Characterization of Extraction Chromatographic Resins based on Monoamide Extractants for the Separation of Transition and Post-Transition Metal Ions

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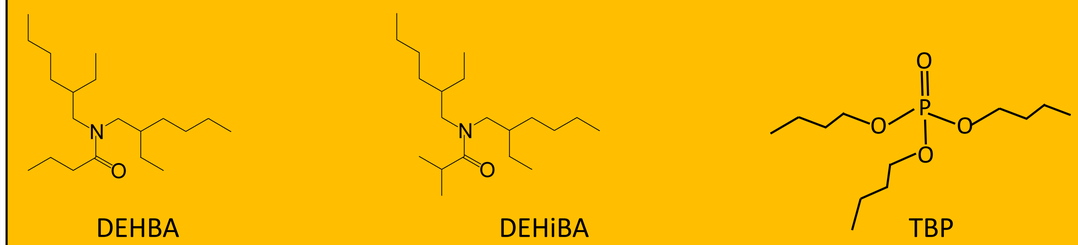
Abstract

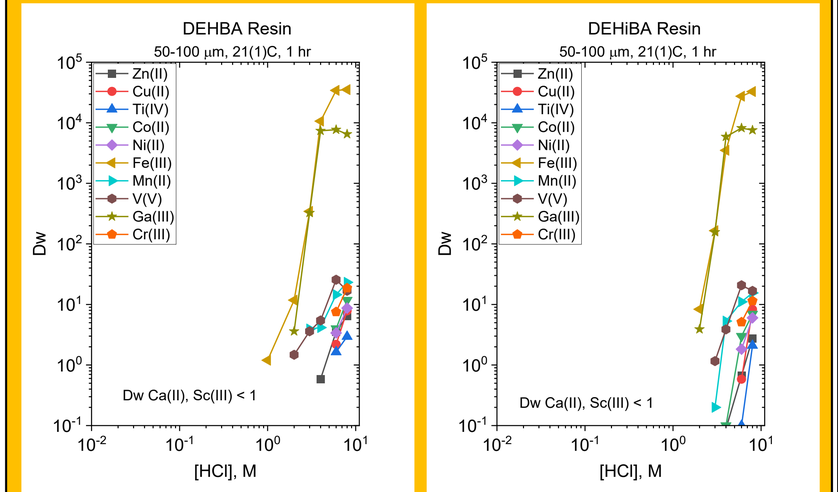
Many radionuclides of the transition and post-transition elements show promise in nuclear medicine imaging and therapy. Monoamide extractants have been studied in solvent extraction processes for the processing of spent nuclear fuel but also exhibit interesting selectivity from hydrochloric acid for important target/product pairs of transition and post transition metal ions. Chromatographic techniques using extraction chromatographic (EXC) materials are commonly used to efficiently separate metal ions from complex mixtures. Extraction chromatography resins produced with monoamides Di-(2-ethylhexyl) butyramide (DEHBA) and Di-(2-ethylhexyl)isobutyramide (DEHiBA) were studied in batch contact methods for the extraction of selected transition and post-transition metals from hydrochloric and nitric acid. From nitric acid, there was little extraction. However, from hydrochloric acid, the EXC resins exhibited selectivity that allows for the efficient separation of indium from cadmium, gallium from zinc, and mercury from gold. Based on the batch retention data, chromatographic separation methods for the separation of ^{111}In from simulated cadmium targets, ^{67}Ga from simulated zinc targets, and ^{197m}Hg from gold targets were developed. The methods allow for high yields of the target radionuclides while also removing the target material and common metal ion impurities and byproducts.

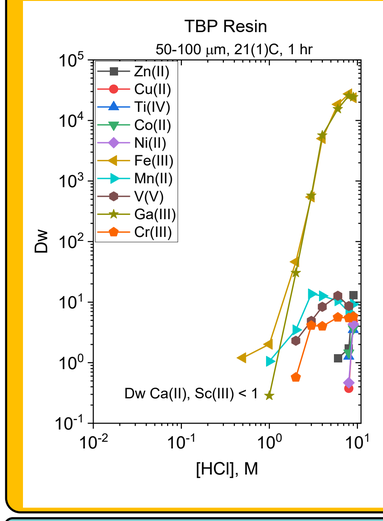
Monoamide Extractants and TBP



The monoamide extractants DEHBA and DEHiBA have been studied as CHON-only (carbon, hydrogen, oxygen, nitrogen) alternatives to tributylphosphate (TBP) for spent nuclear fuel reprocessing by solvent extraction. The monomides exhibit similar extraction properties to TBP and decompose into less troublesome compounds when exposed to harsh chemical conditions or radiation. [1]

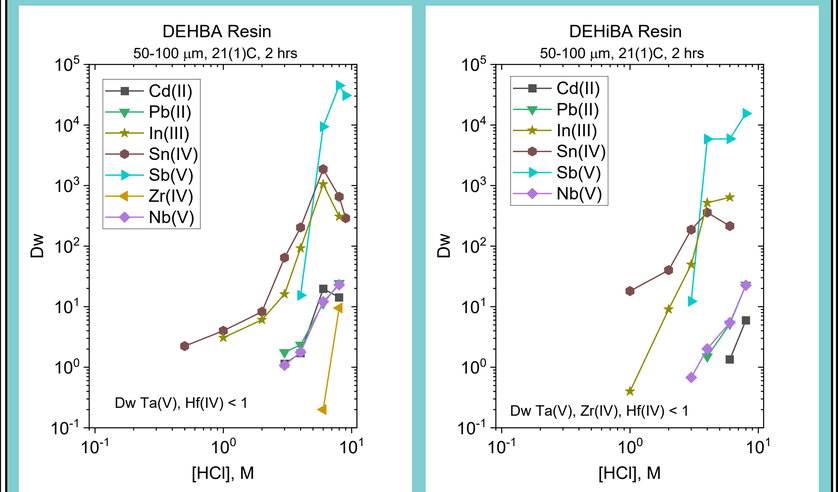
1st Row Transition Metals

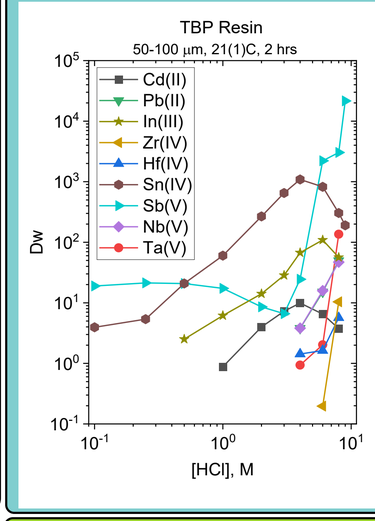




From HNO_3, TBP and the monoamide extractants DEHBA and DEHiBA are poor extractants for most metal ions. However, from HCl, Ga(III) and Fe(III) are strongly extracted as the $[GaCl_4]^-$ and $[FeCl_4]^-$ anions by the protonated extractants R=O- - H^+. This selectivity allows for the scavenging of Fe(III) and Ga(III) from HCl solutions of other mtetal ions and the separation of Ga(III) from Zn(II) targets in the production of ^{67}Ga via the ^{67}Zn(p, n) ^{67}Ga and ^{68}Zn(p,2n)^{67}Zn reactions.

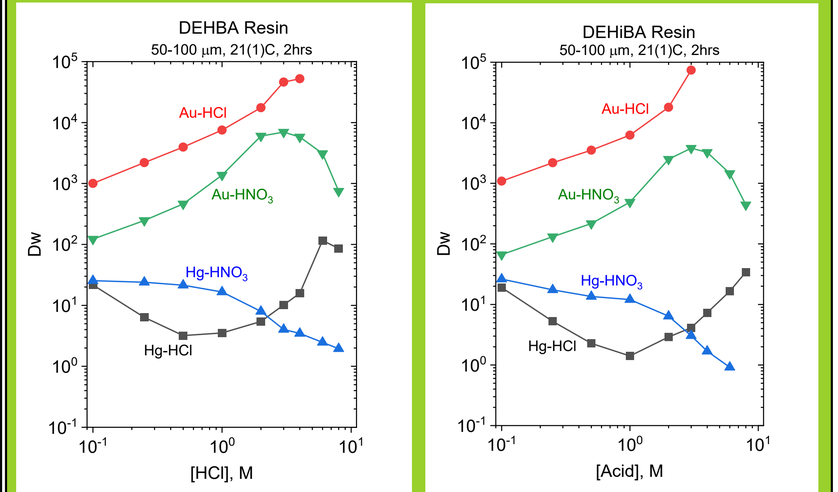
2nd and 3rd Row Transition Metals

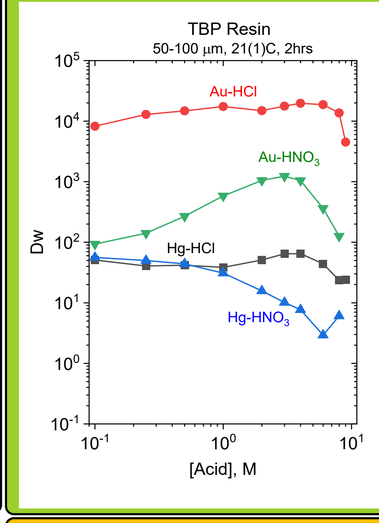




From HCl, In(III), Sn(IV), and Sb(V) are retained by the monoamide and TBP resins, with the DEHiBA resin offering the highest selectivity of In(III) over Cd(II). This selectivity may be utilized for the separation of In from Cd targets in the production of ^{111}In via the ^{111}Cd(p, n)^{111}In and ^{112}Cd(p,2n) ^{111}In reactions. The ^{111}In can be re-covered from the monoamide resins in dilute HCl or buffer solution for further purification on additional columns.

Hg and Au

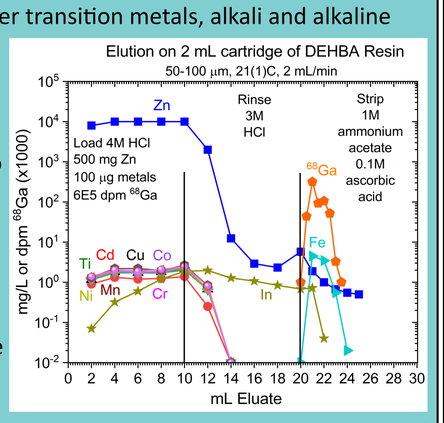


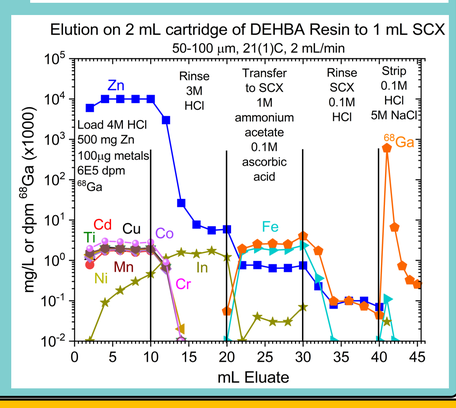


From HNO_3 and HCl TBP and the monoamide extractants strongly retain gold, while poorly retaining Hg(II). This selectivity allows for the separation of Hg(II) from gold targets in the production of ^{197m}Hg/^{197g}Hg via the ^{197}Au(p, n)^{197}Hg reaction. The monoamide resins exhibit higher retention of Au(III) and lower retention of Hg(II) than the TBP resin, allowing removal of Au from the ^{197m}Hg/^{197g}Hg from gold targets dissolved in HNO_3/ HCl and diluted with water..

Ga from Zn

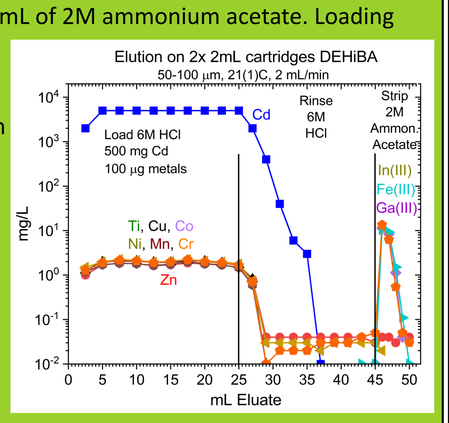
To simulate the purification of ^{67}Ga from proton irradiated zinc, 500 mg of zinc as metal shot or ZnO powder were dissolved with a minimum amount of 1-2M HCl at room temperature. 100 μg of other metal ions and ^{68}Ga tracer were added, and the solution diluted to 10 mL of 4M HCl. The solution was loaded onto a 2 mL cartridge of DEHBA resin trapping the ^{68}Ga. The DEHBA was rinsed with 10 mL of 3M HCl to complete Zn removal and provide additional decontamination from other transition metals, alkali and alkaline earth metals and Al. ^{68}Ga was then recovered from the DEHBA in 10 mL of ammonium acetate buffer with 0.1M ascorbic acid, reducing Fe(III) to Fe(II). Loading the acetate/ascorbic acid buffer onto a 0.25 mL cartridge of strong acid cation exchange silica (SCX) traps ^{68}Ga, providing additional decontamination from Zn and Fe. The SCX cartridge is rinsed with 10 mL of 0.1M HCl for additional cleaning and acetate/ascorbate removal, and ^{68}Ga is recovered in 2-3 mL of 0.1M HCl -5M NaCl.

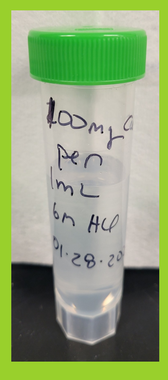




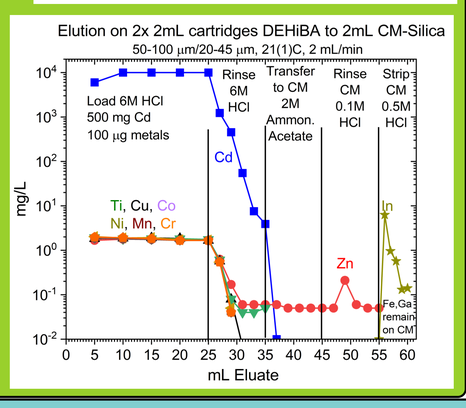
In from Cd

To simulate the purification of ^{111}In from proton irradiated Cd, 500 mg of cadmium metal turnings were dissolved with 6M HCl and heat, concentrated and reconstituted in 25 mL of 6M HCl. 100 μg of other metal ions were added, and the solution was loaded onto 2x 2mL cartridges of DEHiBA resin. The DEHiBA was rinsed with 6M HCl to complete Cd removal and decontaminate from Ti, Cu, Co, Ni, Mn, Cr, alkali metals, alkaline earths, and Al. In was recovered from the DEHiBA with 10 mL of 2M ammonium acetate. Loading the Indium in ammonium acetate onto a 2mL cartridge of CM-silica provides additional decontamination from Zn(II), Cd(II), Ga(III) and Fe(III). Indium is recovered from the CM-silica with 3 mL of 0.5M HCl.

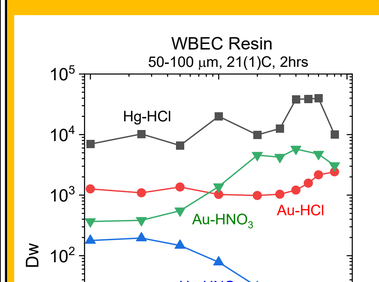




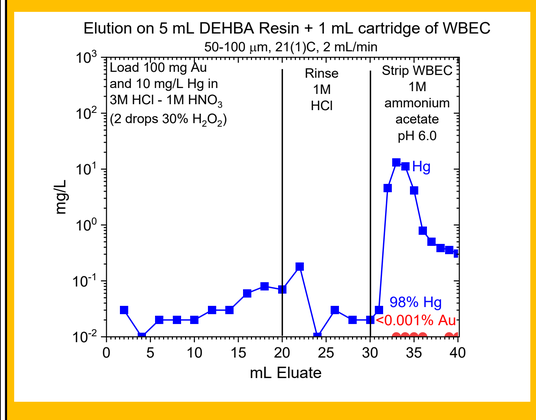
Cd metal turnings dissolved in 6M HCl



Au from Hg



To simulate the purification of $^{197m/197g}$Hg from proton irradiated Au, 100 mg of gold foil was dissolved with 4:1 (v:v) HCl:HNO_3, diluted 4x with DI water, spiked with 100 mg Hg, and loaded directly onto 3x 2 mL cartridges (5 mL total resin) of DEHBA resin and 1 mL cartridge of WBEC resin. The DEHBA retains Au, while the Hg is retained on the WBEC. The Hg is rinsed through the DEHBA with 10 mL of 1M HCl, and Hg is recovered from the WBEC with 5 mL of 1M ammonium acetate, pH 6.0, avoiding time consuming evaporations.



3x 2mL DEHBA cartridges loaded with 100 mg Au. (~35% of capacity)

Conclusions/Future Work

EXC Resins based on the monamides DEHBA and DEHiBA have been characterized for the extraction of selected first and second row transition metals, Hg and Au from HCl, and purification methods developed for ^{67}Ga from Zn, ^{111}In from Cd, and $^{197m/197g}$Hg from Au. Additional work will include evaluation of additional metals and separation systems, as well as optimization of the In and Hg purification using ^{111}In and ^{197}Hg and determination of the effects of larger target sizes on the Ga/Zn, In/Cd and Hg/Au systems.

References

1) www.lhnb.fr/nuclides/Ga-67_tables.pdf

2) The radiochemistry of Cadmium, National Academy of Sciences, National Research Council, Nuclear Science Series, J.R. Devoe, January, 1960.

3) The radiochemistry of Zinc, National Academy of Sciences, National Research Council, Nuclear Science Series, H.G. Hicks, June, 1960.

4) Chen, S.; Bas, M.; Happel, S.; Randhawa, P.; McNeil, S.; Kurakina, E.; Zeisler, S.; Maskell, K.; Hoehr, C.; Ramogida, C.F.; Radchenko, V. Determination of distribution coefficients of mercury and gold on selected extraction chromatographic resins - towards an improved separation method of mercury-197 from proton-irradiated gold targets, Journal of Chromatography A,1688, (2023). https://doi.org/10.1016/j.chroma.2022.463717.