National Physical Laboratory

Expertise in Separation Chemistry

UNIVERSITY OF BIRMINGHAM

Characterisation of Novel Extraction Chromatography Resins for Separation of ^{99}Tc, ^{135}Cs and ^{226}Ra

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2019 Eichrom Workshop/Users group Meeting, 28th October

eichrom

A BRAND OF EICHROM TECHNOLOGIES

Overview

Introduction

National Physical Laboratory
Nuclear Metrology Group
Collaboration with TrisKem

Characterisation

^{99}Tc, ^{135}Cs, ^{226}Ra

Conclusions

Methods Developed
Future Work

National Physical Laboratory (NPL)

1900 - Current

1 UK’s National Metrology Institute

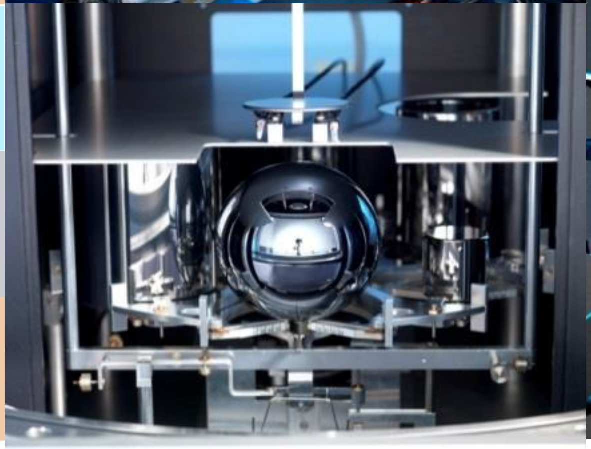
2 Operated and owned by Department for Business Energy and Industrial Strategy (BEIS)

3 National Standards and Measurement Science

Radioactivity measurement since 1913

800 Employees

200 Students



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Nuclear Metrology Group

TRISKEM Expertise in Separation Chemistry

NPL National Physical Laboratory

- First established for the standardisation of radium
- Completed in 1913 by Marie Curie and Ernest Rutherford
- Multiple primary standards of radioactivity
- Secondary calibrations of measurement equipment
- Evaluation of nuclear data
- Underpinning radioactive metrology in UK industry

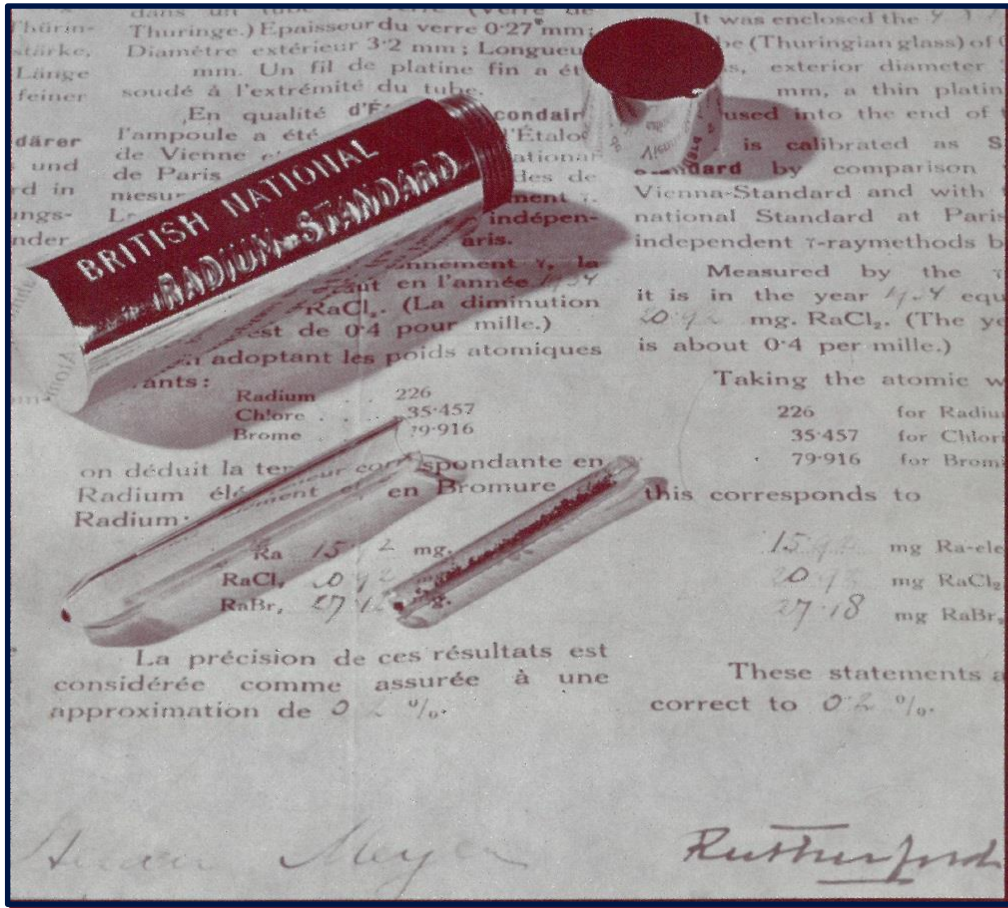
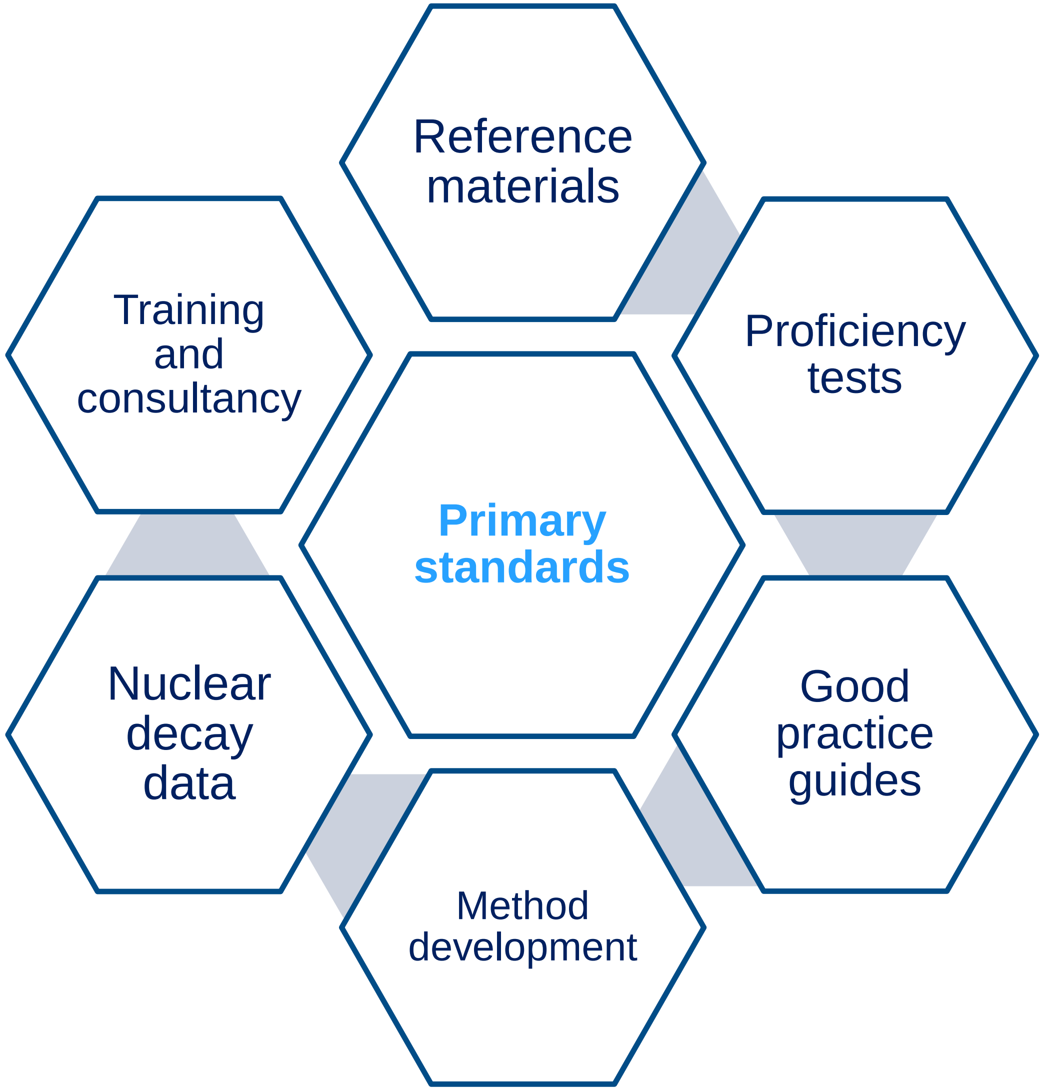


Image: “Radiation Science at the National Physical Laboratory, 1912-1955”, E. E. Smith

Nuclear Metrology Group

Mission:

To enable users of radioactivity to measure radioactivity at an accuracy that is fit-for-purpose and traceable to international standards.



NPL and TrisKem

“TrisKem is the leading European manufacturer and provider of highly specific resins for use in radiochemistry and metals separation.”

NPL has an ongoing collaboration with TrisKem to characterise their resins focusing on radionuclides which have no stable isotopes such as Tc (and Ra).

Resin Characterisation

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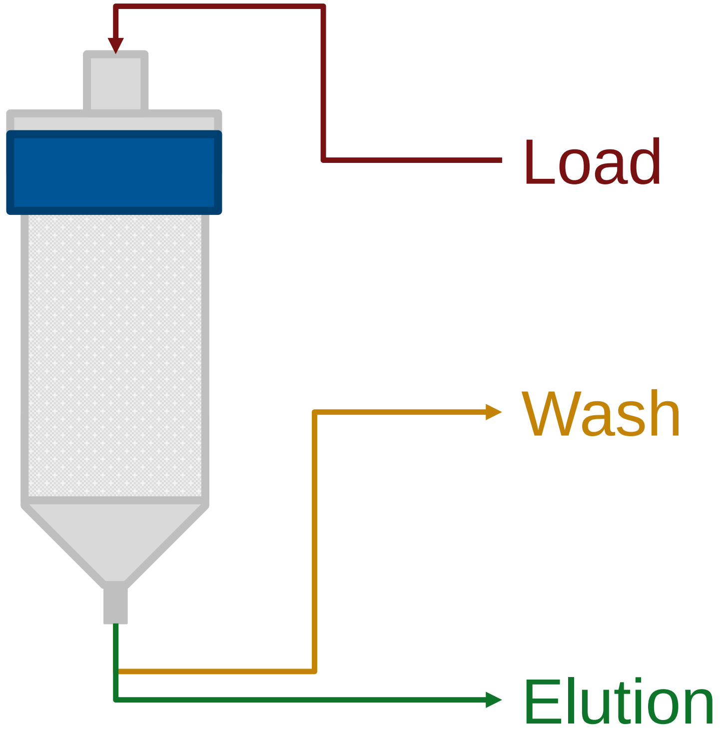
https://www.npl.co.uk/nuclear-metrology

Stages of Resin Characterisation

1. Determine distribution coefficients (K_d) for various elements of interest
2. Identify potential separation conditions for analyte
    1. Load
    2. Wash
    3. Elution
3. Perform elution study
4. Validate with real samples
5. Publication



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Separation of ^{99}Tc

Analysis Requirements
Current Methods
Developments

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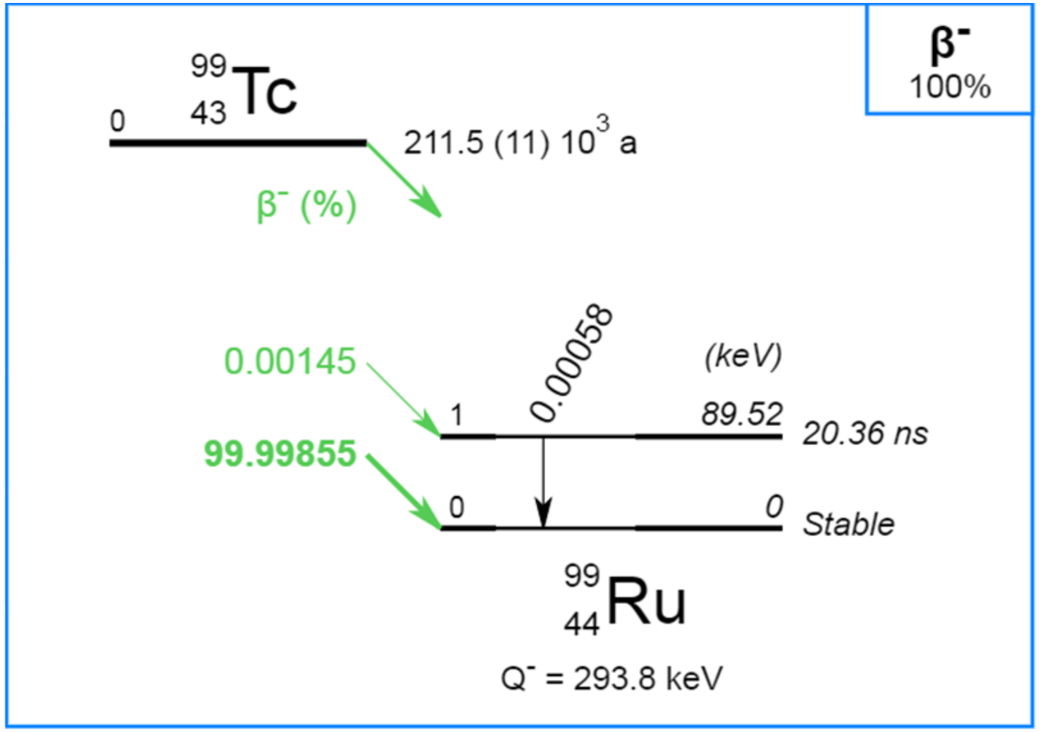
^{99}Tc: Analysis Requirements

- High yield (6.06 %) fission product
- Nuclear Decommissioning
- Environmental Monitoring
- Radiopharmacy and nuclear medicine (^{99m}Tc)

Mediso AnyScan SCP (SPECT-CT-PET) system in the NPL nuclear medicine imaging laboratory

Technetium-99 measurement

Reference	Matrix	Separation	Measurement	LOD
Kabai et al. 2013	Milk	TEVA	LSC	0.2 Bq/L
Temba et al. 2016	Filters	TEVA	LSC	3.15 Bq/L
Guerin et al. 2017	Water	TRU	LSC	5 Bq/L
Su et al. 2017	Cement	TEVA	ICP-MS	8.5 Bq/kg
Sahli et al. 2017	Sediment	TEVA	ICP-MS	0.03 Bq/kg



http://www.lnhb.fr/nuclear-data/module-lara/

Technetium separation with TEVA

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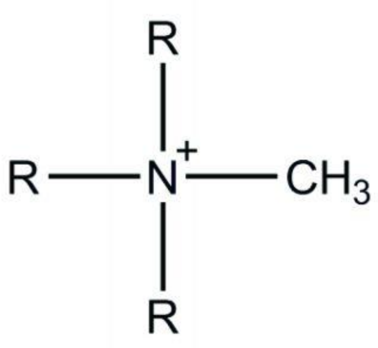
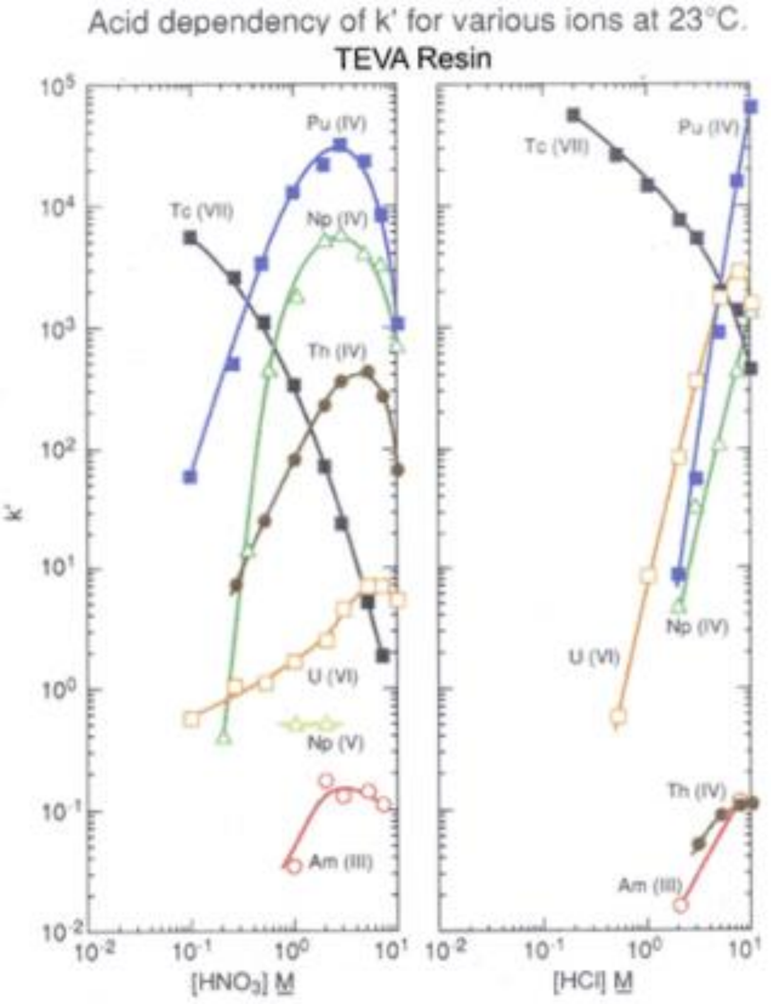
- Trialkyl-methylammonium nitrate/chloride



- Separation of **T**etra**V**alent **A**ctinides

e.g. Th(IV) and Pu (IV).
Load sample in 4 M HNO_3 and elute out Th with 6 M HCl

- Can be applied for Tc analysis as dilute (0.01-1 M) HCl and HNO_3 both retain Tc(VII)
- Tc may be eluted in 8 M HNO_3
- Well established for LSC and ICP-MS

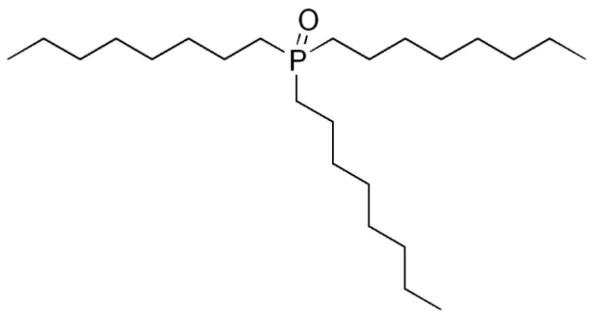


Horwitz et al., Horwitz P., Dietz M., Chiarizia R., Diamond H., Analytica Chimica Acta, 310, pp. 63-78 (1995); HP195.

New Resins

TK200

Based on <u>**T**</u>ri<u>**O**</u>ctyl<u>**P**</u>hosphine <u>**O**</u>xide (TOPO)



TK201

Based on a tertiary amine

Also contains a small amount of a long-chained alcohol (radical scavenger) to increase its radiolysis stability.

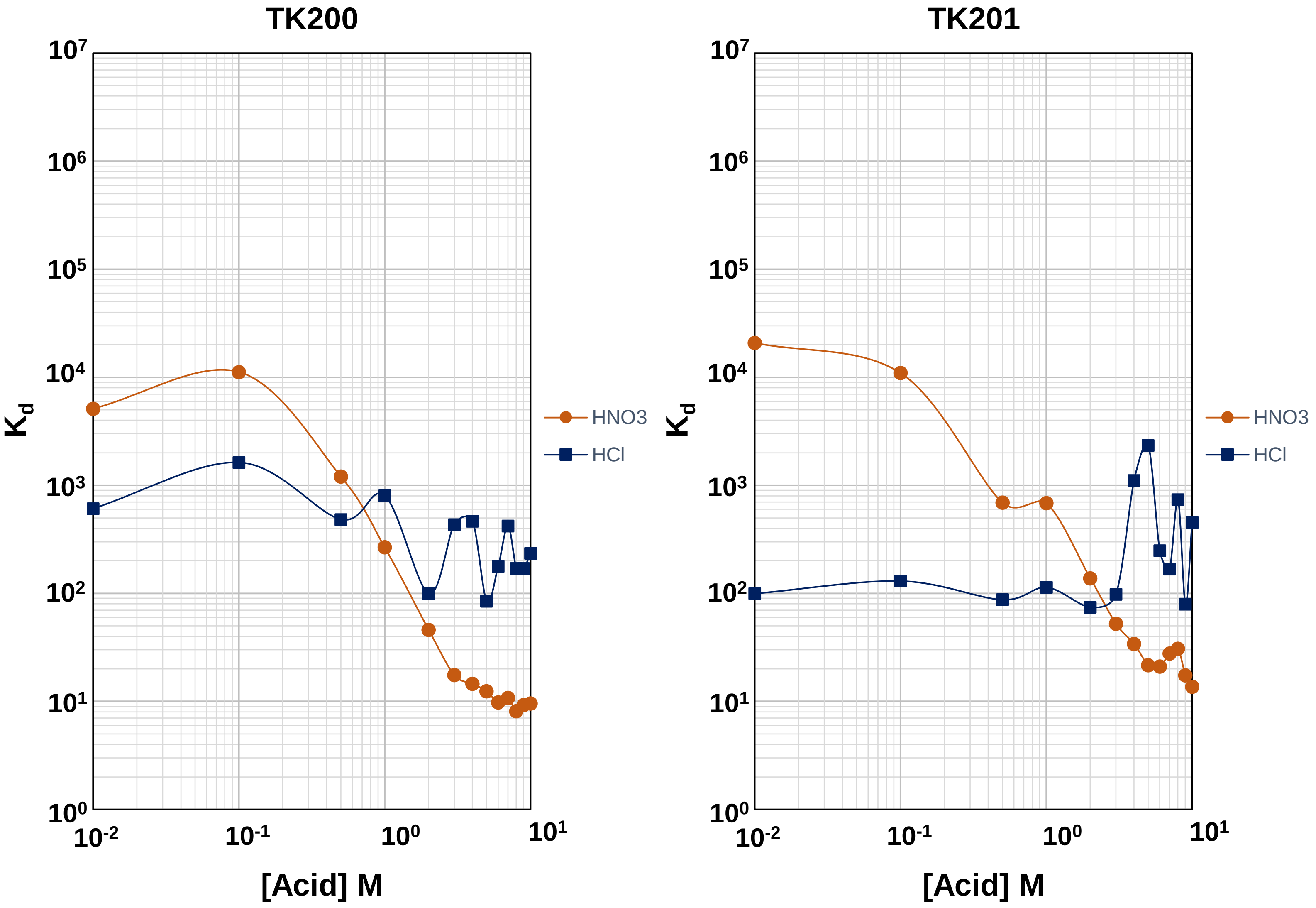
The TK201 Resin acts as a weaker ion pair binding agent than to the TEVA Resin

Potential for softer elution conditions

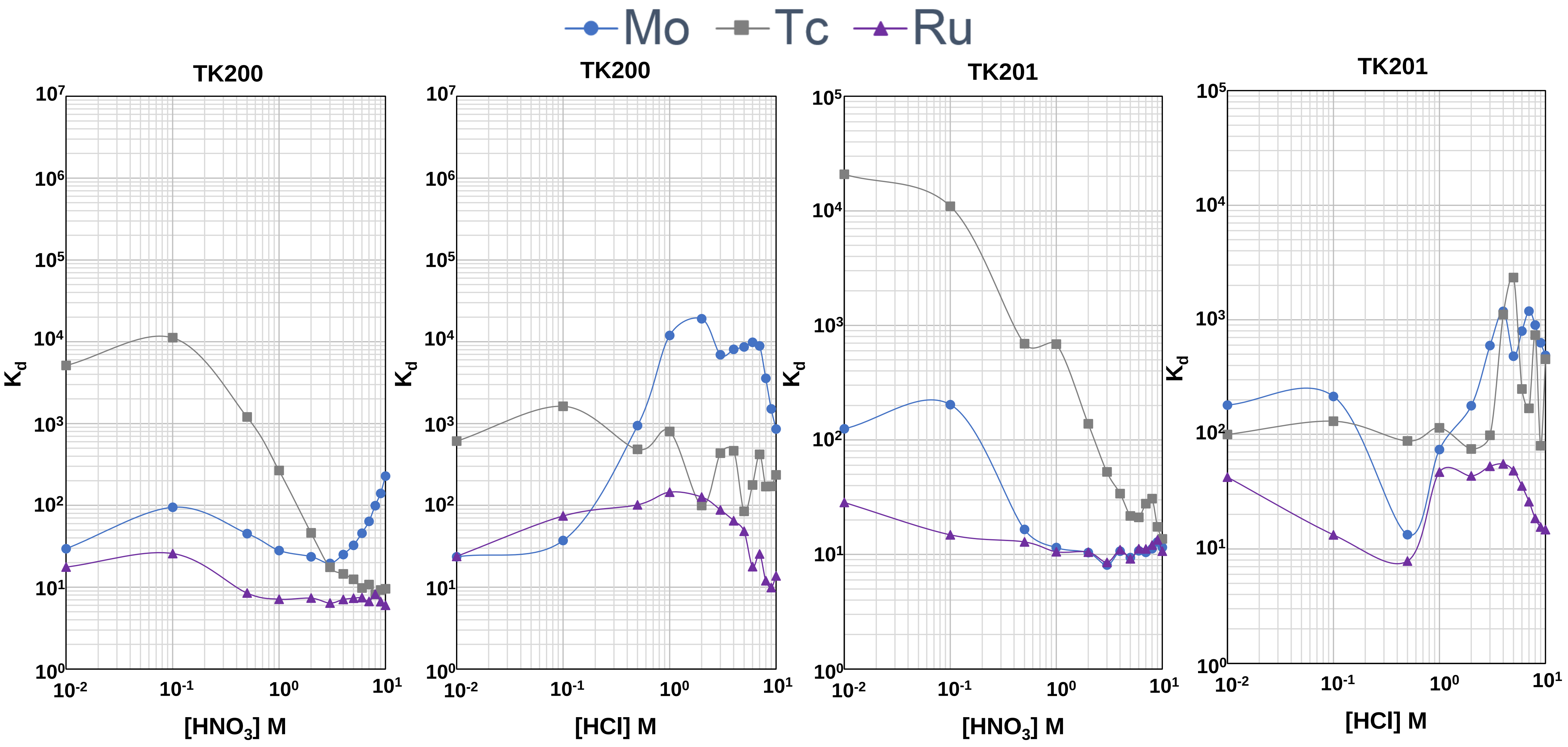
Tc on TK200 and TK201

- Load in dilute acid (0.01 – 1 M)
- Wash (0.01 – 1 M)
- Elute in concentrated acid (> 4 M)
- What about interferences?

^{98}Mo – Tailing
$^{98}Mo^{1}H$ – Polyatomic
^{99}Ru - Isobaric



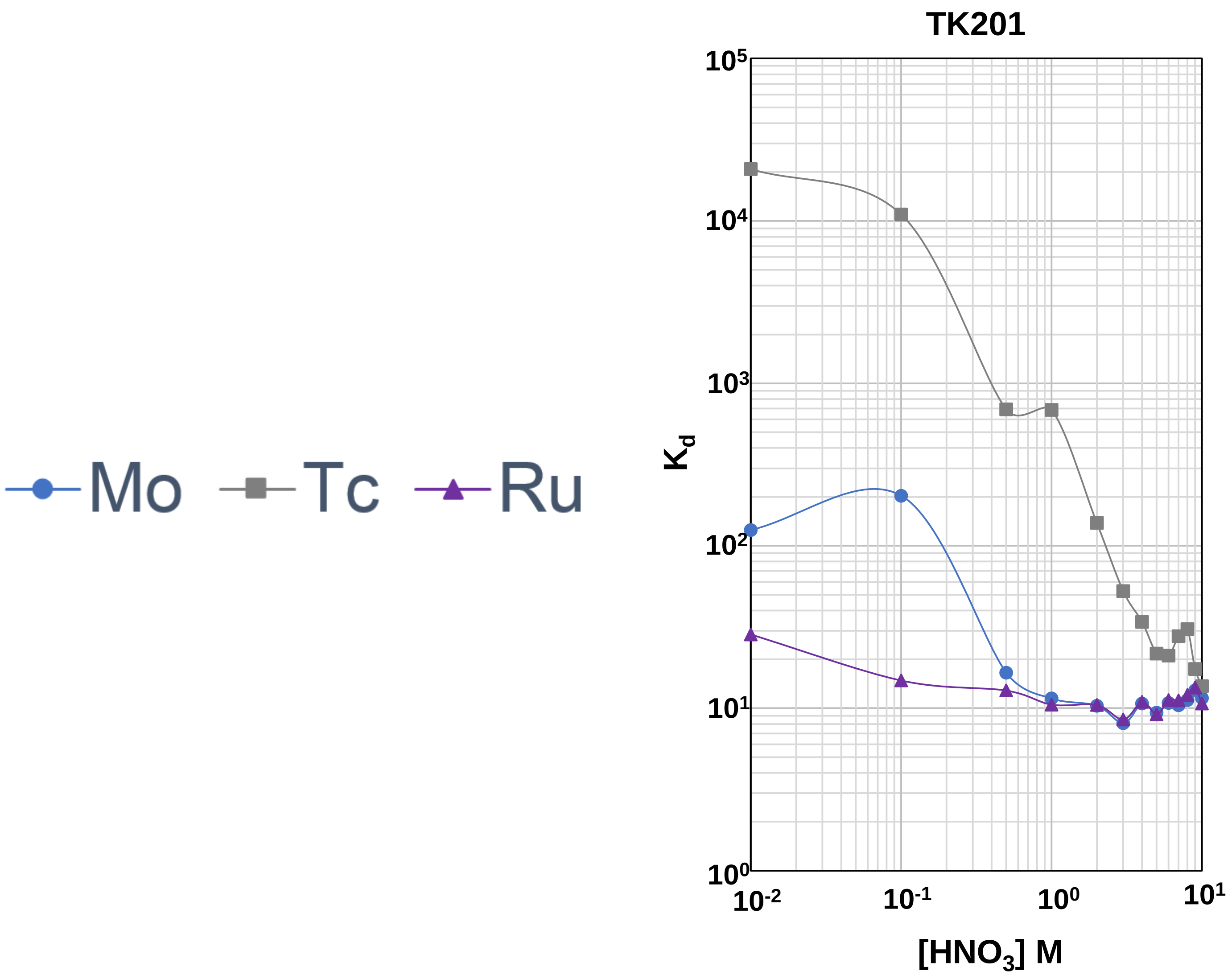
Interference Removal



Proposed Method

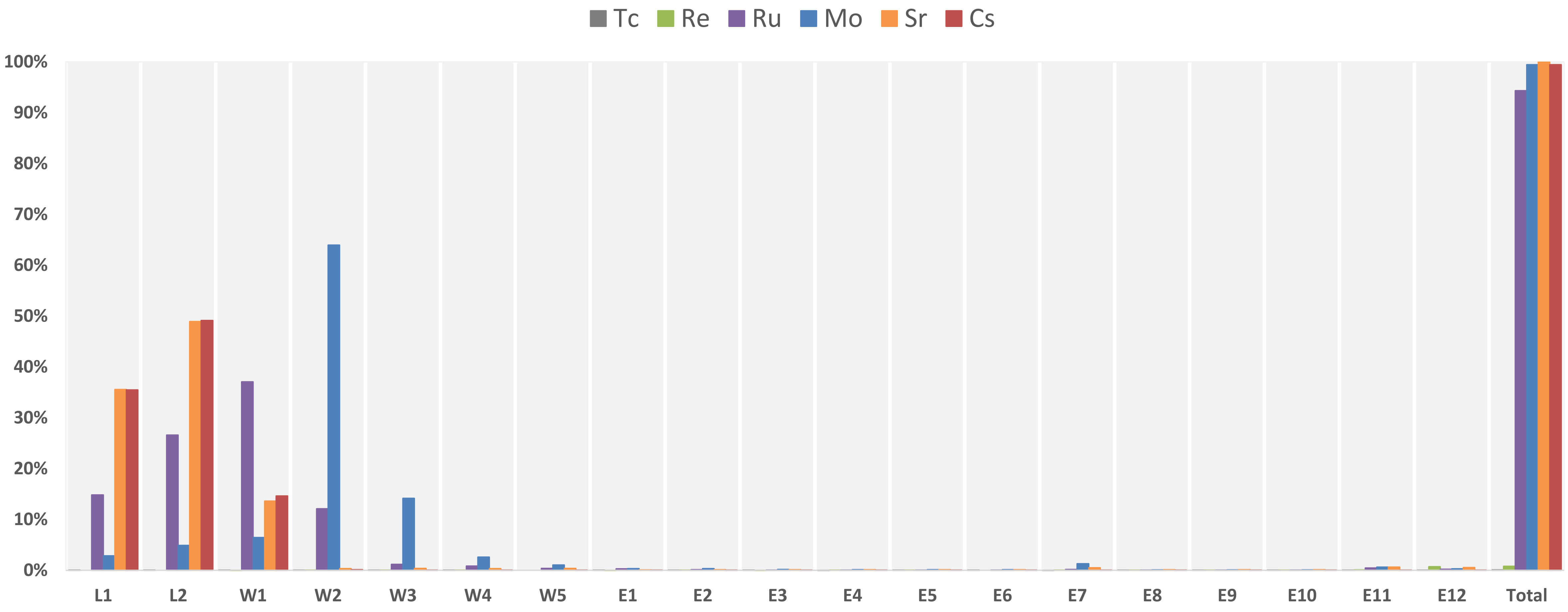
TK201

- Load in 10 mL 0.01 M HNO_3
- Wash with 5 mL 0.01 M HNO_3
- Wash with 20 mL 0.7 M HNO_3
- Elution? 1 M/ 2 M HNO_3 or NH_4OH



Elution Study (TK201) 1 M HNO_3

Load: 10 mL 0.01 M HNO_3
Wash: 5 mL 0.01 M HNO_3
Wash: 20 mL 0.7 M HNO_3
Elution: 20 mL 1 M HNO_3



Elution Study (TK201) 2 M HNO_3

Load: 10 mL 0.01 M HNO_3
Wash: 5 mL 0.01 M HNO_3
Wash: 20 mL 0.7 M HNO_3
Elution: 20 mL 2 M HNO_3

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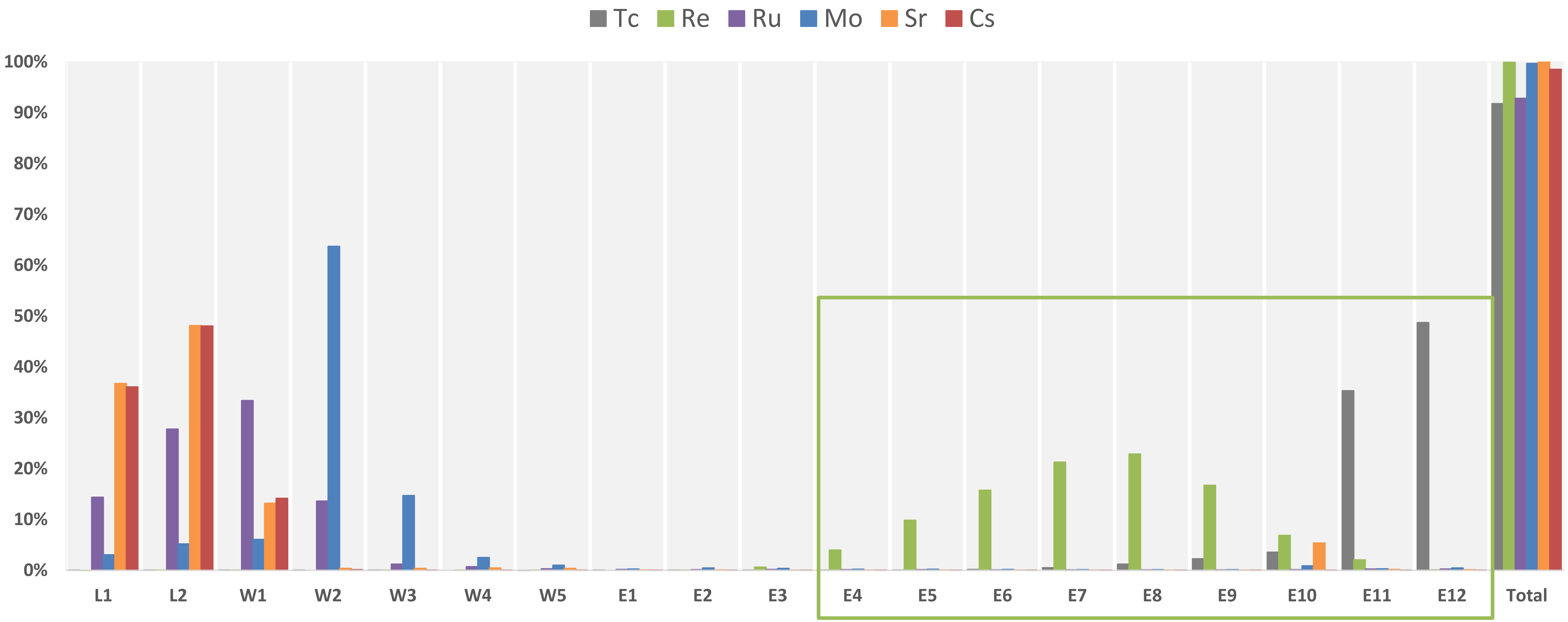

Selectivity is so high that it is important to use analyte instead of chemical analogues

Elution Study (TK201) 0.5 M NH_4OH

Load: 10 mL 0.01 M HNO_3
Wash: 10 mL 0.7 M HNO_3
Wash: 5 mL 0.01 M HNO_3
Elution: 20 mL 0.5 M NH_4OH

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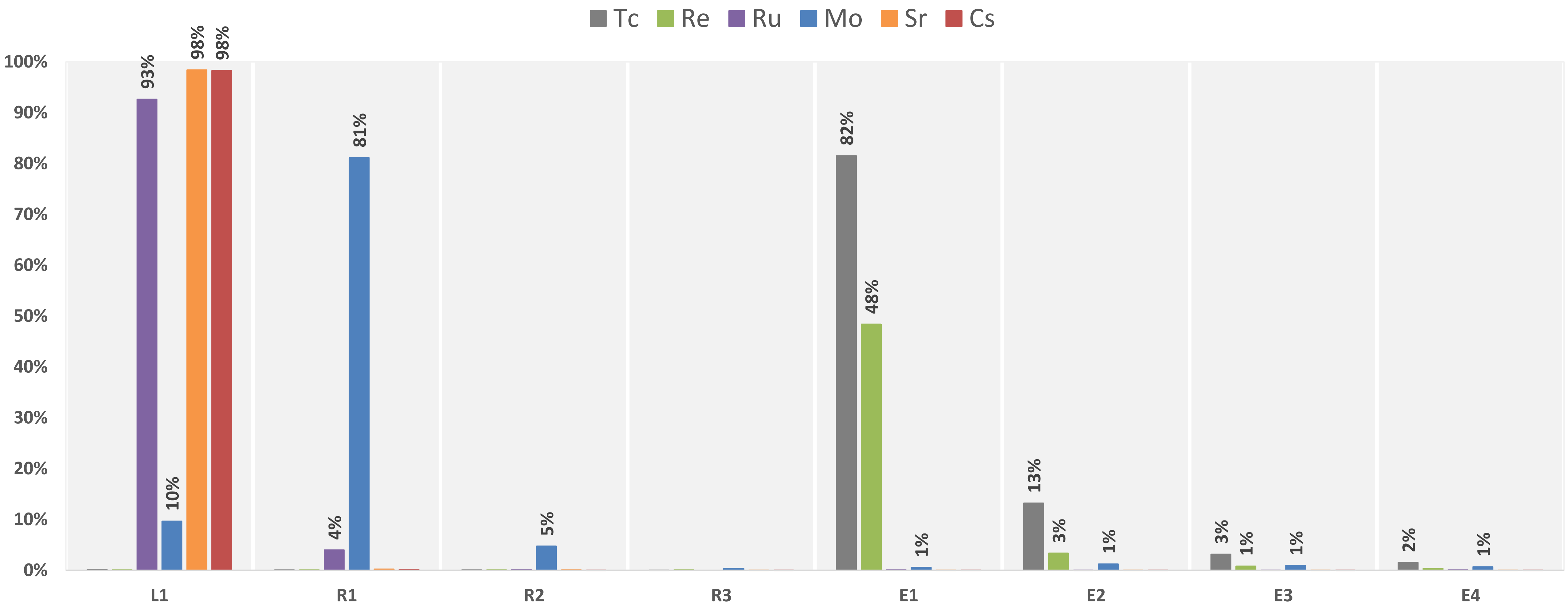
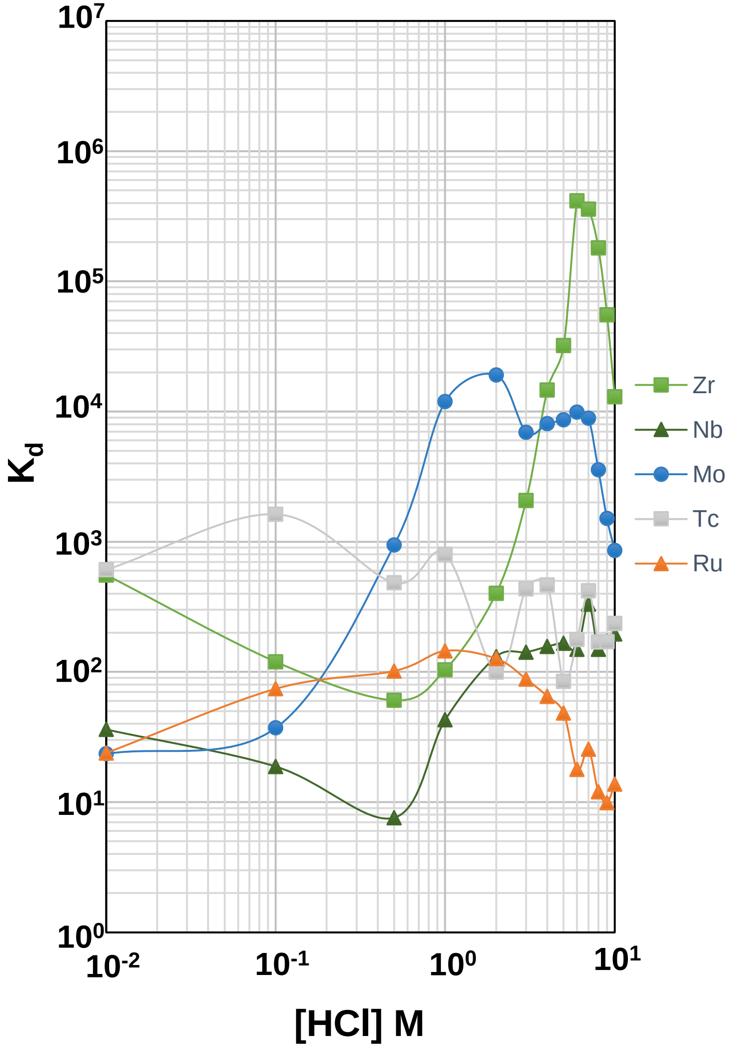
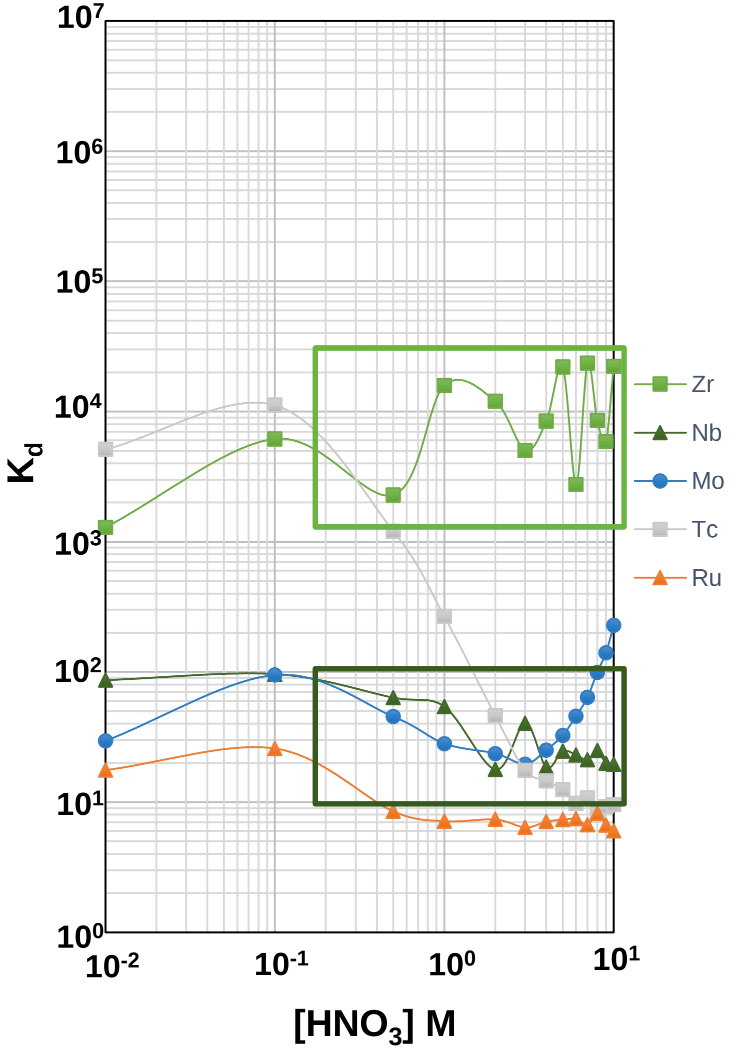


TK200 Transition Metals

Zr/Nb





TK200 Lanthanides and Actinides (+ Bi and Pb)

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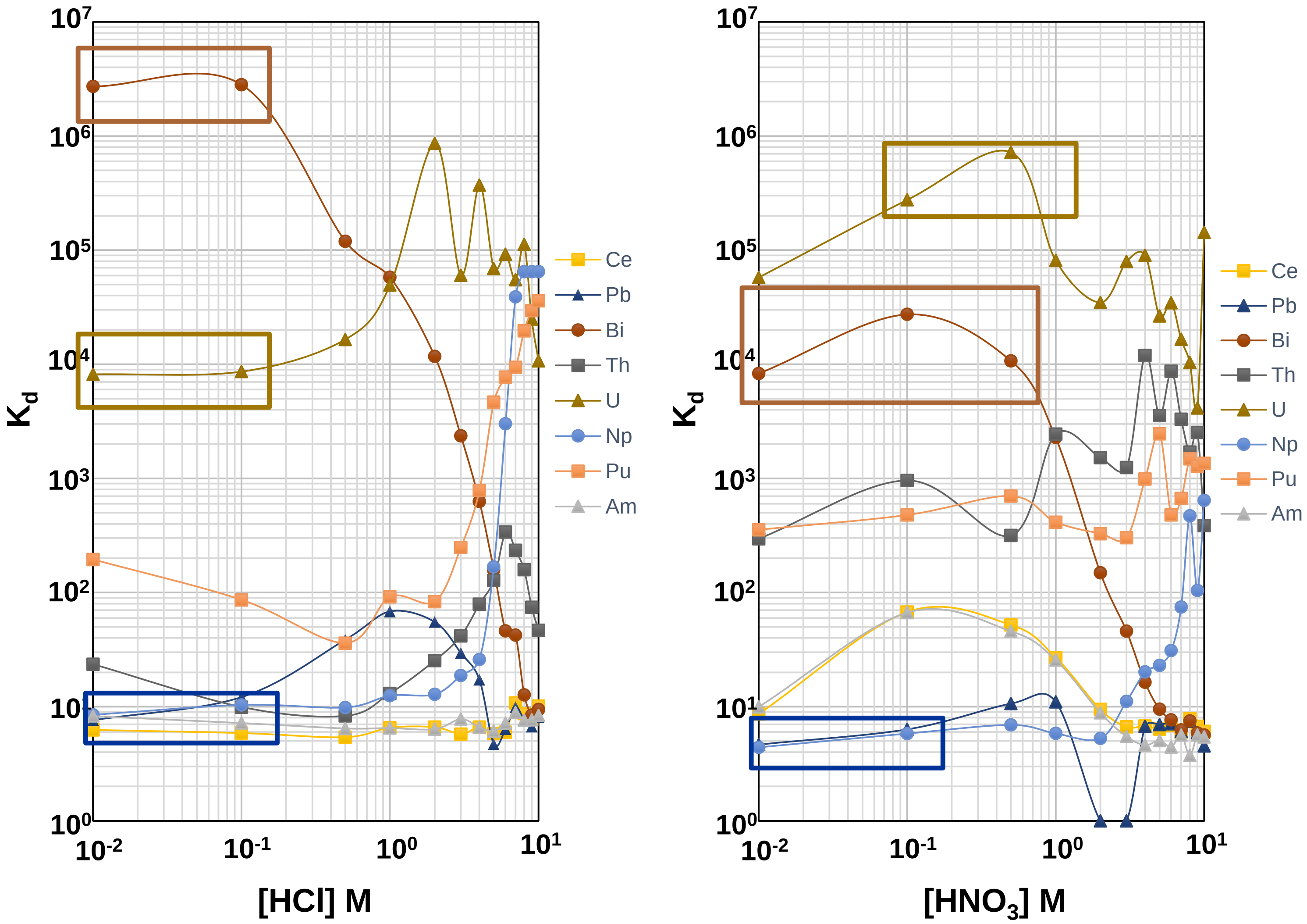
Bi/Pb

U/Np/Am



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TK201 Lanthanides and Actinides (+ Bi and Pb)

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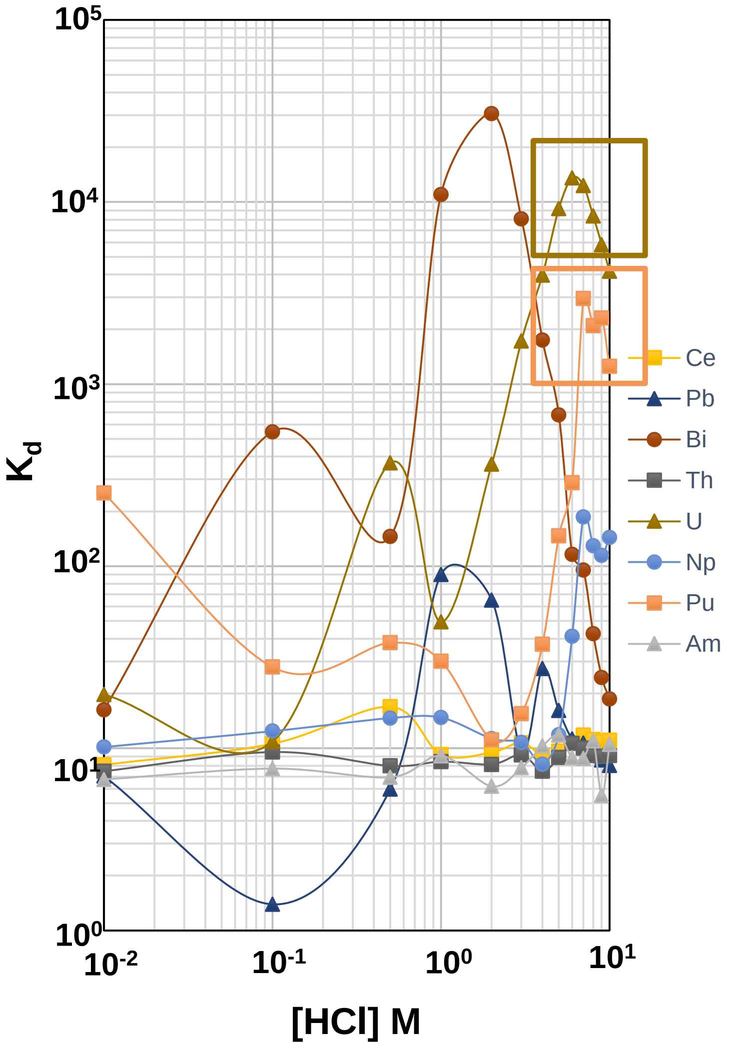
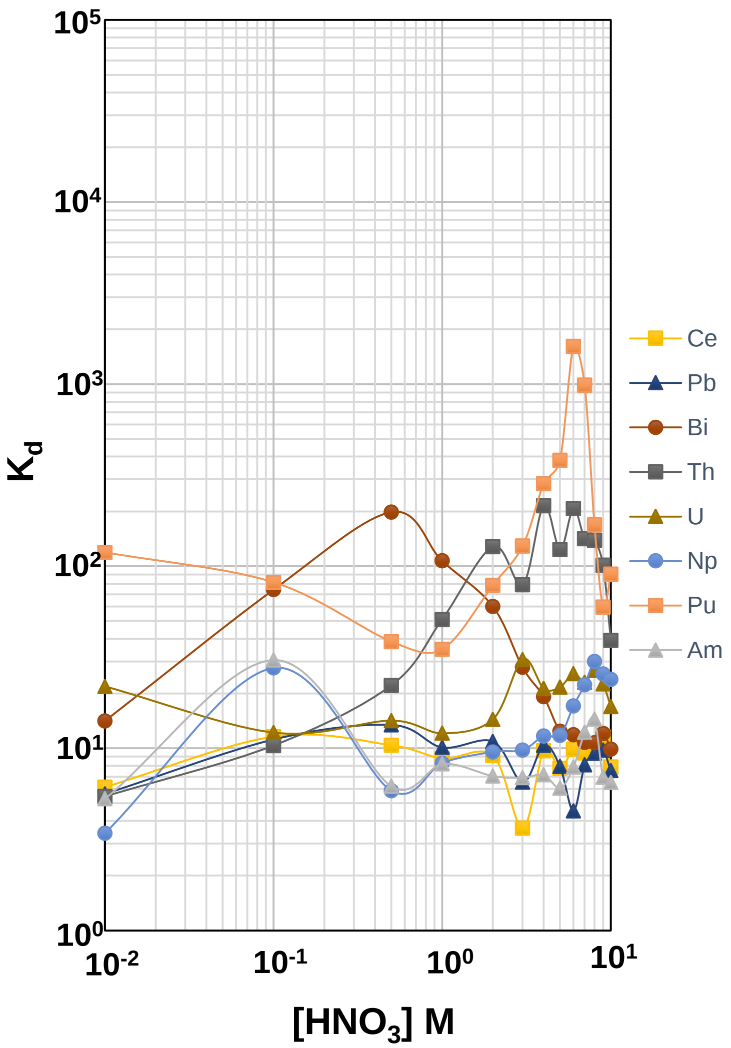
U/Pu from Th/Pb/Am





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Separation of ^{135}Cs

Analysis Requirements
Current Methods
Developments

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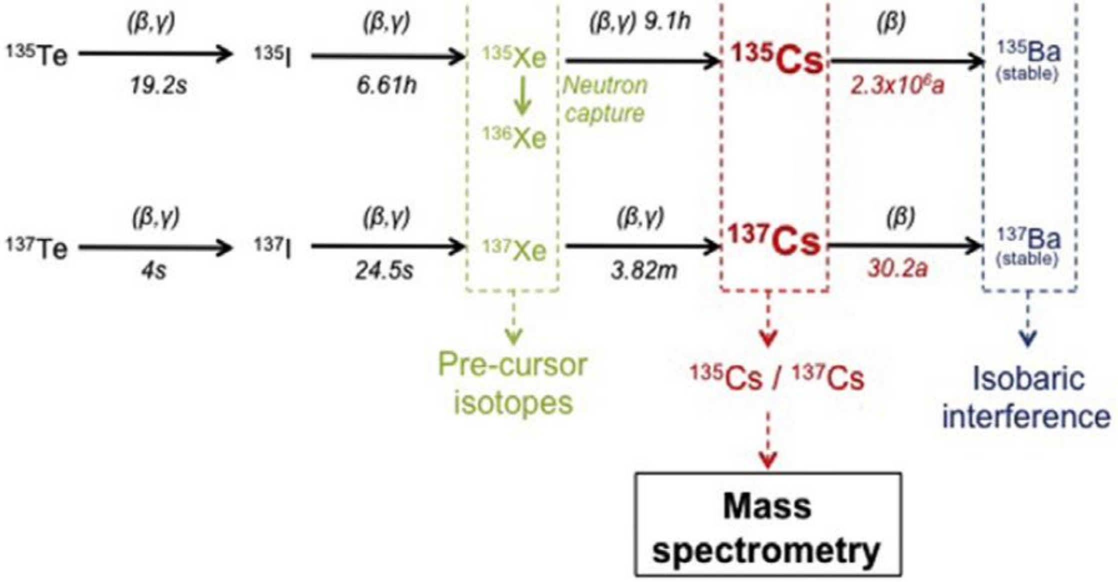
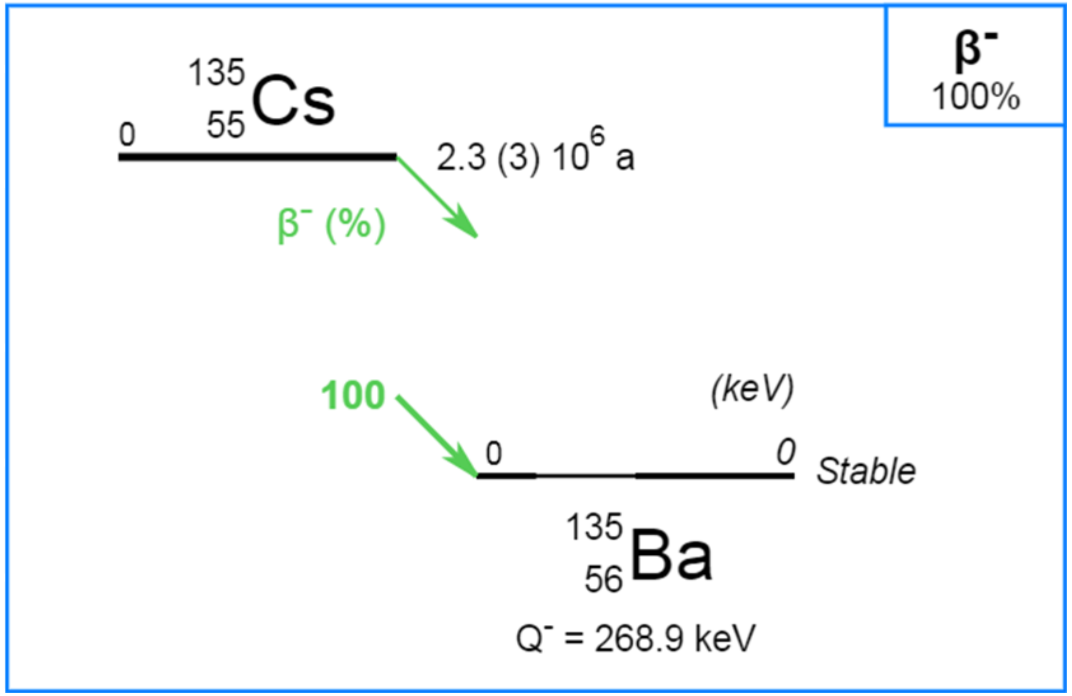
Analysis Requirements

- High yield (6.58 %) fission product
- Nuclear Decommissioning
- Environmental Monitoring (Routine and Radiological Incident
- Long-term Waste Monitoring e.g. Geological Disposal
- Nuclear Forensics ($^{135}Cs/^{137}Cs$ ratios)



Caesium-135 Measurement

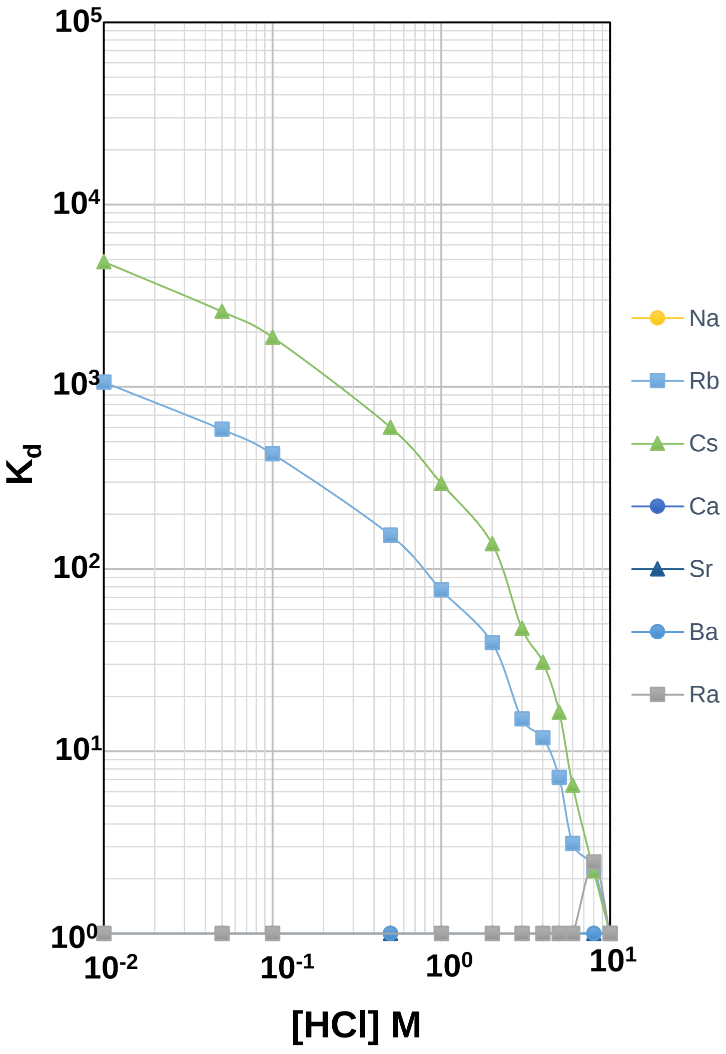
Reference	Matrix	Separation	Measurement	LOD
Taylor et al., 2008	Soil and Sediment	AMP-PAN	DRC-ICPQMS	0.2 ng/L
Liezers et al., 2009	Filters	Online cation exchange (CG3)	ICP-QMS	0.9 pg/L
Delmore et al., 2011	Reactor Effluents	AMP-PAN/ AG1-X8	TIMS	-
Zeng et al., 2014	Environmental Samples	AMP/ AGMP-1M/ AG50W-X8	ICP-MS/MS	-
Russell et al., 2014	Standard	AMP/ AG50W-X8/ Sr resin	ICP-SFMS	0.05 ng/L

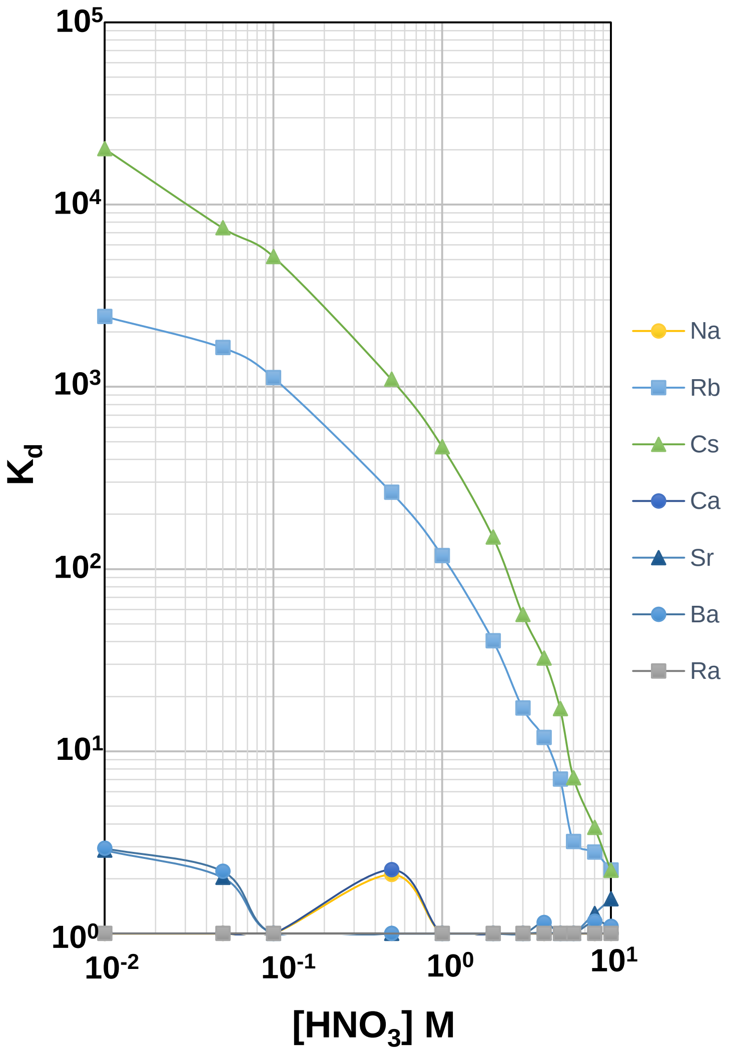


http://www.lnhb.fr/nuclear-data/module-lara/

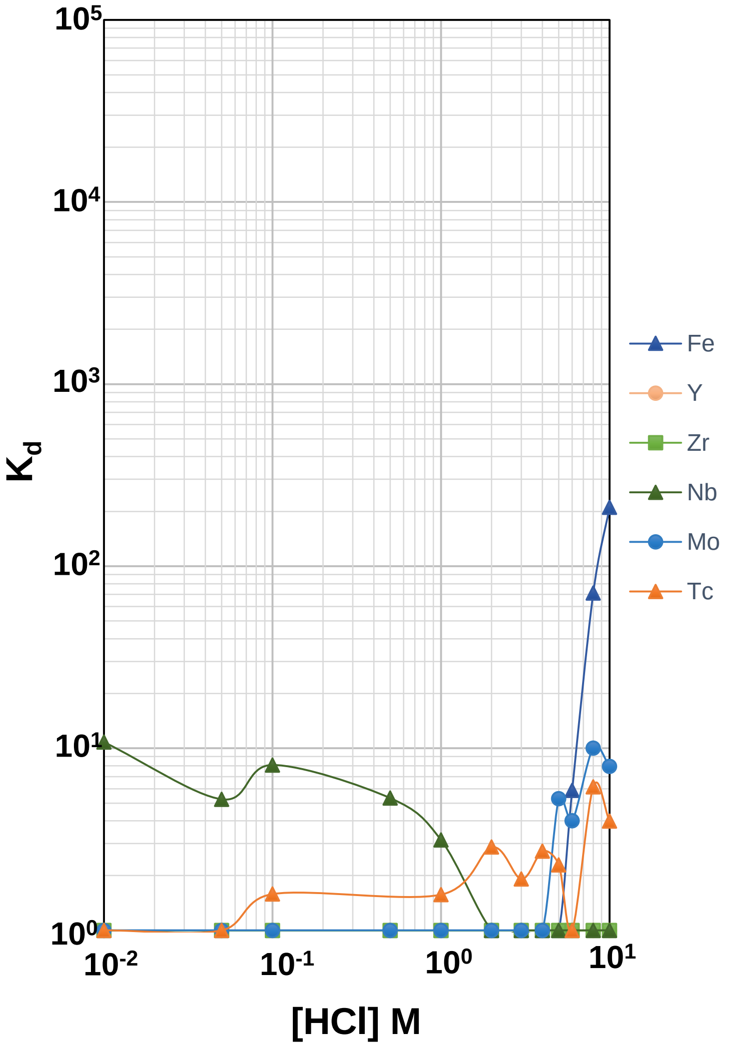
TK300 Group 1 and 2

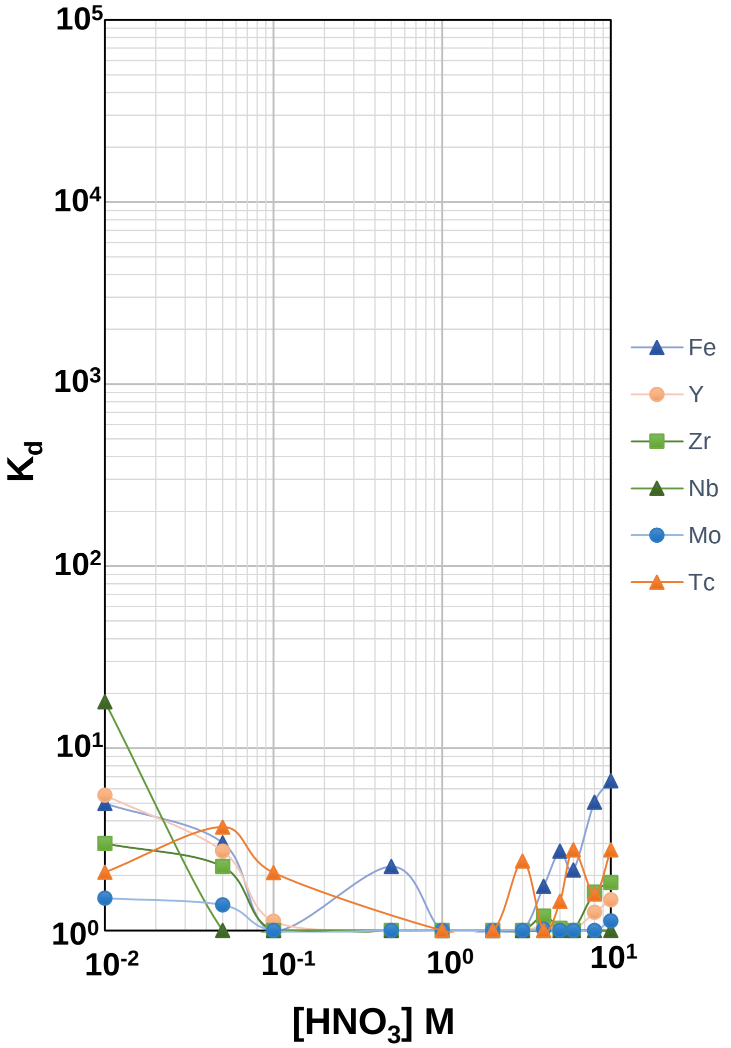
- Separation from Ba
- ICP-MS isobaric interference
- Low retention of other elements





TK300 Transition Metals





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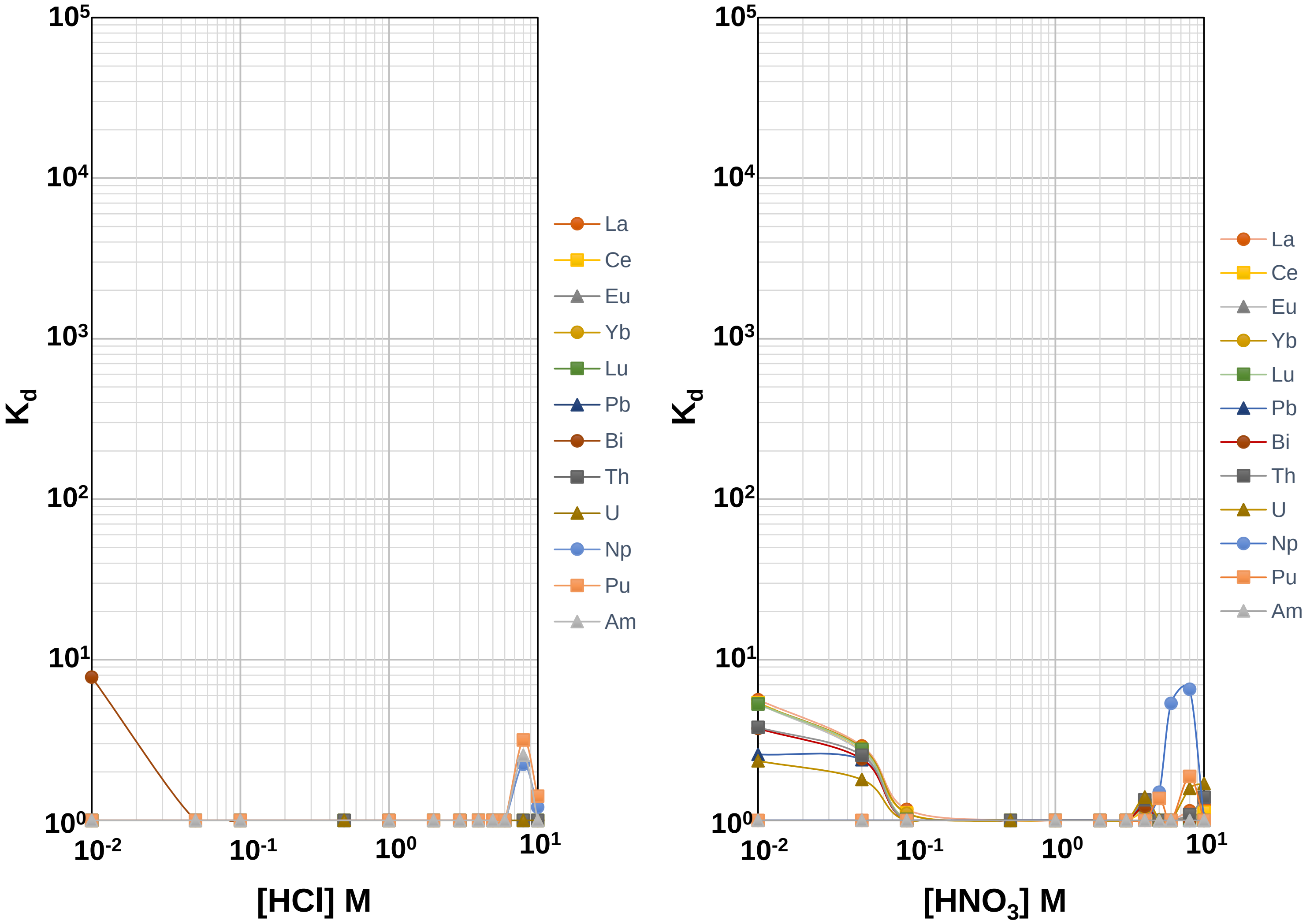
TK300 Lanthanides and Actinides (+ Bi and Pb)



Elution Study (TK300)

Load:	10 mL	0.01 M HNO_3
Wash:	15 mL	0.1 M HNO_3
Wash:	5 mL	1 M HNO_3
Elution:	20 mL	8 M HNO_3

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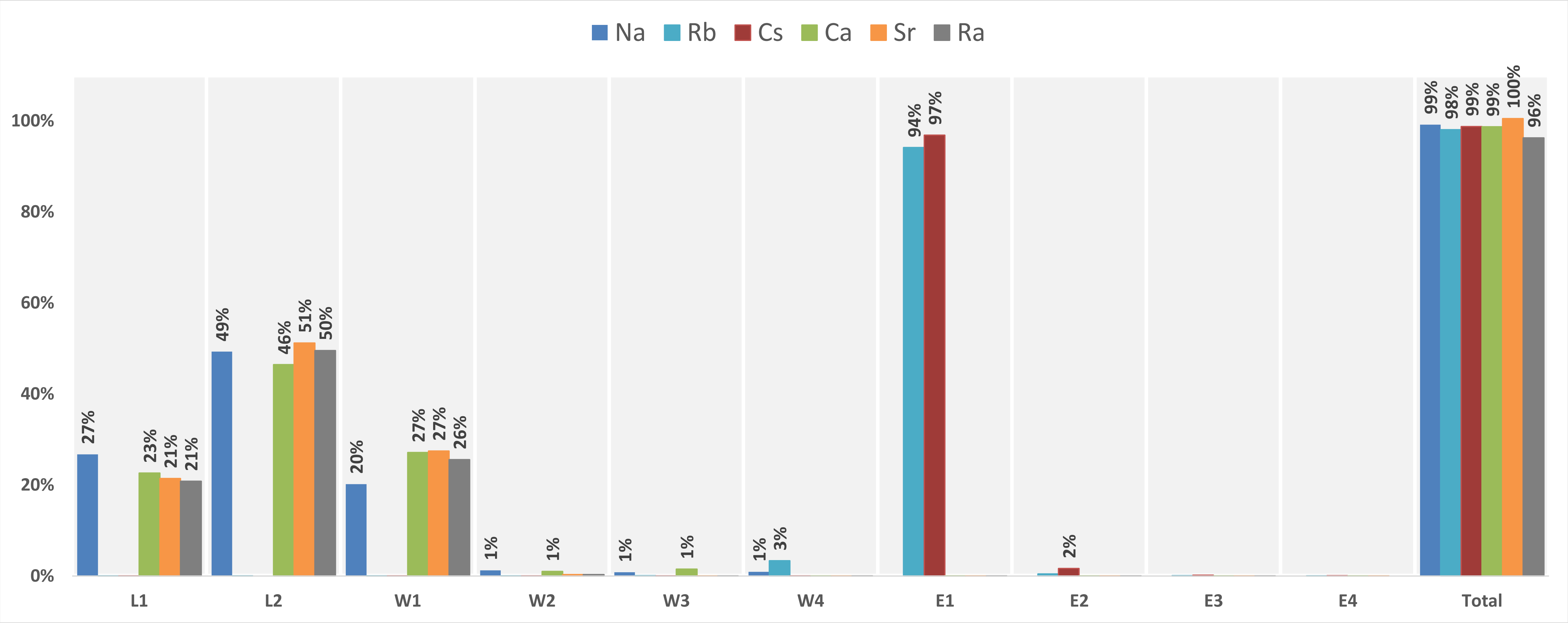

Separation of ^{226}Ra

Analysis Requirements
Current Methods
Developments

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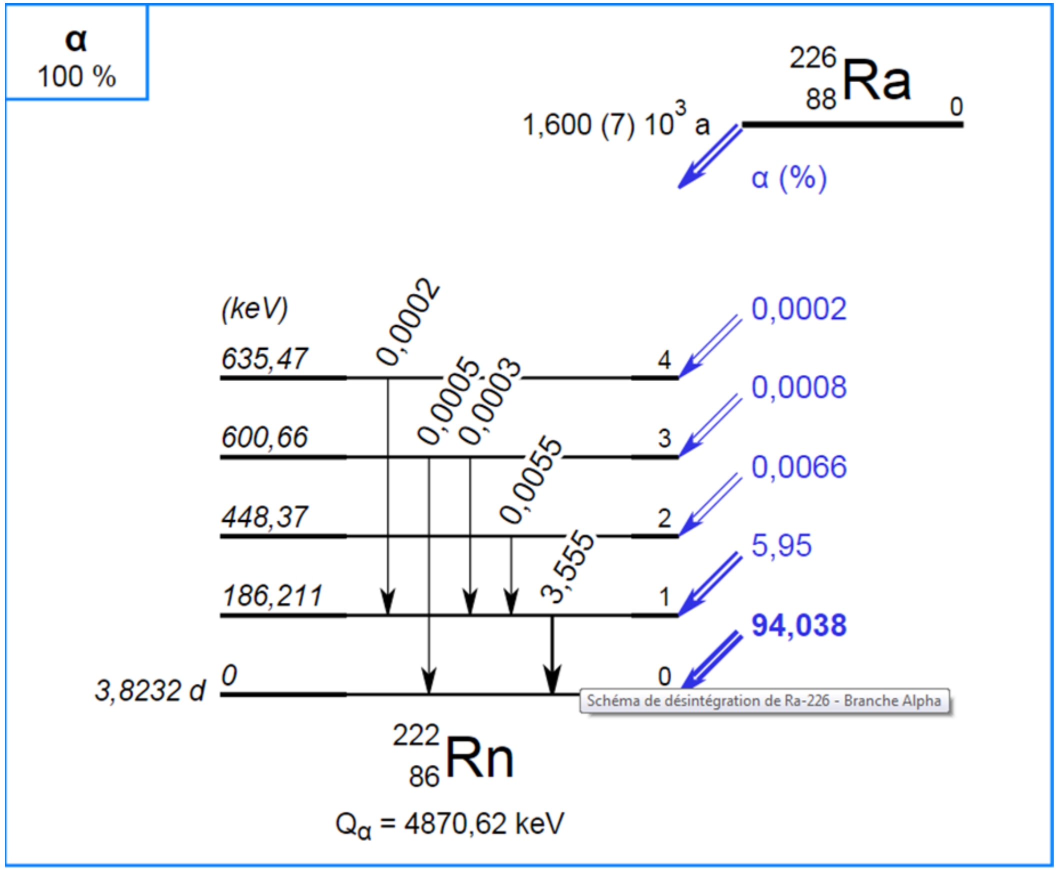
Analysis Requirements (^{226}Ra)

- Naturally Occurring (^{238}U decay series)
- Highly mobile in the environment
- Routine Environmental Monitoring (Natural Waters)
- Waste Characterisation (NORM industries)

Radium-226 Measurement

	Measurement	MDA (mBq L^{-1})	Time of Analysis	Ref
$BaSO_4$ co-precipitation	Gamma spectrometry	-	-	Diab and Abdellah, 2013
Purolite resin	Gamma spectrometry	20	1d	El-Shrakawy et al., 2013
$BaSO_4$ precipitation	Gamma spectrometry	<0.74	1 d	Maxwell et al., 2016
MnO_2 acrylic fibres Burned 600℃	Gamma spectrometry	-	-	Porras et al., 2017
Ln Resin DOWEX- 50WX8	Alpha spectrometry	-	3 d	Bergamini et al., 2016
Ion Exchange, $BaSO_4$ micro co-precipitation	Alpha spectrometry	0.08	20 h	Hu et al., 2017
AG® 50W-X8 $BaSO_4$ micro co-precipitation	Alpha spectrometry	13	3 d	Szabo et al., 2012
MnO_2 resin/ Sr resin	ICP-MS	-	2 d	Amr et al., 2012
AG® 50W-X8, Sr-resin	ICP-MS	0.73	1 d (5 min measurement)	Lagacé et al., 2017
AG® 50W-X8, Sr resin	ICP-MS (Gamma spectrometry)	18,500 ± 15%	< 1 d	Zhang et al., 2015
AG® 50-X12	ICP-QQQ-MS	$< 4 \times 10^{-5}$	1 d	Megard, 2017
AG® 1-X8, Sr resin	MC-ICP-MS	$< 4 \times 10^{-6}$	-	Bourquin et al., 2011
AG® 50W-X8, Sr resin	MC-ICP-MS	4×10^{-9}	2 d	Hsieh et al., 2011
MnO_2 precipitation, Sr resin	MC-ICP-MS	0.01 (^{226}Ra) 3 (^{228}Ra)	2 d	Sharabi et al., 2010
AG® 50W-X8	ICP- SFMS	4×10^{-6}	1 d	Copia et al., 2015
AG® 50W-X8 and Sr resin/ Sr and Ln resin	ICP-SFMS (Gamma spectrometry)	7	8 h	Lariviere et al., 2005



http://www.lnhb.fr/nuclear-data/module-lara/

New Resins

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TK100

Contains crown ether (18-crown-6) and HDEHP

Increased selectivity for Sr in dilute acids

Method already developed for measurement of Ra using TK100

TK101

Crown ether ionic liquid based extraction resin

Developed for the separation of Pb

Easier to elute Pb than Pb/Sr resin

J Radioanal Nucl Chem
DOI 10.1007/s10967-017-5203-4

CrossMark

The behaviour of ^{226}Ra in high-volume environmental water samples on TK100 resin

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ELSEVIER

Development of a method for rapid analysis of Ra-226 in groundwater and discharge water samples by ICP-QQQ-MS

CrossMark

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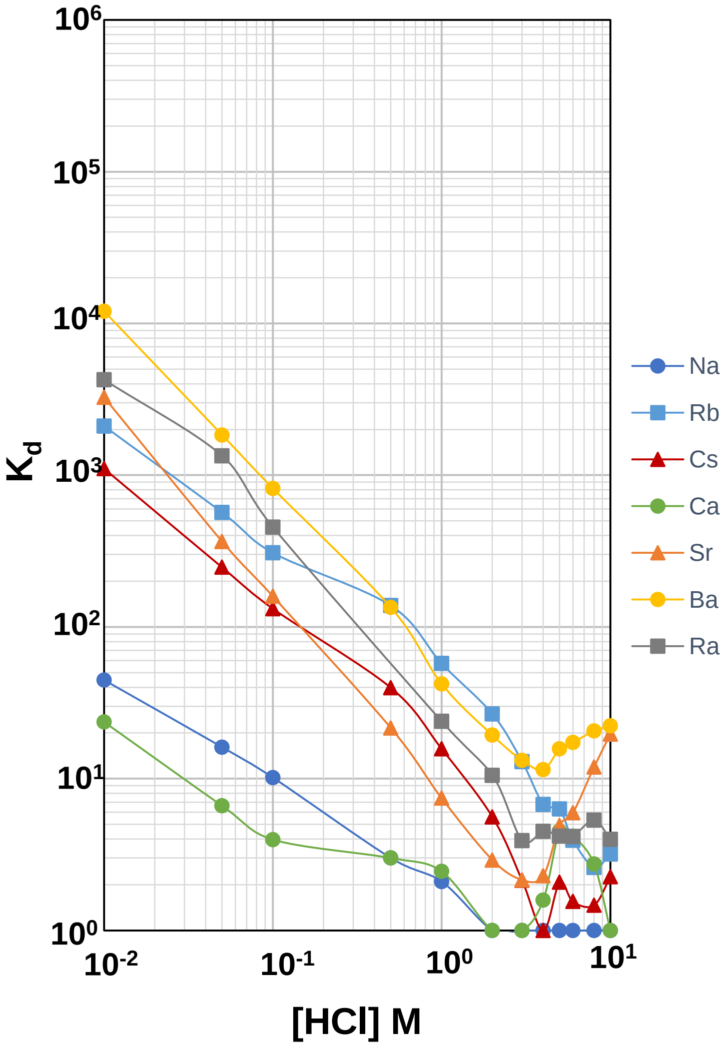
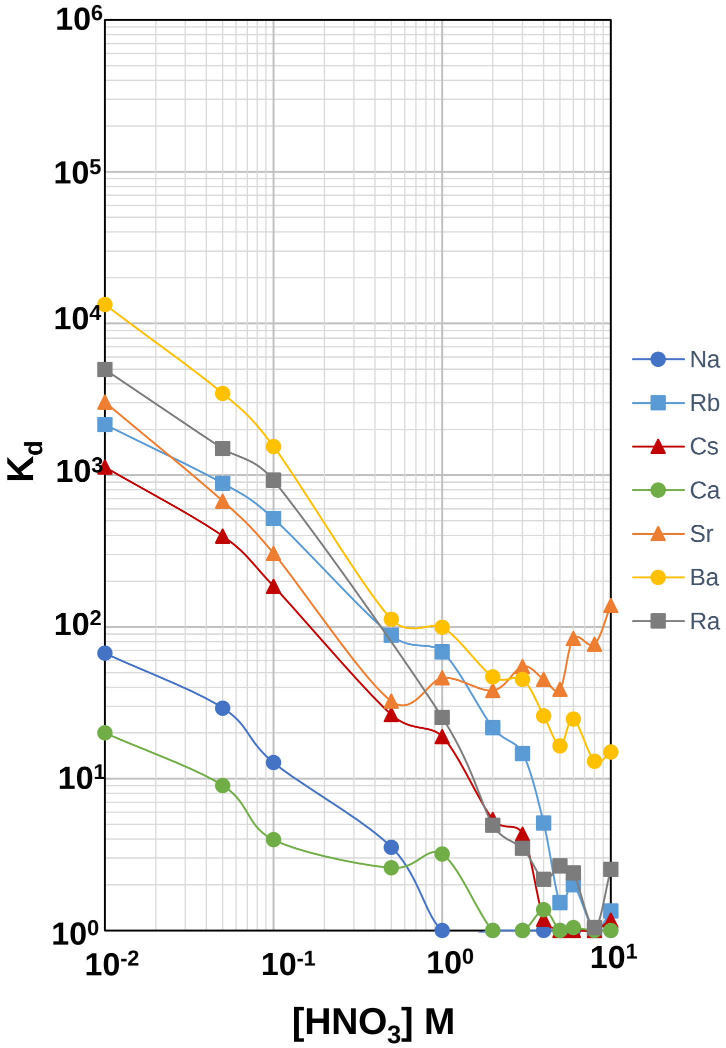
TK101 Group 1 and 2





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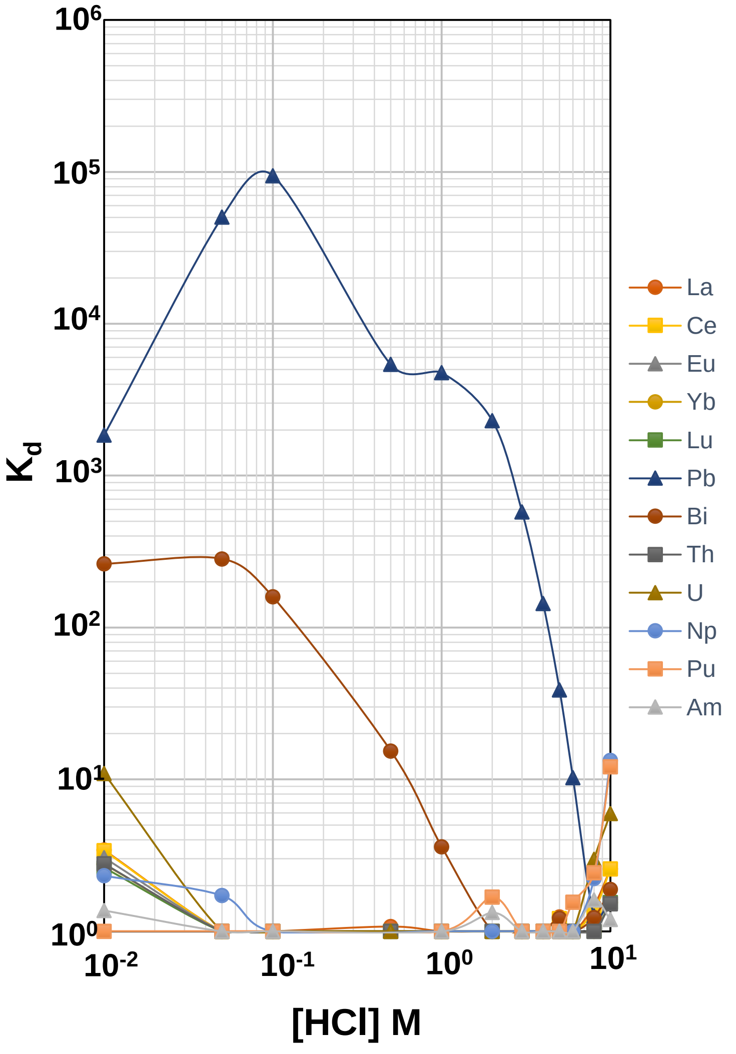
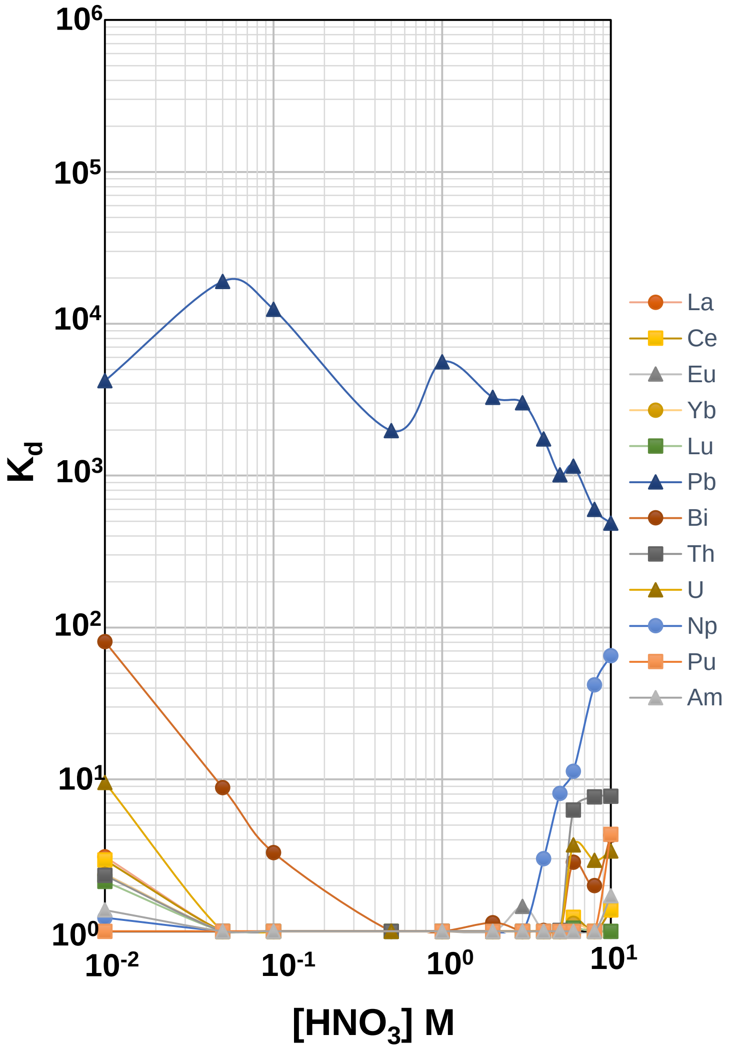
TK101 Lanthanides and Actinides (+ Bi and Pb)





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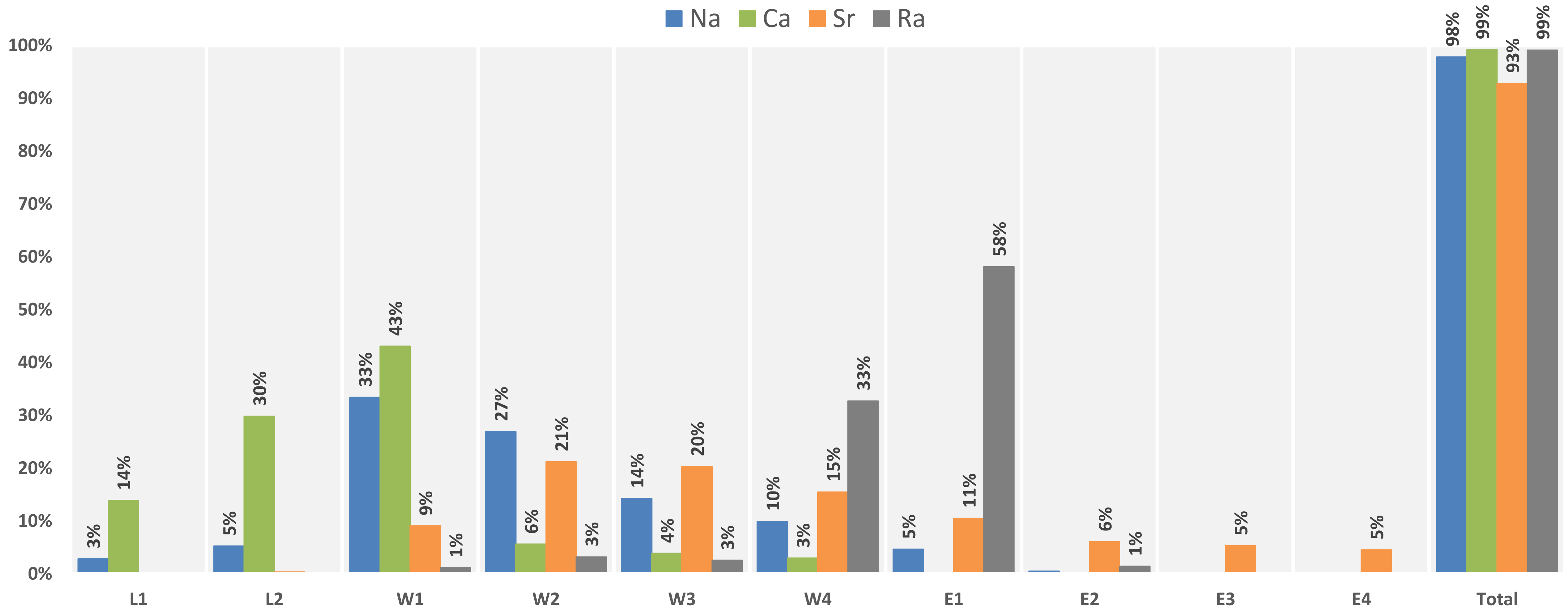
Elution Study (TK101)

Load: 10 mL $0.01\ M\ HNO_3$
Wash: 15 mL $0.1\ M\ HNO_3$
Wash: 5 mL $1\ M\ HNO_3$
Elution: 10 mL $8\ M\ HNO_3$



Elution Study (TK101)

Load:	10 mL	0.01 M HNO_3
Wash:	15 mL	0.1 M HNO_3
Wash:	5 mL	1 M HNO_3
Elution:	10 mL	8 M HNO_3

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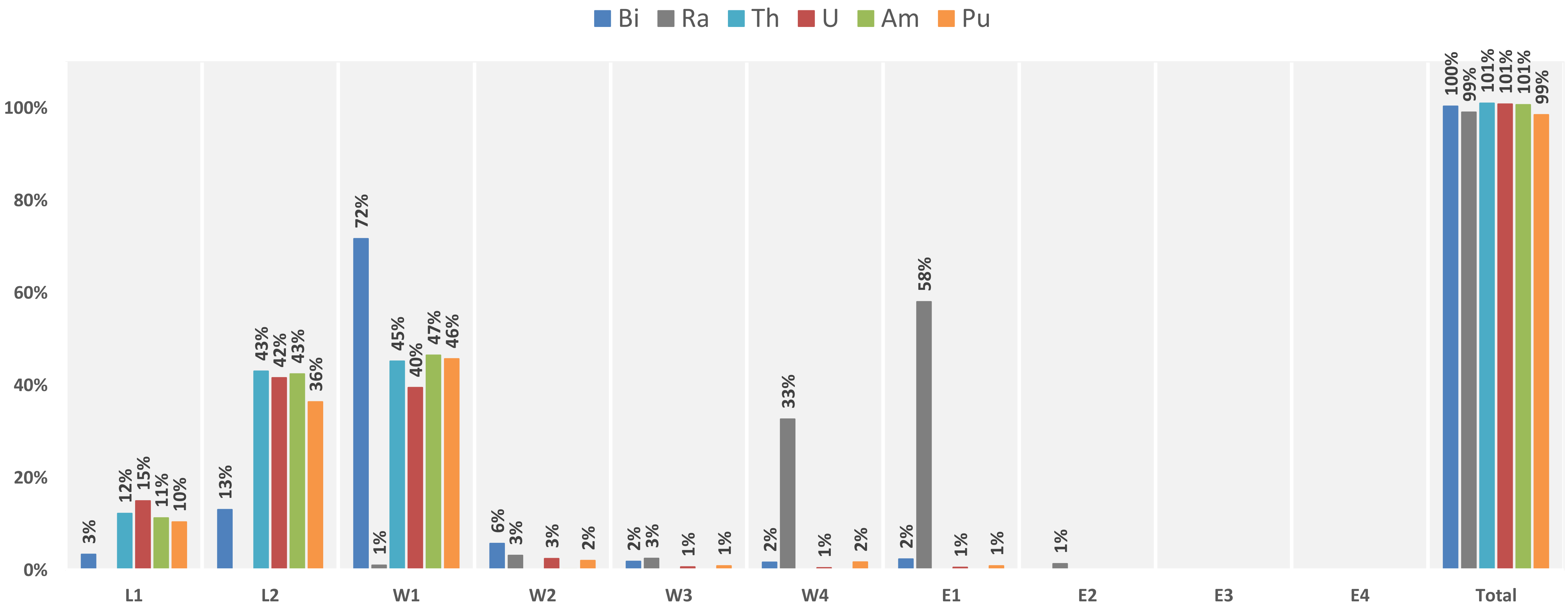
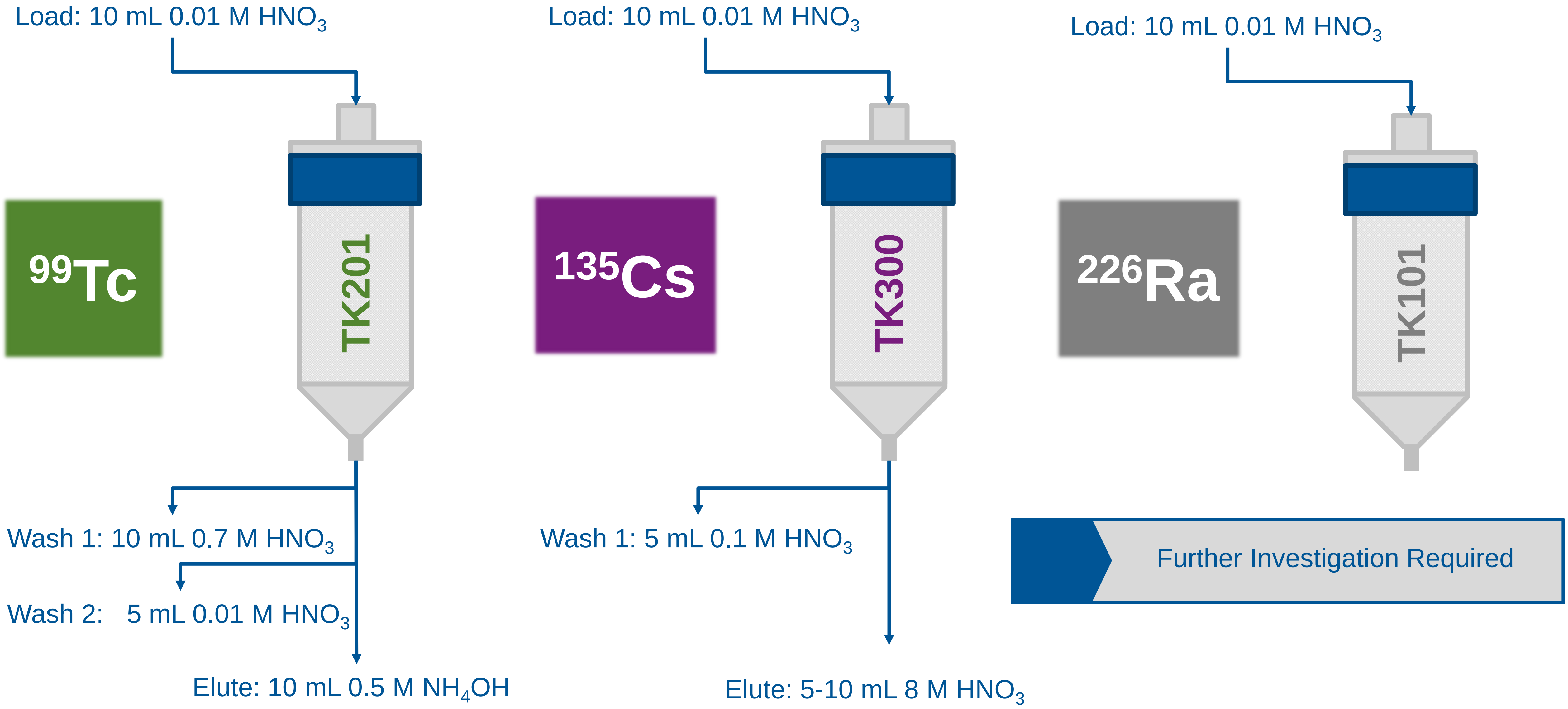


Developed Schemes



Future Work

- Investigate alternate schemes for Ra
- Validate other methods with real samples
- Evaluate how resins cope with higher matrix samples
- Investigate other applications for TK200 and TK201

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Any Questions?

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