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The Chromatographic Separation of Manganese from Simulated Chromium Targets

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Abstract

Manganese-52 is a promising positron emitting radionuclide with a half-life of 5.592 days produced via proton irradiation of chromium targets. Chromatographic techniques using ion exchange and extraction chromatographic (EXC) materials are commonly used to efficiently separate metal ions from complex mixtures. An EXC resin produced with the N,N,N',N'-tetraoctyl-3,6-dioxaoctane diamide (DOODA) extractant exhibits high selectivity for manganese over chromium and other transition metal ions that may be present as impurities in target material or as byproducts from proton irradiation. The DOODA EXC resin was characterized via batch contact experiments from nitric and hydrochloric acids to determine the retention of selected metal ions, including Mn, Cr, and selected main group, transition, rare earth and actinides. Based on the batch retention data, a column chromatographic method was developed to separate Manganese(II) from chromium and other transition metals and main group metals that may be present as impurities in chromium targets or as byproducts from the proton irradiation of chromium. From nitric acid or mixtures of nitric and hydrochloric acid, manganese is efficiently retained and separated from chromium and all other common impurities on the DOODA resin. The manganese can then be recovered in dilute HCl, HNO3 or acetate buffer and further purified on columns of weak cation exchange (CM) silica.

Production and Target Dissolution

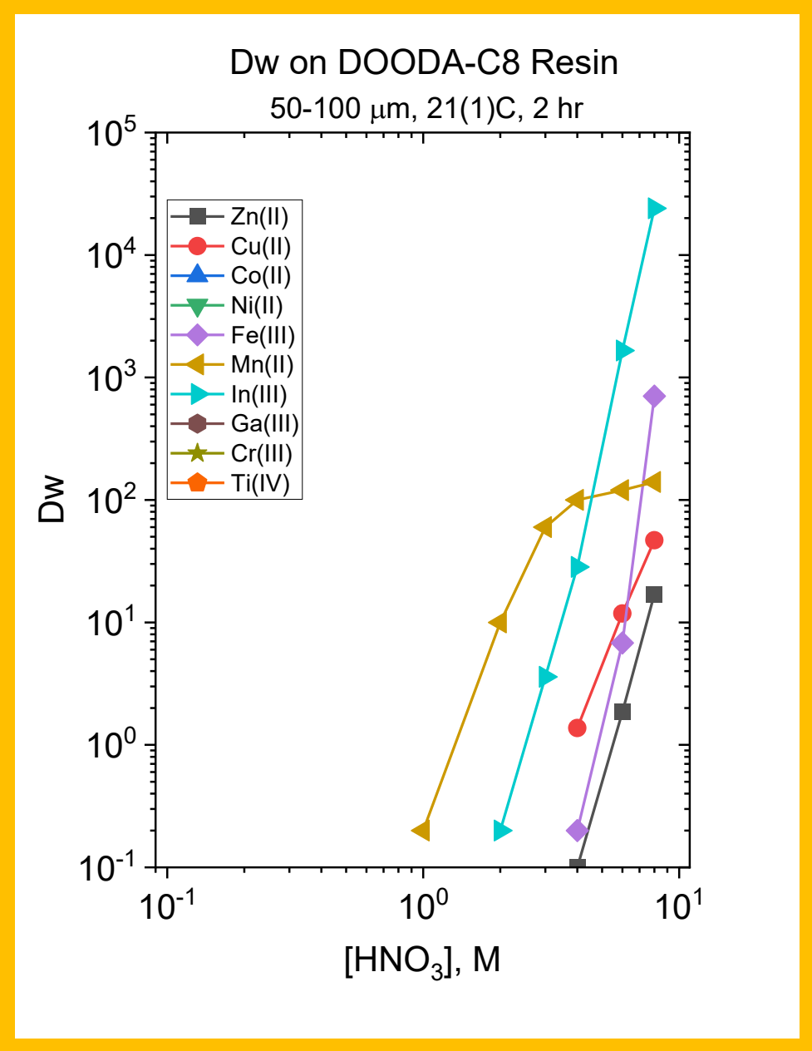
^{52}Mn ($t_{1/2}$ = 5.592 days) decays via electron capture and positron emission and is produced by proton or deuteron bombardment of chromium targets. Chromium metal can be dissolved using HCl at elevated temperature, producing Cr(II) which quickly oxidizes to Cr(III) through interaction with dissolved O_2 or added H_2O_2. HNO_3 tends to passivate chromium metal forming resistant chromium oxide, preventing direct dissolution of chromium metal with HNO_3 or $HNO_3 + H_2O_2$. However, once dissolved in HCl, the chromium solution can be converted to HNO_3 by the addition of HNO_3 and heating to drive off HCl.

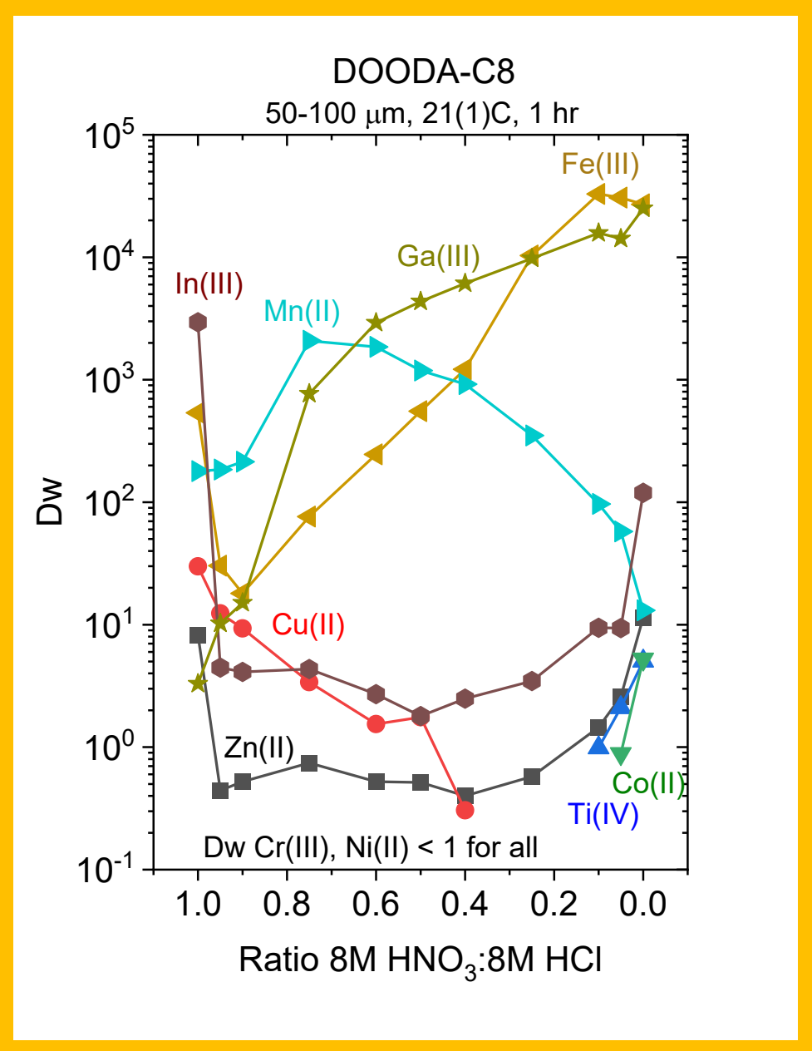
$$Cr_{(s)} + 2HCl \longrightarrow Cr^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + H_{2(g)}$$

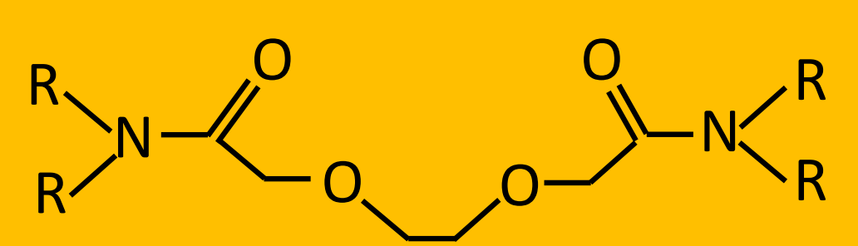
$$4Cr^{2+}_{(aq)} + O_{2(g)} + 4H^{+}_{(aq)} \longrightarrow 4Cr^{3+}_{(aq)} + 2H_2O$$

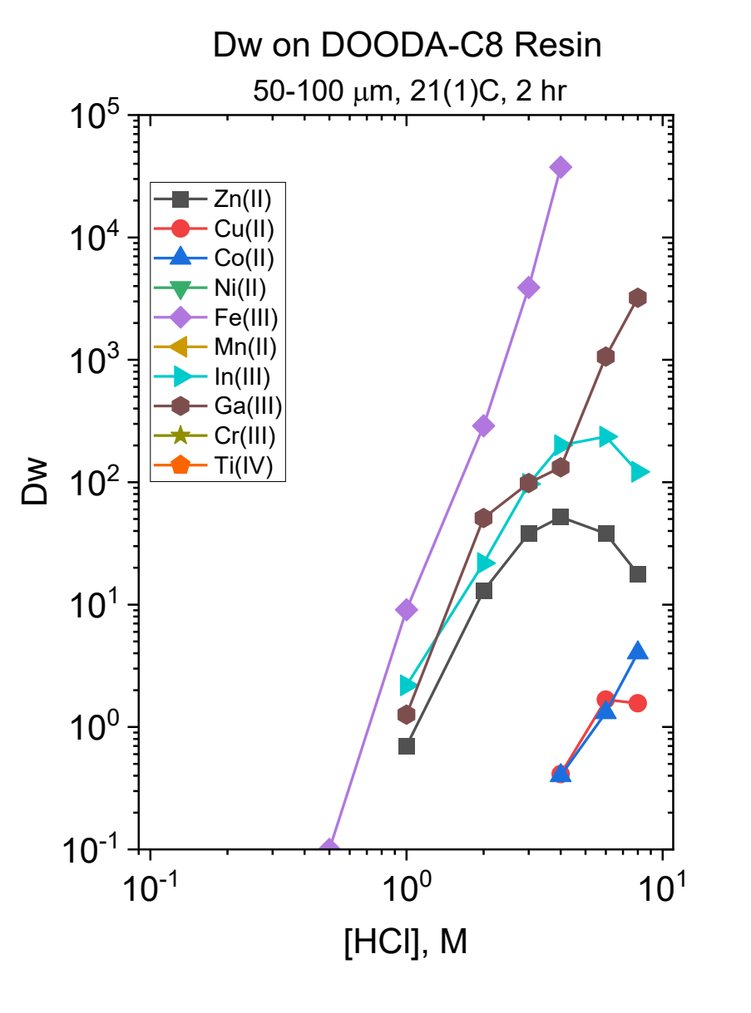
^{nat}Cr (p,xn) ^{52}Mn
^{52}Cr (p,n) ^{52}Mn
^{nat}Cr (d,x) ^{52}Mn
^{52}Cr (d,2n) ^{52}Mn

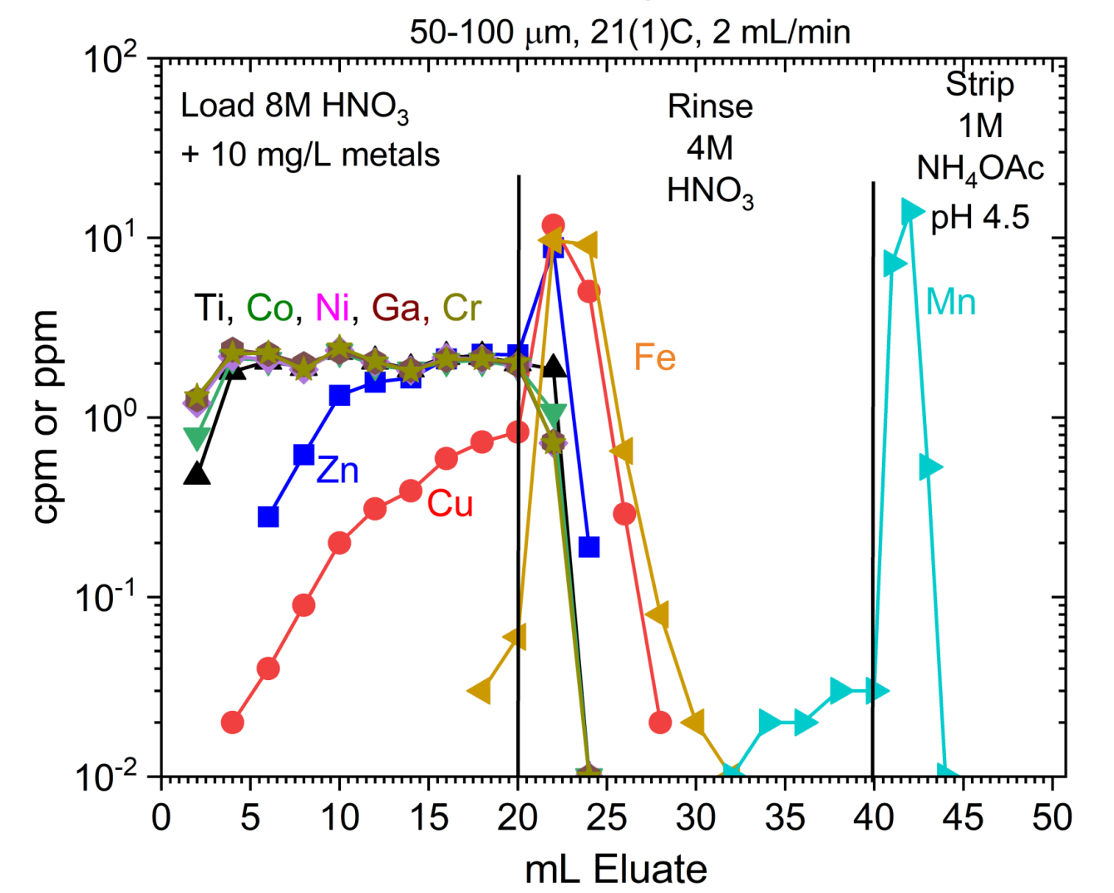
DOODA(C8) Resin



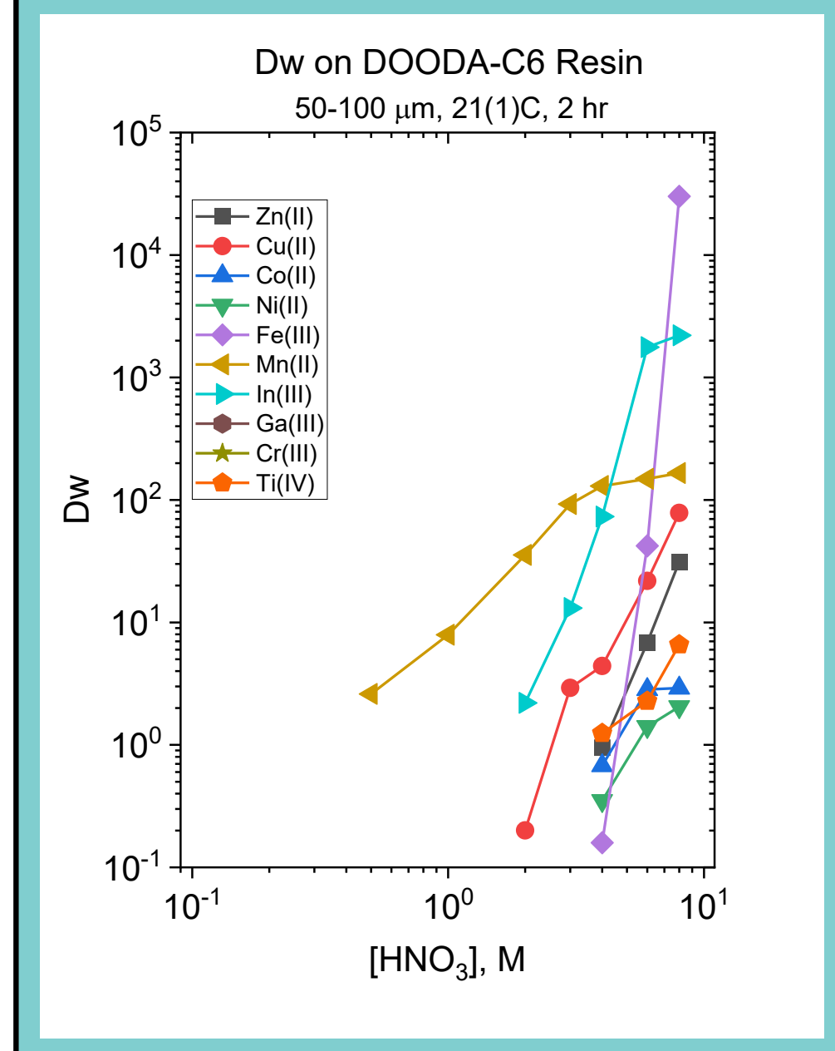


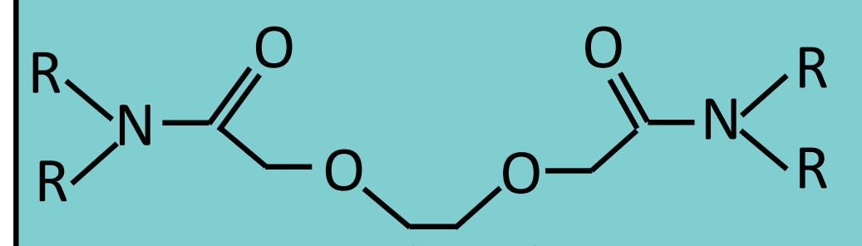

R = n-octyl

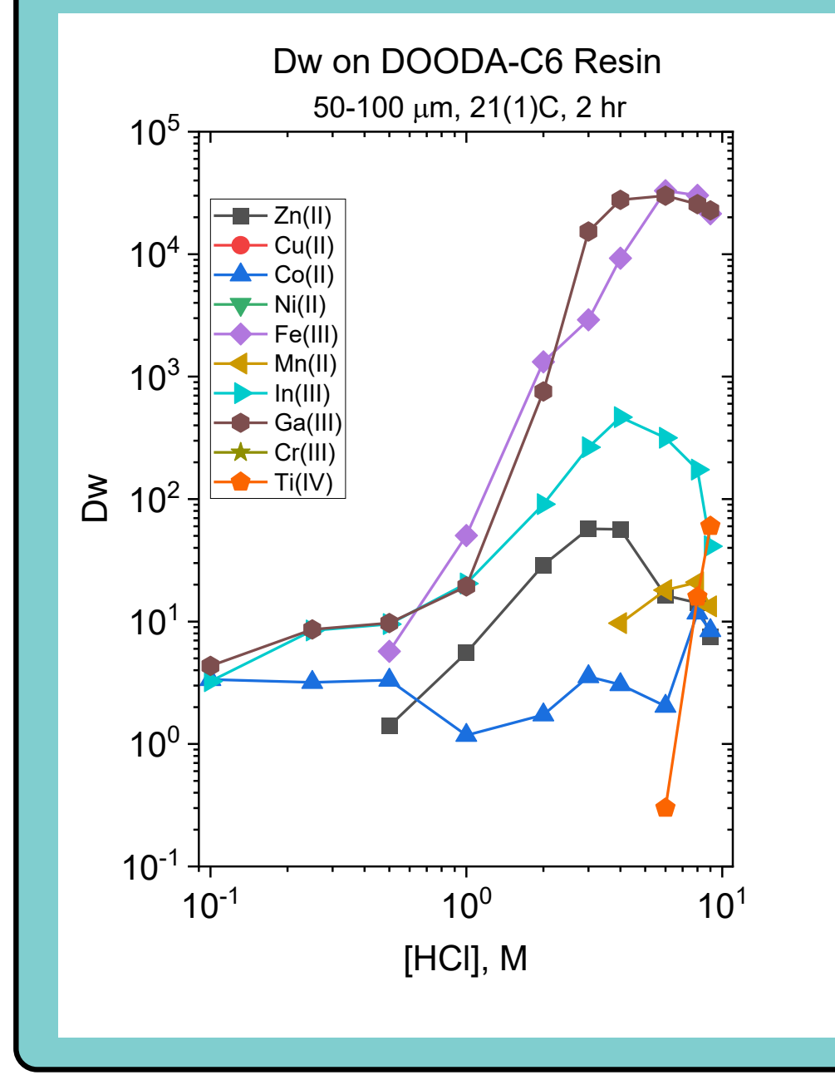




DOODA(C6) Resin




R = n-hexyl

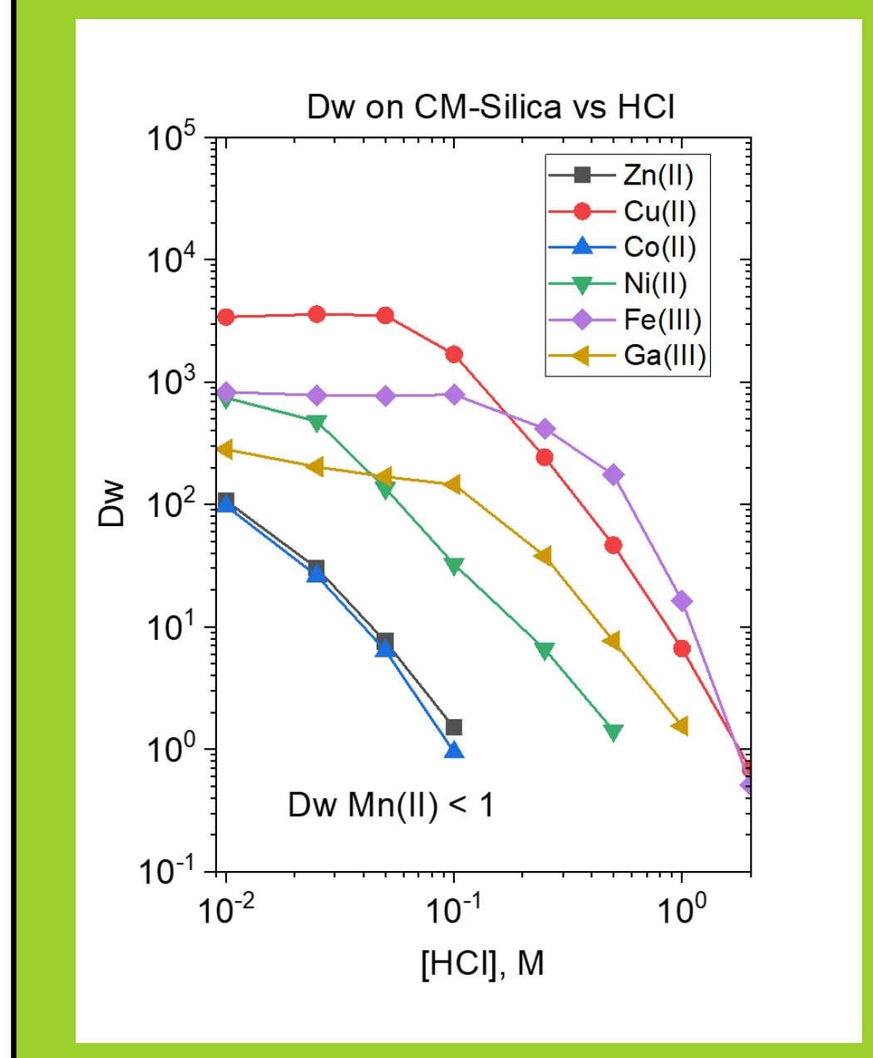


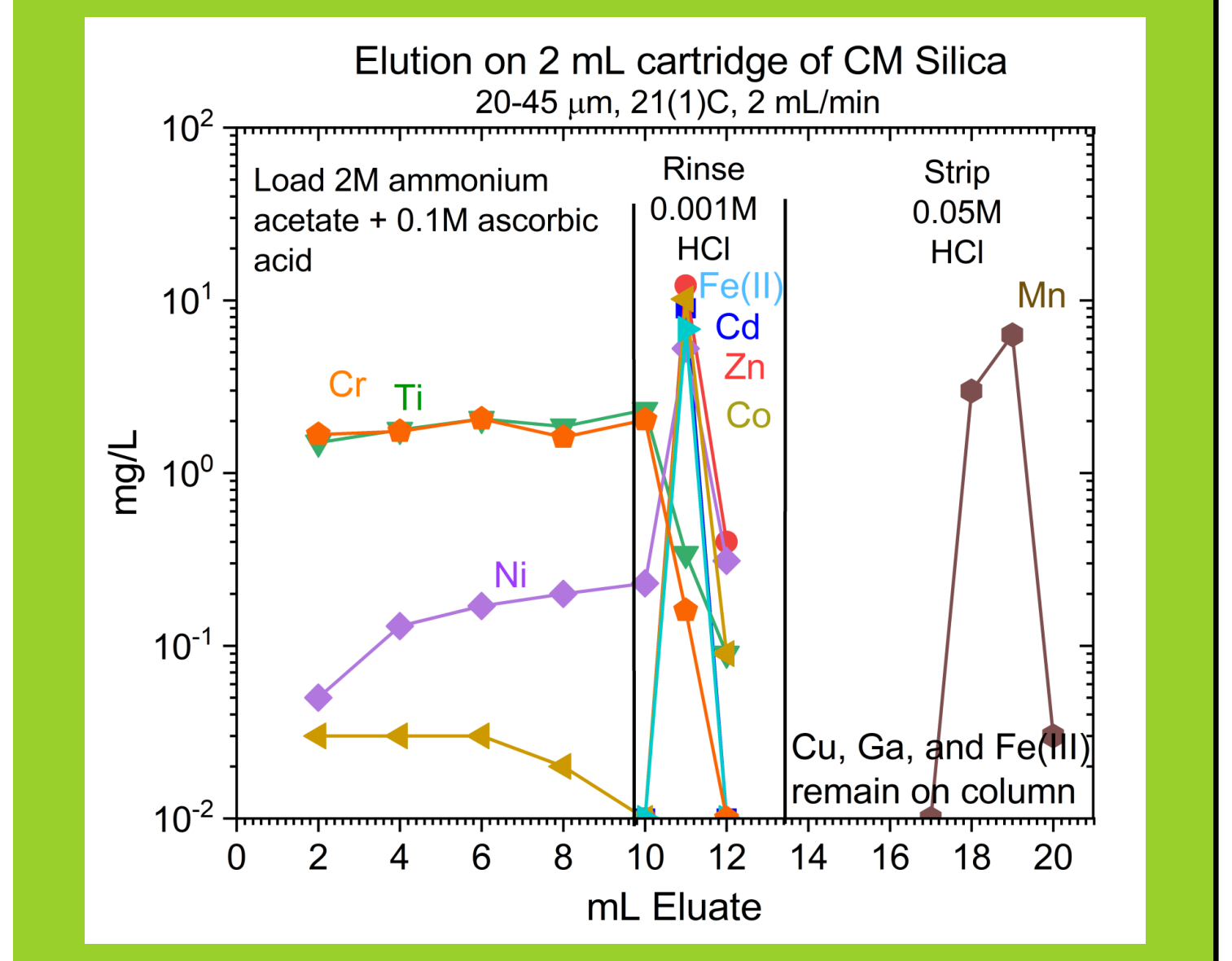
Extraction chromatography resins based on the N,N,N',N'-tetraoctyl-3,6-dioxaoctane diamide (DOODA) extractant exhibit excellent selectivity for Mn(II) over Cr(III) in HNO_3, facilitating the separation of ^{52}Mn from large chromium targets from HNO_3 or mixtures of HNO_3 and HCl, since it not practical to dissolve chromium metal directly in HNO_3.

Hundreds of milligrams of Cr are dissolved in HCl, concentrated and dissolved in 8M HNO_3, yielding a feed of Mn, Cr, and other impurities in 8M HNO_3 withresidual HCl. The residual HCl does not adversely affect the Mn/Cr separation on the DOODA resin for up to 50% residual HCl, with the HCl actually improving decontamination from Zn(II), Cu(II), and In(III).

The feed is loaded onto the DOODA resin, where Mn(II), Fe(III), Cd(II), Cu(II) are retained, while Cr (III), Ga(III) and most other transition metals are rejected. Rinsing the DOODA with 4M HNO_3 removes Fe(III) and Cu(II) and residual Cr(III), and Mn(II) can be recovered in dilute HNO_3, HCl or acetate buffer. Replacing the n-octyl groups of DOODA-C8 with n-hexyl groups (DOODA-C6) increases Mn retention and capacity and allows use of smaller separation columns.

Weak Acid Cation Exchange Silica

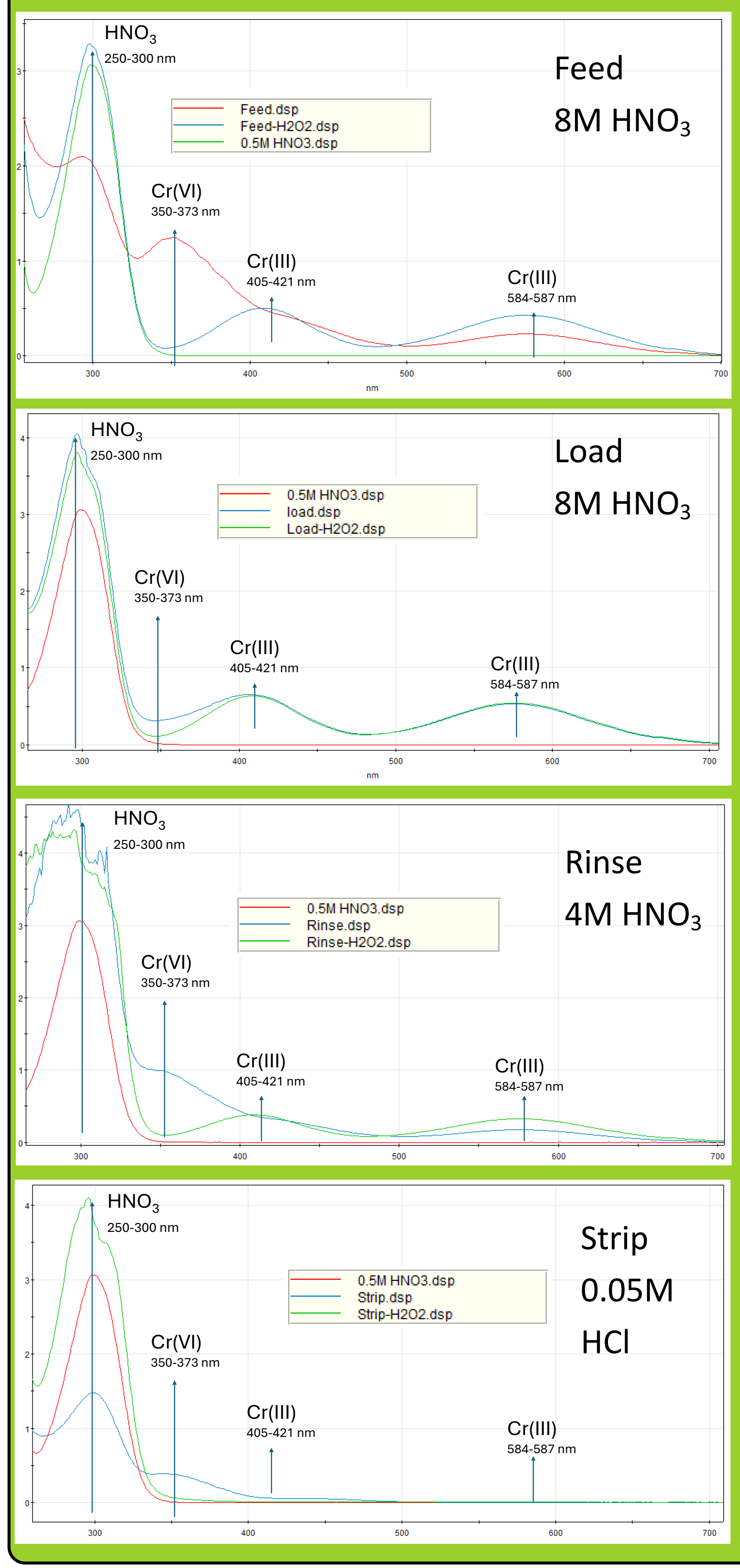




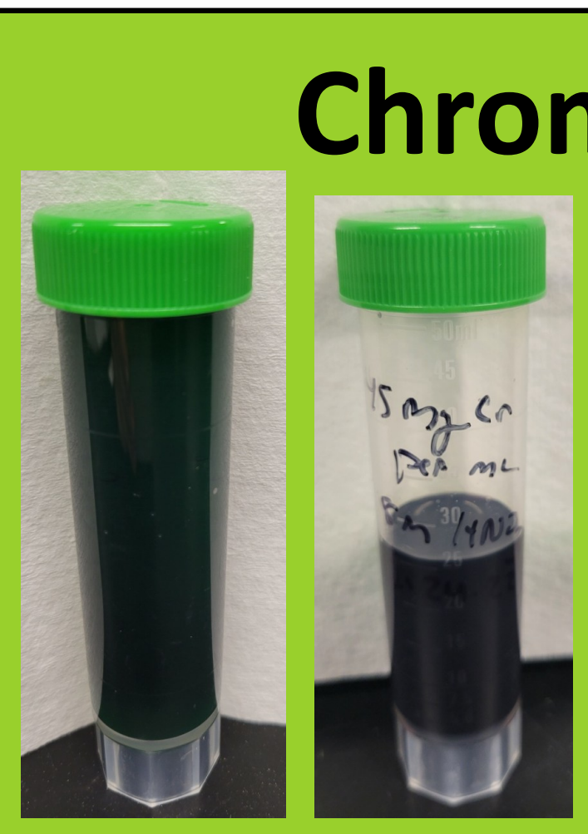
Weak cation exchange silica (CM) functionalized with amino-methyl carboxy groups retain metal ions from dilute HCl or up to 6M ammonium or sodium acetate buffer, allowing transfer of metals from the DOODA-C6 primary separation column to the CM silica for concentration and additional purification. Recovering Mn from the DOODA-C6 in 2M ammonium acetate buffer neutralizes the residual HNO_3 from the load and rinse steps, raising the pH so that Mn is retained on the CM silica. Adding ascorbic acid to the ammonium acetate reduces Fe(III) to Fe(II), improving iron decontamination on the CM silica. Following a small rinse of pH 3 HCl to displace acetate, the Mn is recovered from the CM silica in 2-3 mL of 0.05 M HCl. In addition to the concentration, pH adjustment, and HNO_3 removal, the bonded silica material also reduces the potential for organic impurities than can be leached from the extraction chromatography resin primary separation column.

Chromium oxidation state

UV-VIS Spectra of fractions from DOODA-C6

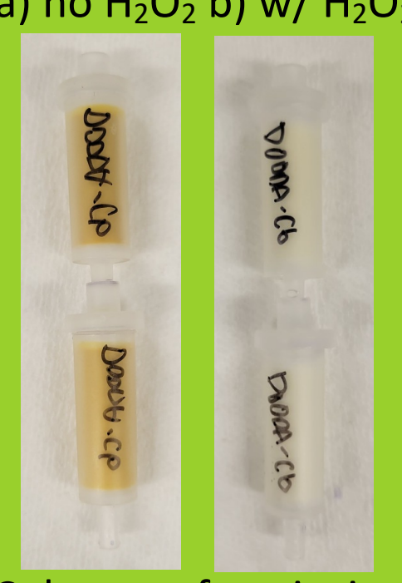


Freshly dissolved Cr(III) in HCl (green)

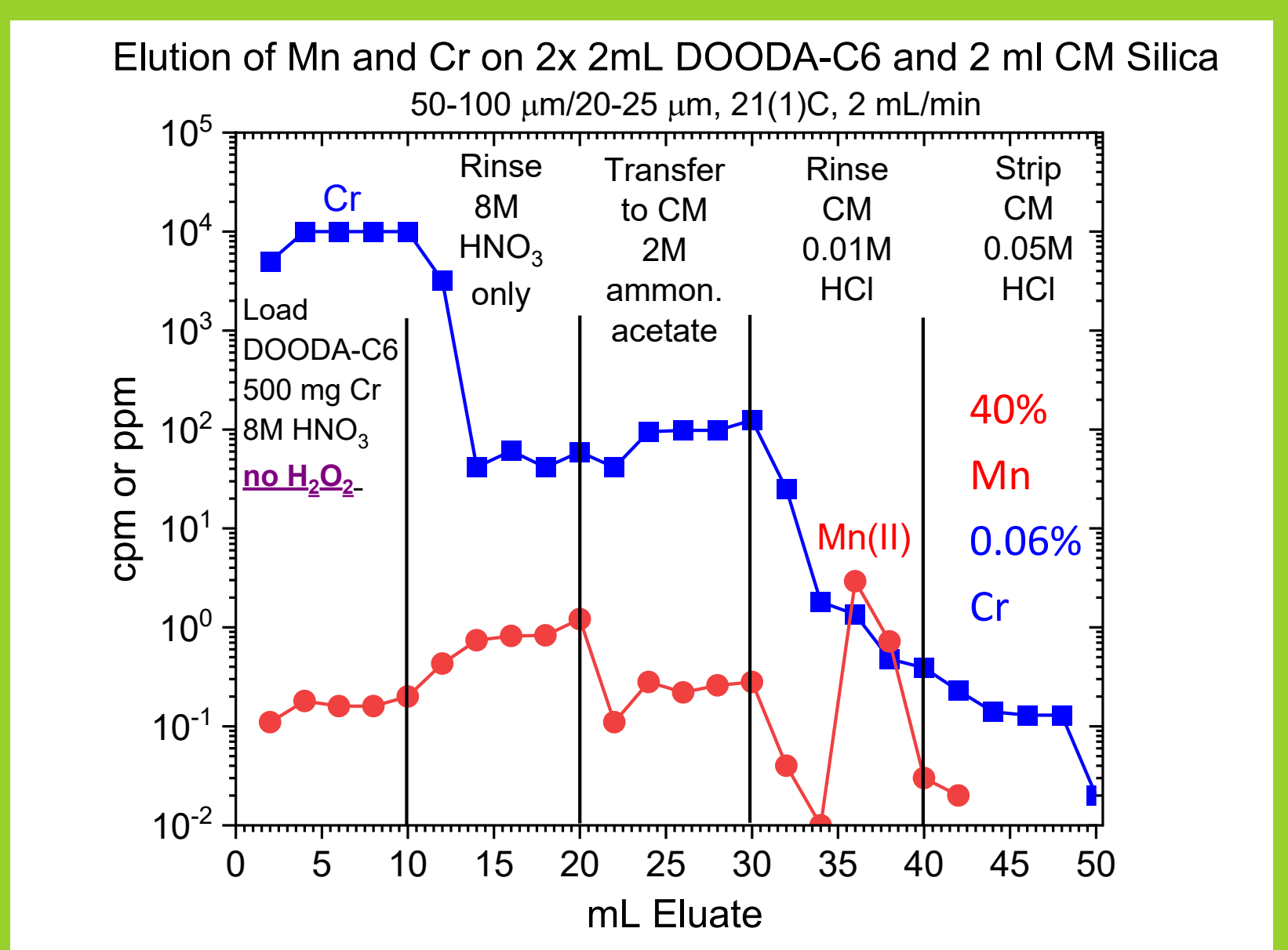


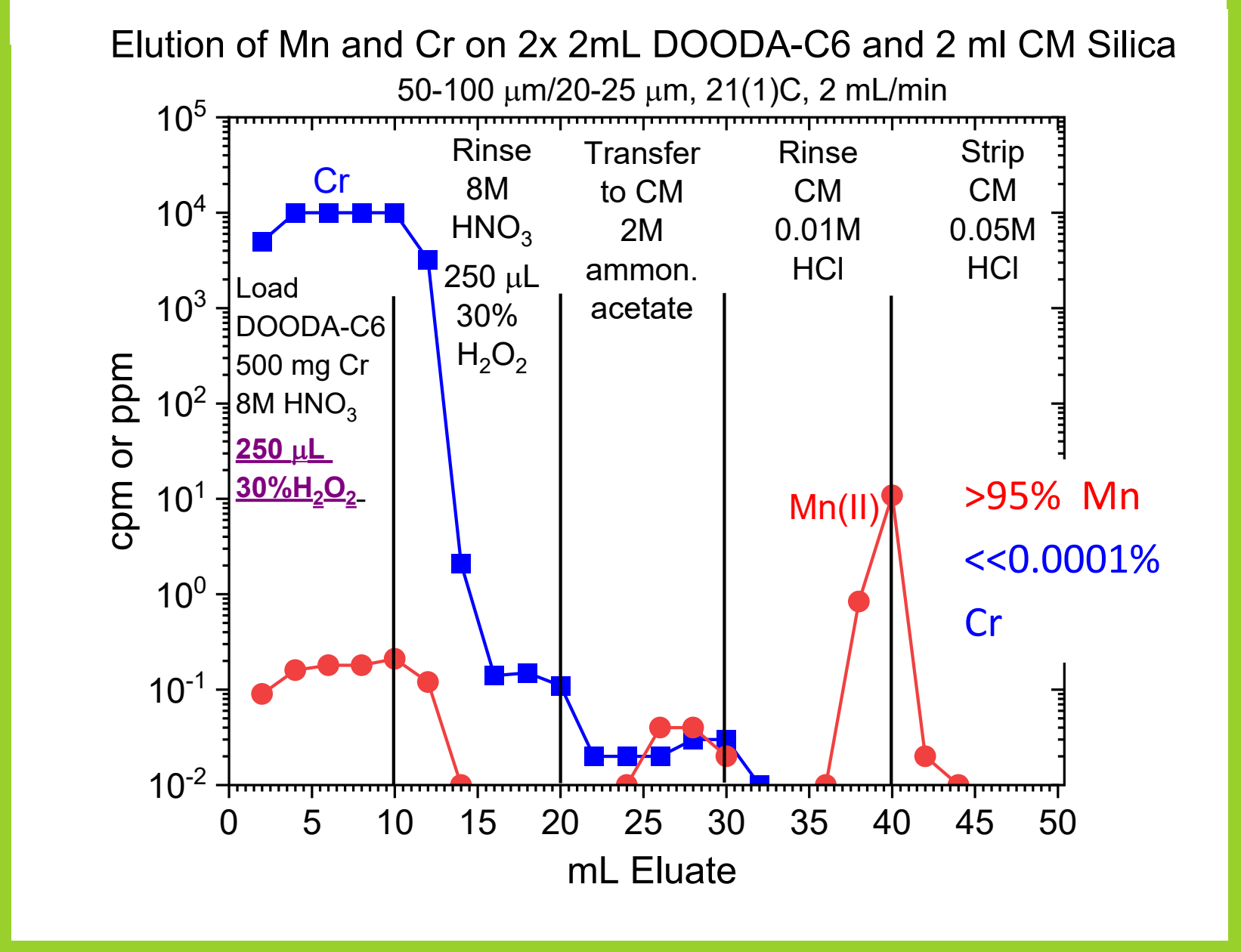
Cr(III) in HNO_3 (purple)

Columns after loading:
a) no H_2O_2 b) w/ H_2O_2



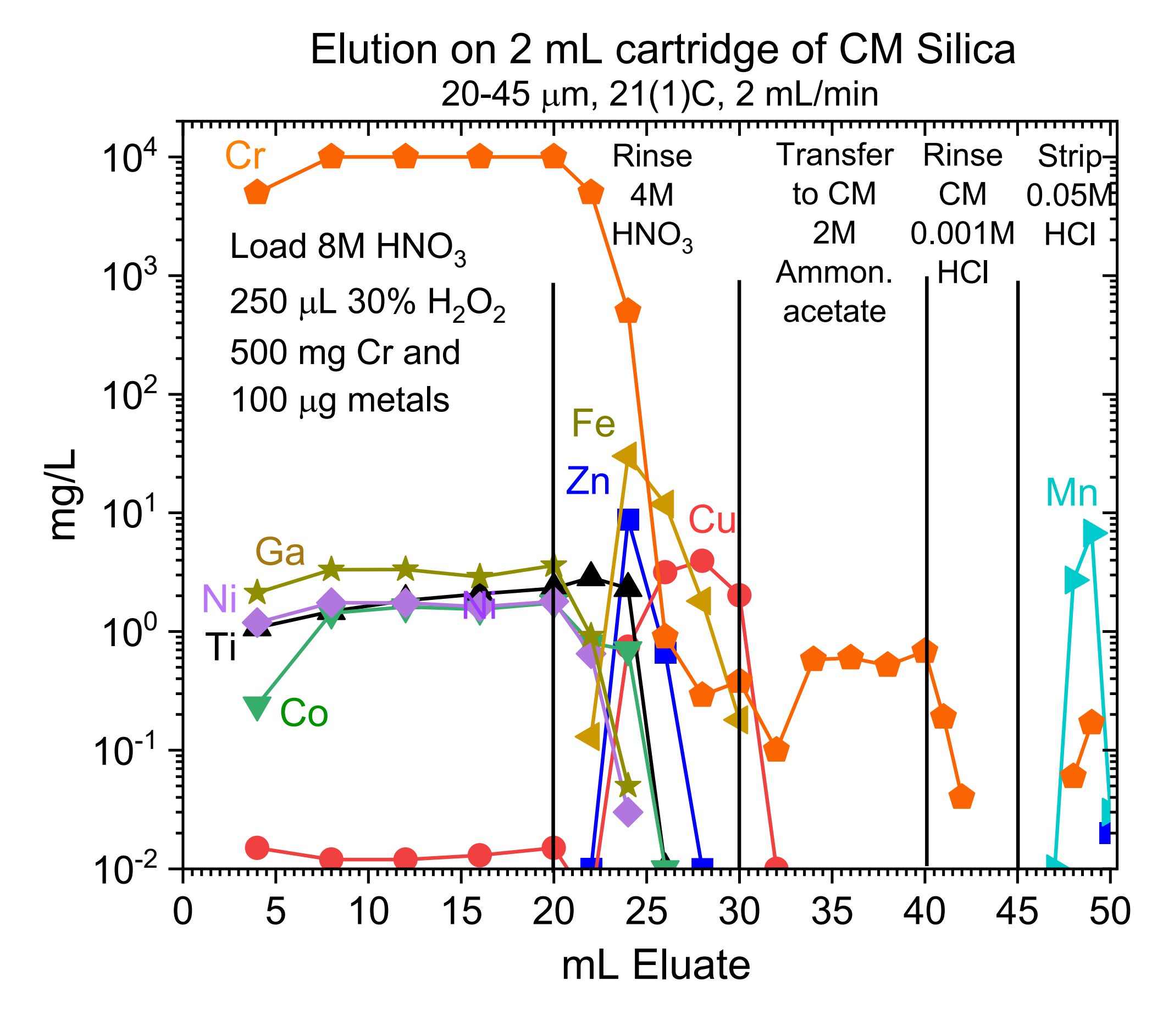
Columns after rinsing:
a) no H_2O_2 b) w/ H_2O_2





Chromium can exist in several oxidation states in aqueous solution, predominantly Cr(III)/(VI). The presence of Cr(VI), and potentially Cr(II), decreases the selectivity of the DOODA-C6 resin for Mn(II), leading to lower Mn yields and higher Cr impurities in the purified Mn. Addition of 30% H_2O_2 to the dissolved Cr target material helps to fix the chromium oxidation state to primarily Cr(III). This is demonstrated by the UV-VIS sepctra and column appearance during the various separation steps. Cr(III), purple color, absorbs at 410 nm and 590 nm, while Cr(VI), yellow color, absorbs at 365 nm. Cr(II) peaks at 410 and 568 nm are obscured by Cr(III). HNO_3 is also visible at 300 nm. The yellow Cr(VI) is clearly visible on the columns in the absence of H_2O_2.

Dual Column Separation



Using the DOODA-C6 and CM-Silica columns in tandem, Mn is obtained in higher purity, smaller volume, and lower acidity, than using DOODA-C6 alone and without HNO_3 contamination. The Cr target material is dissolved in HNO_3. H_2O_2 is added to fix the Cr oxidation state to Cr(III). The dissolved target is loaded onto the DOODA-C6. Rinsing with 4M HNO_3 lowers the acidity and removes Fe(II/III), Zn(II) and Cu(II). Mn is recovered from the DOODA-C6 with acetate buffer, which is collected and mixed before loading on the CM-silica. Adding ascorbic acid to the buffer reduces Fe(III) to Fe(II) improving iron decontamination on the CM-Silica. The CM-silica is rinsed with a small volume of 0.001M HCl to displace the acetate, and Mn is recovered in a small volume of 0.05M HCl in >95% yield and no measureable impurities of the first row transition metals, alkali metals, alkaline earths, Pb, Cd or In. The separation process should be adaptable to automation.

Conclusions/Future work

The separation is effective using up to 500 mg of chromium and μg quantities of othe stable metals. Additional work is being performed to understand how larger chromium targets affect the separation chemistry, and partners are being sought to test the chemistry on irradiated targets with ^{52}Mn. Optimization of the chromium target dissolution is also ongoing. Initial work has shown that residual HCl has no adverse effects on the Mn separation chemistry, so dissolution using HCl is also an option. However, the separation on the DOODA-C6 must be carried out in HNO_3.

References

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