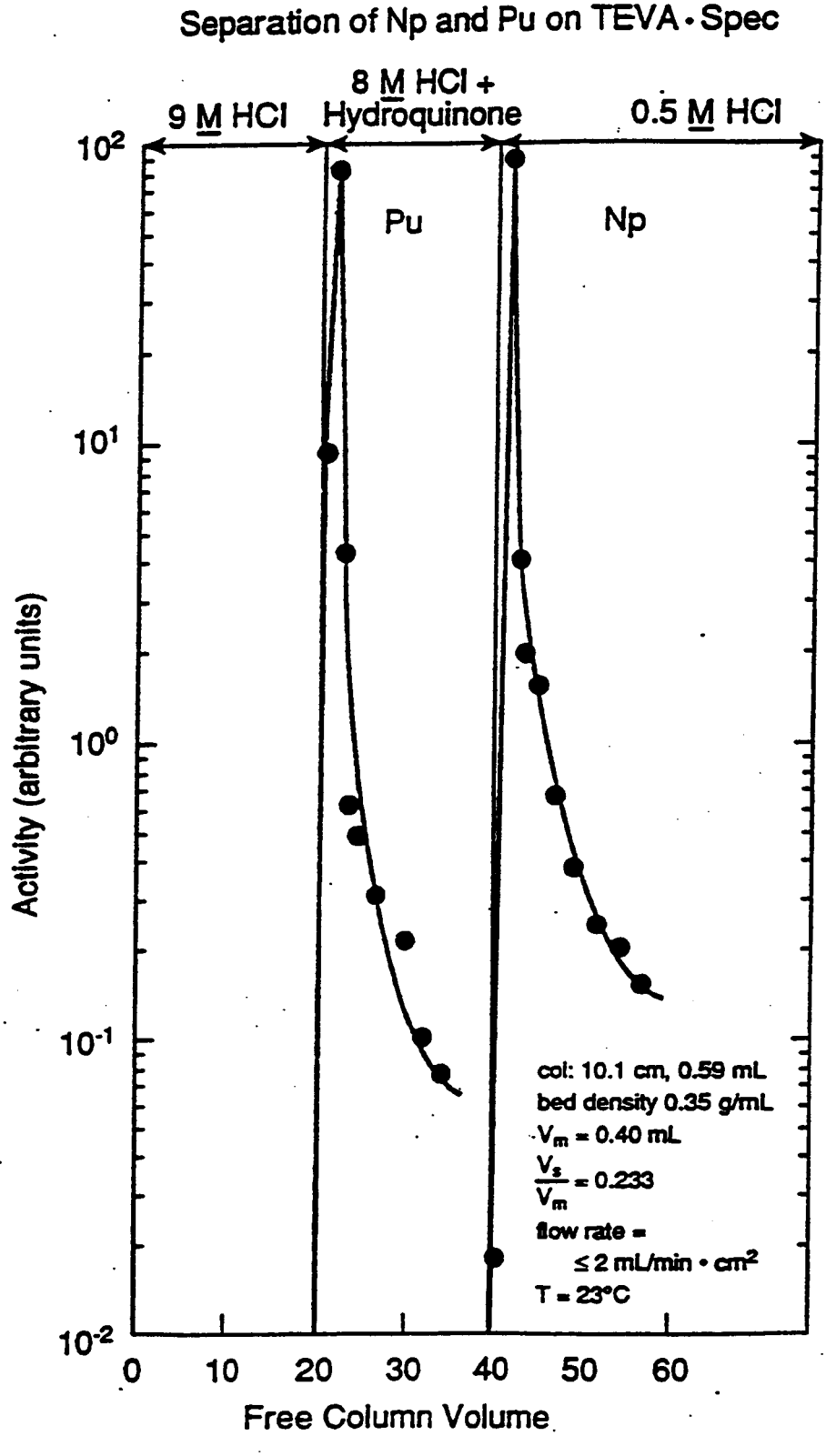
Effect of Matrix Constituents on Neptunium Retention

TEVA • Spec/2 M HNO_3



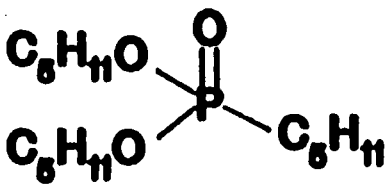

Effect of Matrix Constituents on Neptunium Retention
TEVA • Spec/5 M HNO3
10^4
10^3
10^2
10^1
10^0
k'Np (IV)
UO2 (NO3)2
Th (NO3)4
10^-3
10^-2
10^-1
10^0
[Salt], M


Separation of U(VI), Th (IV),
and Np (IV) on TEVA•Spec
2 M HNO3
6 M HCl
0.5 M HCl
U (VI)
Th (IV)
Np (IV)
or
Pu (IV)
Activity (arbitrary units)
10^2
10^1
10^0
10^-1
10^-2
col: 10.1 cm, 0.59 mL
bed density 0.35 g/mL
Vm = 0.40 mL
Vs/Vm = 0.233
flow rate =
≤ 2 mL/min • cm2
T = 23°C
0
10
20
50
60
70
80
90
Free Column Volume


Separation of Np and Pu on TEVA • Spec
9 M HCl
8 M HCl + Hydroquinone
0.5 M HCl
Pu
Np
Activity (arbitrary units)
10²
10¹
10⁰
10⁻¹
10⁻²
0
10
20
30
40
50
60
Free Column Volume
col: 10.1 cm, 0.59 mL
bed density 0.35 g/mL
Vm = 0.40 mL
Vs/Vm = 0.233
flow rate =
≤ 2 mL/min • cm²
T = 23°C

U/TEVA·Spec

Extractant:



DP[PP]

Diluent: None

Extraction Equilibria:

$$UO_2^{2+} + 2NO_3^- + \overline{2E} \rightleftharpoons \overline{UO_2(NO_3)_2 \cdot E_2}$$

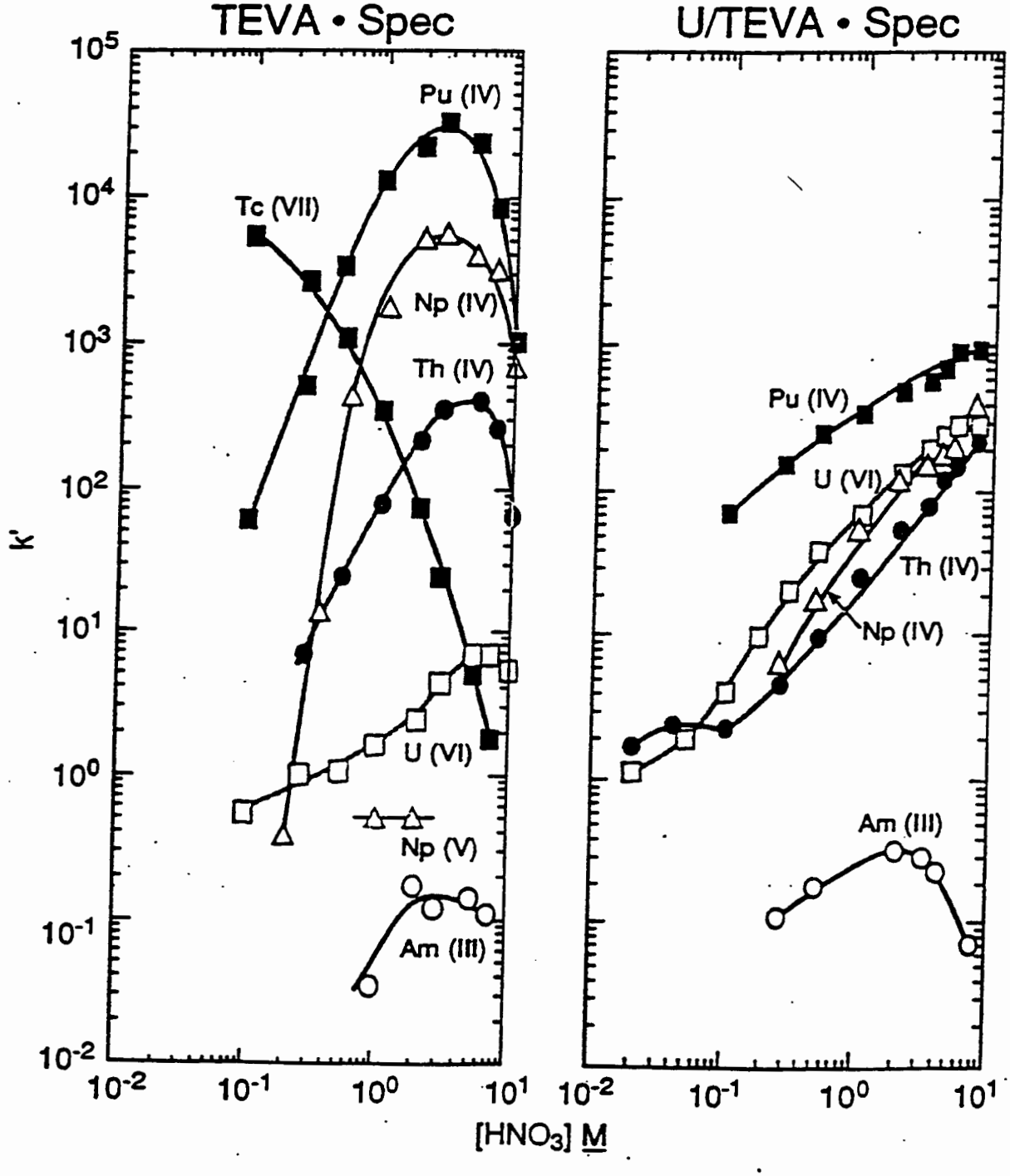
$$Th^{4+} + 4NO_3^- + \overline{3E} \rightleftharpoons \overline{Th(NO_3)_4 \cdot E_3}$$

Characteristics of the U/TEVA•Spec extraction chromatographic material and packed columns.

Bulk Material	
Stationary Phase	Diamyl amylphosphonate (ρ = 0.926 g/ml)
Support	Amberchrom™ CG-71 or Amberlite™ XAD-7
Particle Diameter	50-100 µm (Amberchrom); 80-160 µm; 100-125 µm
Extractant Loading	40 weight percent
Average Density of Extractant-Loaded Beads[a]	1.10 g/mL
Packed Columns	
v_s	0.167 mL/mL of bed
Bed Density	0.386 g/mL
v_m (also FCV)	0.65 mL/mL of bed
v_s/v_m	0.257
Calculated Capacity	37 mg U/mL of bed
Experimentally Measured Capacity	37 mg U/mL of bed

a Picnometric density and flotation density were 1.065 and 1.133, using the 50-100 µm particle size resin. The calculated density is 1.094 g/ml assuming 100% pore filling and no swelling.

Acid dependency of k' for various ions at 23°C.



Elution behavior of selected elements on a U/TEVA•Spec (fine particle) column.

	Portion eluting (%)[a]						
	← 2 M HNO_3						→ ← 0.02 M HNO_3 →
	Number of free column volumes[b]						
Element	1-5	6-10	11-15	16-20	21-25	26-30	31-40
Li	99.4	—	—	—	—	—	—
Na	95.0	<1.2	—	—	—	—	—
Mg	101	—	—	—	—	—	—
Al	92.0	<5.8	—	—	—	—	—
K	<123	—	—	—	—	—	—
Ca	92.4	<13.3	—	—	—	—	—
Cr	94.7	<3.3	—	—	—	—	—
Mn	96.5	<0.7	—	—	—	—	—
Fe	94.0	<0.3	—	—	—	—	—
Co	99.1	<7.1	—	—	—	—	—
Ni	97.8	<2.0	—	—	—	—	—
Cu	98.1	<2.6	—	—	—	—	—
Zn	96.8	<1.2	—	—	—	—	—
Rb[c]	102	—	—	—	—	—	—
Sr	101	—	—	—	—	—	—
Y	97.9	<2.9	—	—	—	—	—
Zr	56.4	35.7	(1.4)	—	—	—	—
Ru	59.6	<19.2	<19.2	—	—	—	—
Rh	91.7	—	—	—	—	—	—
Ag	103	—	—	—	—	—	—
Cd	96.4	<0.7	—	—	—	—	—
Cs[d]	100	—	—	—	—	—	—
Ba	96.6	<14.4	—	—	—	—	—
La	108	—	—	—	—	—	—
Ce	96.3	<25	—	—	—	—	—
Pr	(136)	—	—	—	—	—	—
Nd	99.0	—	—	—	—	—	—
Sm	120	—	—	—	—	—	—
Eu	100	—	—	—	—	—	—
Pb	98.4	<5.8	—	—	—	—	—
U[e]	—	—	—		—	—	>99

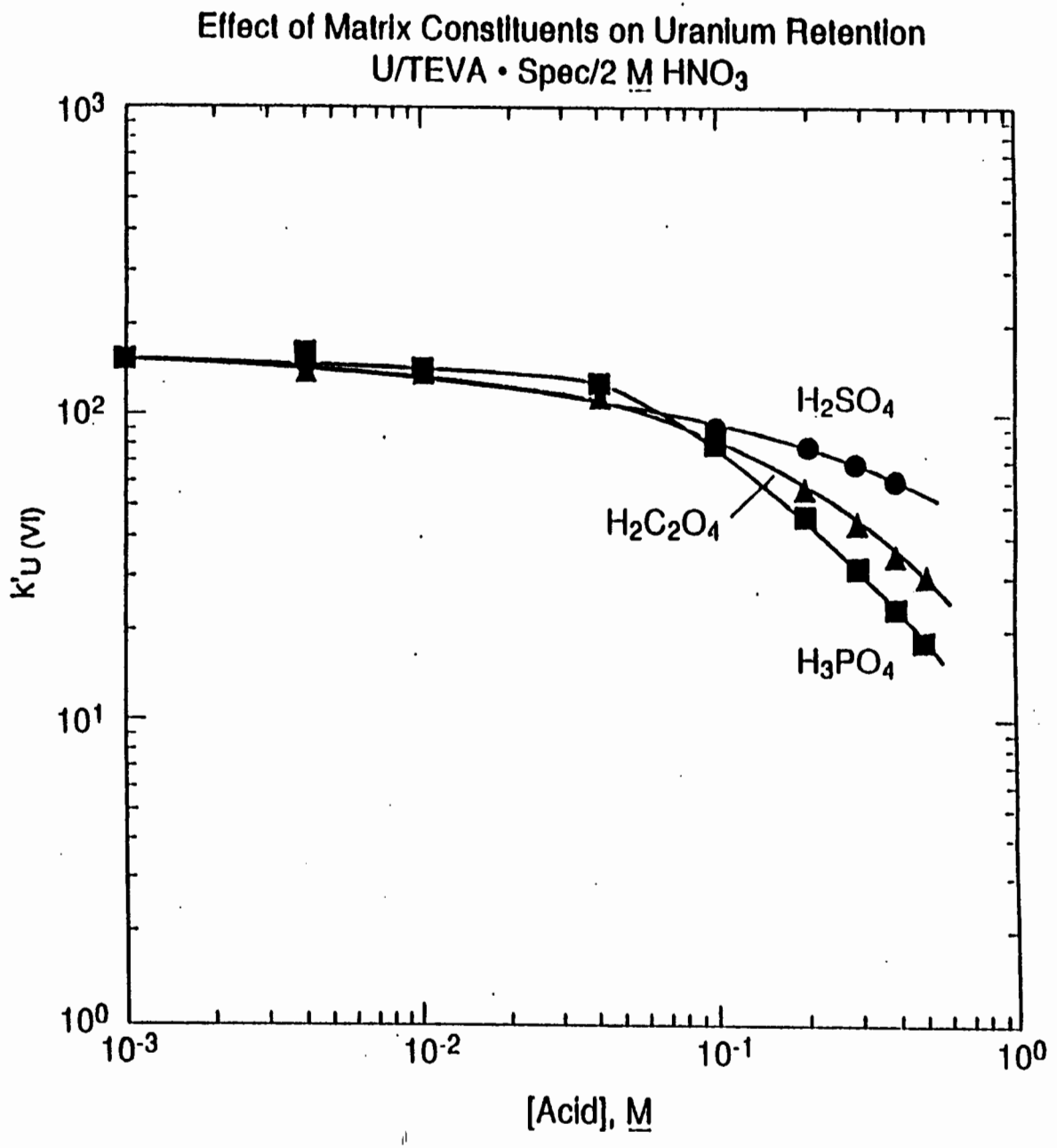
[a] Because of uncertainties inherent in the ICP-AES method used for quantitation, the fractions shown for a given element may not total 100%. Values in parentheses are subject to considerable uncertainty and are intended only as a guide. Feed solution contained ~0.02 M oxalic acid to solubilize zirconium.

[b] 1 FCV = 0.60 mL here.

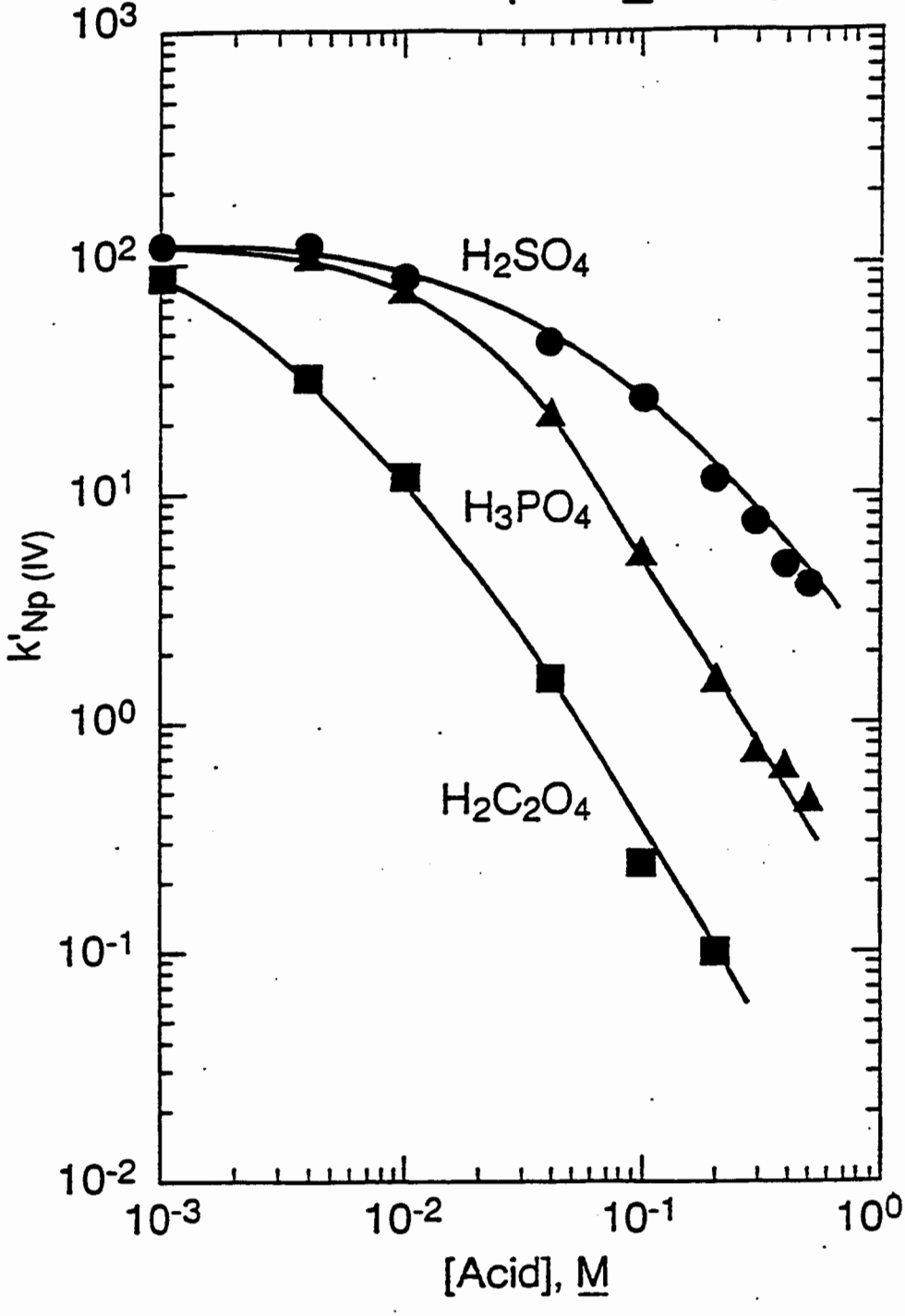
[c] By flame atomic emission.

[d] By atomic absorption.

[e] Radiometric.

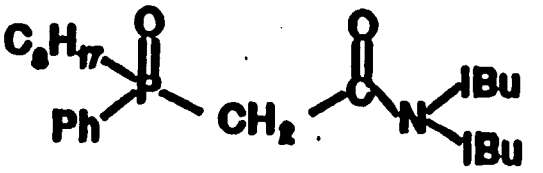

Effect of Matrix Constituents on Uranium Retention
U/TEVA • Spec/2 M HNO3
10^3
10^2
10^1
10^0
k'U (VI)
H2SO4
H2C2O4
H3PO4
10^-3
10^-2
10^-1
10^0
[Acid], M

Effect of Matrix Constituents on Neptunium Retention
U/TEVA • Spec/2 M HNO_3



TRU·Spec

Extractant:



CMPO

Diluent: TBP

Extraction Equilibria:

$$Am^{3+} + 3NO_3^- + \overline{3E} \rightleftharpoons \overline{Am(NO_3)_3 \cdot E_3}$$
$$(Ln^{3+})$$

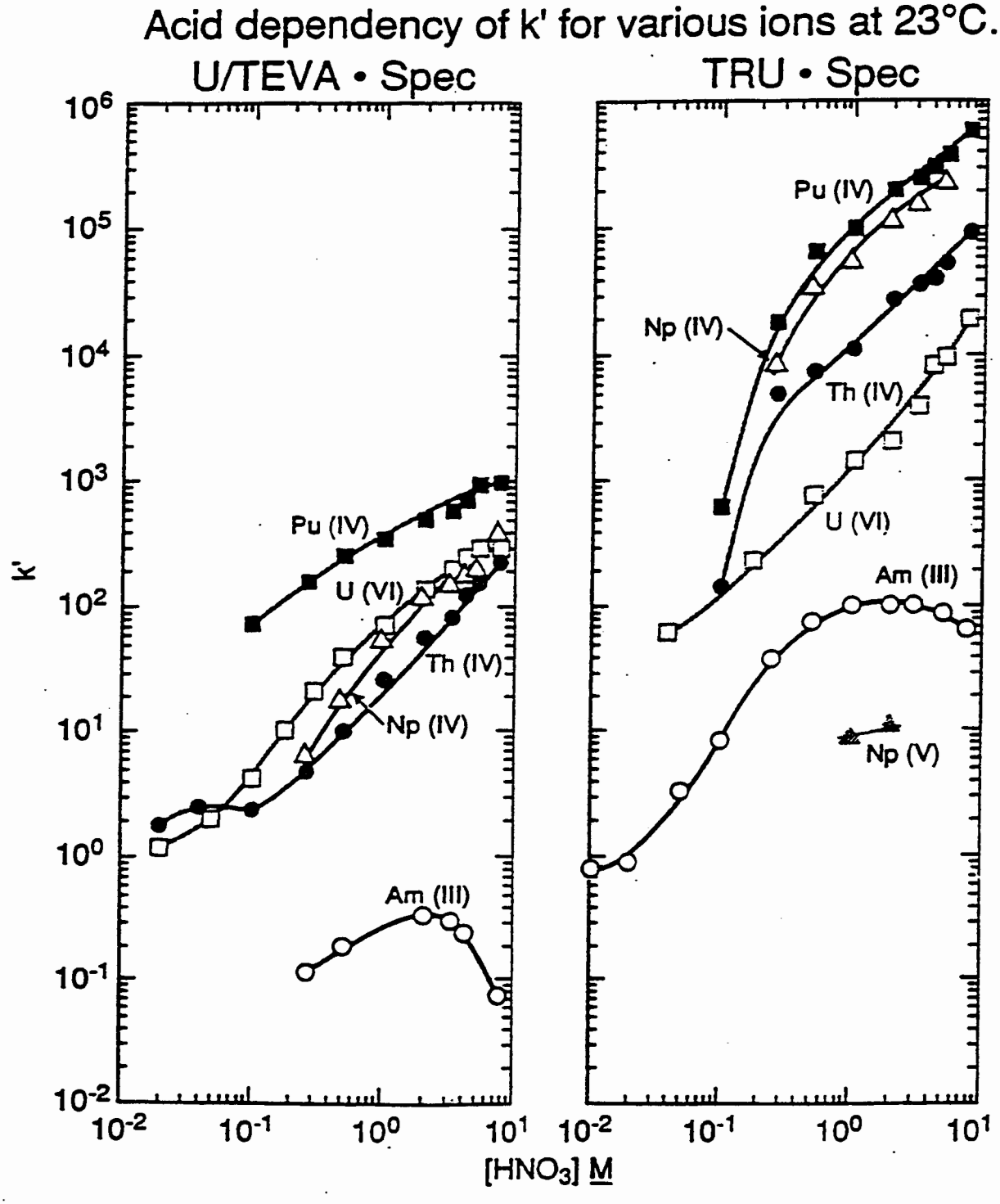
$$Pu^{4+} + 4NO_3^- + \overline{2E} \rightleftharpoons \overline{Pu(NO_3)_4 \cdot E_2}$$
$$(Np^{4+})$$

$$UO_2^{2+} + 2NO_3^- + \overline{2E} \rightleftharpoons \overline{UO_2(NO_3)_2 \cdot E_2}$$

Characteristics of the TRU-Spec extraction chromatographic material and packed columns.

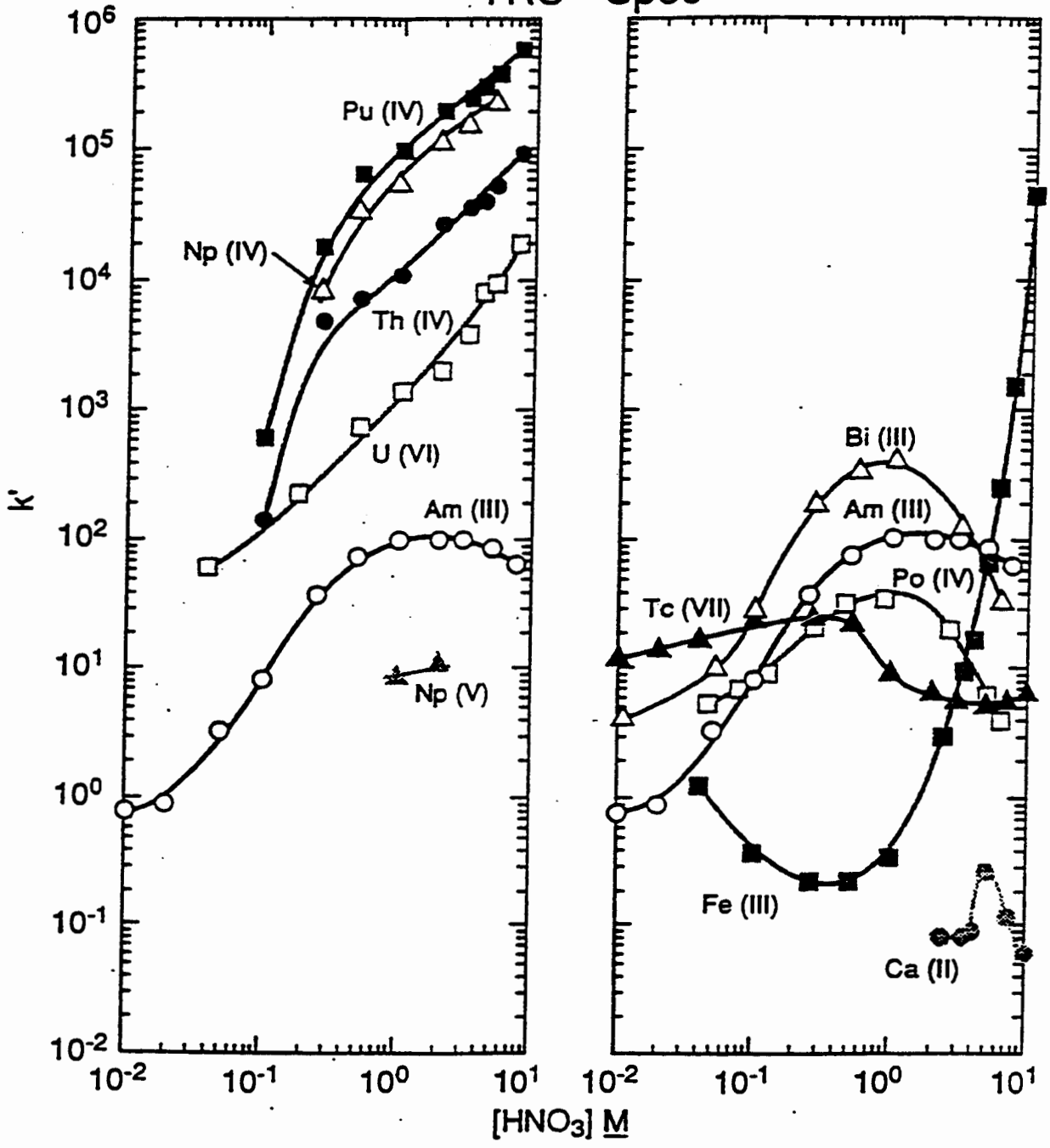
Bulk Material	
Stationary Phase	0.75 M CMPO in TBP (ρ = 0.971 g/ml)
Support	Amberchrom™ CG-71
Particle Diameter	50-100 μm and 80-160 μm
Extractant Loading	40%
Average Density of Extractant-Loaded Beads[a]	1.12 g/mL
Packed Columns	
v_s	0.152 mL/mL of bed
Bed Density	0.370 g/mL
v_m (also FCV)	0.68 mL/mL of bed
v_s/v_m	0.223
Calculated Capacity	5.49 mg Nd or 9.18 mg ^{241}Am/mL of bed
Experimentally Measured Capacity	4.1 mg Nd or 6.8 mg ^{241}Am/mL of bed

[a] Picnometric density and flotation density were 1.081 (in water) and 1.158 (in 4.9 M HNO3) g/mL,respectively, using the 50-100 μm particle size resin. The calculated density is 1.094 g/ml assuming 100% pore filling and nc swelling.

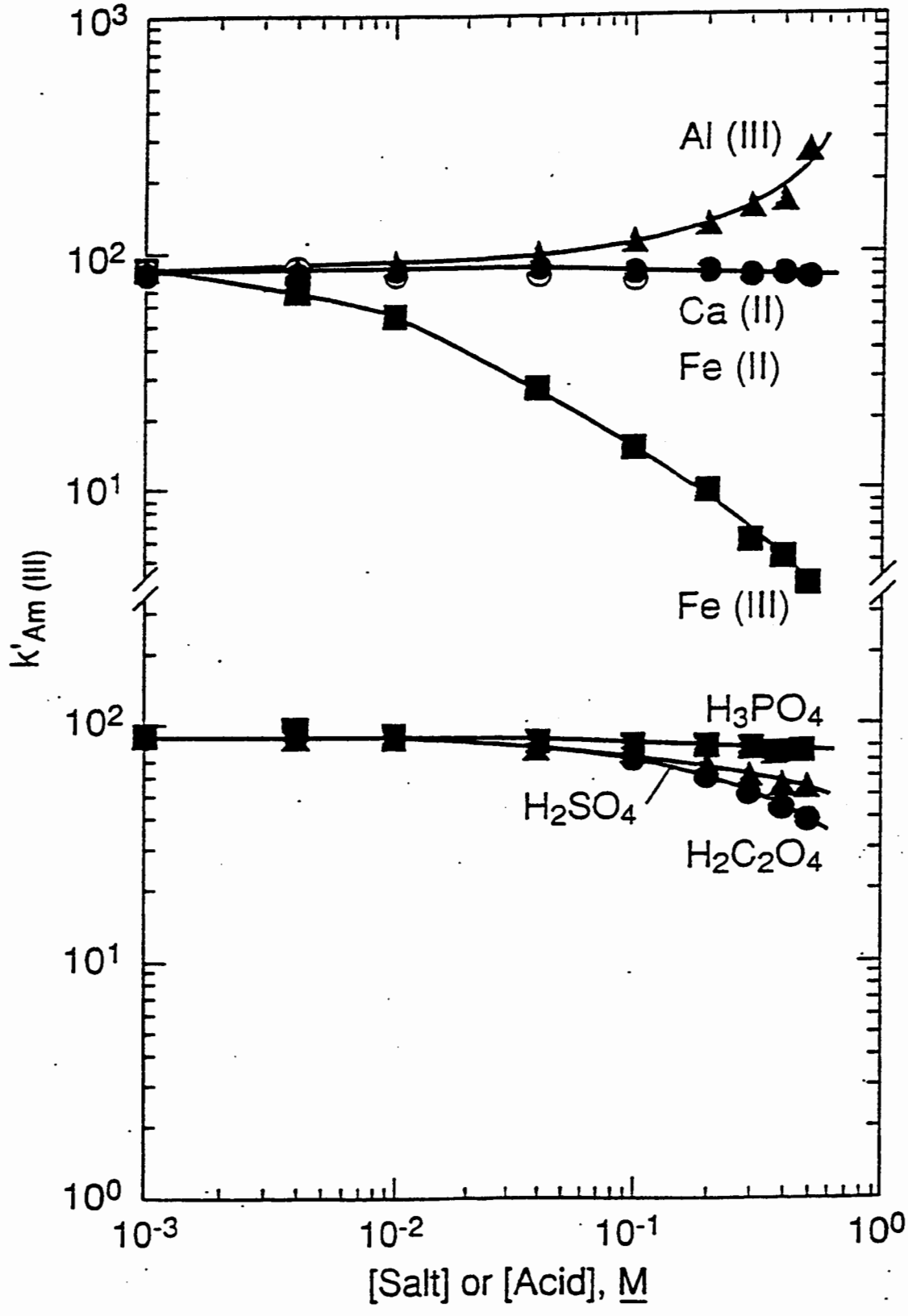

Acid dependency of k' for various ions at 23°C.
U/TEVA • Spec
TRU • Spec
k'
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
Pu (IV)
U (VI)
Th (IV)
Np (IV)
Am (III)
Np (V)
10^{-2}
10^{-1}
10^0
10^1
[HNO_3] M

Acid dependency of k' for various ions at 23-25°C.

TRU • Spec



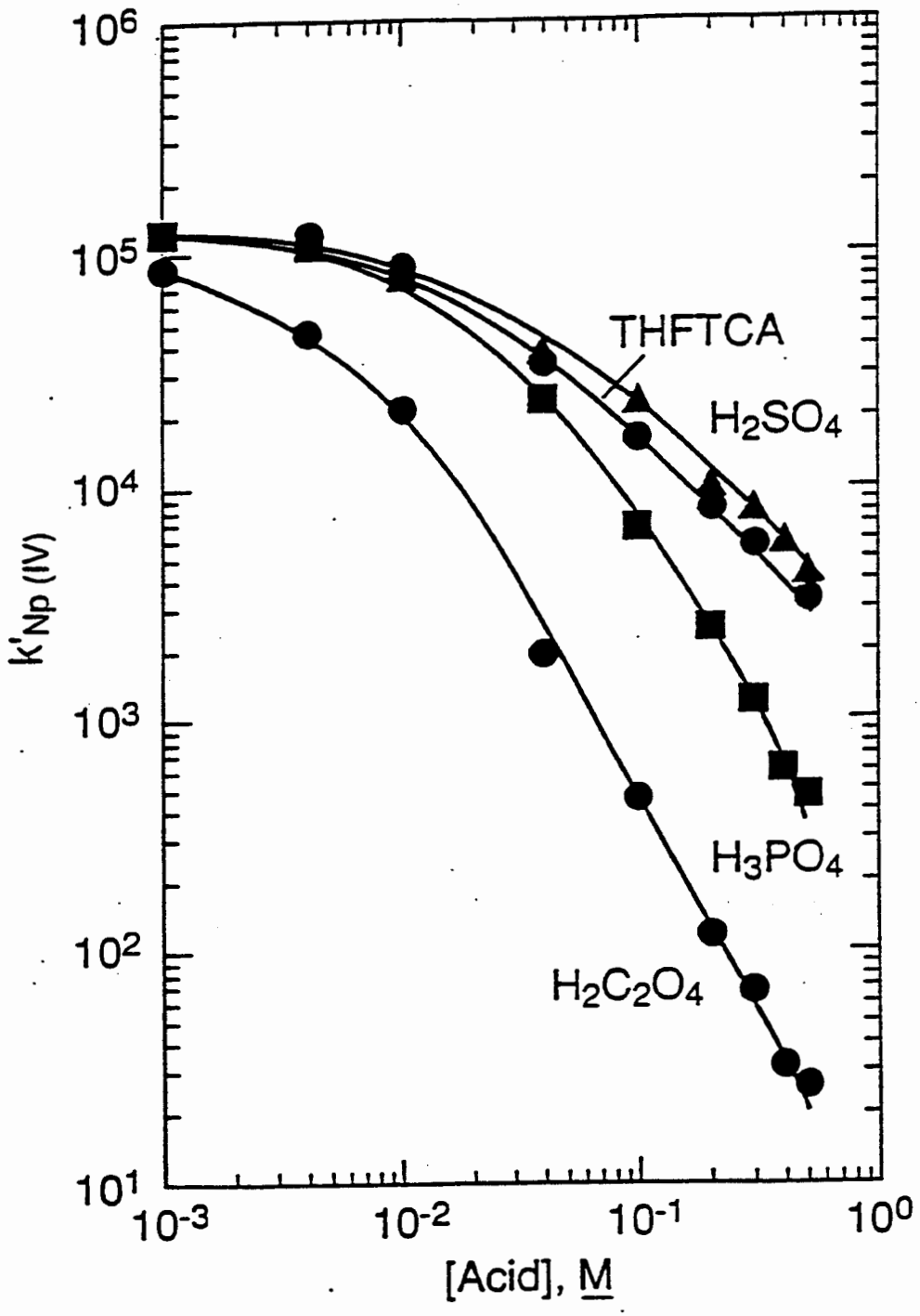
Effect of Matrix Constituents on Americium Retention
TRU • Spec/2 M HNO_3



Effect of Fe on Am Uptake by TRU Spec
(Reference k'_{Am} at 2M HNO_3, 23 °C = 98)

mg of Fe/10mL	M of Ascorbic Acid	k'_{Am}
25	–	28
50	–	17
100	–	9.1
25	0.3	88
50	0.3	72
100	0.3	65

Effect of Matrix Constituents on Neptunium Retention
TRU • Spec/2 M HNO_3



Elution of Selected Elements on a TRU•Spec Column

(fine particles)

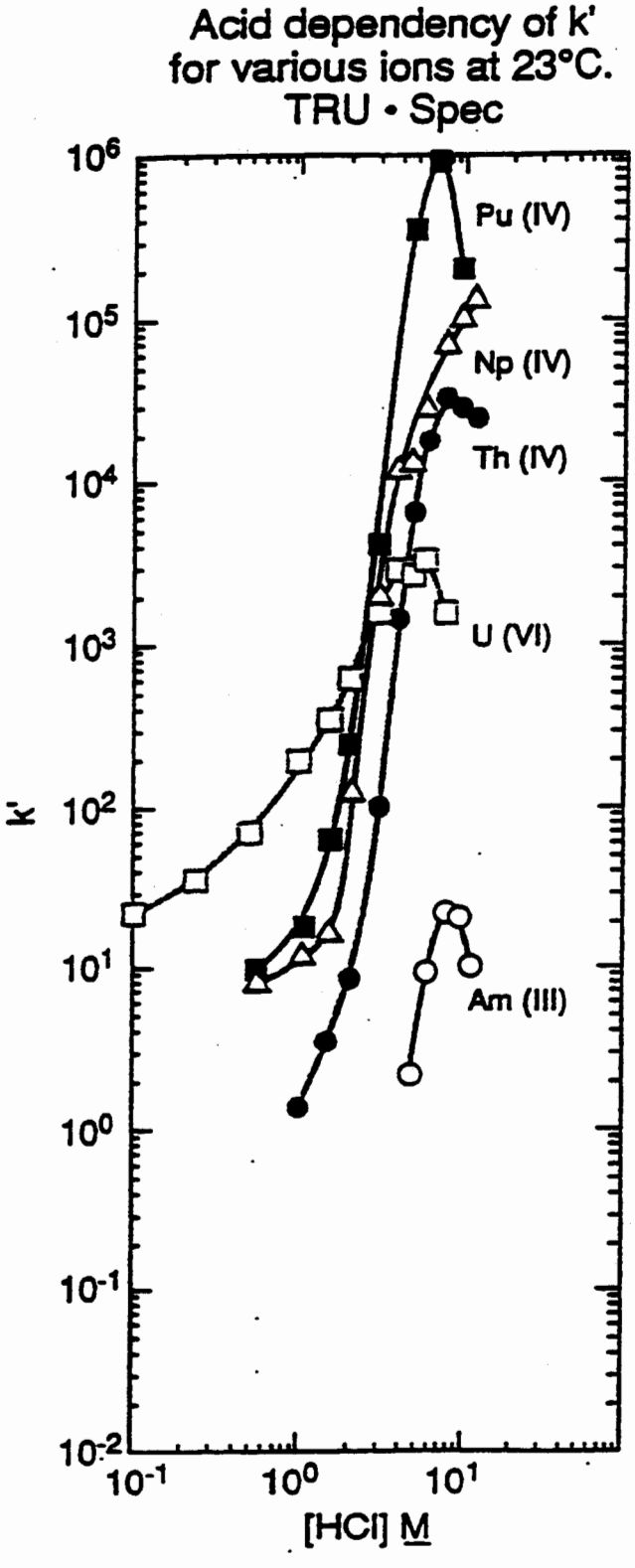
Element	Fraction Eluting [%] by number of free column volumes						
	1–5	6–10	11–15	16–20	21–25	25–30	31–40
Li	98.4	<1.9	–	–	–	–	–
Na	92.8	<1.2	–	–	–	–	–
Mg	100	–	–	–	–	–	–
Al	99.8	<2.9	–	–	–	–	–
K	81.8	40.9	–	–	–	–	–
Ca	100	–	–	–	–	–	–
Cr	100	–	–	–	–	–	–
Mn	100	–	–	–	–	–	–
Fe	102	12.3	–	–	–	–	–
Co	100	–	–	–	–	–	–
Ni	100	–	–	–	–	–	–
Cu	100	–	–	–	–	–	–
Zn	100	–	–	–	–	–	–
Sr	100	–	–	–	–	–	–
Y	23.4	76.8	3.5	–	–	–	–
Zr	–	–	–	–	–	–	75.0
Ru	82.6	<19.2	–	–	–	–	–
Rh	100	–	–	–	–	–	–
Ag	100	–	–	–	–	–	–
Cd	100	–	–	–	–	–	–
Ba	100	–	–	–	–	–	–
La	–	–	–	–	–	30.0	72.0
Ce	–	–	–	–	–	<25.0	75.0
Pr	–	–	–	–	–	–	100
Nd	–	–	–	–	–	–	96.0
Sm	–	–	–	–	–	–	100
Eu	–	–	–	–	–	–	>99
Hg	(100)	(60)	(19)	–	–	–	–
Pb	100	–	–	–	–	–	–
Am*	–	–	–	–	–	–	>99

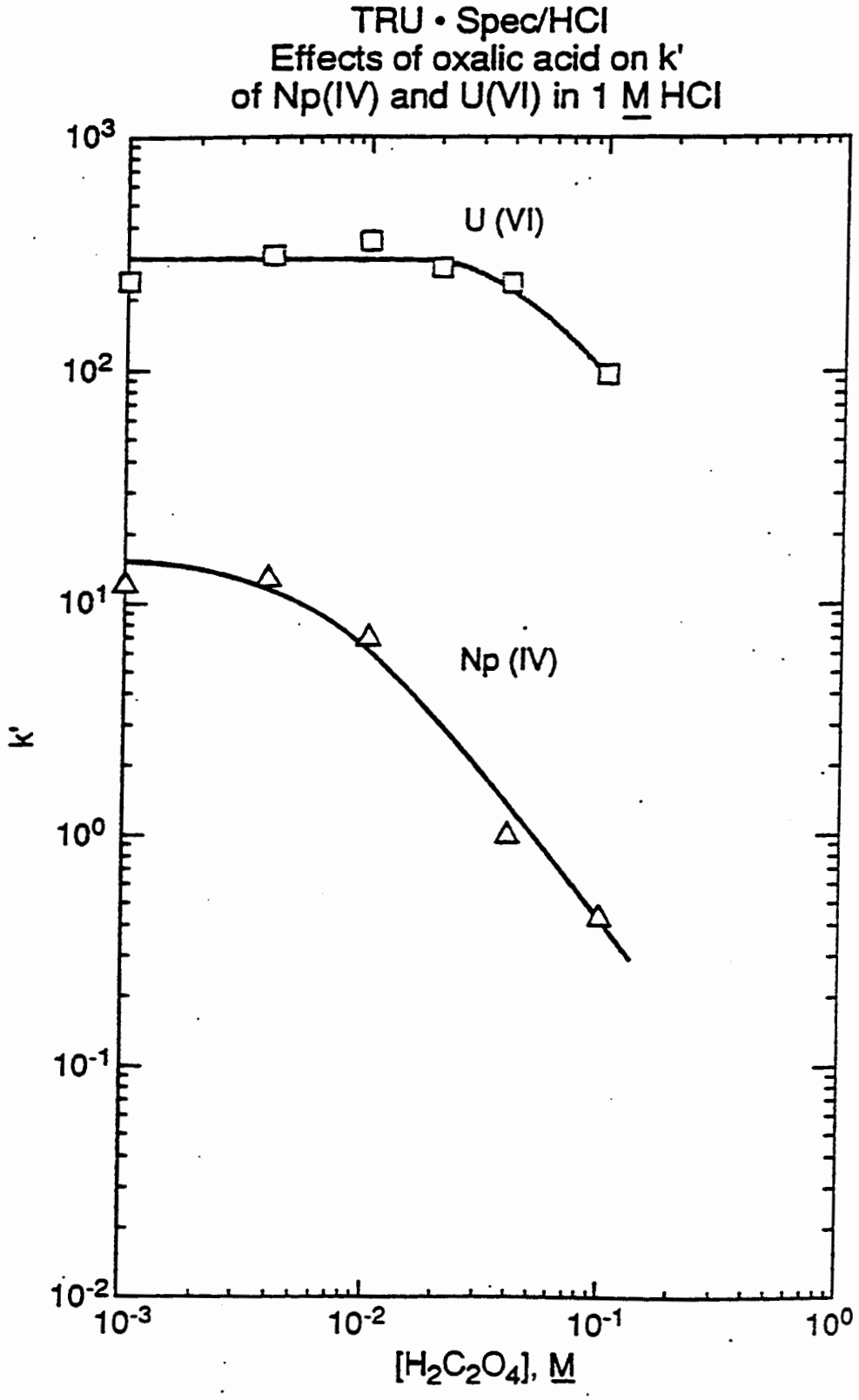
* radiometric

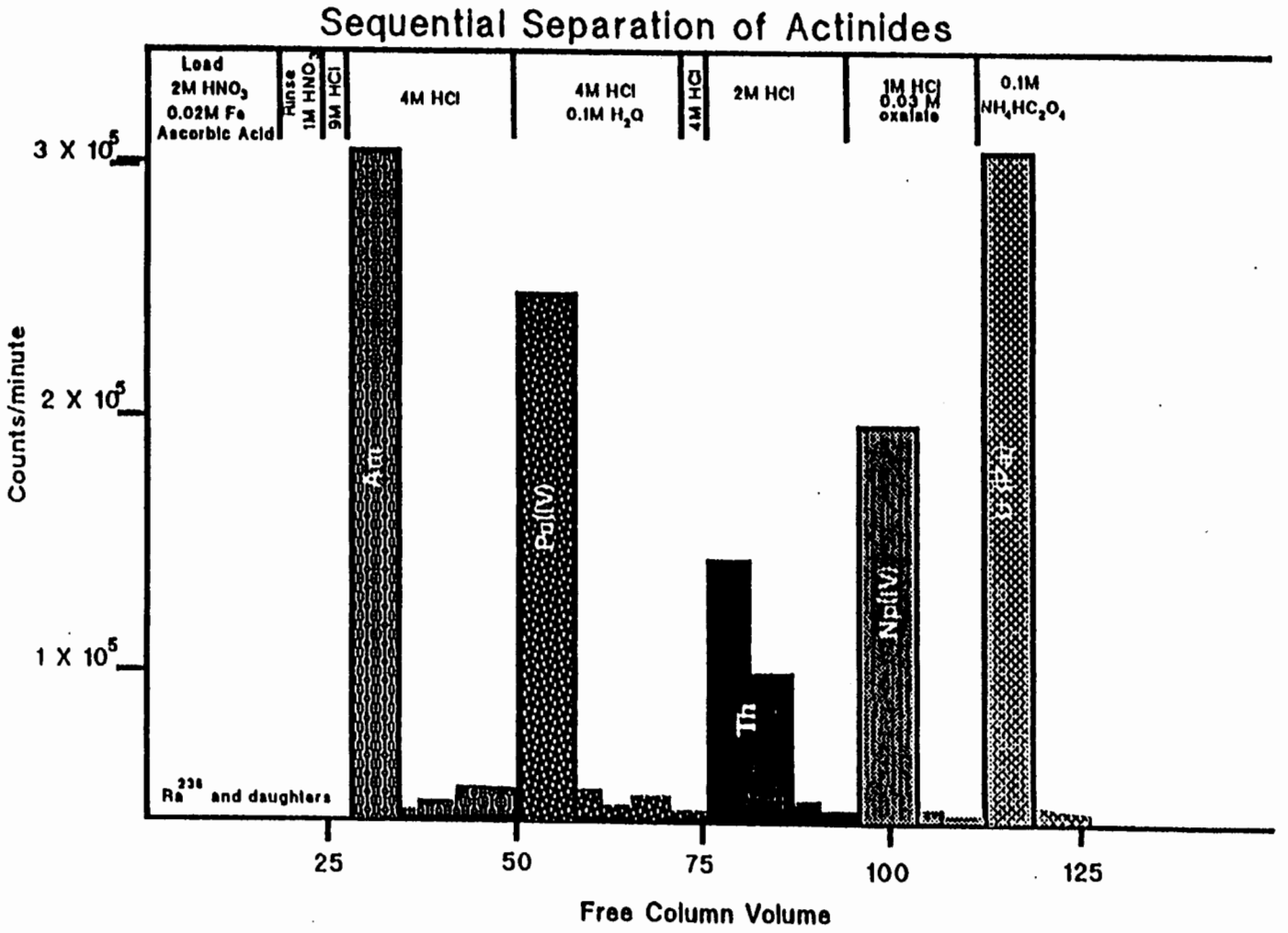
1–30 f.c.v. : 2M HNO_3

31–40 f.c.v. : 0.05M HNO_3

note: Because of uncertainties inherent in the ICP-AES method, the fractions shown for each element may not total to 100%. Values in parentheses are subject to considerable uncertainty and are intended only as a rough guide.

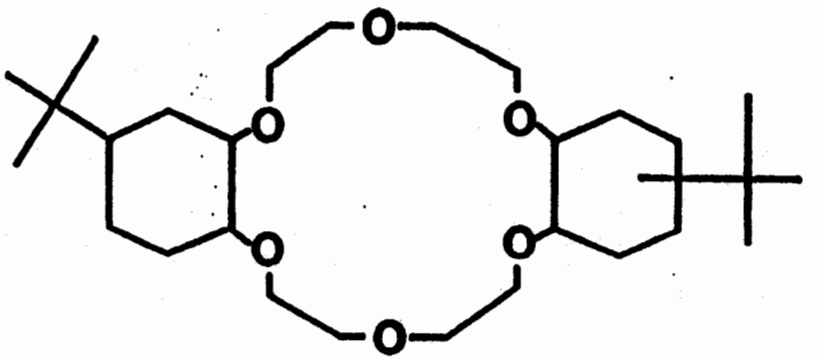

Acid dependency of k'
for various ions at 23°C.
TRU • Spec
Pu (IV)
Np (IV)
Th (IV)
U (VI)
Am (III)
k'
[HCl] M


TRU • Spec/HCl
Effects of oxalic acid on k'
of Np(IV) and U(VI) in 1 M HCl
U (VI)
Np (IV)
k'
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-2}
10^{-1}
10^0
$[H_2C_2O_4]$, M


Sequential Separation of Actinides
Load
2M HNO3
0.02M Fe
Ascorbic Acid
Rinse
1M HNO3
9M HCl
4M HCl
4M HCl
0.1M H2O
4M HCl
2M HCl
1M HCl
0.03 M
oxalate
0.1M
NH4HC2O4
3 X 10^5
2 X 10^5
1 X 10^5
Counts/minute
Am
Pa(IV)
Th
Np(V)
U+Pu
Ra^226 and daughters
25
50
75
100
125
Free Column Volume

Sr·Spec

Extractant: bis-t-Butyl-cis-Dicyclohexano-18-Crown-6



Diluent: 1-Octanol ($C_8H_{17}OH$)

Extraction Equilibrium:

$$Sr^{2+} + 2NO_3^- + \overline{Cr} \rightleftharpoons \overline{Sr(Cr)(NO_3)_2}$$

CHARACTERISTICS OF STRONTIUM-SELECTIVE EXTRACTION CHROMATOGRAPHIC MATERIAL AND PACKED COLUMNS

BULK MATERIAL	
Stationary Phase	1.0 M DtBuCH18C6 in 1-octanol[a] (ρ = 0.912 g/mL)
Support	Amberchrom™ CG-71 or Amberlite™ XAD-7
Particle Sizes (diam.)	50-100 µm; 80-160 µm; 100-125 µm
Extractant Loading	40 weight percent
Average Density of Extractant-Loaded Beads[b]	1.12 g/ml

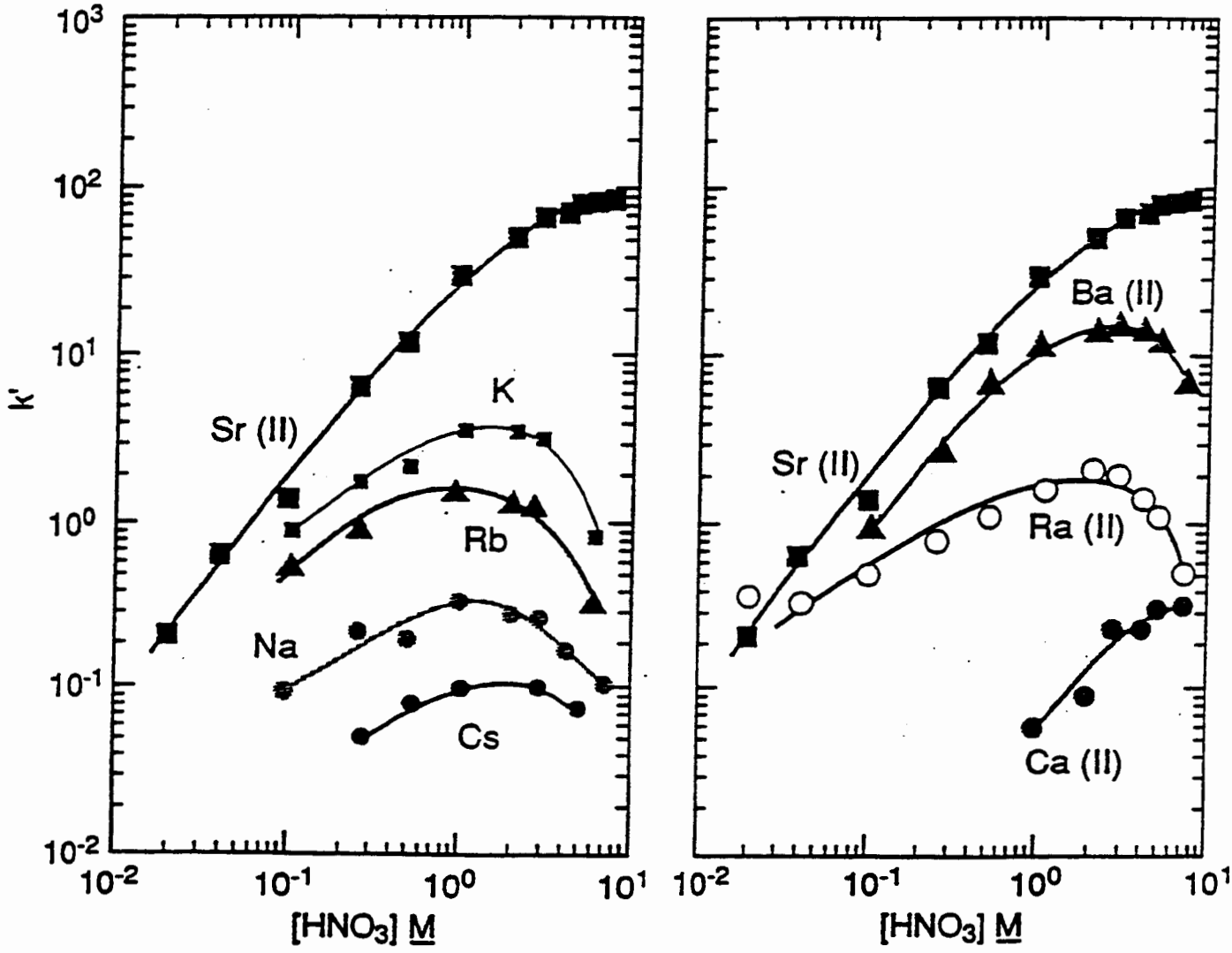
PACKED COLUMN	Particle Size	
	50-100 µm	80-160 µm
v_s, ml/ml of Bed[c]	0.146±0.004	0.152±0.004
Bed Density (g/ml)	0.33	0.35
v_m (Also F.C.V.), ml/ml of Bed[c]	0.71±0.01	0.69±0.01
v_s/v_m[c]	0.21±0.01	0.22±0.01
Capacity:		
Calc. mg Sr/ml of Bed	12.8	13.3
Exp. mg Sr/ml of Bed	10.6	—

[a] 1 M concentration of DtBuCH18C6 in 1-octanol is close to a saturated solution; therefore, the Sr retention from nitric acid is close to the maximum that can be achieved with this system.

[b] Picnometric density and flotation density values were 1.079 and 1.157 g/ml, respectively, using the 50-100 µm particle size resin. The calculated density is 1.094 g/ml, assuming 100% pore filling and no swelling.

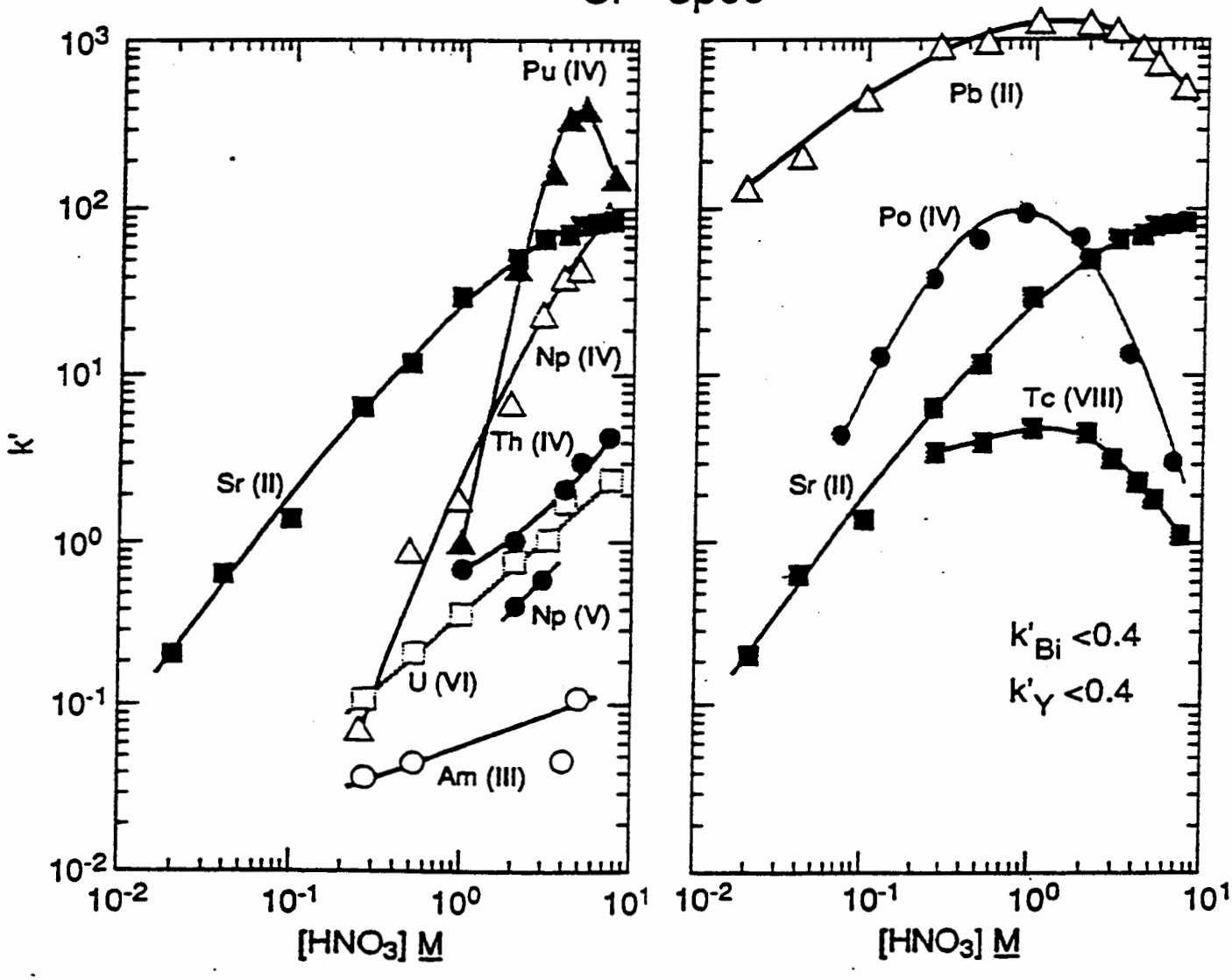
[c] Average of five measurements: error is one σ.

Acid dependency of k' for various ions at 23-25°C.
Sr • Spec

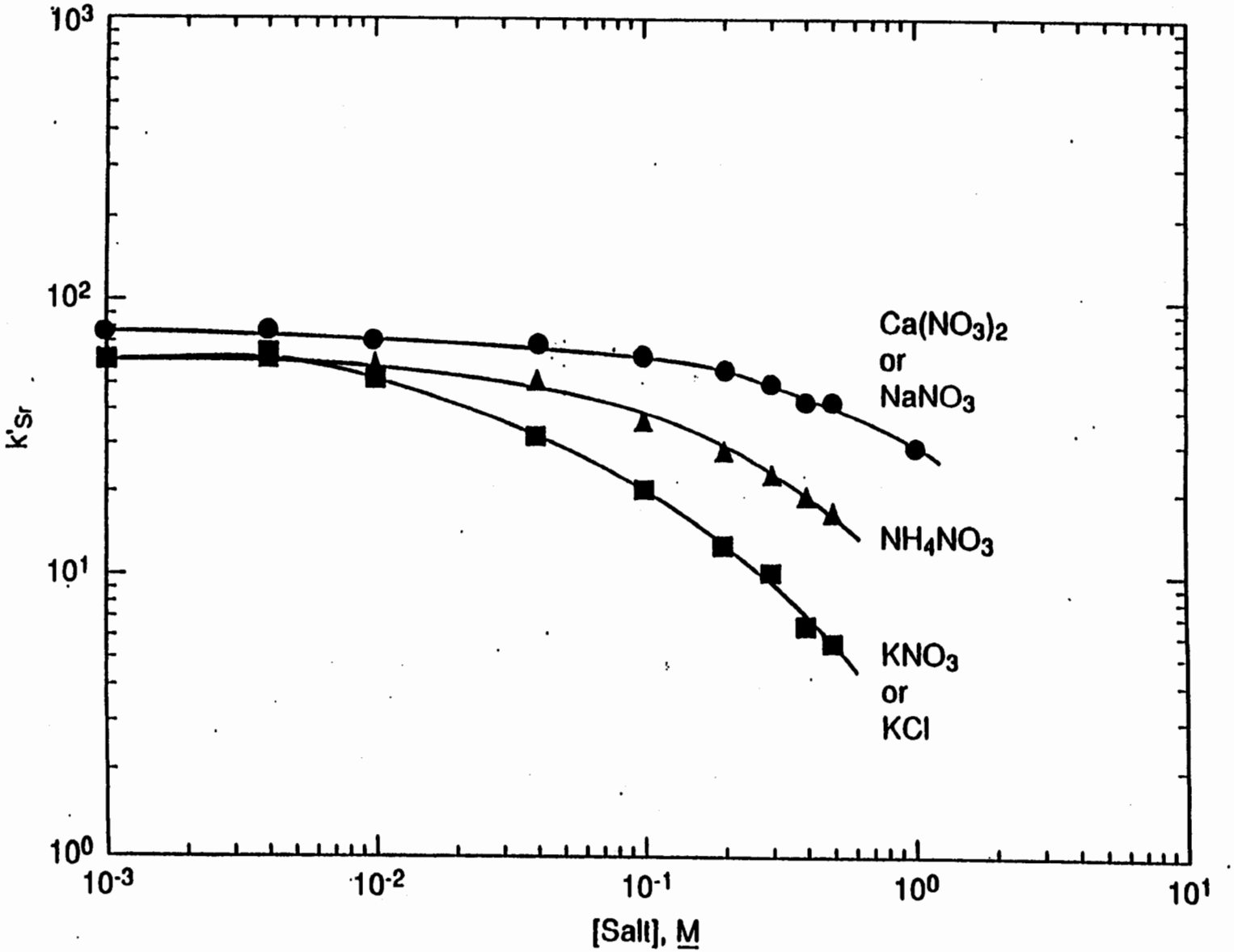


Acid dependency of k' for various ions at 23-25°C.

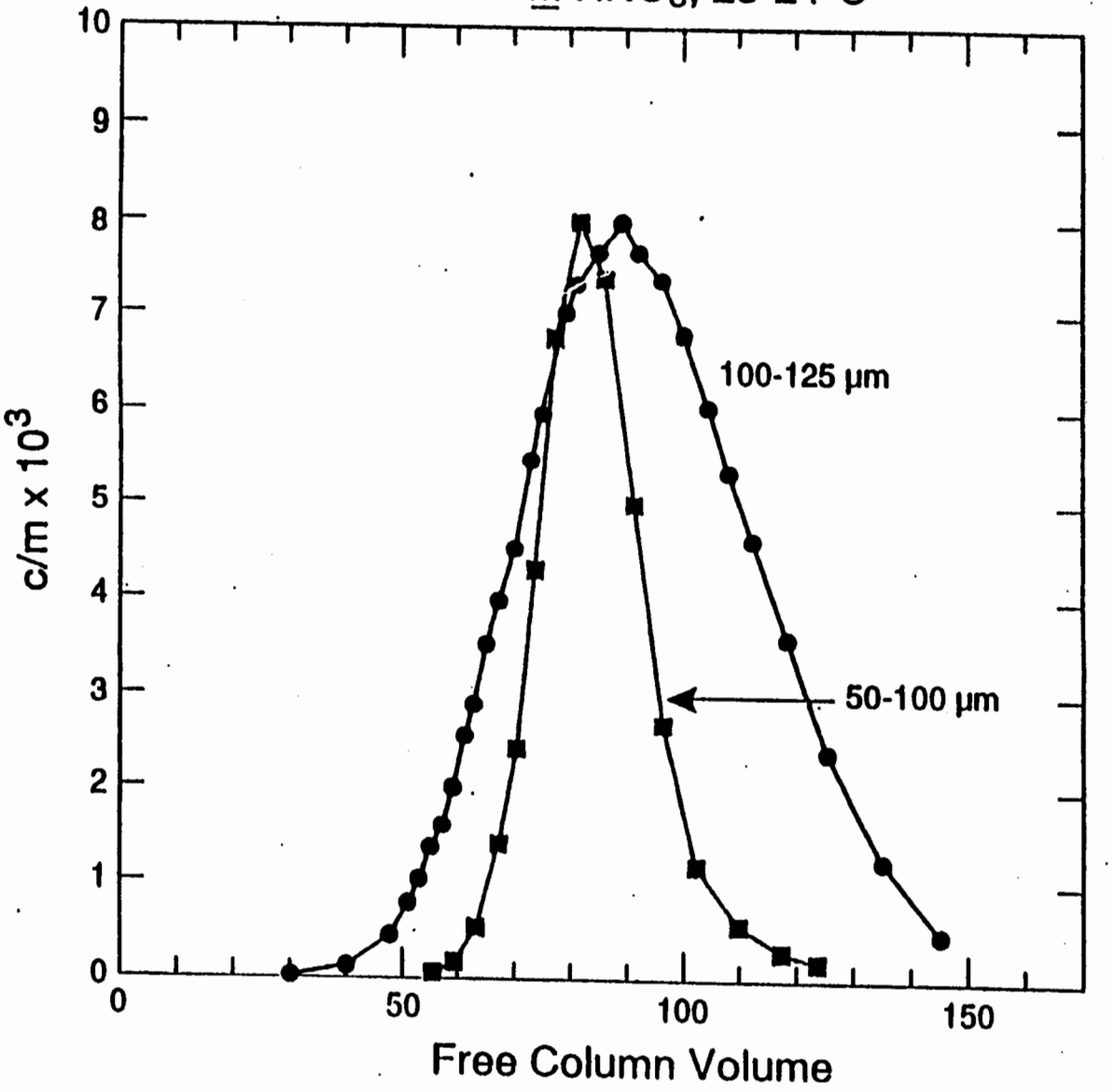
Sr • Spec



Effect of Matrix Constituents on Strontium Retention
Sr • Spec/3 M HNO_3



Comparison of Elution Curves for Sr^{2+}
for Two Particles of Sr • Spec
Elutrient 3.2 M HNO_3, 23-24°C



ELUTION BEHAVIOR OF COMMON ELEMENTS AND FISSION PRODUCTS ON THE STRONTIUM-SELECTIVE RESIN

	PERCENT OF ELEMENT FOUND IN F.C.V. #							
	3 M HNO_3 - 0.01 M Oxalic Acid						0.05 M HNO_3	
Element	1-5	6-10	11-15	16-20	21-25	26-30	31-40	F.C.V.
Li	100	—	—	—	—	—	—	
Na	100	—	—	—	—	—	—	
K	66	35	—	—	—	—	—	
Rb	100	—	—	—	—	—	—	
Cs	100	—	—	—	—	—	—	
Mg	100	—	—	—	—	—	—	
Ca	100	—	—	—	—	—	—	
Sr	—	—	—	—	—	—	99	
Ba	—	—	53	42	6	0.7	—	
Ra	99		1	—	—	—	—	
Al	100	—	—	—	—	—	—	
Cr	100	—	—	—	—	—	—	
Mn	100	—	—	—	—	—	—	
Fe	99	0.6	0.2	0.4	—	—	—	
Co	100	—	—	—	—	—	—	
Ni	100	—	—	—	—	—	—	
Cu	100	0.2	—	—	—	—	—	
Zn	100	0.2	—	—	—	—	—	
Y	100	0.1	—	—	—	—	—	
Zr	91	0.4	0.2	—	—	—	—	
Mo	84		16		—	—	—	
Tc	57	43	—	—	—	—	—	
Ru	100	—	—	—	—	—	—	
Rh	100	—	—	—	—	—	—	
Pd	100	—	—	—	—	—	—	
Ag	15	88	2	—	—	—	—	
Cd	100	0.1	—	—	—	—	—	
La-Eu	100	0.1	—	—	—	—	—	
Hg	5	5	19	40	19	10	5	

Column parameters: Particle size = 50-100 μm, Bed Volume = 1.0 cm^3, Bed height = 5.0 cm, and 1 F.C.V. = 0.60 mL.