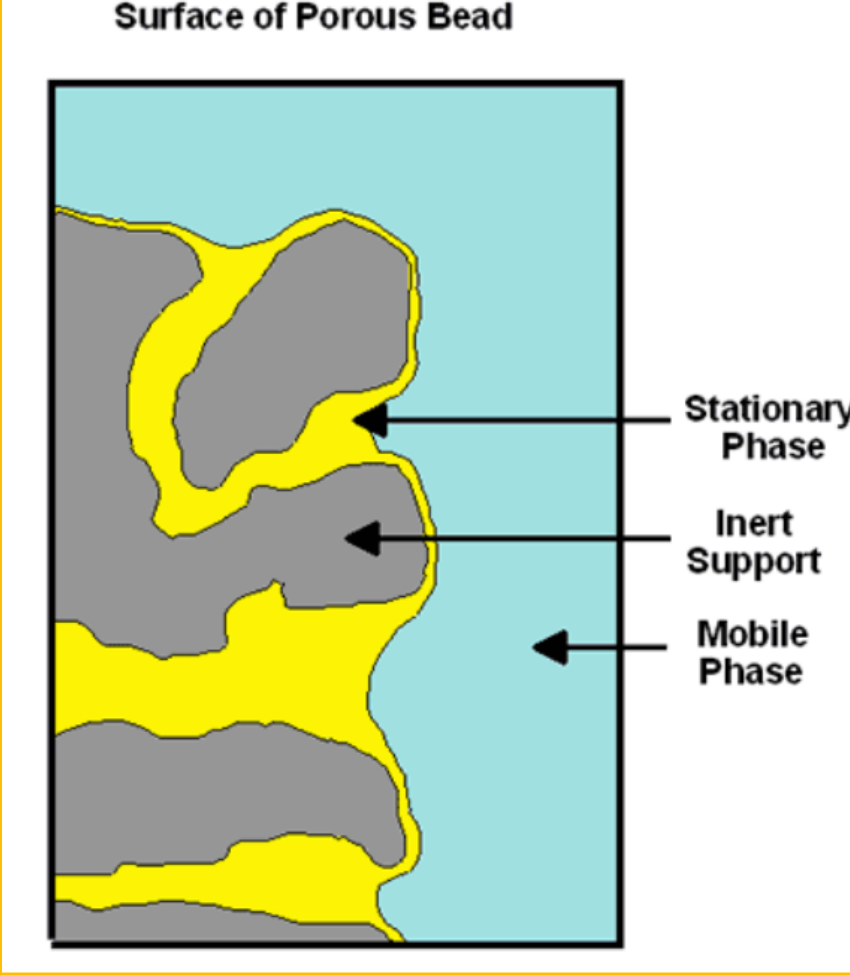
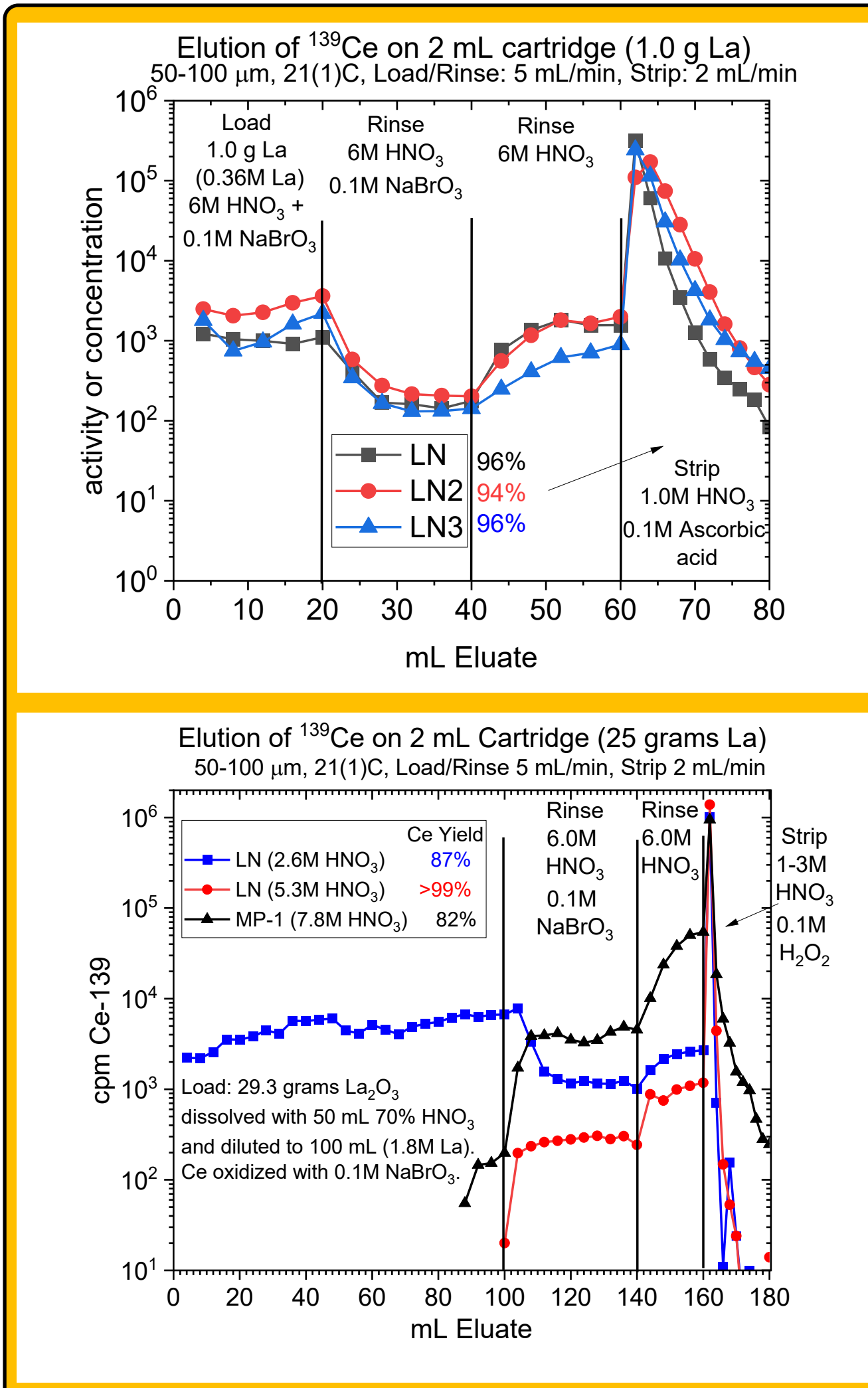
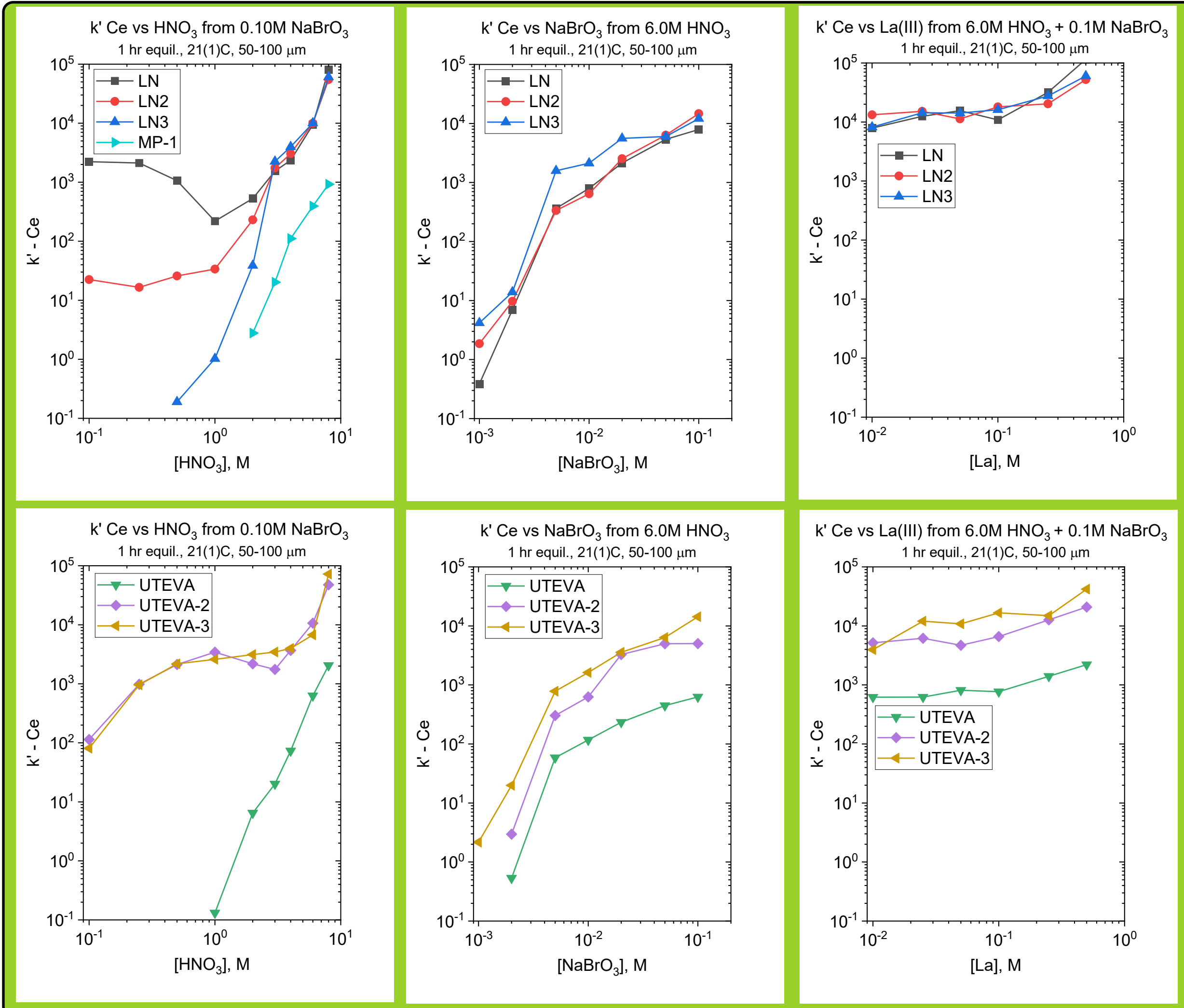
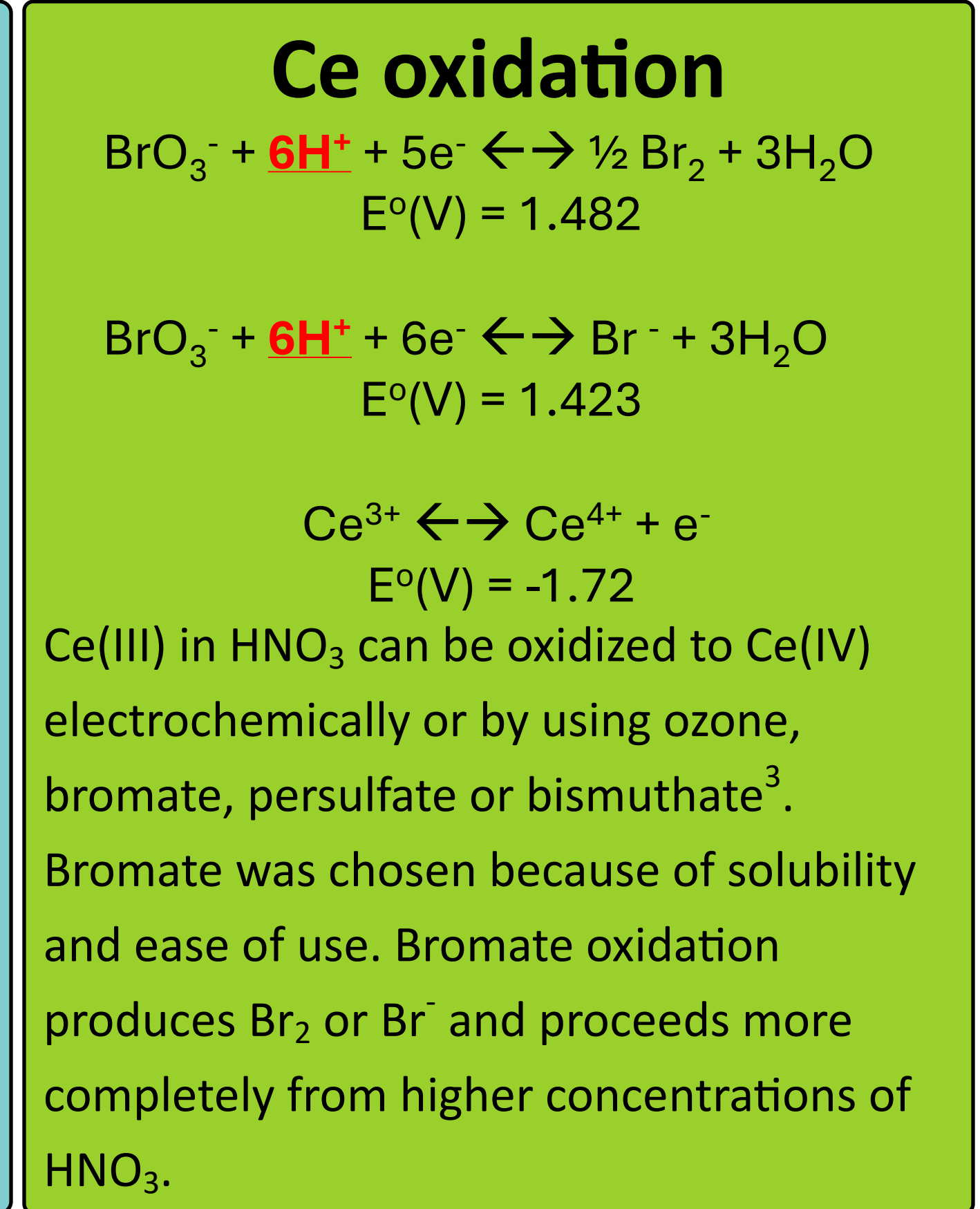
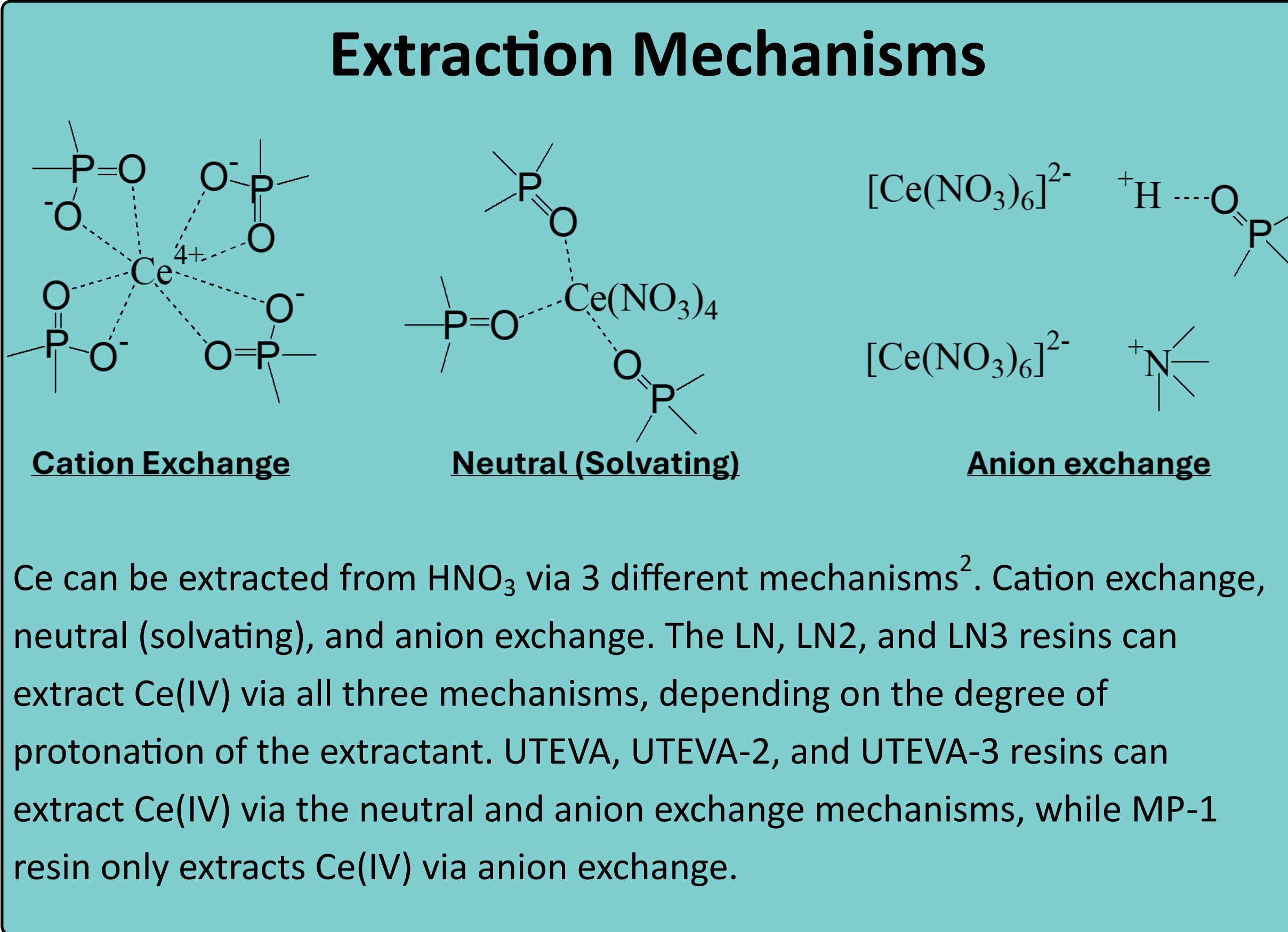
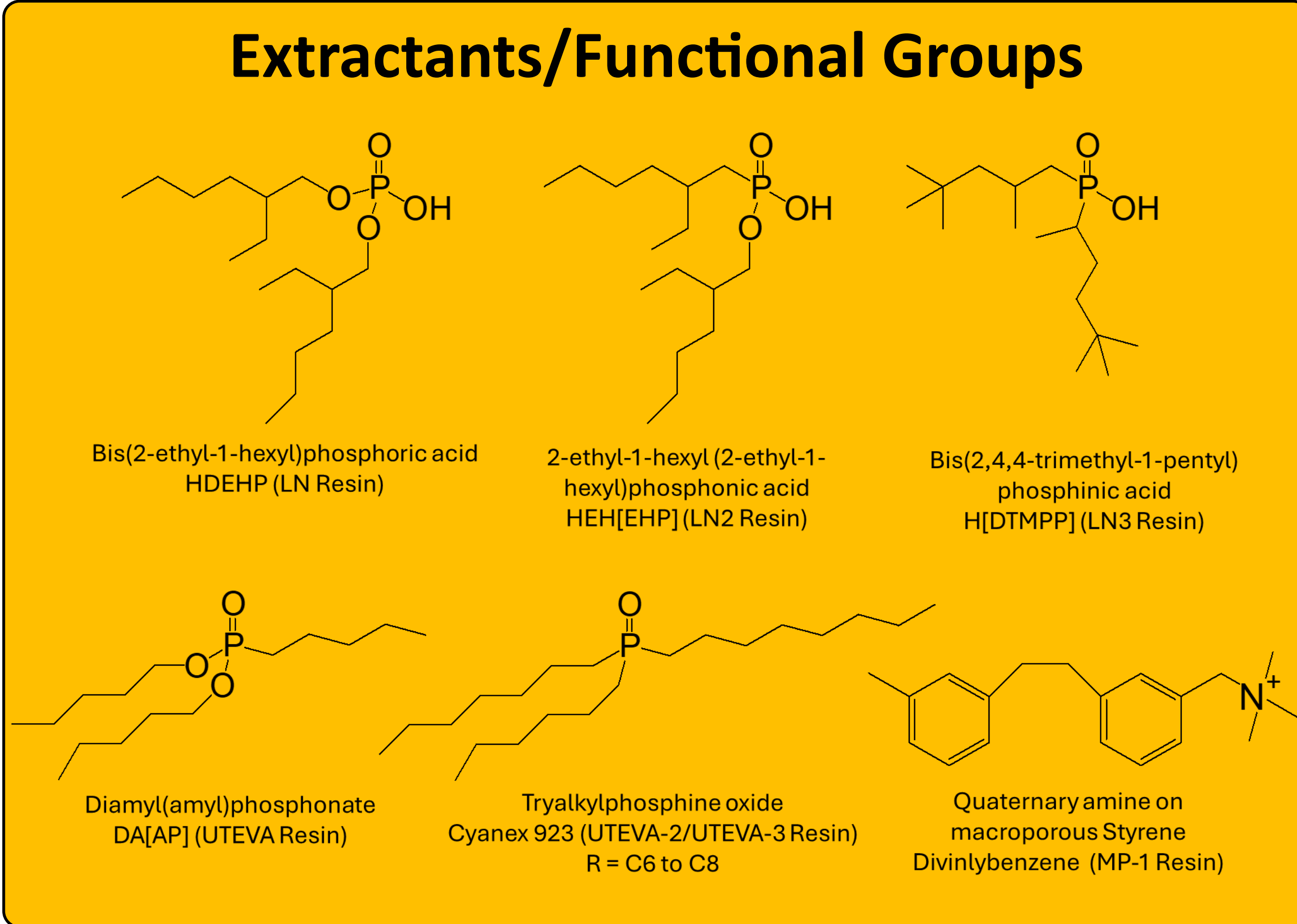


The Separation of Radio-Cerium from Simulated Irradiated Lanthanum Oxide Target

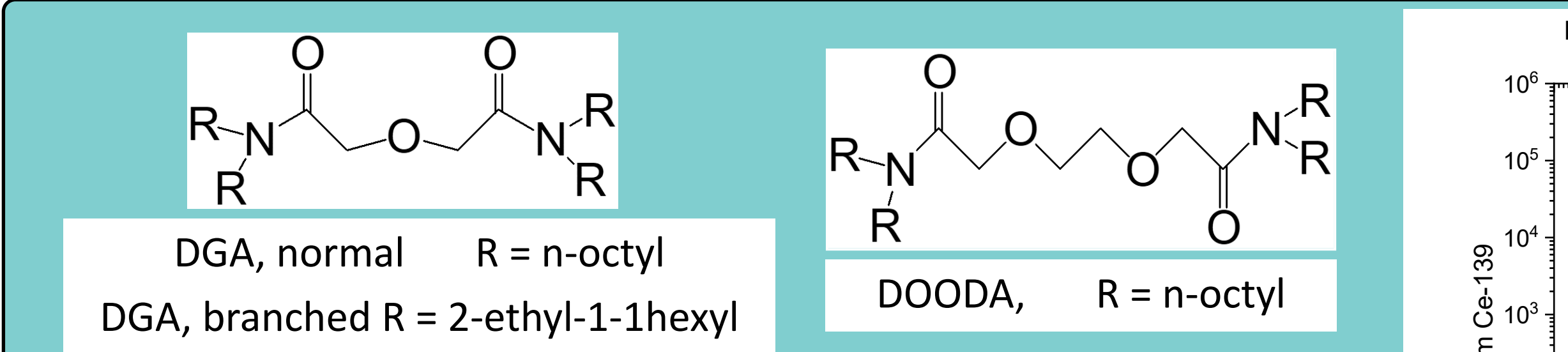
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Abstract The radionuclide pair ¹³⁴Ce/¹³⁴La has been proposed as a positron emission tomography (PET) imaging partner to the targeted alpha therapy radionuclide ²²⁵Ac. ¹³⁴Ce is produced by the proton irradiation of lanthanum targets and decays (t_{1/2} = 3.2 days) via electron capture into the positron emitting ¹³⁴La (t_{1/2} = 6.45 min). Results for the separation of cerium from up to 25 grams of La are provided, comparing anion exchange resin (AGMP-1) to extraction chromatography (EXC) resins containing acidic and neutral organophosphorus extractants. ¹³⁹Ce (t_{1/2} = 137.6 days) is used as a surrogate for ¹³⁴Ce throughout. Following dissolution of La₂O₃ with HNO₃, Ce(III) is oxidized to Ce(IV) using sodium bromate in HNO₃ and separated from the bulk lanthanum using AGMP-1 or EXC resin. Once recovered from the primary separation column using HNO₃ + H₂O₂, the Ce is concentrated using EXC resins containing DGA or DOODA extractants and recovered in a medium that will allow a second Ce oxidation and separation cycle to provide additional decontamination from the very large mass of La target. The separation of Ce from La using EXC resins produces cerium in high yield and purity with options for recovery of the radionuclide in dilute HNO₃, HCl, or sodium acetate buffer.

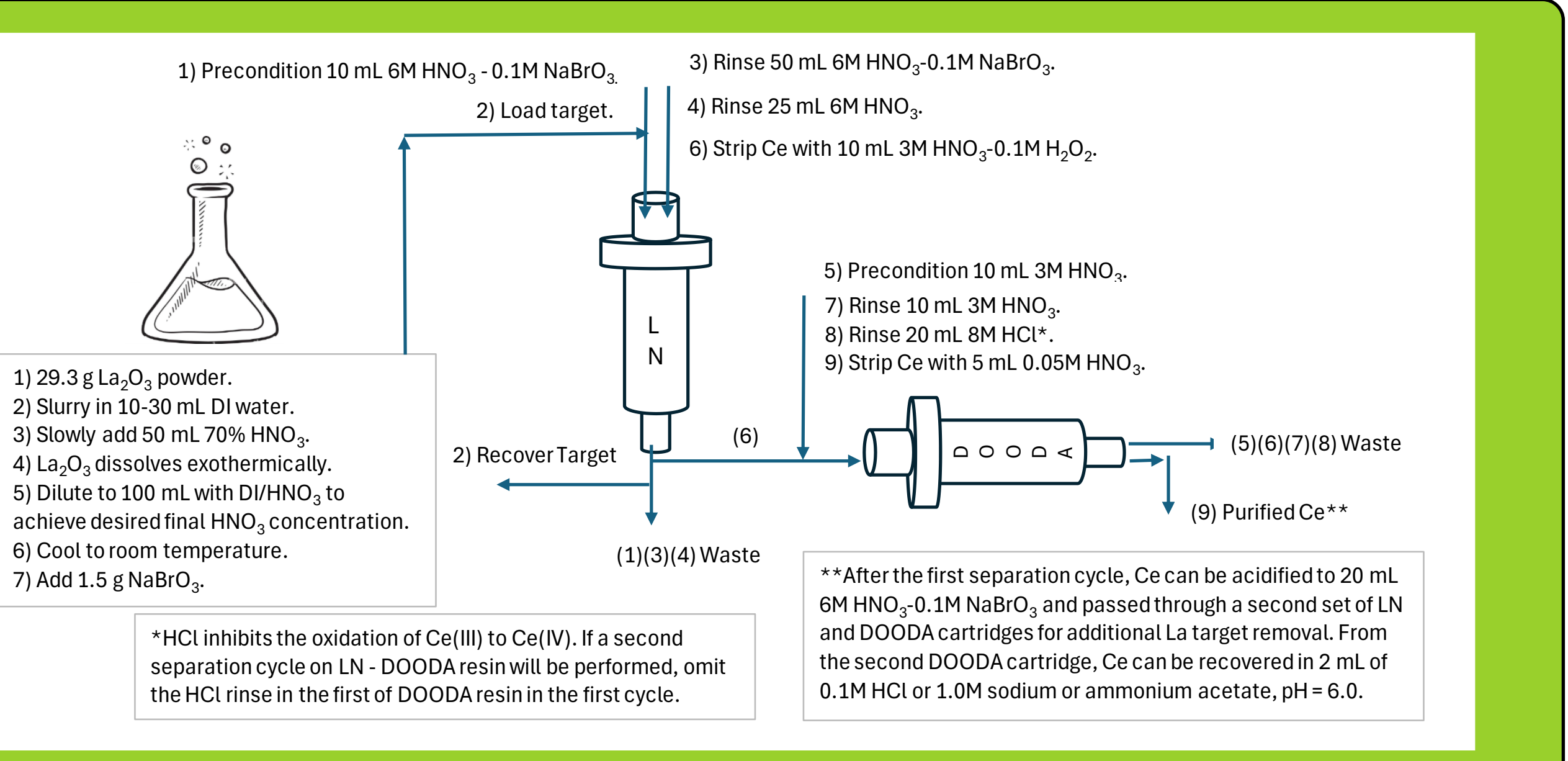
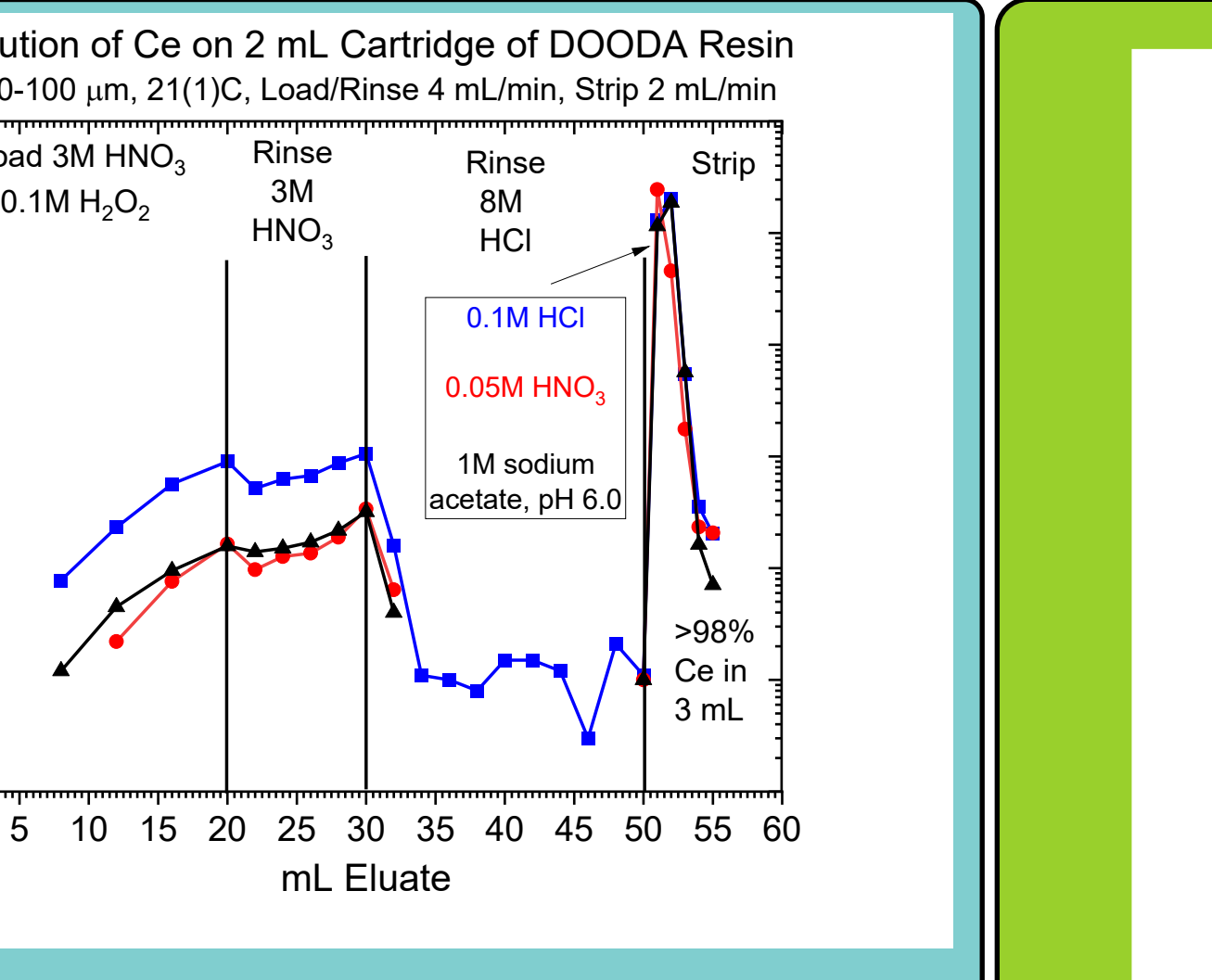
EXC Resins contain lipophilic extractants physisorbed onto an inert porous support. The extractant is not covalently bonded to the support, but held in the pores of the resin through hydrophobic interactions. This limits the mobile phases compatible with EXC resins to aqueous solutions. However, the resulting material retains the selectivity of the extractant in liquid-liquid solvent extraction.

Primary Column Batch retention data for Ce exhibited a positive correlation with the concentration of HNO₃, NaBrO₃, and La(NO₃)₃. Higher concentrations of HNO₃ and NaBrO₃ promote more efficient oxidation to Ce(IV), while higher HNO₃ and La(NO₃)₃ concentrations provide NO₃⁻ to promote extraction via the neutral and anion exchange mechanisms. Preliminary column experiments were performed with all resins using 1 gram of La. For the LN, LN2, LN3 resins, Ce recovery ranged from 94-96%, while for the UTEVA resin Ce recovery was 65-70%, UTEVA-2 94-95%, and UTEVA-3 91-95%. Recovery of Ce from the loaded resins was tested using 1.0M HNO₃ with 0.1M H₂O₂ or ascorbic acid added to reduce Ce(IV) to Ce(III). Ce was recovered in a smaller volume using H₂O₂ as the reducing agent, so subsequent experiments utilized only 1-3M HNO₃ + 0.1M H₂O₂ to recover Ce. Up to 3M HNO₃ did not decrease the efficiency of Ce recovery from the LN or UTEVA resins. Full scale tests with 25 grams of La were performed on 2 mL cartridges of LN and MP-1 resins. From 2.6M HNO₃, significant loss of Ce was observed during loading of LN resin, likely due to incomplete oxidation of Ce(III) to Ce(IV). Increasing to 5M HNO₃ decreased Ce breakthrough and led to >99% recovery of Ce on LN resin. Separation on MP-1 required 6-8M HNO₃ due to the lower retention of Ce, yielding 82% Ce recovery. The higher HNO₃ concentration used in the MP-1 separation also led to gas evolution, likely Br₂.



Secondary Column After recovery from the primary column in HNO₃-H₂O₂, the Ce can be retained on a secondary column of DGA or DOODA resin. The secondary column does not provide additional decontamination from La, but does allow concentration of the Ce, removal of NaBrO₃, Br⁻, Br₂, and H₂O₂, and exchange of the matrix from HNO₃ to HCl or buffer. DGA, normal or branched can be used for recovery of Ce in HCl, while DOODA resin allows recovery in dilute HNO₃ or HCl or 1M sodium or ammonium acetate buffer. From a 2 mL cartridge of DOODA resin, >98% of the Ce can be recovered in 2-3 mL of 0.05M HNO₃, 0.10M HCl or 1.0M ammonium acetate, pH 6.0. For additional decontamination from La, the Ce can be stripped from the primary column directly onto DOODA resin. Omitting the HCl rinse, the Ce is then recovered from the DOODA resin in 0.05M HNO₃, HNO₃ and NaBrO₃ are added, and a second separation cycle is performed on LN and DOODA or DGA resins.



Flowsheet The complete flowsheet for separation of Ce from 25 grams of La is presented above. After a single LN - DOODA resin cycle, stripping the Ce from DOODA in 10 mL of 0.05M HNO₃, the recovery of Ce was 98% with 1.5-2.5 ug of La impurity. Following two LN - DOODA cycles, recovering Ce from DOODA in 3 mL of 1.0M ammonium acetate, pH 6.0 in the second cycle, the recovery of Ce was >95% with the lanthanum impurity below the limit of detection via atomic emission spectrometry (AES), < 0.01 ug La.

References

- 1) a) T.A. Bailey, et al. "Developing the ¹³⁴Ce and ¹³⁴La pair as companion positron emission tomography diagnostic isotopes for ²²⁵Ac and ²²⁷Th radiotherapeutics," Nature Chemistry, 13, pp. 284-289 (2021). b) K.N. Boba, et al. "Evaluation of ¹³⁴Ce/¹³⁴La as a PET imaging theranostic pair for ²²⁵Ac α-Radiotherapeutics," Journal of Nuclear Medicine, 64(7), pp. 1076-1082 (2023).
- 2) a) J. Zhao, et al. "Liquid-Liquid extraction of cerium(IV) from nitric acid media by di-(2-ethylhexyl)-2-ethylhexyl phosphonate (DEHEHP)," Solv. Extr. Ion Exch., 22(3), pp. 429-447 (2004). b) O.S. Helaly, et al. "Extraction of cerium(IV) using tributyl phosphate impregnated resin from nitric acid medium," Trans. Nonferrous Met. Soc. China, 22, pp. 206-214 (2012).
- 3) 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).

