Laboratoire de Radioécologie

SEPARATION AND ANALYSIS OF Sr-90 AND Zr-90 FOR NUCLEAR FORENSIC APPLICATIONS

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CRTI-IRTC
Initiative de recherche et de technologie CBRN

Agilent Technologies

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Availability of ^{90}Sr sources

RTG

- $^{90}SrTiO_3$
- Fairly common in Russia
- Activity ~10^{15} Bq/RTG

Nuclear waste

Fission product of ^{235}U (reactors)

Medical isotopes

- Production of ^{90}Y
- Cancer treatment

M. Ajaz, I. Amundsen. *Strålevern Rapport* **2009,** *13*, 1-39.

Radiological properties

Parameters	Information
Appearance	Type of material (e.g. powder)
Dimensions and isotopic composition	Type of reactor
Impurities	Process, Geolocation
Surface	Production plant
$^{18}O/^{16}O$	Geolocation
Microstructure	Process
Age	Production date

M. Wallenius, K. Mayer, I. Ray, *Forensic Science International* **2006**, *156*, 55–62.

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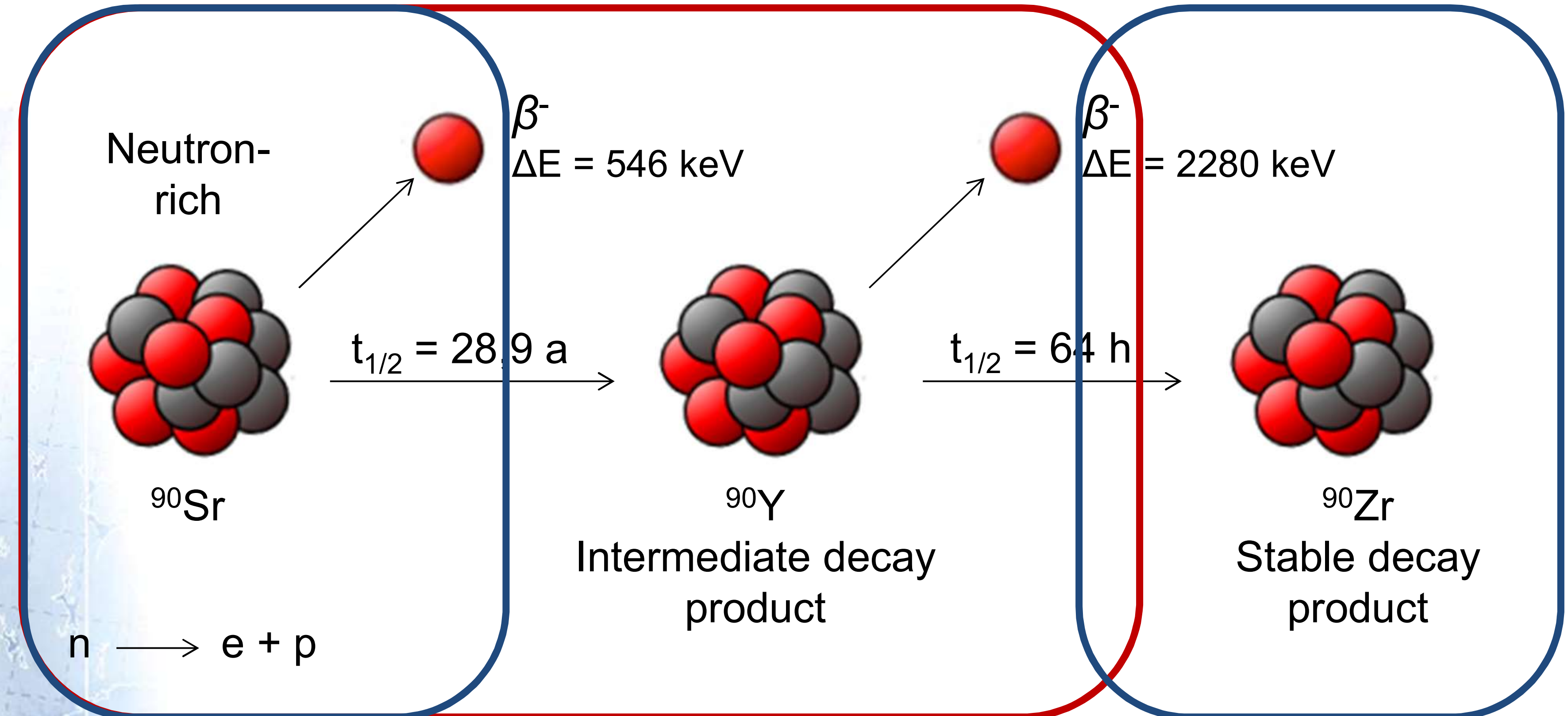
Origin

M. Wallenius, K. Mayer, I. Ray, *Forensic Science International* **2006**, *156*, 55–62.

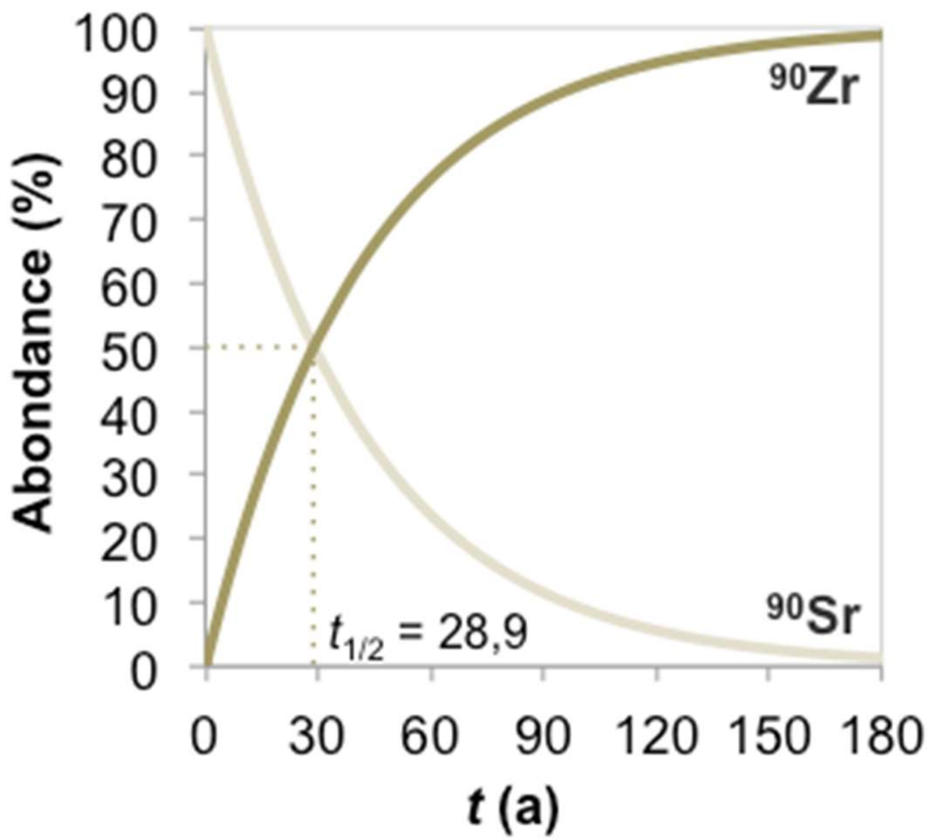
Decay scheme of ^{90}Sr



Radiometric approaches

Mass spectrometric approaches

Radiochronometry



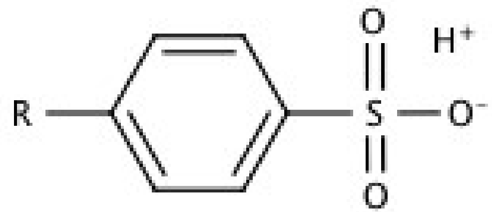
Age
Time since the last purification

Production or purification ➔ *t* = 0
100 % ^{90}Sr
0% ^{90}Zr

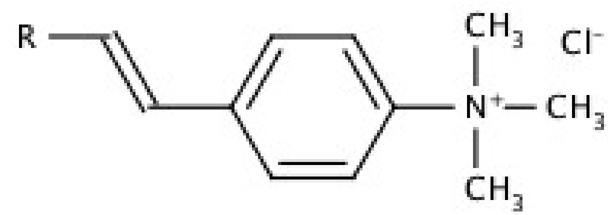
$$t = \frac{28,9}{ln\,2} \ln\left(1 + \frac{[^{90}Zr]}{[^{90}Sr]}\right)$$

Choices

Ion-exchange resin ➔ Charged active site

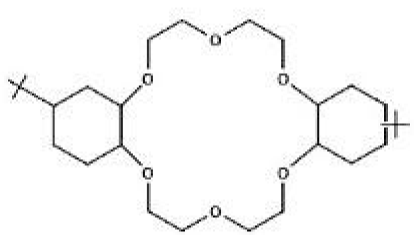


Cationic

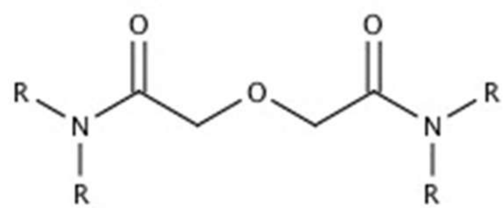


Anionic

Extraction resins ➔ Chelating agents



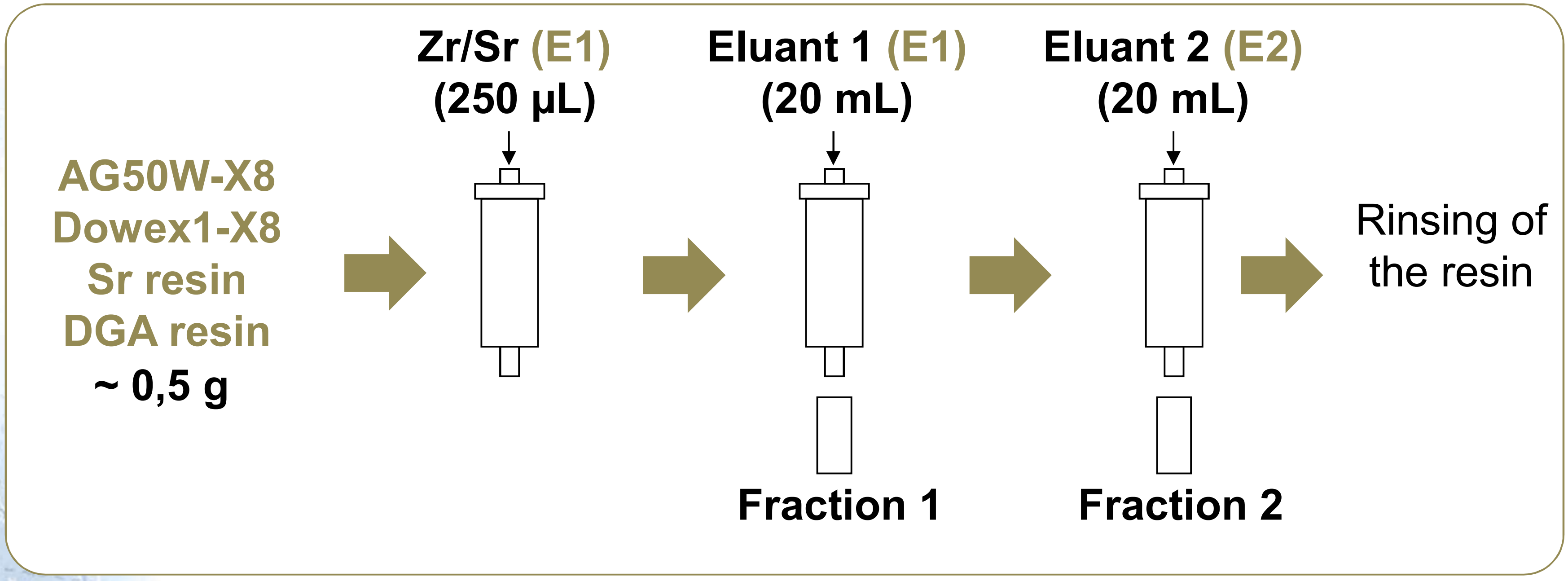
Sr Resin



DGA

F. W. E. Strelow, *Analytical Chemistry* **1959**, *31*, 1974-1977
L. R. Bunney, N. E. Ballou, J. Pascual, S. Foti, *Analytical Chemistry* **1959**, *31*, 324-326
E. P. Horwitz, R. Chiarizia, M. L. Dietz, *Solvent Extraction and Ion Exchange* **1992**, *10*, 313-336
D. W. Pawlak, J. L. Parus, T. D, A. Muklanowicz, R. Mikolajczak, *Talanta* **2013**, *114*, 1-4

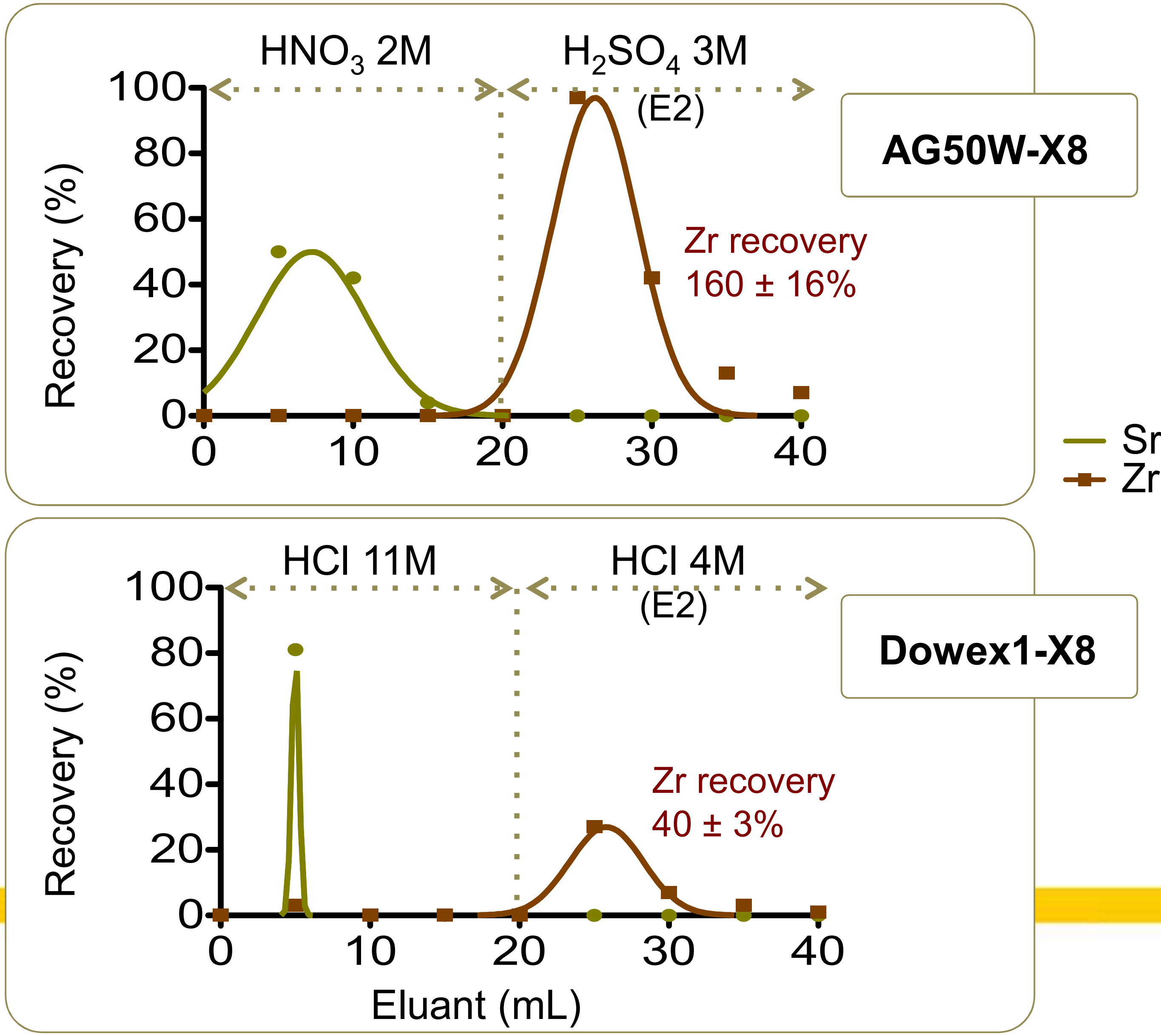
Separation scheme



- E1 ➔ *Partitioning coefficient very different*
- Preliminary tests ➔ Stable isotopes

- Zr separation ➔ Interference removal
- Zr recovery ➔ Radioactive source determination

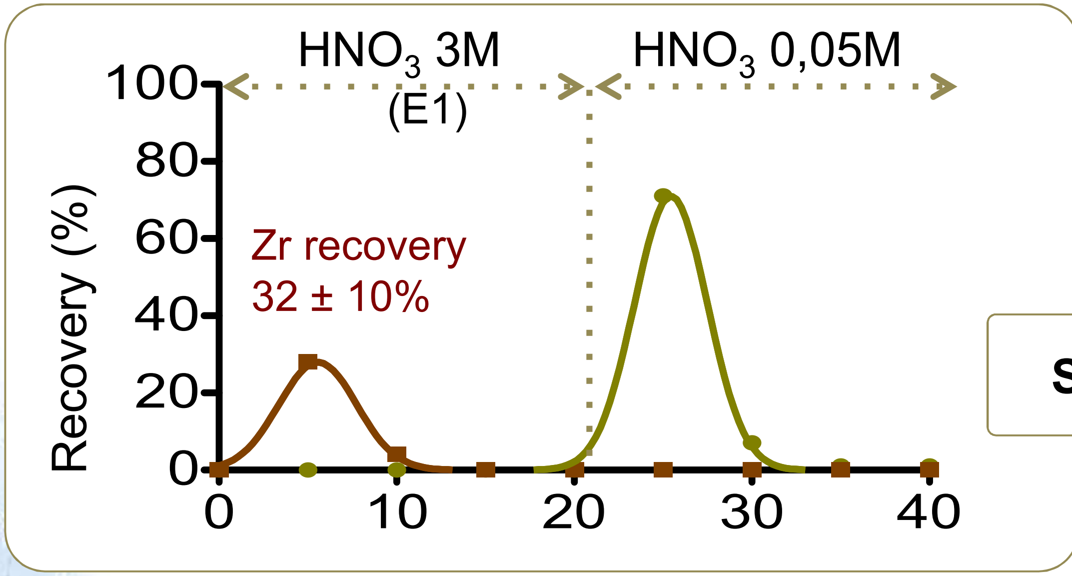
Ion-exchange resins

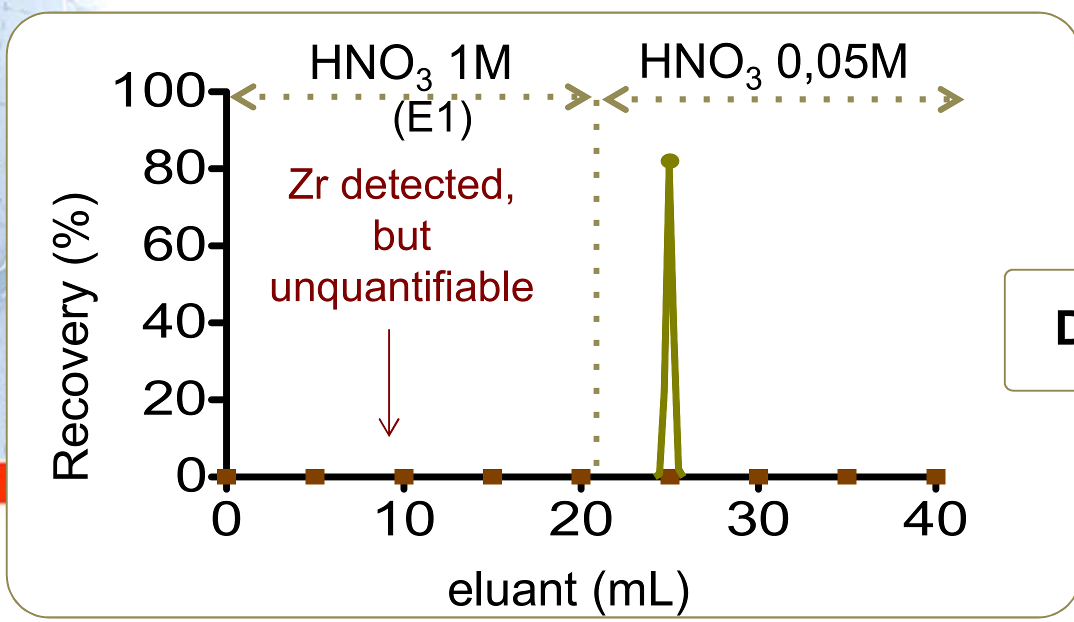


Extraction resins

Zr in 1st fraction

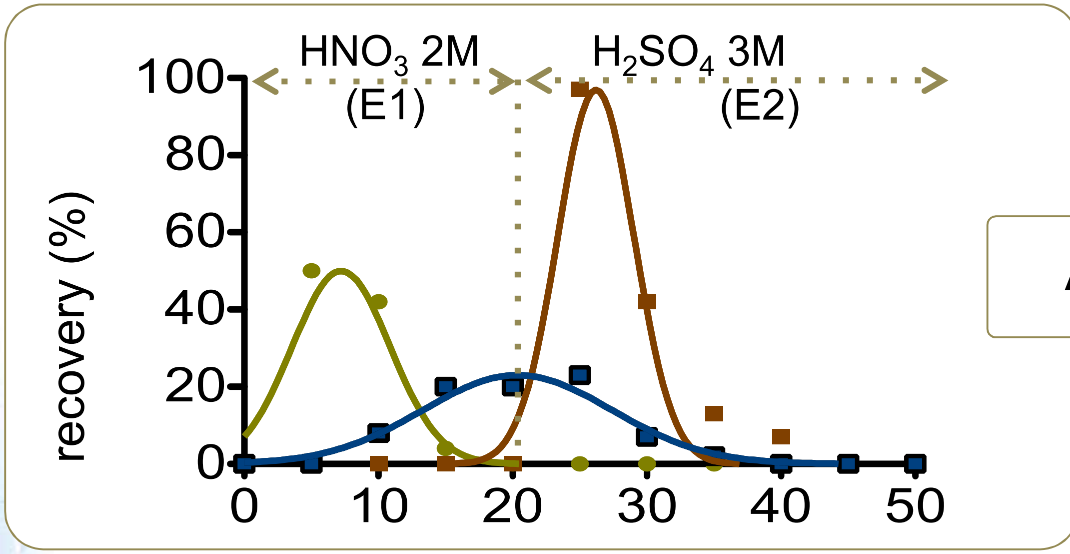
- Faster
- Limited exposure to radioactivity





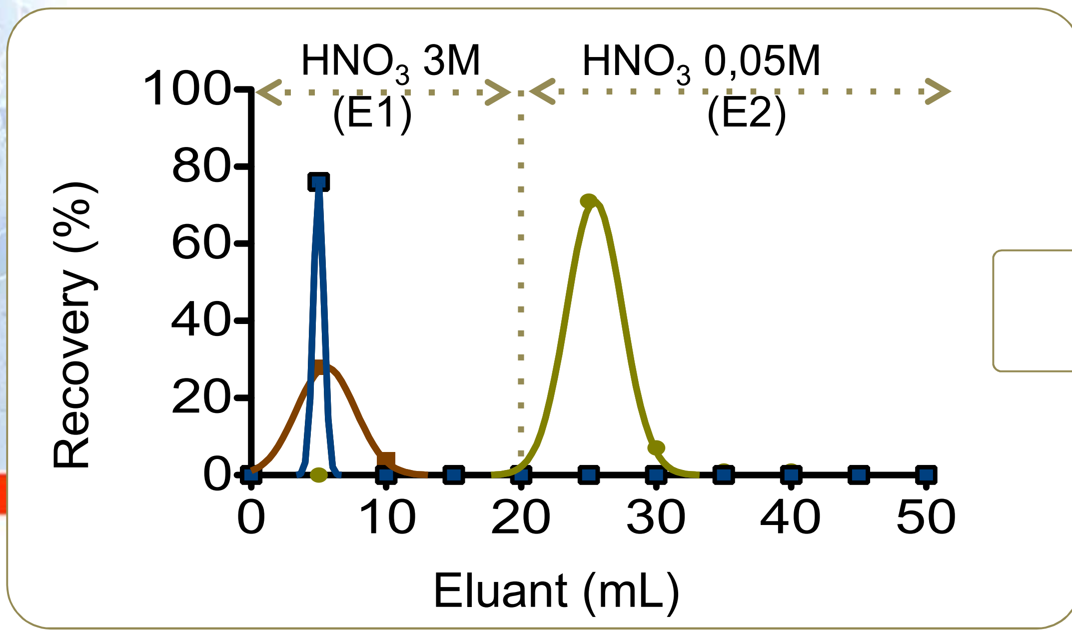
Limitations

Zr
Not isolated from Y



AG50W-X8

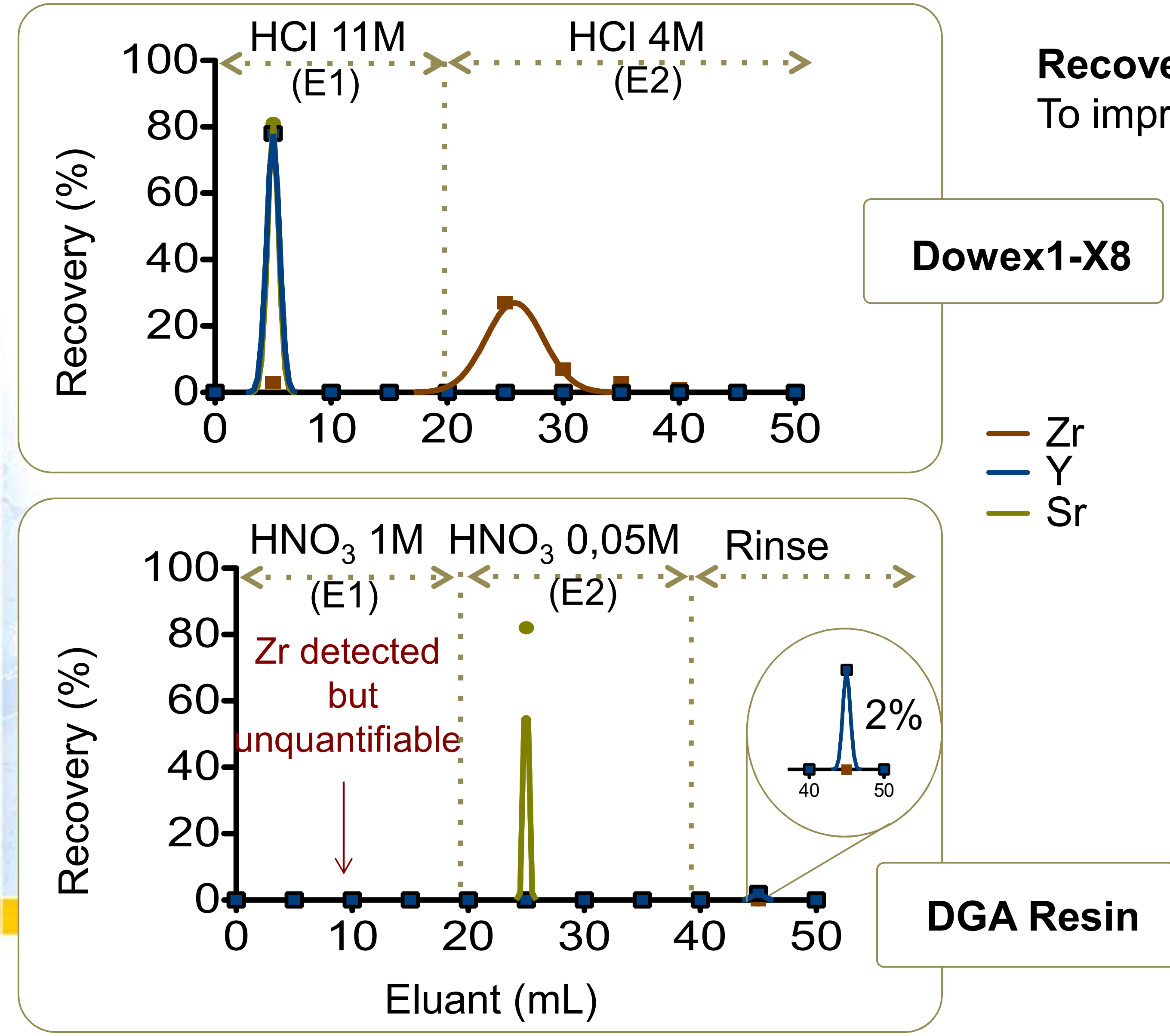
Zr
Y
Sr



Sr Resin

Limitations

Recovery yield
To improve



Zr recovery

Sample preparation
Addition of F^- to complex Zr

Anionic exchange resin
- Neutral or positive complexes
- Zr less retain ➔ effect on separation

DGA Resin
- Neutral complex➔ Zr more retained
- Increased affinity on the resin ➔ effect on recovery yield

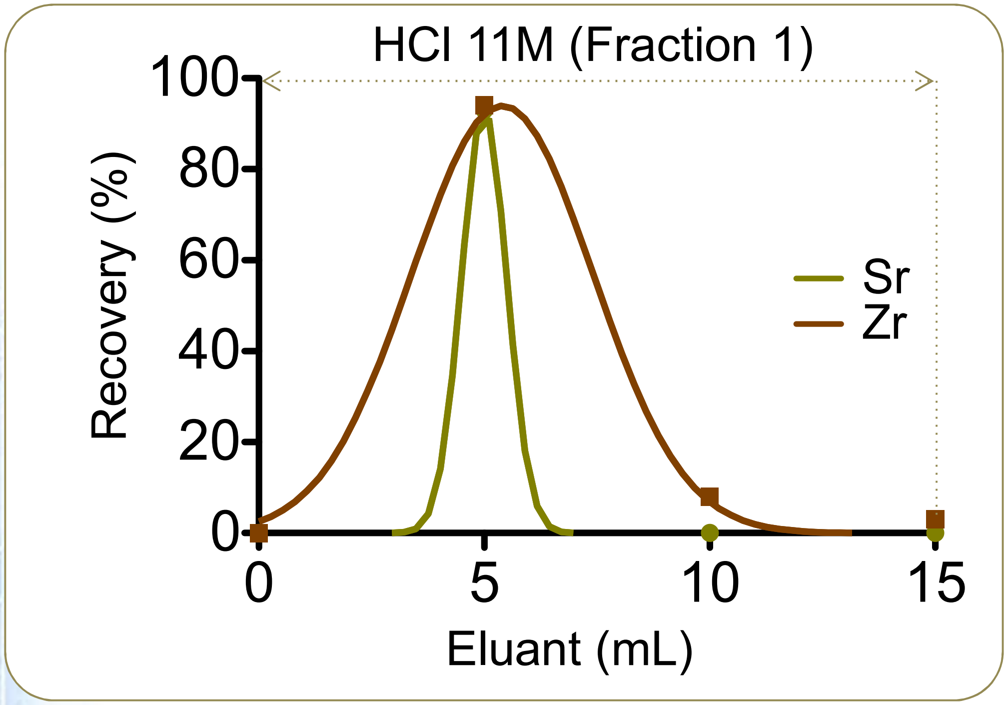
$$[Zr]^{4+} + F^- \leftrightharpoons [ZrF]^{3+}$$
$$[ZrF]^{3+} + F^- \leftrightharpoons [ZrF_2]^{2+}$$
$$[ZrF_2]^{2+} + F^- \leftrightharpoons [ZrF_3]^{+}$$
$$[ZrF_3]^{+} + F^- \leftrightharpoons [ZrF_4]$$
$$[ZrF_4] + F^- \leftrightharpoons [ZrF_5]^{-}$$
$$[ZrF_5]^{-} + F^- \leftrightharpoons [ZrF_6]^{2-}$$

Which species will be favored?

R. L. Davidovich, D. V. Marinin, V. Stavila, K. H. Whitmire, *Coordination Chemistry Reviews* **2013**, *257*, 3074-3088.

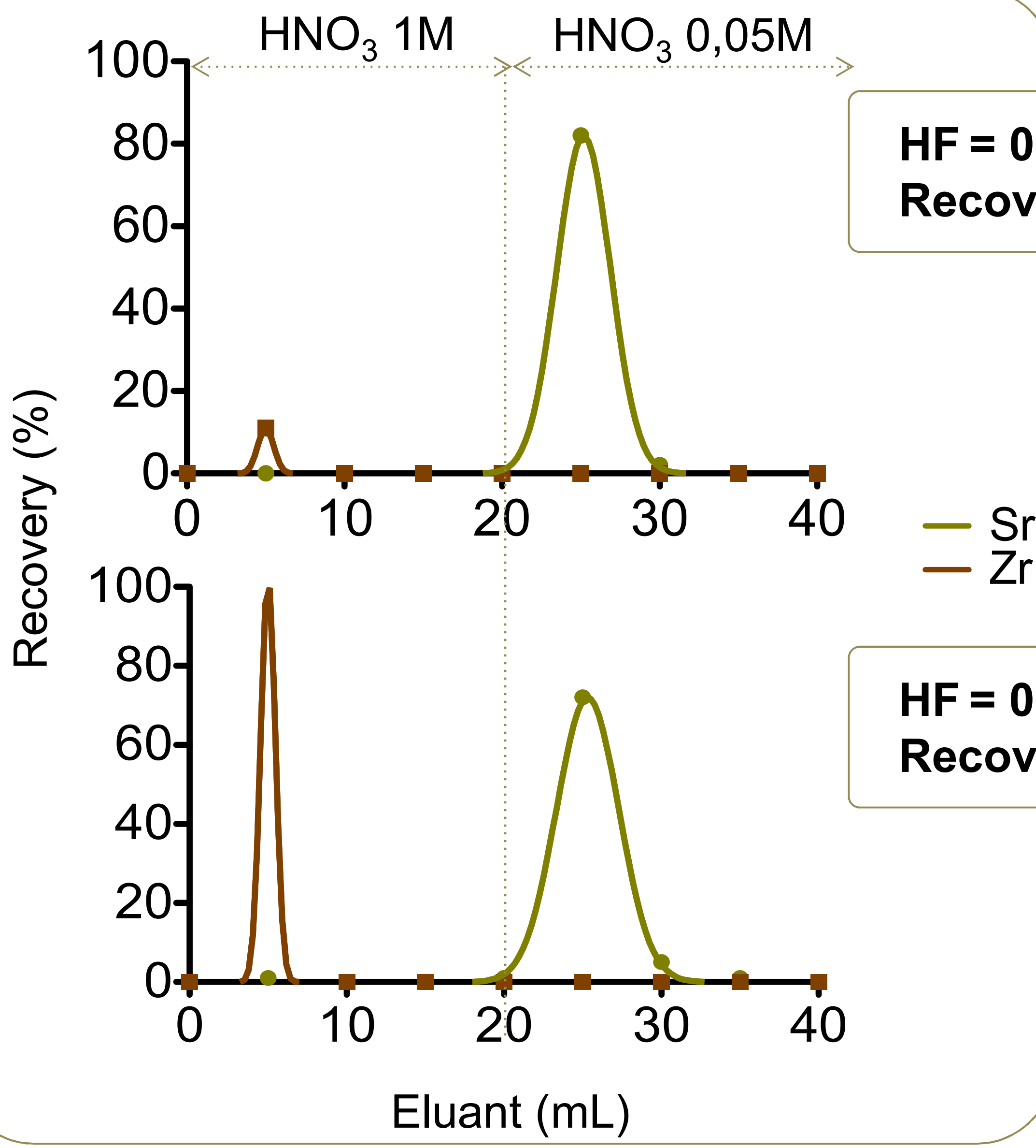
F^- - Dowex1-X8

Sample preparation ➔ E1 + HF 0,01M
Zr recovery yield = 124 ± 11 %



Neutral complex forming!!!

F^- DGA-resin



HF = 0,01M
Recovery = 11 ± 1 %

HF = 0,2M
Recovery = 102 ± 10%

Comparison

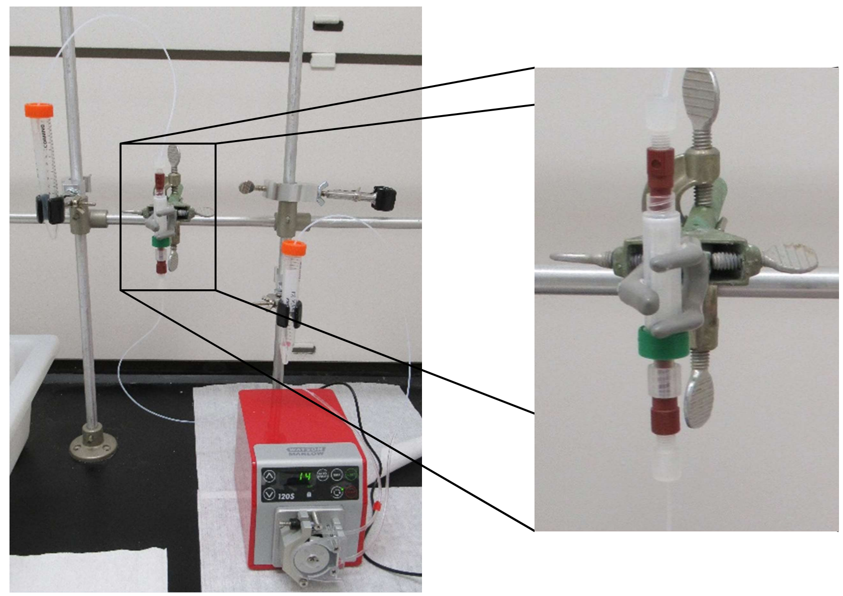
Resin	Sr removal	Y removal	HF
AG50W-X8	✓	✗	✗
Dowex1-X8	✓	✓	✗
Sr	✓	✗	✗
DGA	✓	✓	✓

Adding HF in the sample

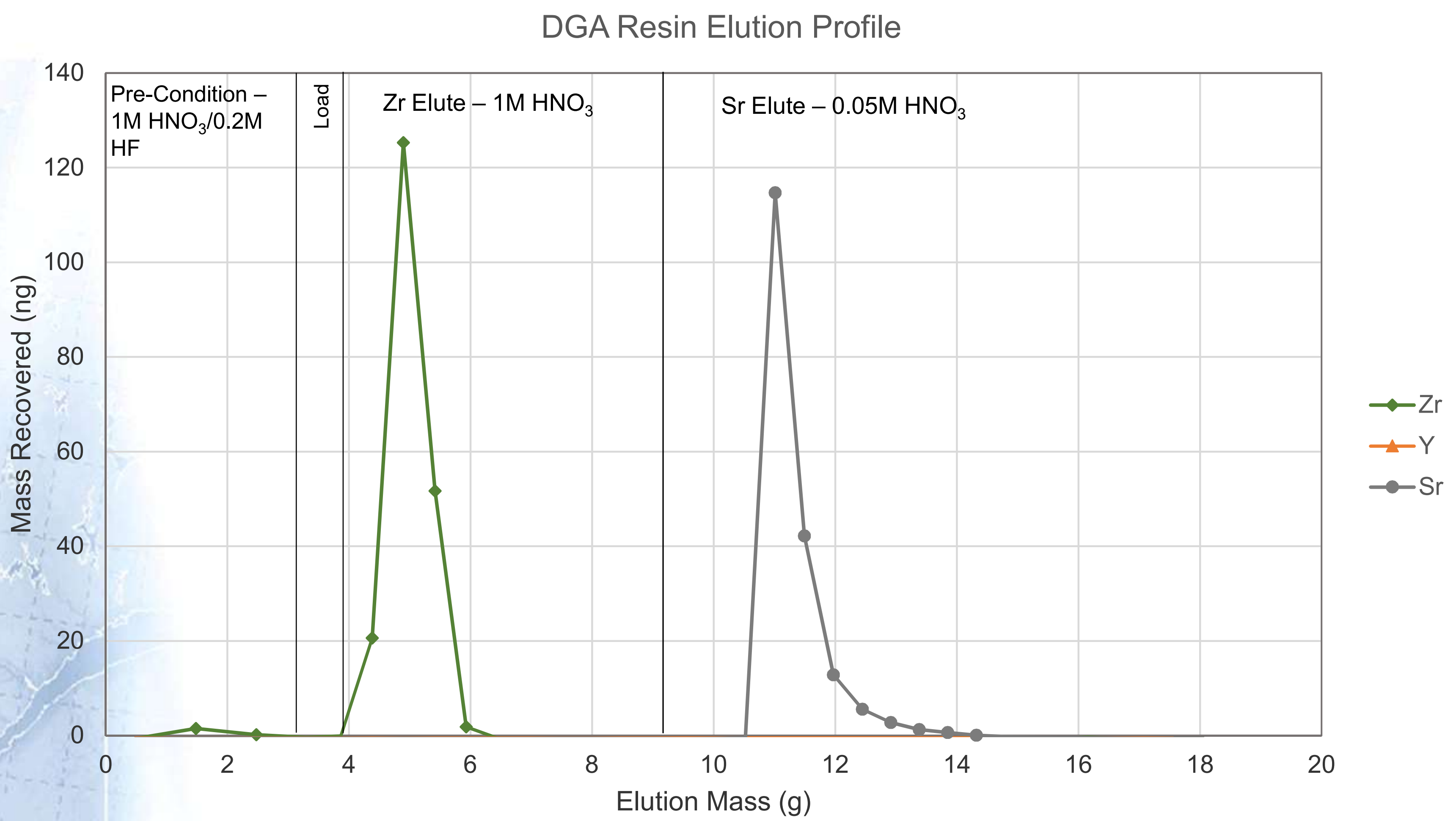
DGA resin ➔ Excellent alternative for proper separation-recovery

New Procedure

- DGA Resin
  - Wash
    - DIW
  - Pre-Condition
    - 1 M HNO_3/0.2 M HF
  - Load
    - 1 M HNO_3/0.2 M HF
  - Elute Zr
    - 1 M HNO_3
  - Elute Sr
    - 0.05 M HNO_3



Separation Results – DGA Resin



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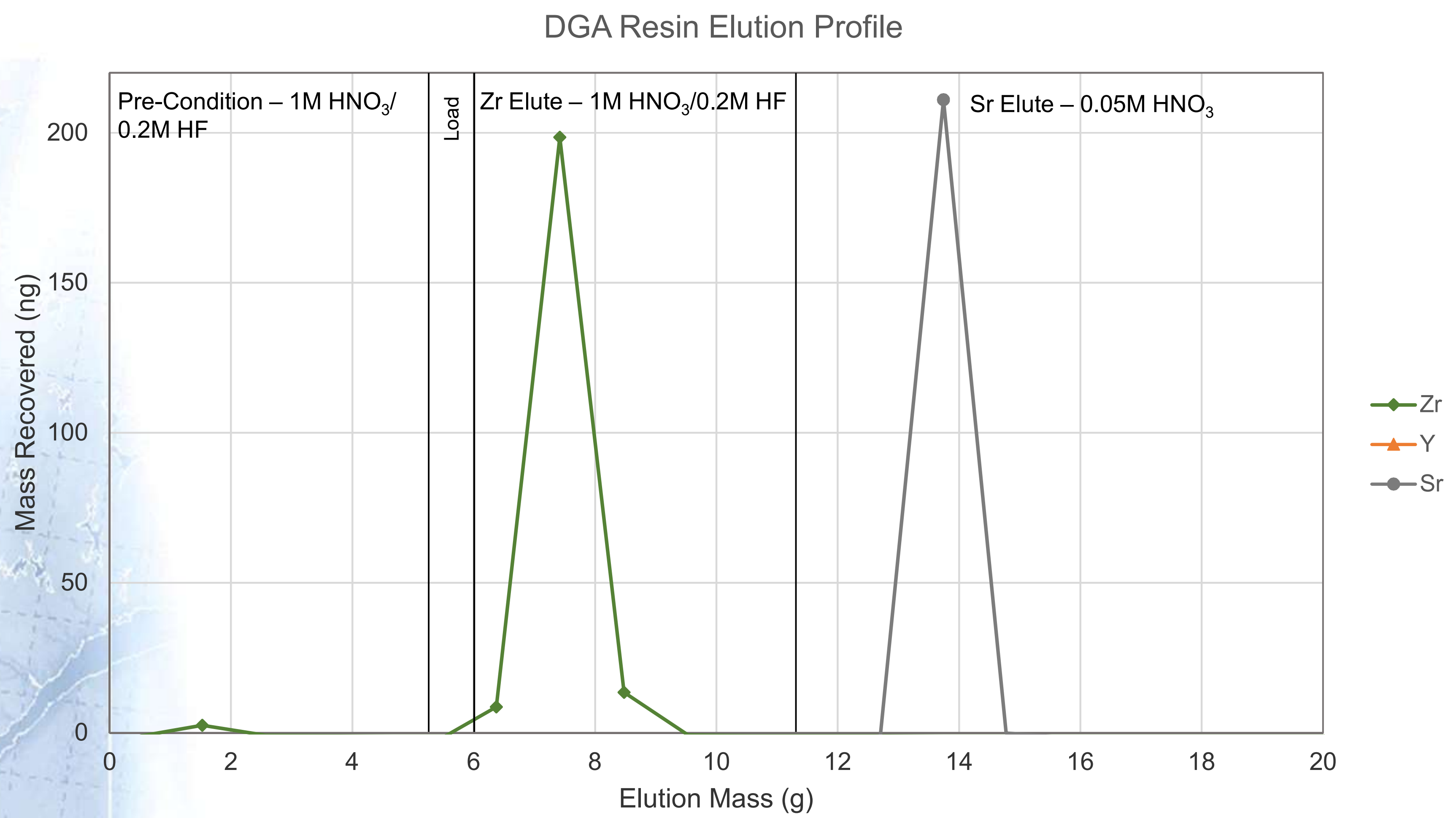

Recovery Comparison

Sr Resin Separation % Recovery

Element	Load Fraction	Rinse Fraction	Sr Elution Fraction
Zr	0.00 ± 0.00	100.19 ± 2.72	0.01 ± 0.02
Y	0.00 ± 0.00	99.91 ± 2.40	0.00 ± 0.00
Sr	0.01 ± 0.02	0.03 ± 0.01	97.33 ± 1.09

- Minor Sr cross-contamination
- Minor Zr cross-contamination
- Quantitative recovery of Zr/Y
- Nearly quantitative recovery of Sr
- RSD for calculated age: 2.99%

DGA Resin Separation % Recovery

Element	Load Fraction	Zr Elution Fraction	Sr Elution Fraction
Zr	0.00 ± 0.01	99.88 ± 0.43	0.12 ± 0.19
Y	0.93 ± 3.21	0.00 ± 0.00	0.00 ± 0.00
Sr	0.00 ± 0.00	0.00 ± 0.01	100.94 ± 0.57

- Minor Zr cross-contamination
- Quantitative recovery of Zr
- Quantitative recovery of Sr
- RSD for calculated age: 1.51%

DGA Resin – High Fidelity Measurements

Sample ID	Sr in Sample (ng)	Y in Sample (ng)	Zr in Sample (ng)	Zr/Sr Ratio
Process Blank - Zr	<1.0	<1.0	<1.0	-
Process Blank - Sr	<1.0	<1.0	<1.0	
DGA Resin 1 - Zr	<1.0	<1.0	102.2	0.979
DGA Resin 1 - Sr	104.4	<1.0	<1.0	
DGA Resin 2 - Zr	<1.0	<1.0	100.7	0.959
DGA Resin 2 - Sr	105.1	<1.0	1.1	
DGA Resin 3 - Zr	<1.0	<1.0	101.9	0.986
DGA Resin 3 - Sr	103.3	<1.0	<1.0	
DGA Resin 4 - Zr	<1.0	<1.0	102.7	0.980
DGA Resin 4 - Sr	104.8	<1.0	<1.0	
DGA Resin 5 - Zr	<1.0	<1.0	101.1	0.984
DGA Resin 5 - Sr	102.7	<1.0	<1.0	
			Average	0.978
			SD	0.011
DGA Resin Spike 1	99.9	43.8	98.2	0.983
DGA Resin Spike 2	100.2	43.9	98.4	0.983
DGA Resin Spike 3	100.3	43.9	98.3	0.980
			Average	0.982
			SD	0.002

Conclusions/Future Plans

- Conclusions
  - DGA Resin procedure works at least as well as Sr Resin separation
    - Load and Elute Zr in 1 M HNO_3/0.2 M HF
  - Resin requires cleaning
    - ~1.5 ng Zr/g DGA resin
- Future Work
  - Test re-usability
    - Likely possible with 0.05 M HCl