ON THE DEVELOPMENT AND CHARACTERISATION OF AN HYDROXAMATE BASED EXTRACTION CHROMATOGRAPHIC RESIN

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Introduction

Zr separation chemistry is of increasing interest in various domains. Long-lived Zr-93 ($t_{1/2}$ = 1.61(6) 10^6 a, E_{β^-}, = 58.5(15) keV with P=73(5)% and 90.3(15) keV with P=27(5)%) frequently needs to be determined in decommission and radioactive waste samples. It is often quantified by mass spectrometry, accordingly isobaric interferences and matrix elements need to be removed very thoroughly before measurement. Zr-89 on the other hand is gaining more and more interest in immuno-PET due to its favorable physical properties ($t_{1/2}$ = 78.42(13) h, 100% EC/β^+, E_γ = 908.97(3) keV with P=99.03(2)%). It is usually cyclotron produced via a (p,n) reaction from natural Y targets. Hydroxamate based resins as e.g. described by Jason et al. are often used to separate Zr from the Y targets. The synthesis of the described resin involves the use of irritating (GHS07) and hygroscopic reagents such as 2,3,5,6-tetrafluorophenol. In order to overcome this drawback a stable and ready to use hydroxamate based extraction chromatographic resin was developed, and will soon be commercially available under the designation ZR Resin.

Determination of D_W values

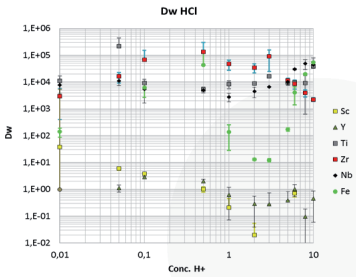

Fig. 1: D_W values, Hydroxamate resin, HCl, various elements

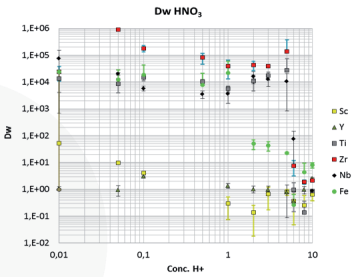

Fig. 2: D_W values, Hydroxamate resin, HNO_3, various elements

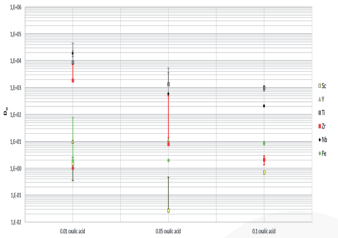

Fig. 3: D_W values, Hydroxamate resin, oxalic acid, various elements

- Zr, Nb and Ti show high D_W in HCl
- No selectivity for Y and Sc, low selectivity for Fe(III) at medium high HCl
  - Zr/Y and Ti/Sc separations seem possible
  - At pH2 selectivities corresponding to Ti/Sc generator
- High selectivity for Zr, Ti and Nb for c(HNO_3) < 6M
- No selectivity for Y and Sc, low selectivity for Fe(III) at medium to high HNO_3
- High D_W values for Zr, Nb and Ti in 0.01M oxalic acid
  - Low D_W for Fe(III)
- High D_W values for Nb and Ti high in 0.05M oxalic acid, low D_W values for Zr
  - Zr/Nb separation seems possible

Elution studies

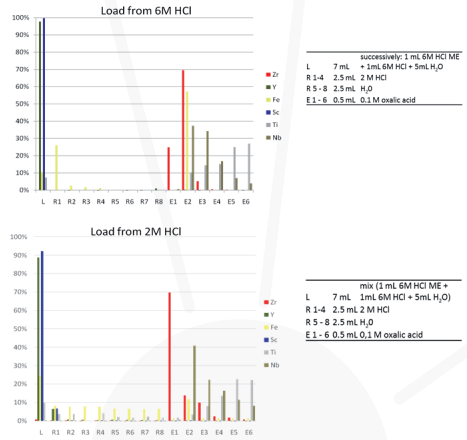

Fig. 4 a – b: Elution study Hydroxamate resin, 100 mg, load from 6M HCl, 2M HCl respectively, multielement solution (ME), fractions analysed by ICP-MS

- High selectivity for Zr over Y at 2M and 6M HCl
- 100 mg column efficiently retains and separates Zr even at 300 mg Y in load solution
- Nb, Fe(III) and Ti also retained

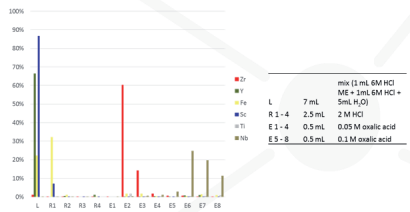

Fig. 5: Elution study Hydroxamate resin, 100 mg, load from 2M HCl, multielement solution (ME), fractions analysed by ICP-MS

- Zr/Nb separation feasible through variation of oxalic acid concentrations

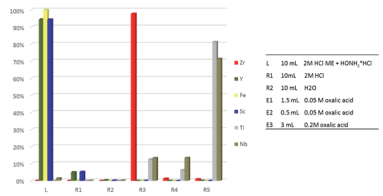

Fig. 6: Elution study Hydroxamate resin, 100 mg, load from 2M HCl, reducing conditions ($HONH_2$*HCl), multielement solution (ME), fractions analysed by ICP-MS

- Facile Fe removal by loading under reducing conditions e.g. using $HONH_2$*HCl

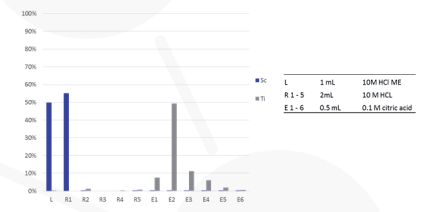

Fig. 7: Elution study Hydroxamate resin, 100 mg, load from 10M HCl, multielement solution (ME), fractions analysed by ICP-MS

- High Ti uptake at 10M HCl
- Very good selectivity for Ti over Sc

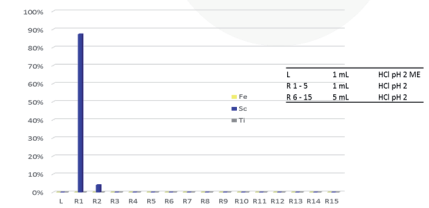

Fig. 8: Elution study Hydroxamate resin, 100 mg, load from 0.01M HCl, multielement solution (ME), fractions analysed by ICP-MS

- High Ti uptake at 0.01M HCl
- Very good selectivity for Ti over Sc
- No Ti breakthrough of Ti after extended rinse
  - Evaluation of potential for use in Ti/Sc generator

Conclusions

- Hydroxamate resin shows high Zr, Nb and Ti uptake over wide HCl and HNO_3 concentration ranges
- High Zr/Y and Ti/Sc selectivities, especially in HCl, allow for clean and facile separation even in presence of up to 300mg Y
- Zr elution possible with oxalic acid at concentrations equal or greater than 0.05M
- Nb/Zr separation possible by subsequent elution at different oxalic acid concentrations
- Facile Zr/Fe separation under reducing conditions (e.g. $HONH_2$*HCl)
- Resin shows interesting Ti/Sc selectivity at pH 2 HCl => potential for use as generator

Literature

[LNHB recommended data, http://www.nucleide.org/DDEP_WG/DDEPdata.htm, accessed 08/10/15

Jason P. Holland, D.Phil, Yiauchung Sheh, Jason S. Lewis, Ph.D: "Standardized methods for the production of high specific-activity zirconium-89", Nucl Med Biol., 36(7), 2009, 729–739; doi:10.1016/j.nucmedbio.2009.05.007

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