Extraction Chromatography Separation of Zirconium-93

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Overview

NPL National Physical Laboratory

- Importance of zirconium-93
- Measurement of zirconium-93
- Batch separation results
- Chromatographic separation results
- Conclusions and future work

Zirconium-93

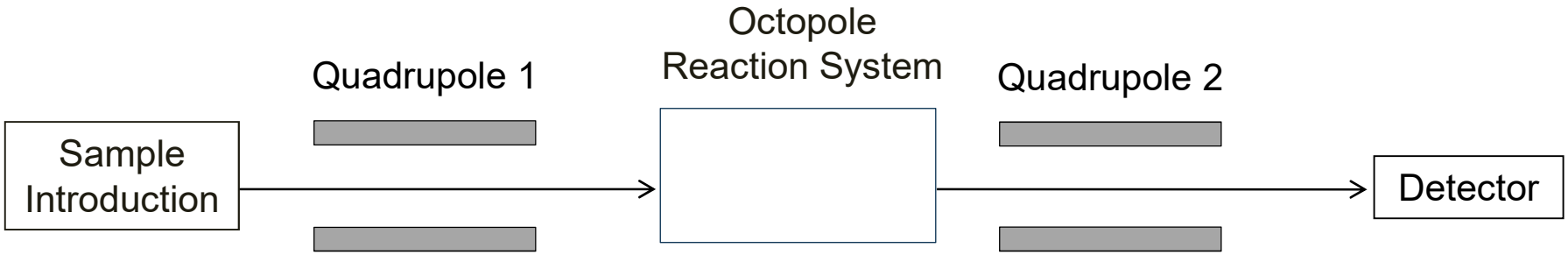
- High yield fission product (6.35 %), and activation of stable Zr in zircalloy fuel cladding
- Significant contributor to total waste inventory over longer timescales
- Half-life = 1.64 x 10^6 years
- Beta-emitter (maximum decay energy 60 keV)
- Measurable by LSC and ICP-MS
- Interference separation required prior to measurement
  - Mass spectrometric interference from **^{93}Nb** and ^{93}Mo

Zirconium-93 Standardisation

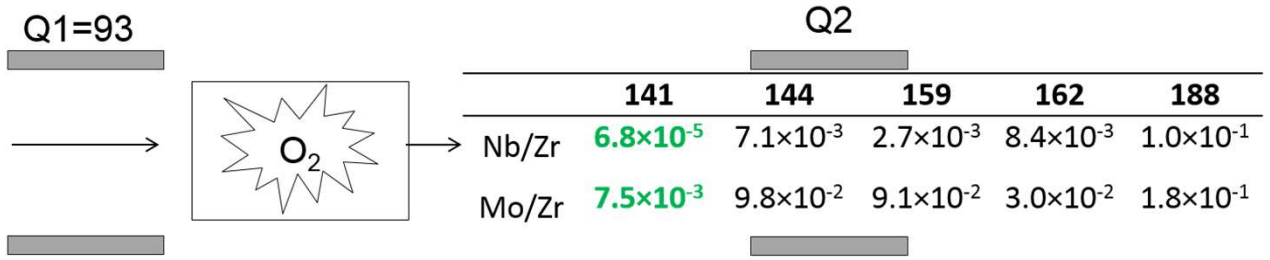
Technique	Activity (Bq/g)
CIEMAT/NIST	1046 ± 24
TDCR	1030 ± 23
DCC	1028 ± 17
Average	**1035 ± 24 (k=1)**

- ^{93m}Nb impurity of 6.4 ± 1.3 Bq/g
- ^{93}Zr dilutions measured by LSC down to 1 Bq/g

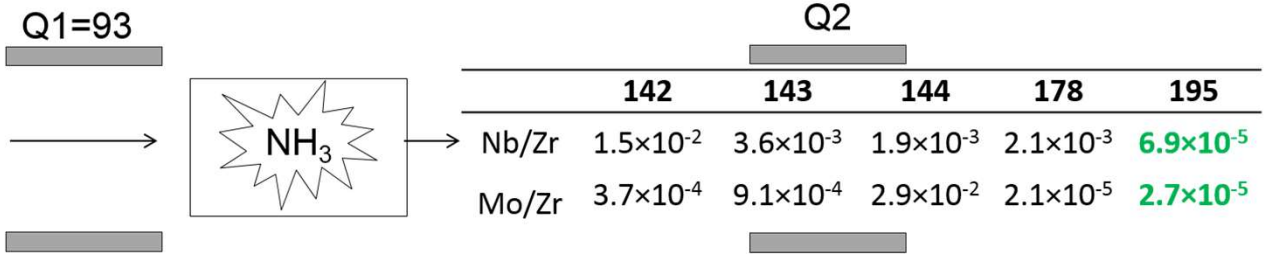
ICP-MS/MS



- Initial trials using stable element standards of Zr, Nb and Mo
- O_2 and NH_3 reaction gases investigated for Zr/Nb and Zr/Mo separation as rapid support to offline chemical separation

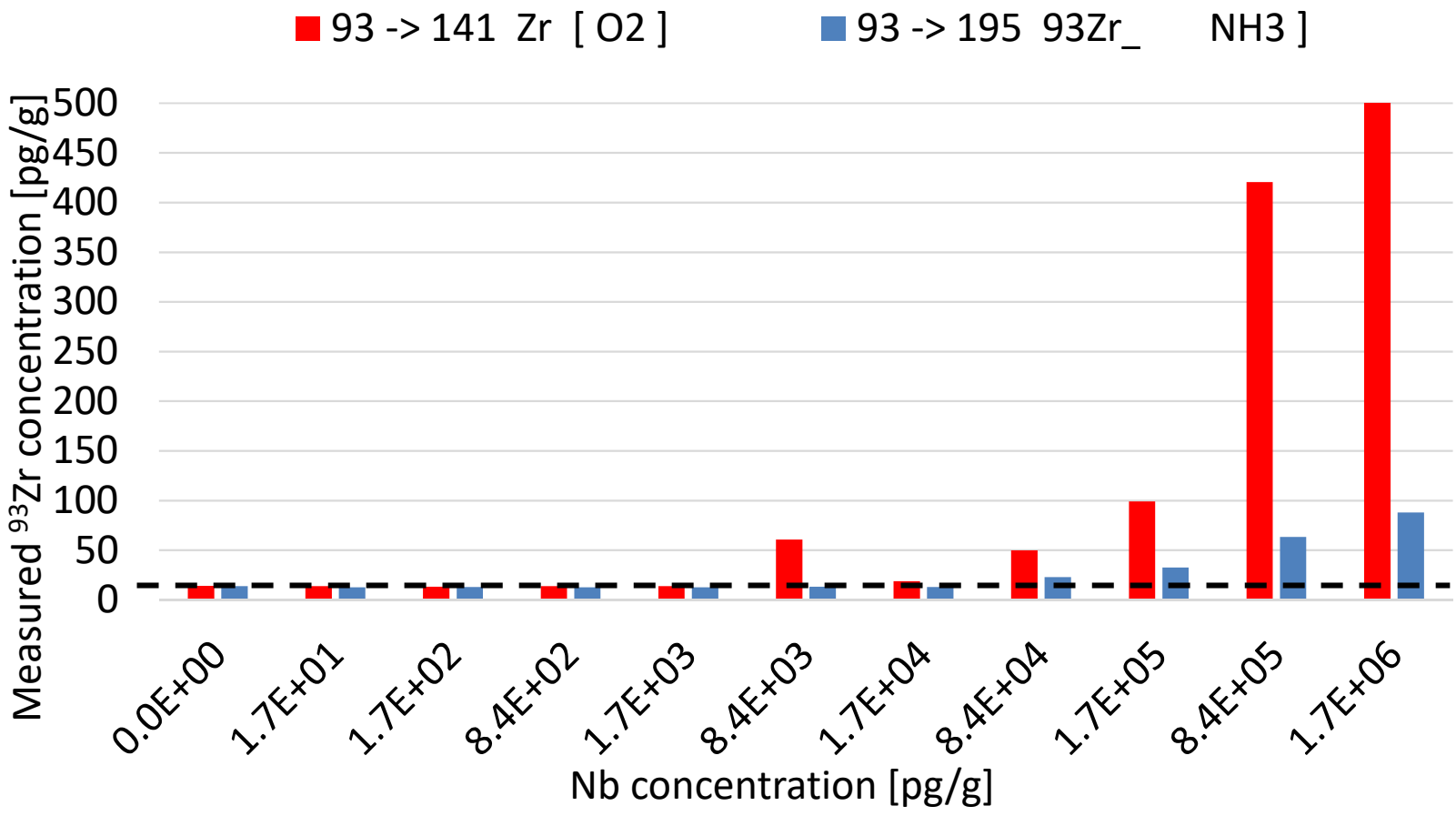


	141	144	159	162	188
Nb/Zr	6.8×10^{-5}	7.1×10^{-3}	2.7×10^{-3}	8.4×10^{-3}	1.0×10^{-1}
Mo/Zr	7.5×10^{-3}	9.8×10^{-2}	9.1×10^{-2}	3.0×10^{-2}	1.8×10^{-1}



	142	143	144	178	195
Nb/Zr	1.5×10^{-2}	3.6×10^{-3}	1.9×10^{-3}	2.1×10^{-3}	6.9×10^{-5}
Mo/Zr	3.7×10^{-4}	9.1×10^{-4}	2.9×10^{-2}	2.1×10^{-5}	2.7×10^{-5}

Reaction cell separation of ^{93}Zr spiked with ^{93}Nb



- ICP-MS/MS can be used to support chemical separation

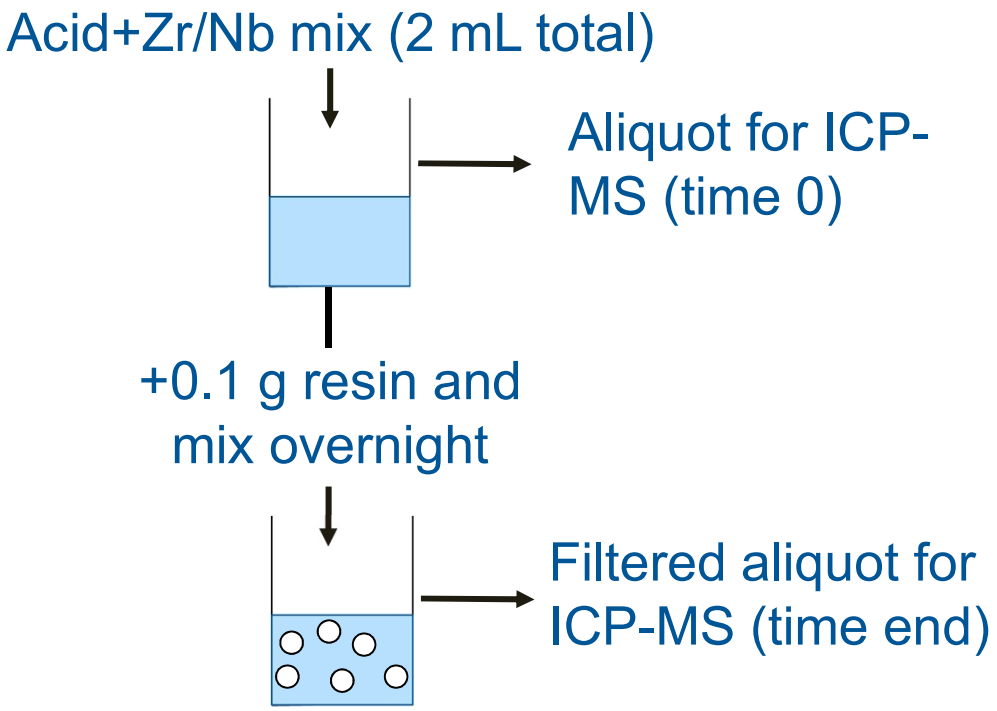
Chemical separation of Zr/Nb: previous methods

Reference	Resin	Zr elution	Nb elution
Triskem	UTEVA	0.1-0.5 M $H_2C_2O_4$	9 M HNO_3/100µL H_2O_2
Busse et al. (2002)	AG1-X8	8M HCl	3 M HCl or 7M HCl + 0.1 M $H_2C_2O_4$
Oliveira (2010 and 2014)	TRU TEVA	2M HCl (12 mL) DI water (12 mL)	
Radchenko et al. (2014)	AG-1 UTEVA	2 M HCl 0.5 % H_2O_2 5.5 M HCl	 2.2 M HCl
Shimada et al. (2014)	TEVA	10 M HCl/0.1 M HF	8-10 M HNO_3/0.1 M HF
Dulanska et al. (2012)	AG-1	20 mL 35 % HCl with 20 mL 0.5 M HF	
Remenec et al. (2014)	TEVA	7 M HCl	

Batch separation

- Triskem resins investigated in HCl and HNO_3
- Mixed stable Zr and Nb measured by ICP-MS

- TEVA
- UTEVA
- TRU
- TBP
- Zr-resin
- TK100
- TK101

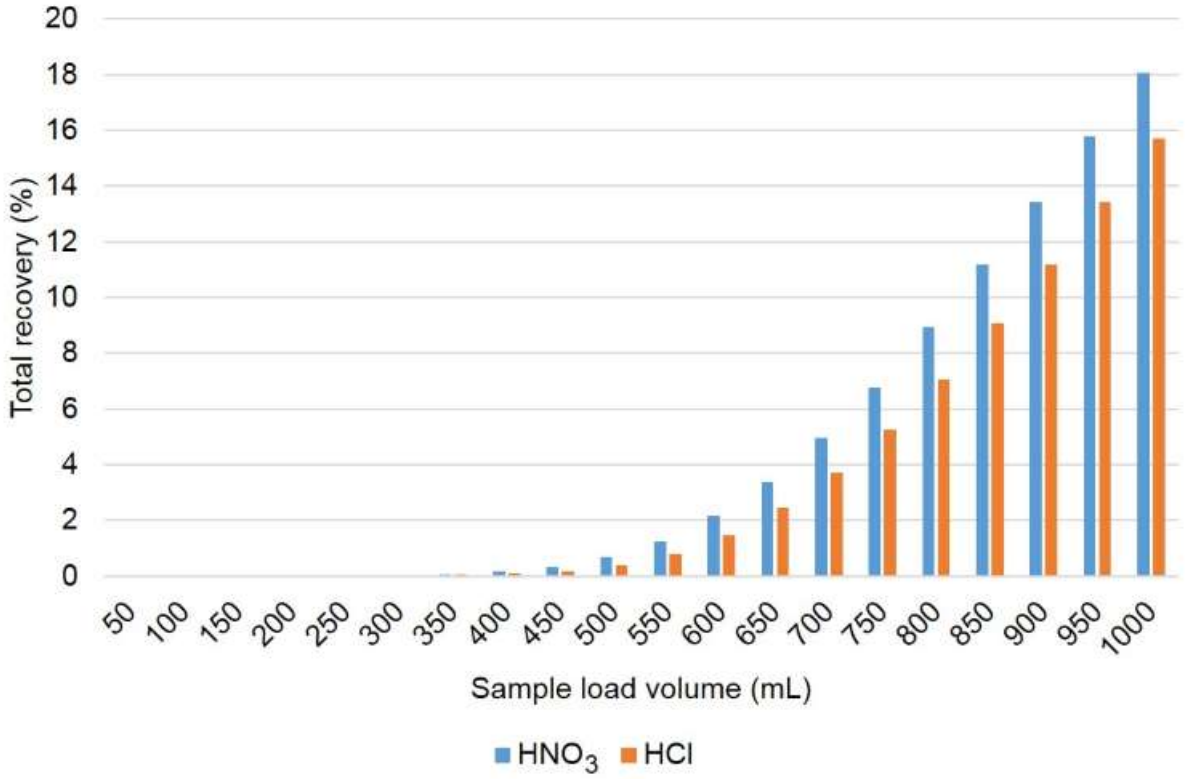


Batch separation results

- Similar distribution coefficients for Zr and Nb for multiple resins:

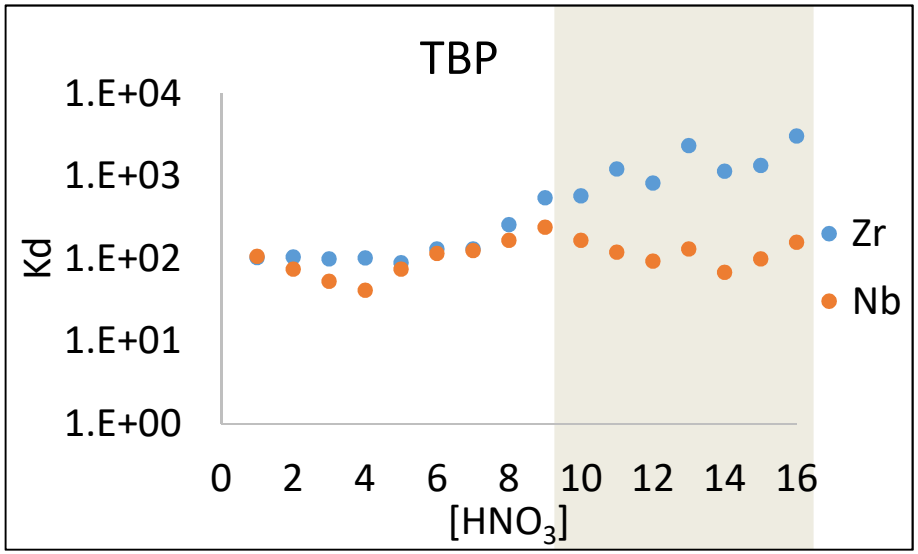
  - **TK100** (10^4-10^5 achievable)
  - TK101
  - TEVA (HNO_3)
  - TBP (HCl)
  - **Zr-resin** (10^4-10^5 achievable)
  - TRU (HCl)

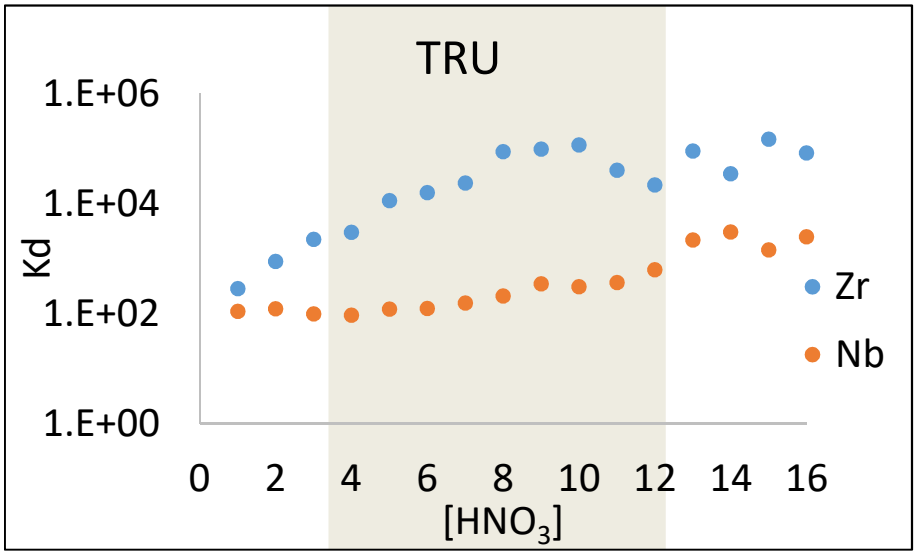
TK100 resin for high volume water samples

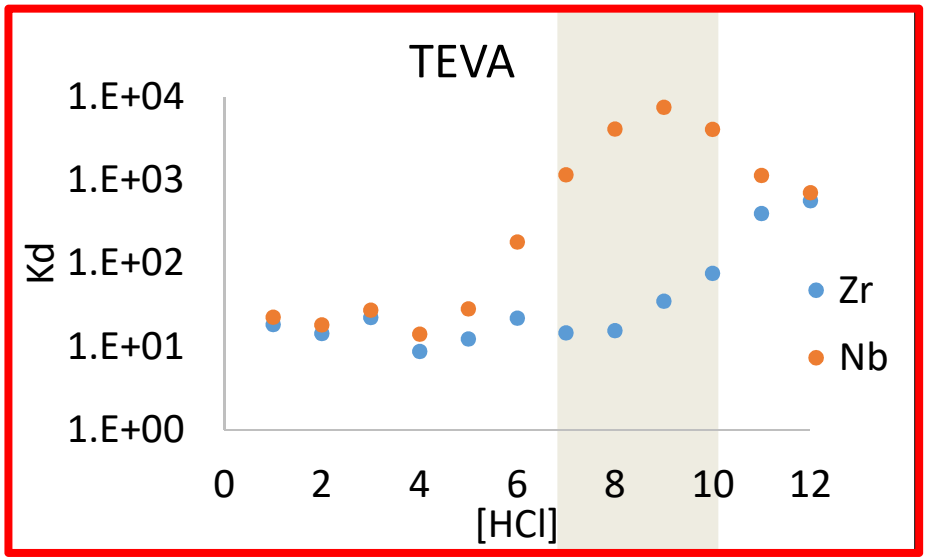


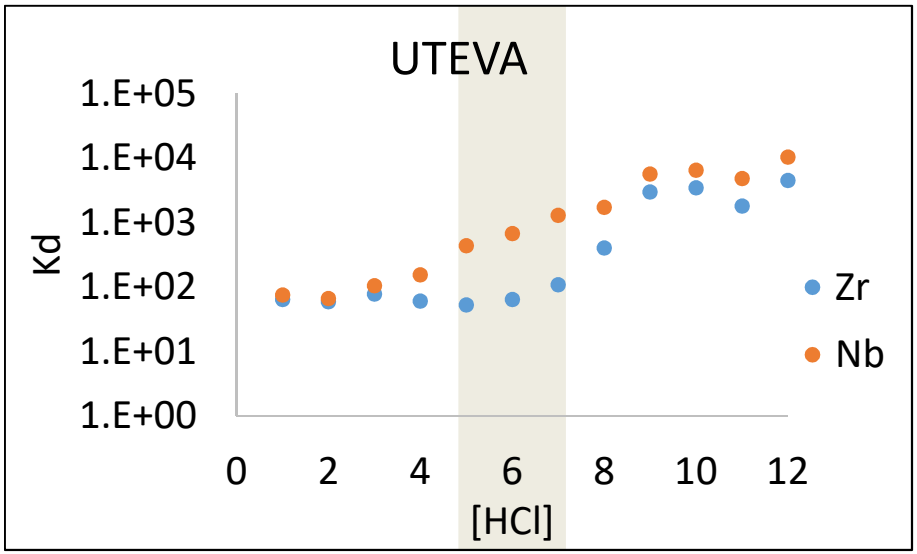
- No ^{90}Sr loss up to 400 mL, or ^{226}Ra up to 1 L
- No elution of Zr

Batch separation results



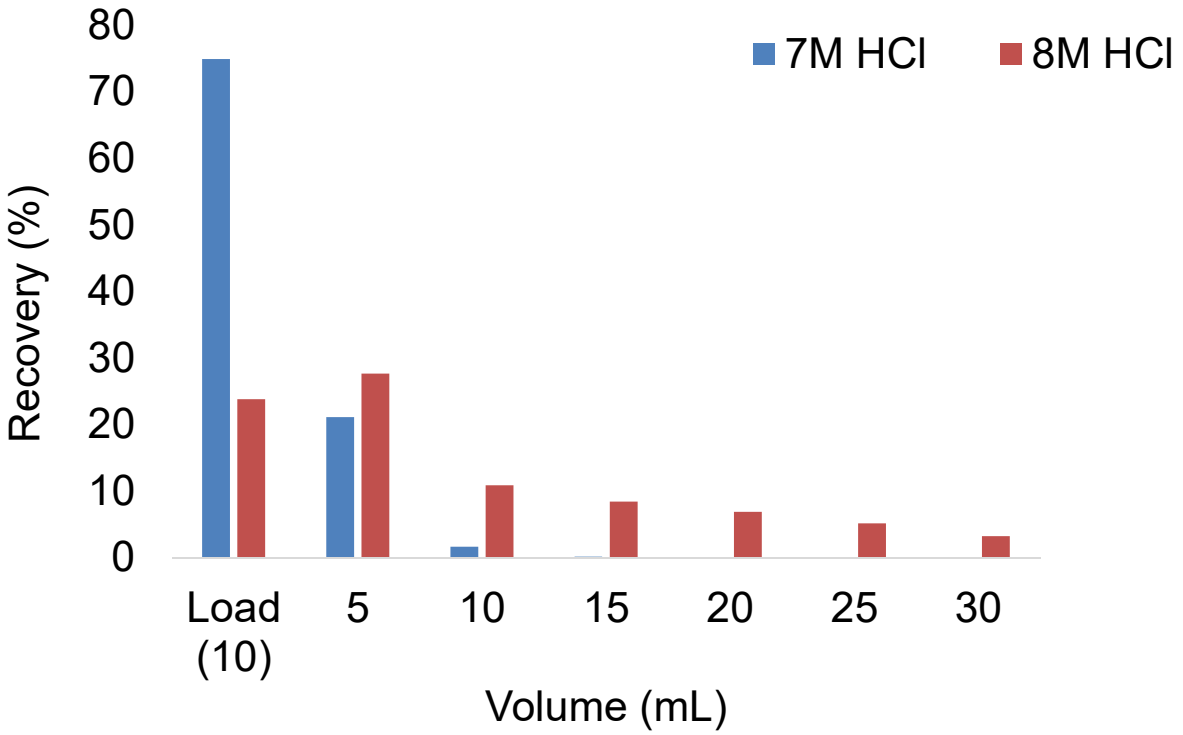






Chromatographic separation

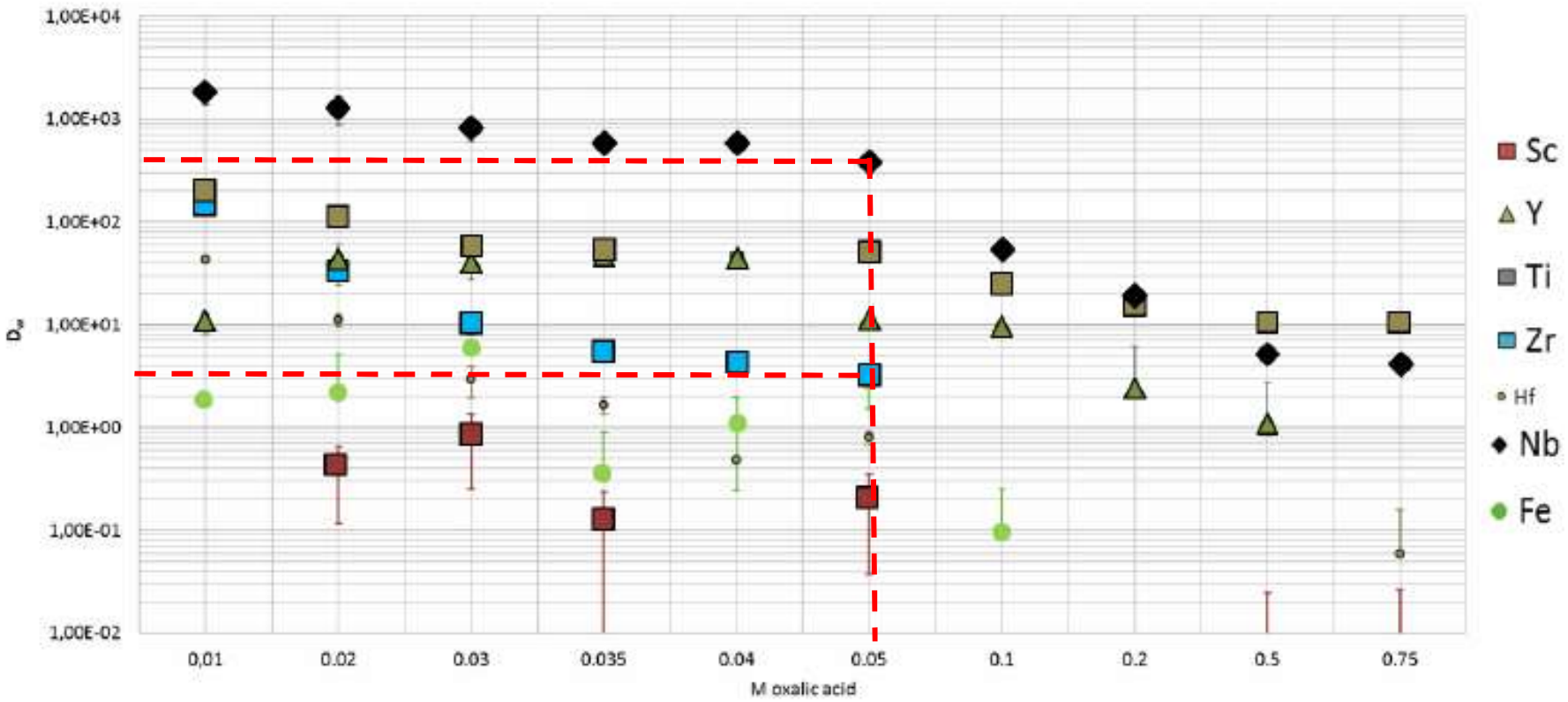
- TEVA based on lower distribution coefficient for Zr compared to Nb in 7-9 M HCl
- 2 mL pre-packed column using a vacuum box



Total Zr recovery:
7M = 98.0%
8M = 86.1%
9M = <1%

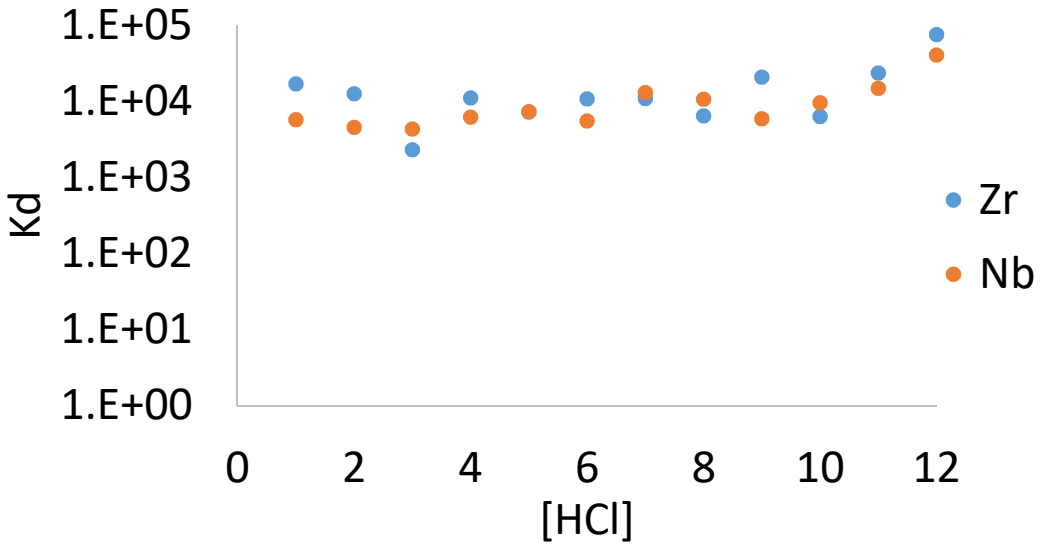
Nb < 1% for all conditions tested

Zr-resin


1,00E+04
1,00E+03
1,00E+02
1,00E+01
1,00E+00
1,00E-01
1,00E-02
D
0,01
0.02
0.03
0.035
0.04
0.05
0.1
0.2
0.5
0.75
M oxalic acid
Sc
Y
Ti
Zr
Hf
Nb
Fe

Zr-resin

- Good retention of Zr and Nb in HCl
- Zr more readily eluted in oxalic acid



- Load in 7 M HCl
- 10 mL water wash
- 10 mL 0.01 – 0.1M oxalic acid
- Optimal conditions not yet determined

Oxalic acid concentration (M)	Recovery in 10 mL	
	Zr recovery (%)	Nb recovery (%)
0.01	26.6	1.2
0.05	26.5	4.0
0.1	41.4	34.6

Conclusions and future work

- Zirconium-93 a key long-lived fission and activation product for decommissioning and long term monitoring of nuclear waste
- Multiple extraction chromatography resins tested- TEVA and Zr-resin most promising
- Additional resins to be tested e.g. TK400 to establish optimal procedure
- Procedure will then be applied to ^{93}Zr in dissolved steel

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