Separation of radio-cerium from simulated irradiated lanthanum targets

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Introduction

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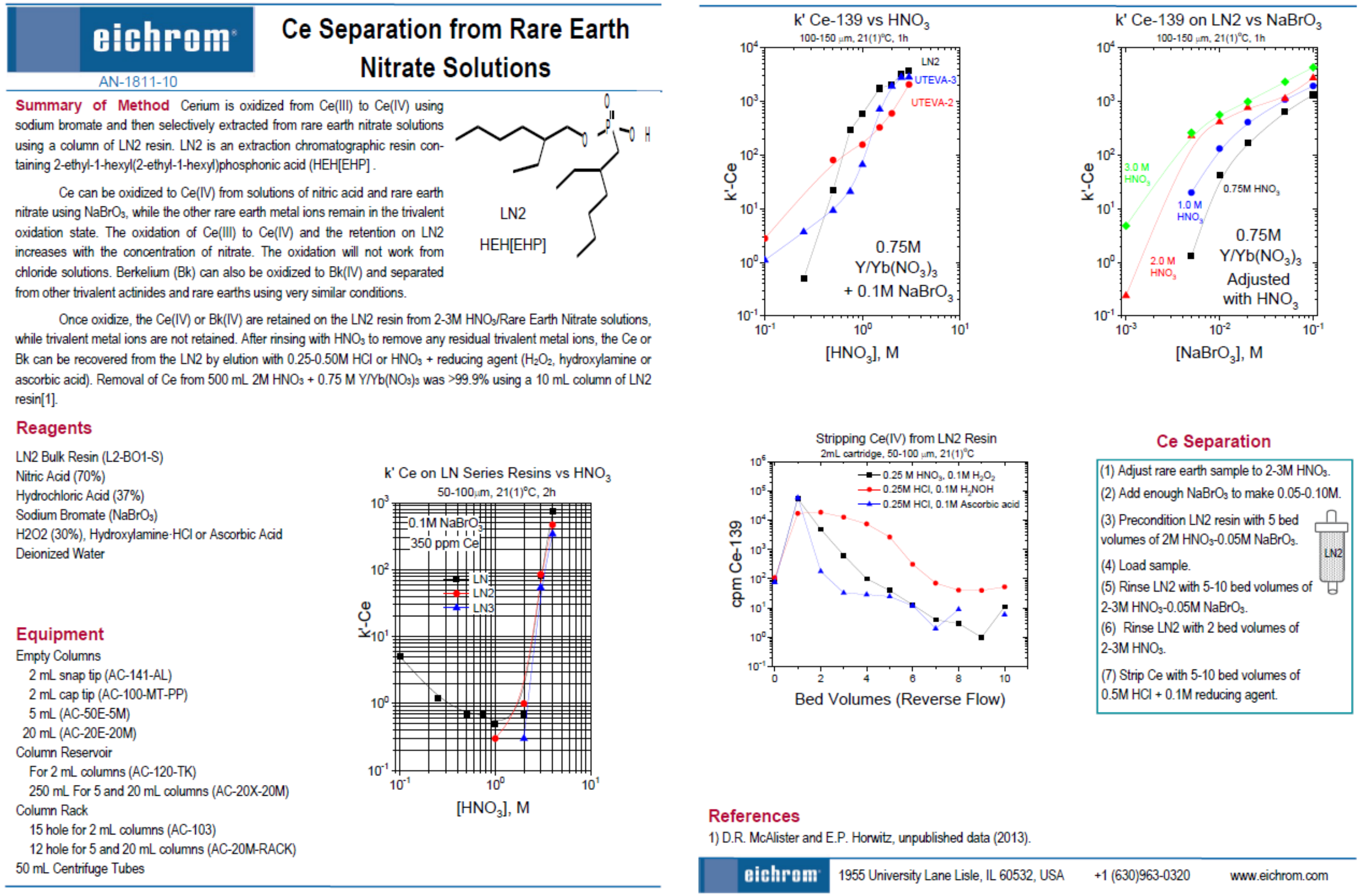

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AN-1811-10

Ce Separation from Rare Earth Nitrate Solutions

Summary of Method Cerium is oxidized from Ce(III) to Ce(IV) using sodium bromate and then selectively extracted from rare earth nitrate solutions using a column of LN2 resin. LN2 is an extraction chromatographic resin containing 2-ethyl-1-hexyl(2-ethyl-1-hexyl)phosphonic acid (HEH[EHP]).

LN2

HEH[EHP]

Ce can be oxidized to Ce(IV) from solutions of nitric acid and rare earth nitrate using $NaBrO_3$, while the other rare earth metal ions remain in the trivalent oxidation state. The oxidation of Ce(III) to Ce(IV) and the retention on LN2 increases with the concentration of nitrate. The oxidation will not work from chloride solutions. Berkelium (Bk) can also be oxidized to Bk(IV) and separated from other trivalent actinides and rare earths using very similar conditions.

Once oxidize, the Ce(IV) or Bk(IV) are retained on the LN2 resin from 2-3M HNO_3/Rare Earth Nitrate solutions, while trivalent metal ions are not retained. After rinsing with HNO_3 to remove any residual trivalent metal ions, the Ce or Bk can be recovered from the LN2 by elution with 0.25-0.50M HCl or HNO_3 + reducing agent (H_2O_2, hydroxylamine or ascorbic acid). Removal of Ce from 500 mL 2M HNO_3 + 0.75 M $Y/Yb(NO_3)_3$ was >99.9% using a 10 mL column of LN2 resin[1].

Reagents

LN2 Bulk Resin (L2-B01-S)
Nitric Acid (70%)
Hydrochloric Acid (37%)
Sodium Bromate ($NaBrO_3$)
H2O2 (30%), Hydroxylamine·HCl or Ascorbic Acid
Deionized Water

Equipment

Empty Columns
2 mL snap tip (AC-141-AL)
2 mL cap tip (AC-100-MT-PP)
5 mL (AC-50E-5M)
20 mL (AC-20E-20M)
Column Reservoir
For 2 mL columns (AC-120-TK)
250 mL For 5 and 20 mL columns (AC-20X-20M)
Column Rack
15 hole for 2 mL columns (AC-103)
12 hole for 5 and 20 mL columns (AC-20M-RACK)
50 mL Centrifuge Tubes

Ce Separation

(1) Adjust rare earth sample to 2-3M HNO_3.
(2) Add enough $NaBrO_3$ to make 0.05-0.10M.
(3) Precondition LN2 resin with 5 bed volumes of 2M HNO_3-0.05M $NaBrO_3$.
(4) Load sample.
(5) Rinse LN2 with 5-10 bed volumes of 2-3M HNO_3-0.05M $NaBrO_3$.
(6) Rinse LN2 with 2 bed volumes of 2-3M HNO_3.
(7) Strip Ce with 5-10 bed volumes of 0.5M HCl + 0.1M reducing agent.

References

1) D.R. McAlister and E.P. Horwitz, unpublished data (2013).

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Application note AN-1811-10

Phosphors in CFL bulbs contain rare earth elements:

Y, Eu, Tb, Ce

red phosphor Y2O3:Eu3+ (YOX)

green phosphors
LaPO4:Ce3+Tb3+ (LAP)

(Gd,Mg)B5O12:Ce3+Tb3+ (CBT)

(Ce,Tb)MgAl11O19 (CAT)

blue phosphor BaMgAl11O17:Eu2+

Introduction

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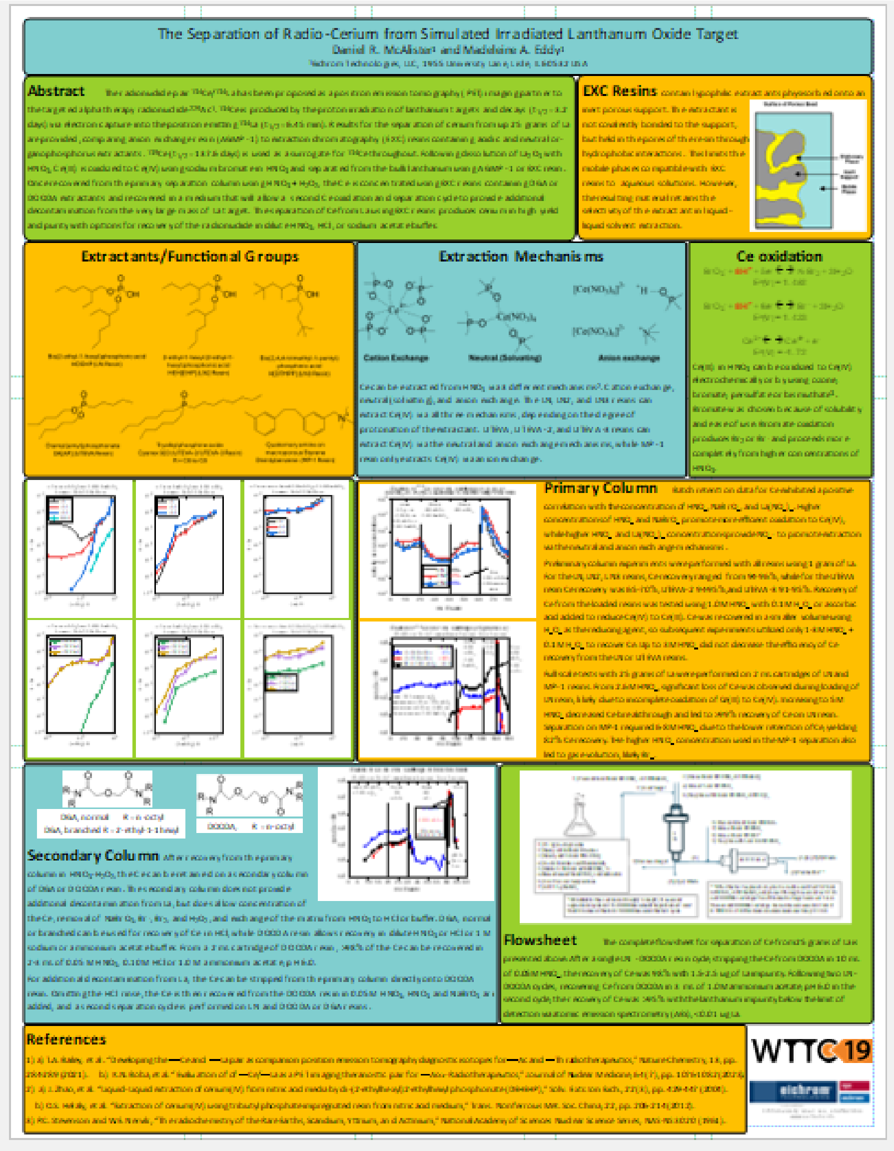


Poster WTTC19, August 2024

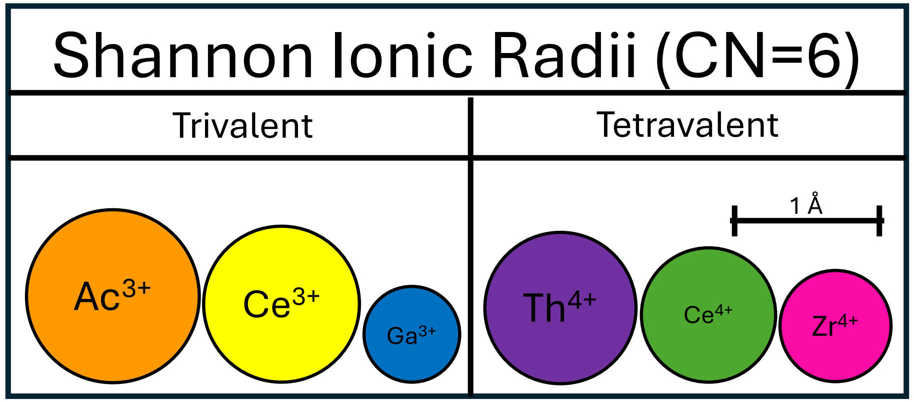
^{134}Ce ($t_{1/2}$ = 3.16 days) decays via electron capture to

^{134}La ($t_{1/2}$ = 6.45 minutes) ε/β^+

Proposed as the imaging part of a theranostic pair with:

^{225}Ac / ^{134}Ce(III)

^{227}Th / ^{134}Ce(IV)



Produced by proton irradiation of large La targets

T.A. Bailey, et al. "Developing the ^{134}Ce and ^{134}La pair as companion positron emission tomography diagnostic isotopes for ^{225}Ac and ^{227}Th radiotherapeutics," Nature Chemistry, 13, pp. 284-289 (2021).

REEE extraction

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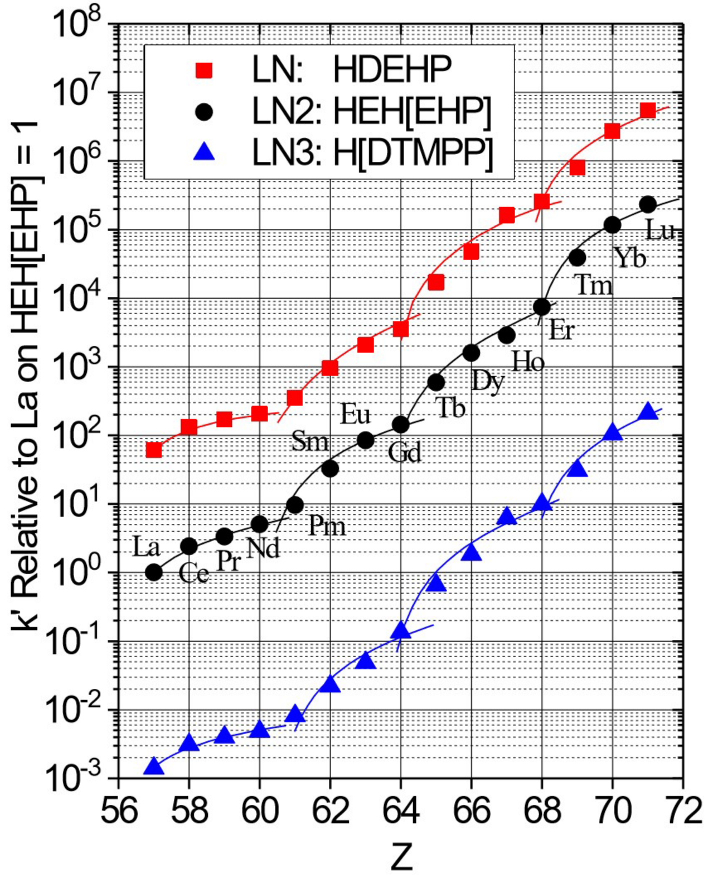

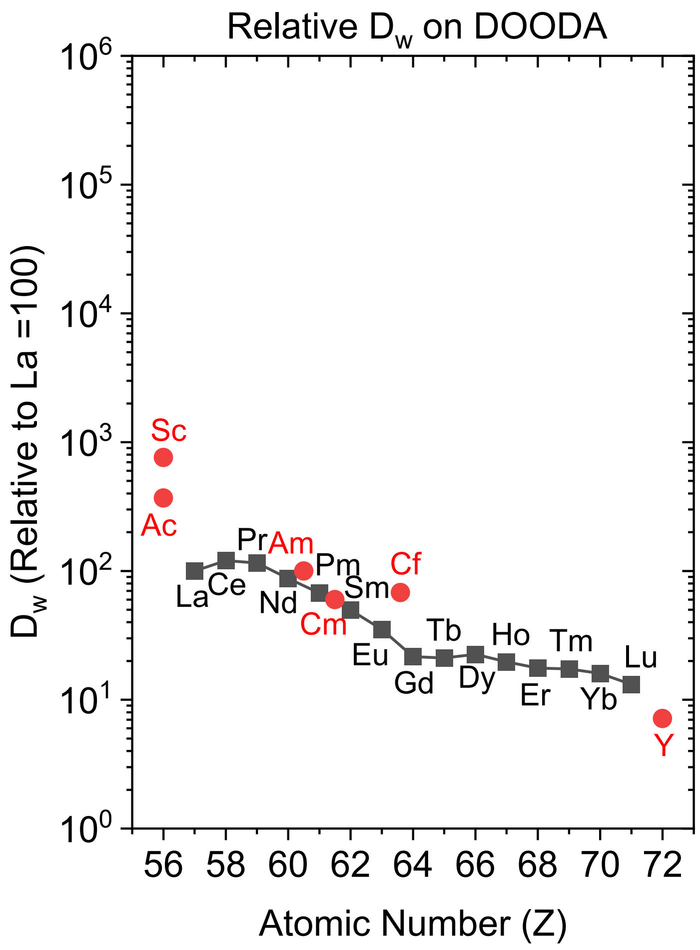

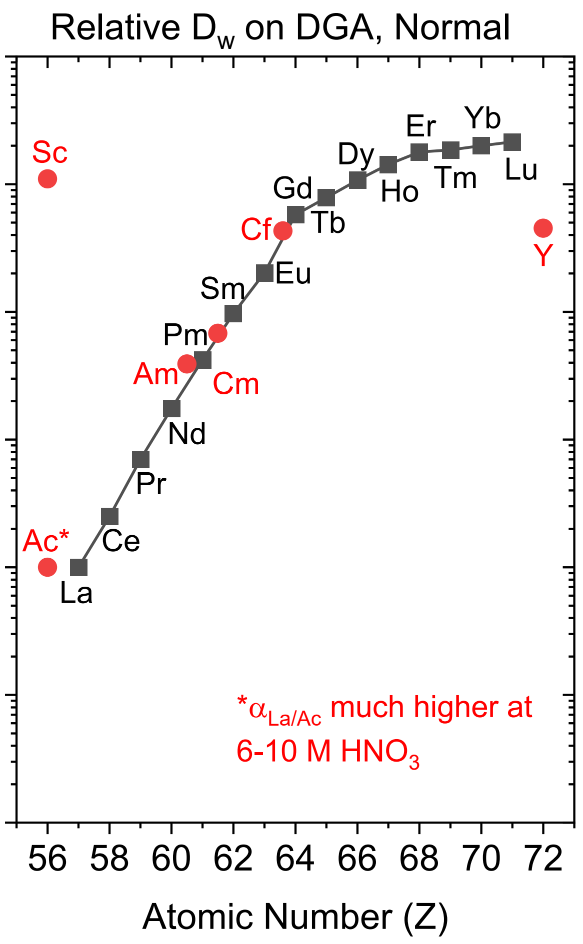

Difficult to separate adjacent REE(III), but Ce(III) can be oxidized to ***Ce(IV)***.

Ce oxidation with bromate

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$BrO_3^- + \mathbf{6H^+} + 5e^- \leftrightarrow \frac{1}{2} Br_2 + 3H_2O$

$E^o(V) = 1.482$

$BrO_3^- + \mathbf{6H^+} + 6e^- \leftrightarrow Br^- + 3H_2O$

$E^o(V) = 1.423$

$Ce^{3+} \leftrightarrow Ce^{4+} + e^-$

$E^o(V) = -1.72$

$NaBrO_3$ can be used to oxidize Ce(III) to Ce(IV).

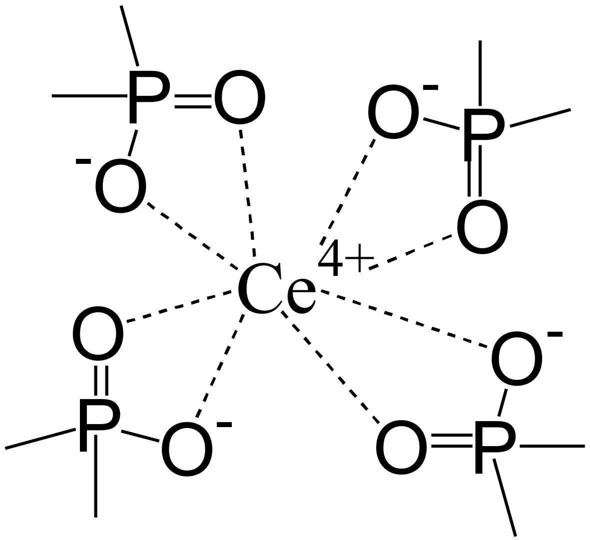
Oxidation proceeds more completely at higher HNO_3 concentrations.

Does not work in HCl.

Byproducts include Br_2 and Br^-.

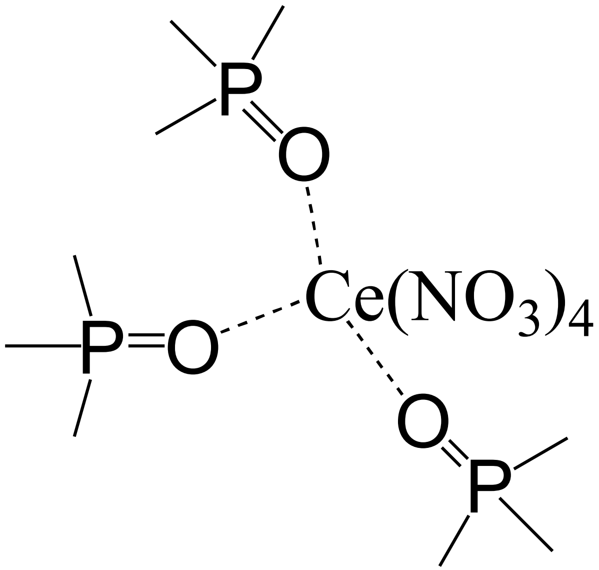
P.C. Stevenson and W.E. Nervik, "The radiochemistry of the Rare Earths, Scandium, Yttrium, and Actinium," National Academy of Sciences Nuclear Science Series, NAS-NS 3020 (1961).

Extraction mechanisms



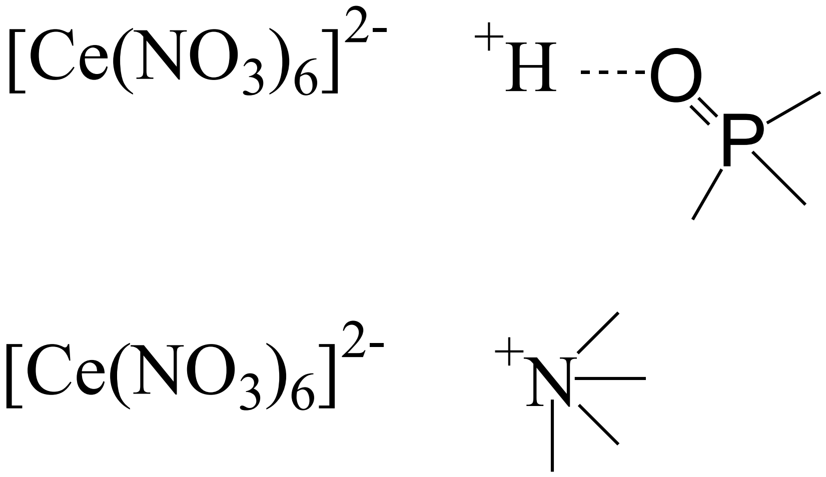
Cation Exchange

LN, LN2, LN3



Neutral (Solvating)

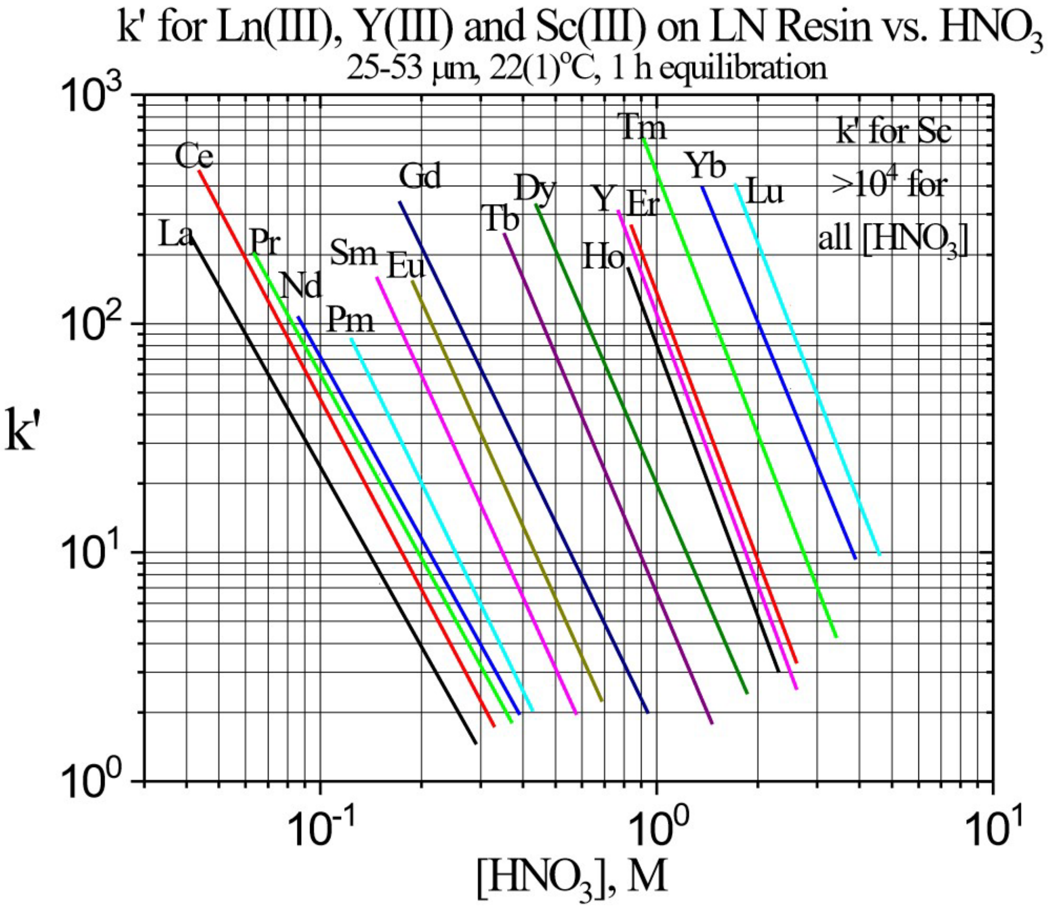
UTEVA, UTEVA-2, UTEVA-3

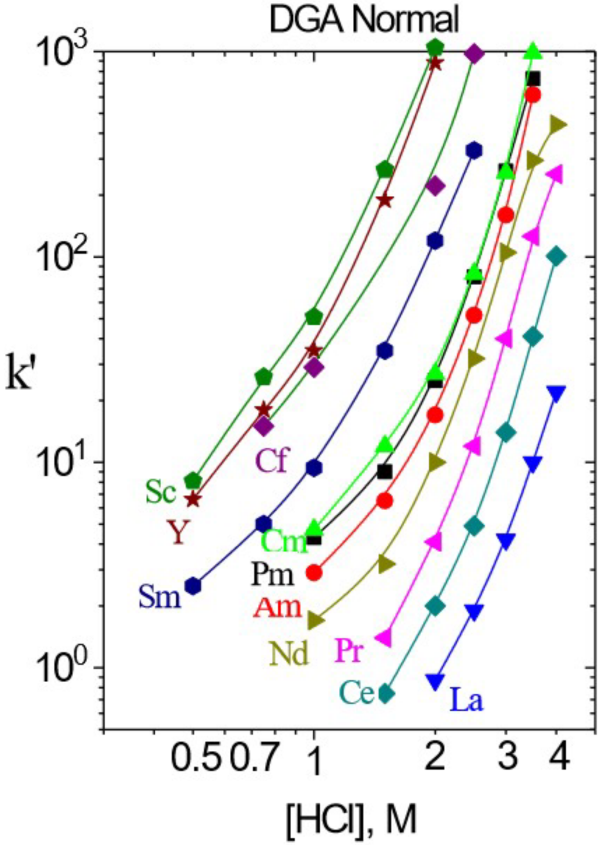


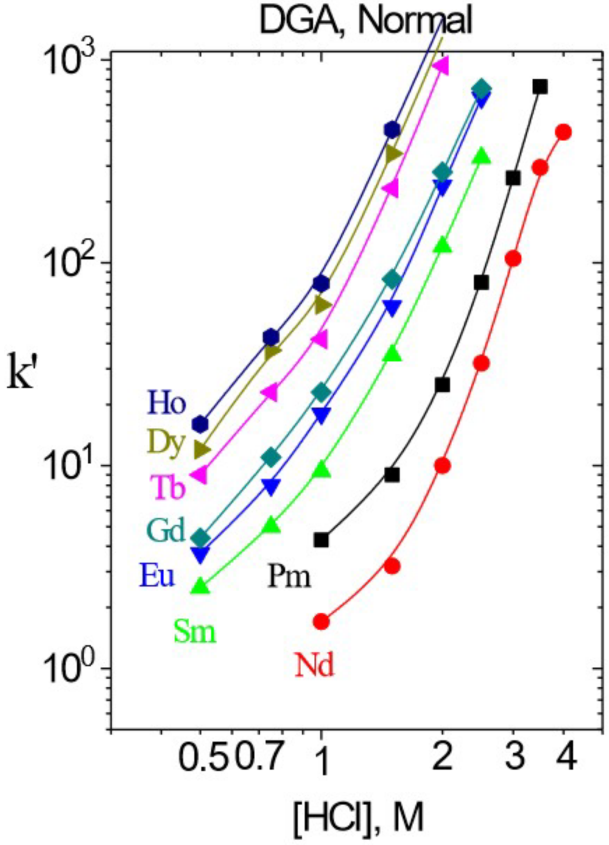
Anion exchange

1x8, TEVA

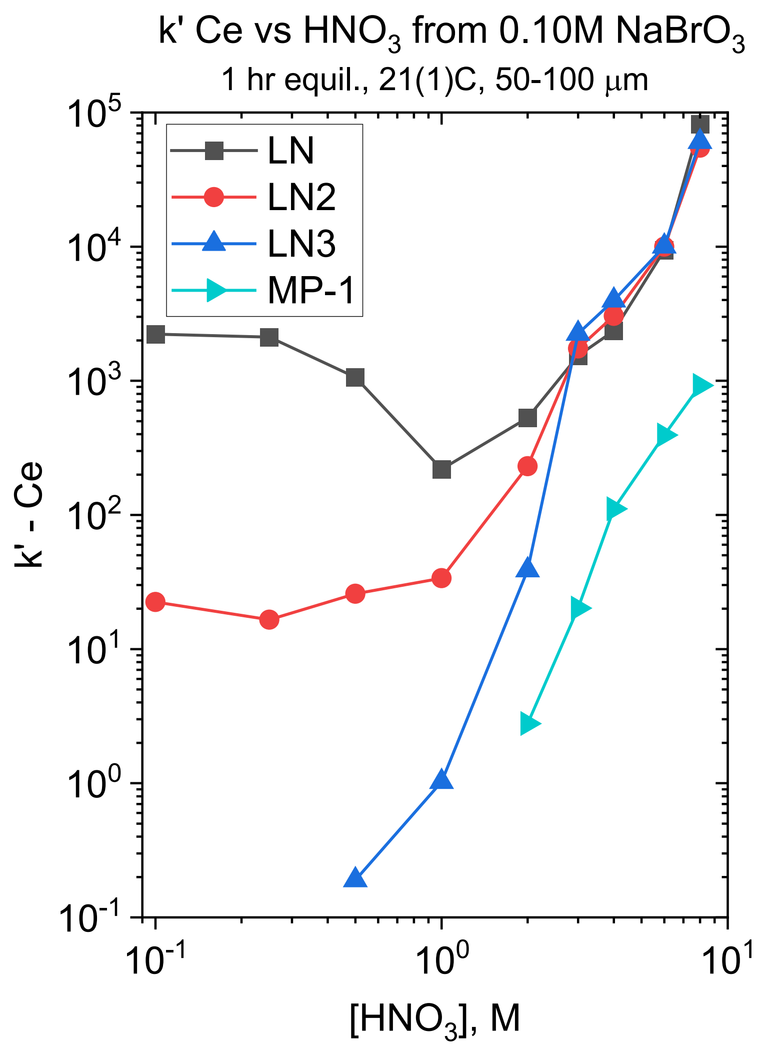
REE extraction

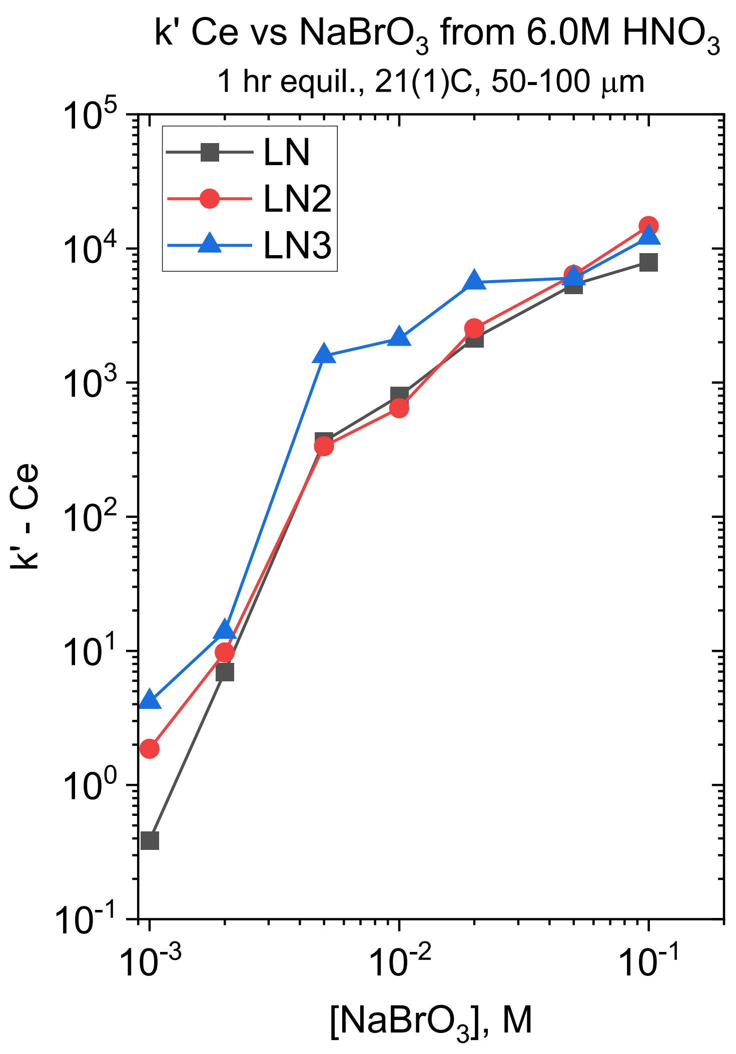


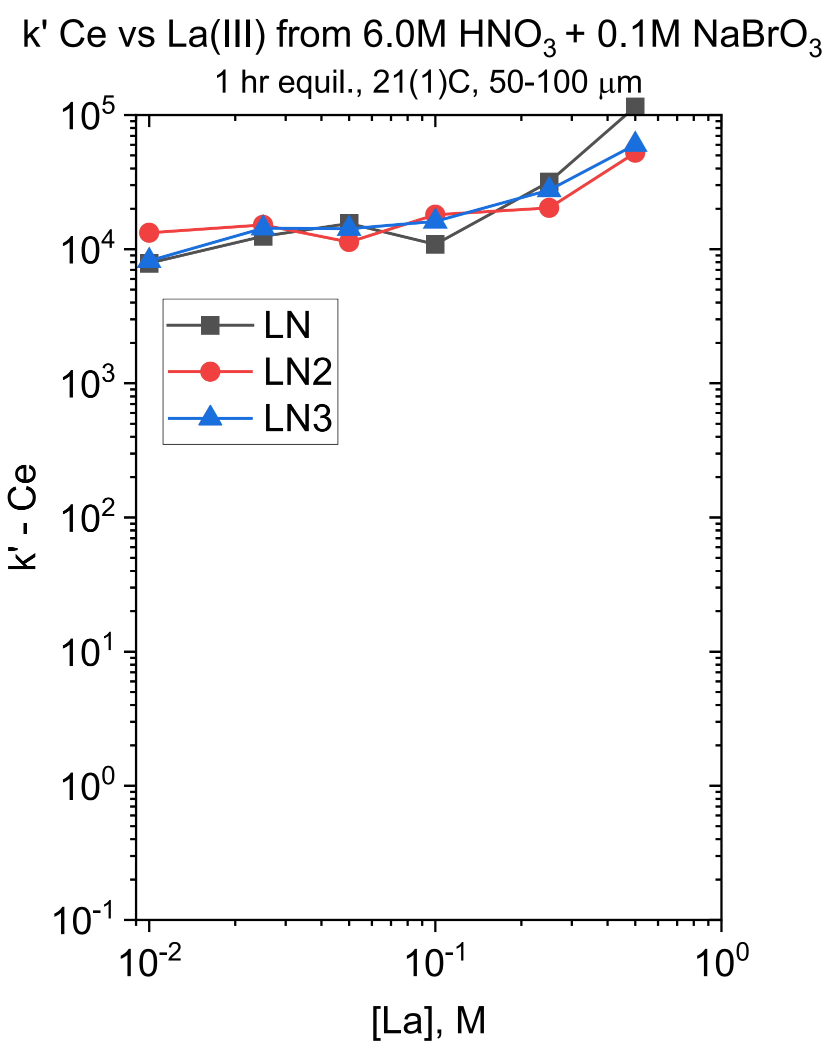




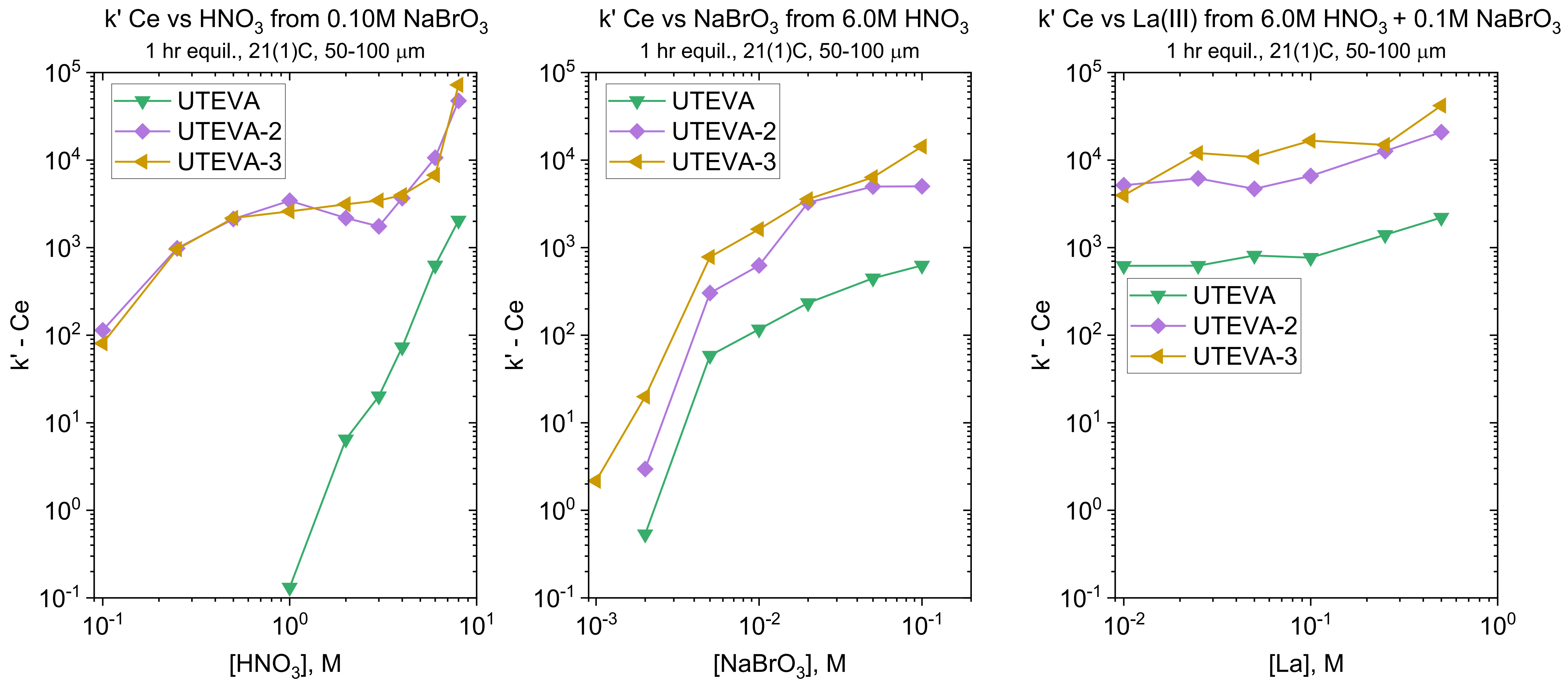
Ce extraction (acidic extractants)



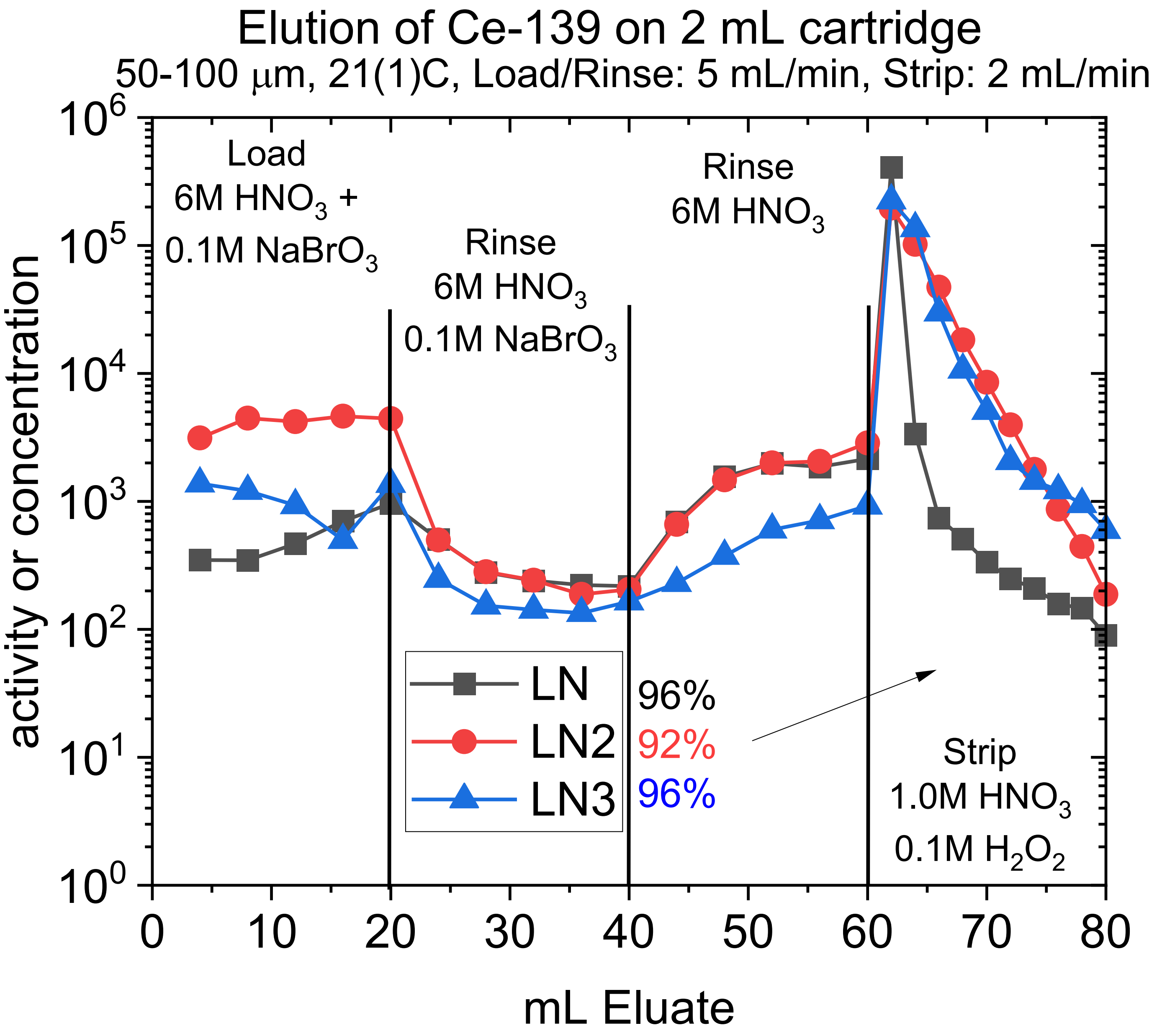




Ce extraction (neutral/solvating extractants)



Ce separation (acidic extractants)



1 g simulated La target

Rinse with 6M HNO_3

Recovery in HNO_3/H_2O_2

>92% recovery for LN, LN2, and LN3

Ce separation (acidic extractants)

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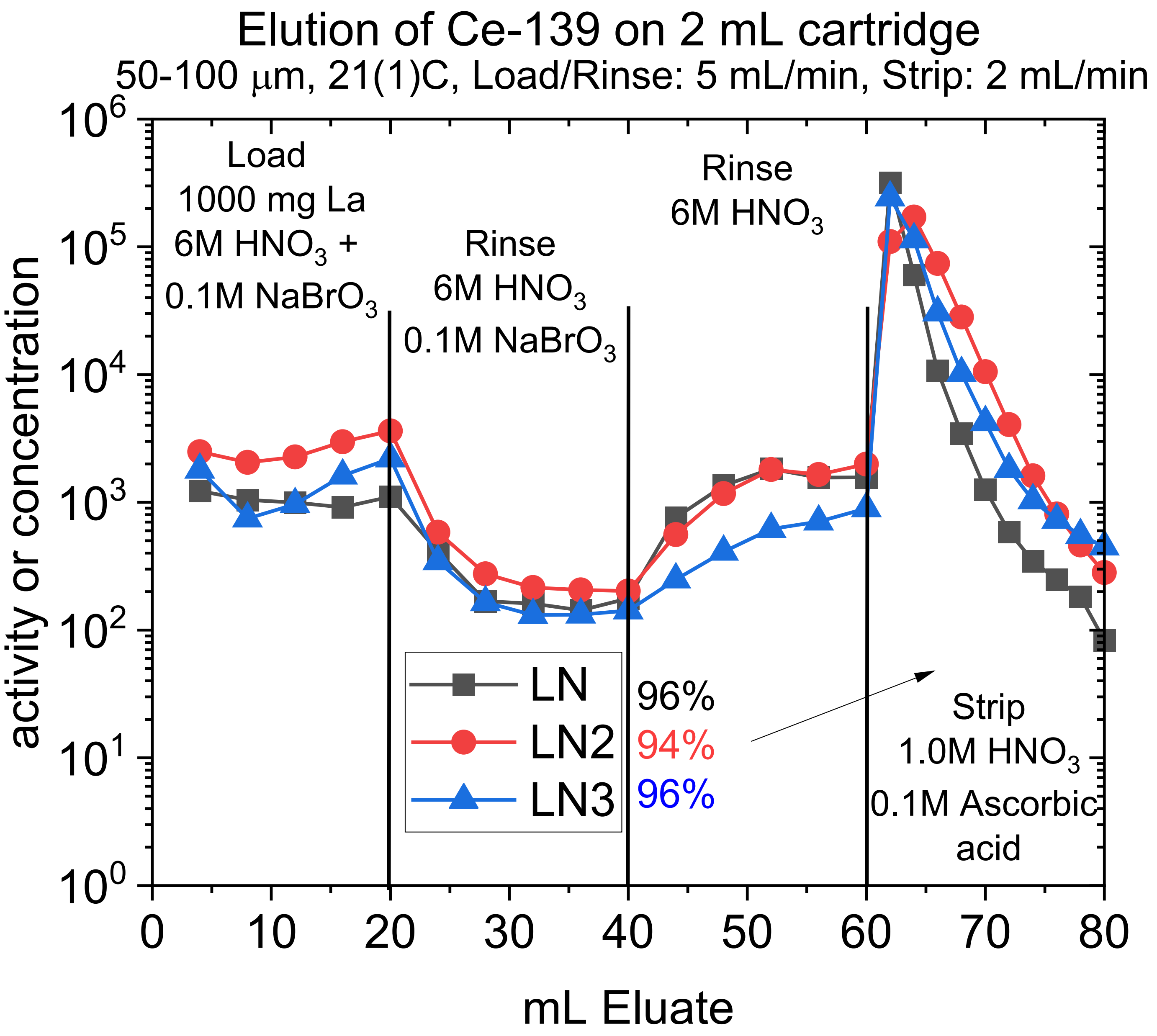


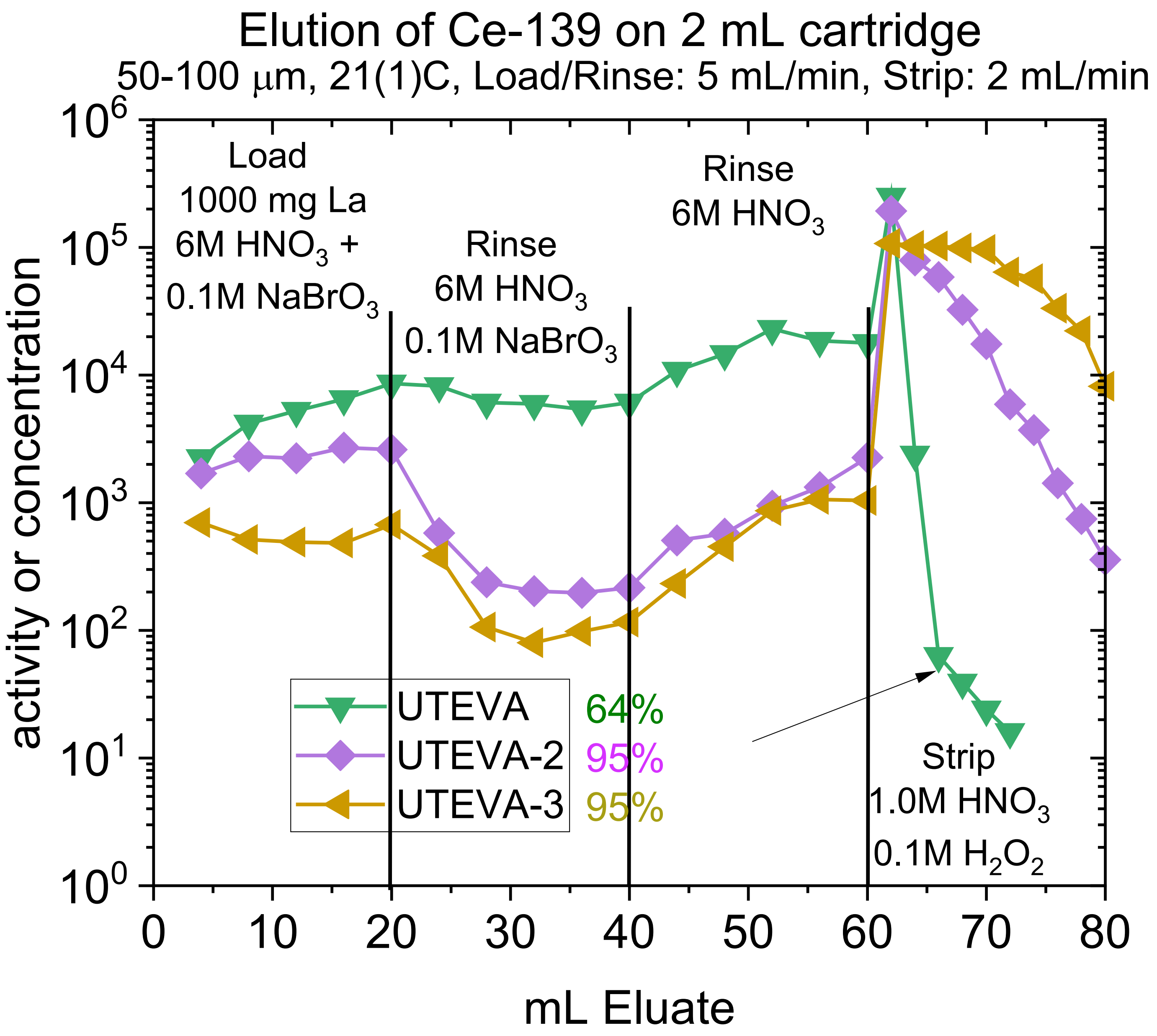
1 g simulated La target

Rinse with 6M HNO_3

Recovery in HNO_3 / ascorbic acid

>94% recovery for LN, LN2, and LN3

Ce separation (neutral/solvating extractants)



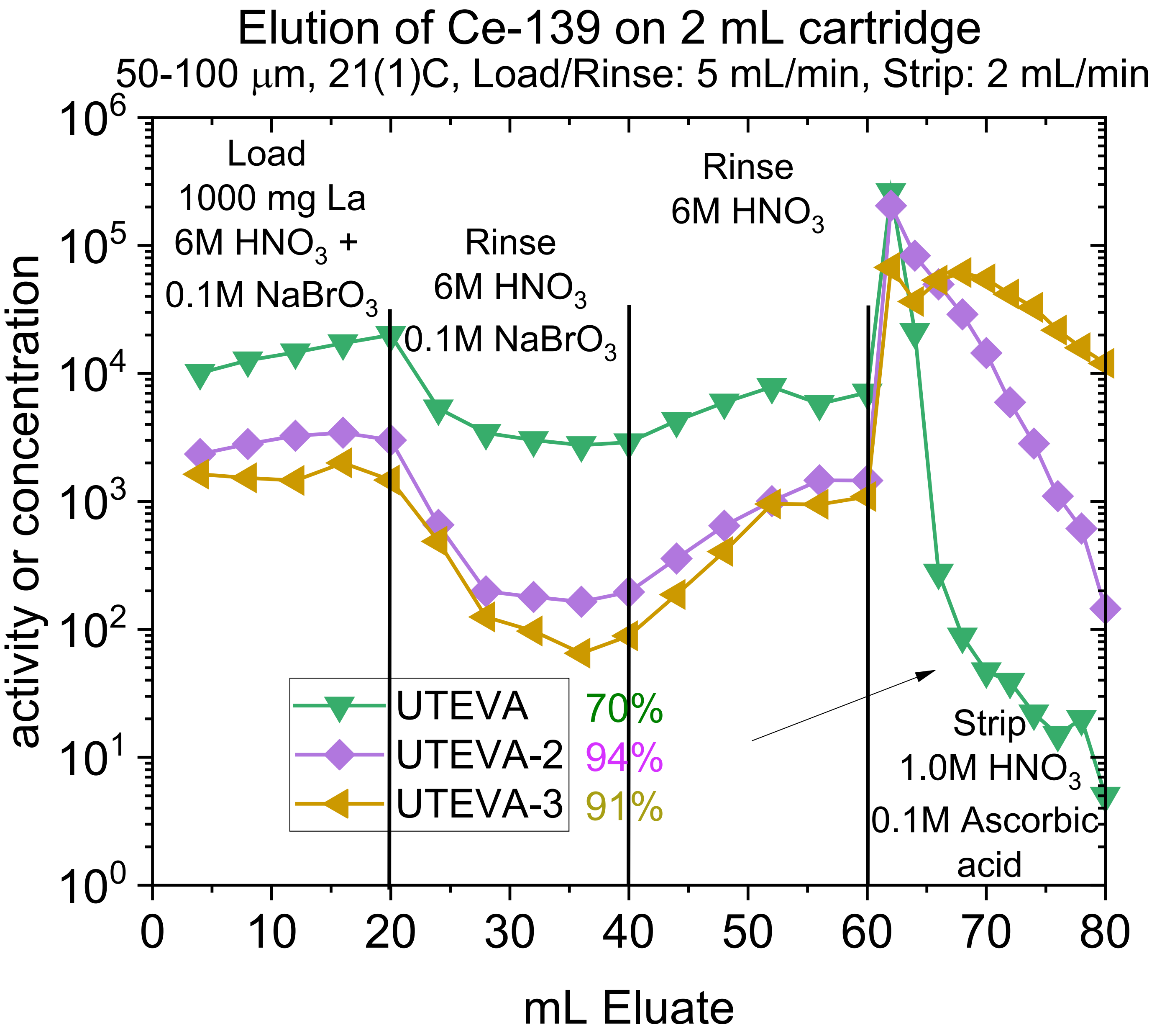
1 g simulated La target

Rinse with 6M HNO_3

Recovery in HNO_3/H_2O_2

>95% recovery for UTEVA-2, UTEVA-3

Ce separation (neutral/solvating extractants)



1 g simulated La target

Rinse with 6M HNO_3

Recovery in HNO_3 / ascorbic acid

>91% recovery for UTEVA-2 and UTEVA-3

Secondary Column

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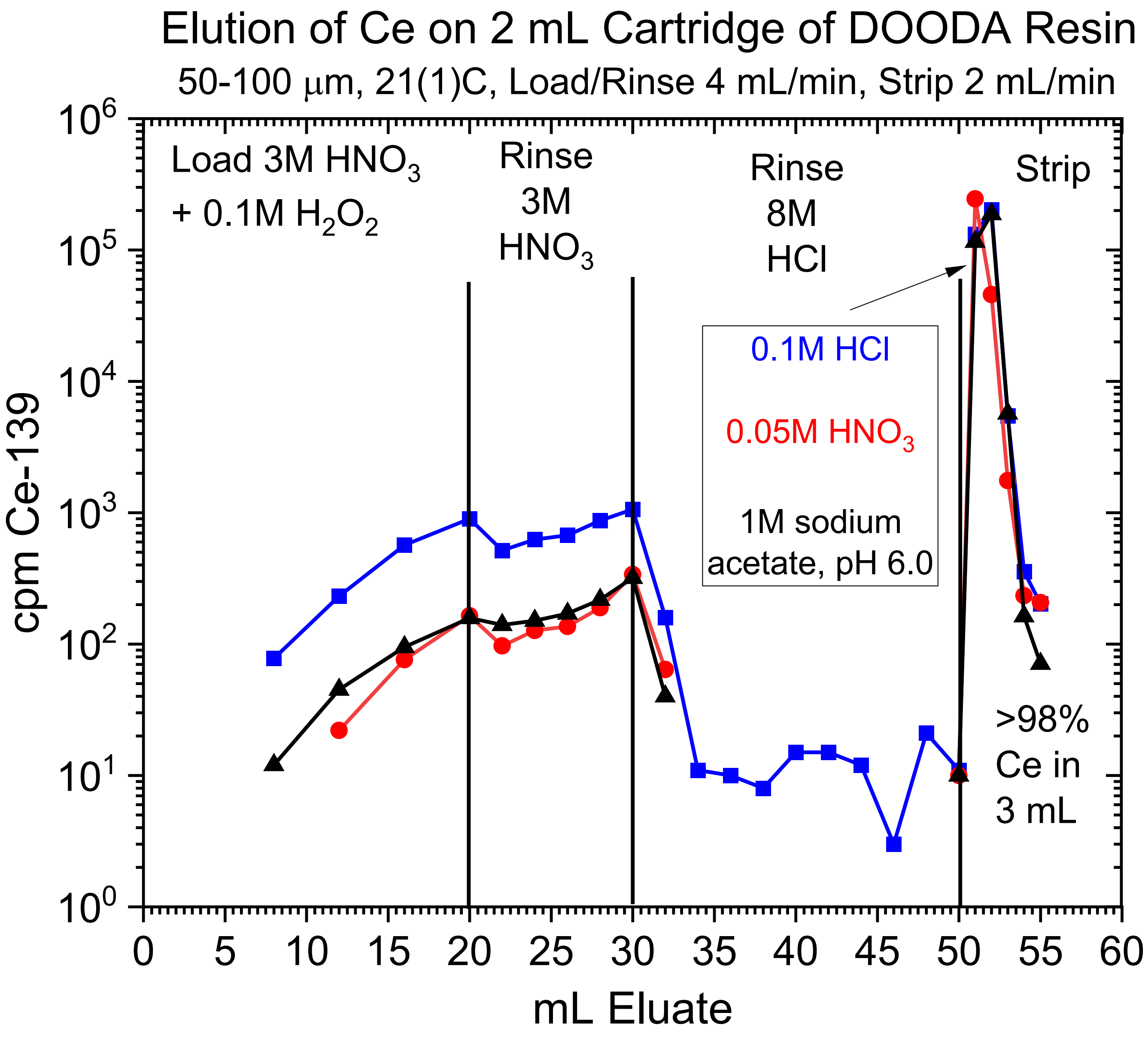

Secondary column of DOODA or DGA resin.

Concentrate

Remove reducing agent

Change matrix

- Additional purification
- Dilute HCl or buffer for radiolabeling

Flowsheet

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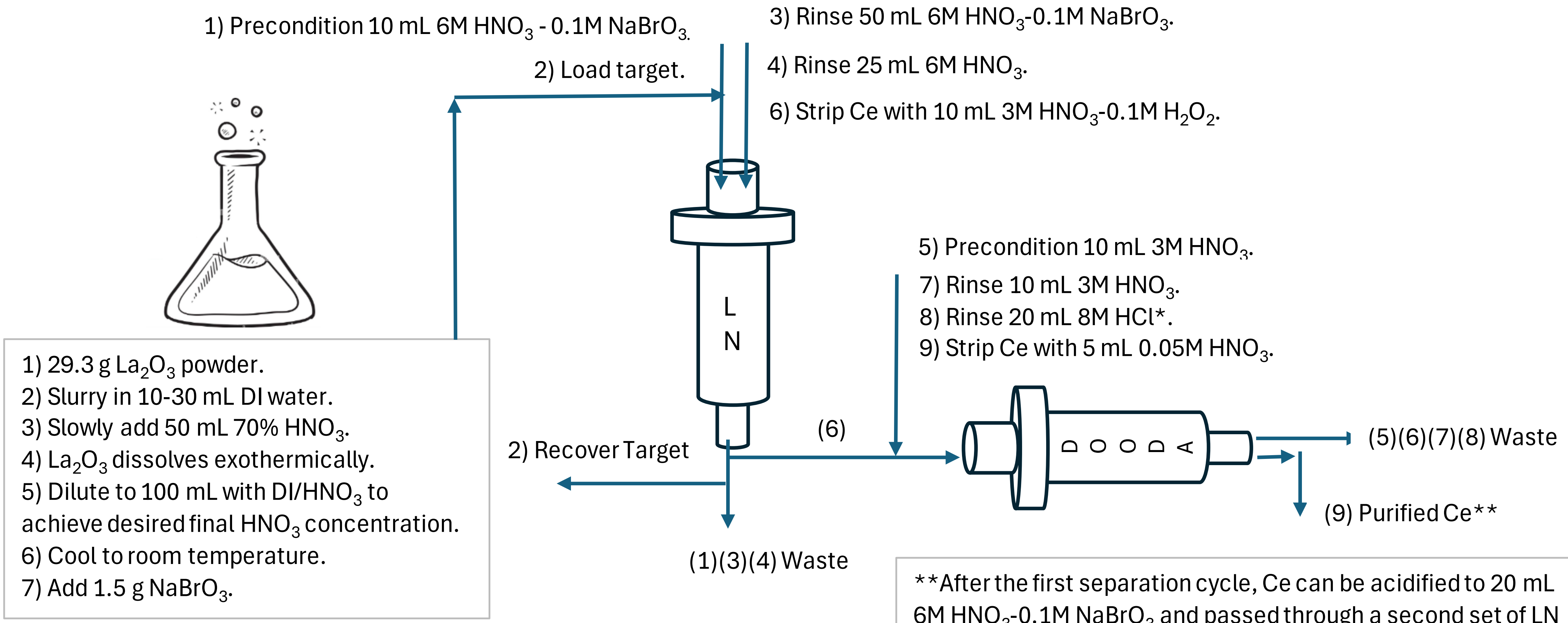

*HCl inhibits the oxidation of Ce(III) to Ce(IV). If a second separation cycle on LN - DOODA resin will be performed, omit the HCl rinse in the first of DOODA resin in the first cycle.

**After the first separation cycle, Ce can be acidified to 20 mL 6M HNO_3-0.1M $NaBrO_3$ and passed through a second set of LN and DOODA cartridges for additional La target removal. From the second DOODA cartridge, Ce can be recovered in 2 mL of 0.1M HCl or 1.0M sodium or ammonium acetate, pH = 6.0.

Full scale (25g La Target)

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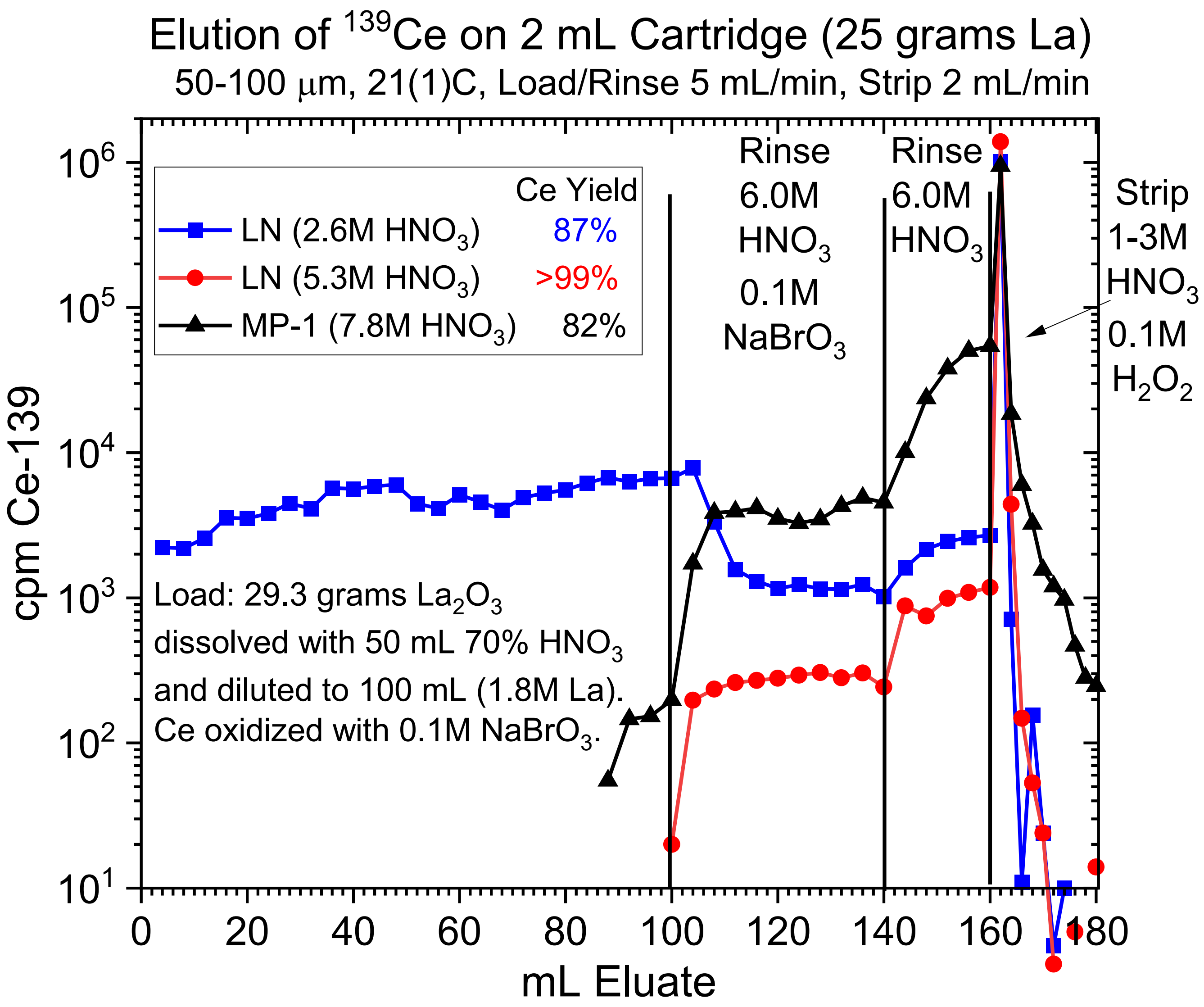

Single LN - DOODA resin cycle stripping the Ce from DOODA in 10 mL of 0.05M HNO_3

98% Ce with 1.5-2.5 ug of La.

Two LN - DOODA cycles, recovering Ce from DOODA in 3 mL of 1.0M ammonium acetate, pH 6.0 in the second cycle,

>95% Ce with the impurity < 0.01 ug La (LOD by MP-AES).

Questions???