Advances Made in Technetium Separation and Tracer Production

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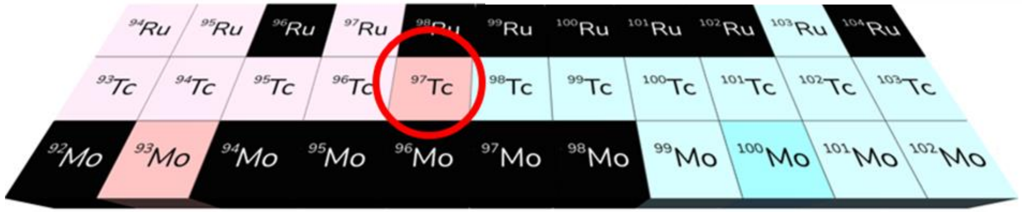
Overview

Research Motivation
- Importance of Tracers

Separation of ^{99}Tc
- Existing Tracers for Tc
- Separation Methods

Results
- Method Development – TK202 Resin
- Method Validation

Next Steps



Research Motivation - ^{99}Tc Measurement

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^{99}Tc: Important radionuclide for routine environmental monitoring

- Prevalent in the environment - Sellafield (UK) has discharged 1720 TBq over the period of 1952-2008
- Forms highly mobile ions: $Tc(VII)O^{4-}$ (under oxidising conditions)
- Long half-life ($T_{1/2}$: $2.111 \times 10^{5}(12)$ y)

Reference	Source	^{99}Tc release (TBq)
Cefas, 2008	Sellafield reprocessing plant (1952-present)	1720
Shi *et al.*, 2012a	La Hague reprocessing plant (1966-present)	154
Aarkrog *et al.*, 1986	Atmospheric weapons testing (1940s-70s)*	140
Uchida *et al.*, 1999	Chernobyl nuclear accident	0.97
Bailly du Bois *et al.*, 2012	Fukushima-Daiichi nuclear accident⁺	220

* Calculated from Cs-137 fallout and fission yield of ^{99}Tc

⁺ Calculated from seawater Tc/Cs ratio of 0.01, with 22PBq estimated Cs release

^{99}Tc Measurement – Importance of Tracers

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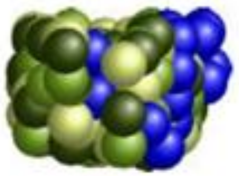
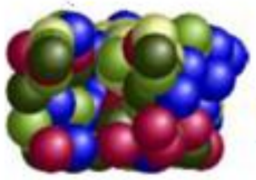
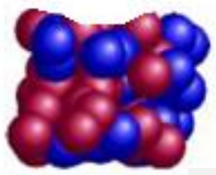
Tracers are required to determine the chemical yield of a process e.g., separation scheme.
No stable isotopes of technetium exist ∴ need for a supply of radiotracers to support analysis of ^{99}Tc.

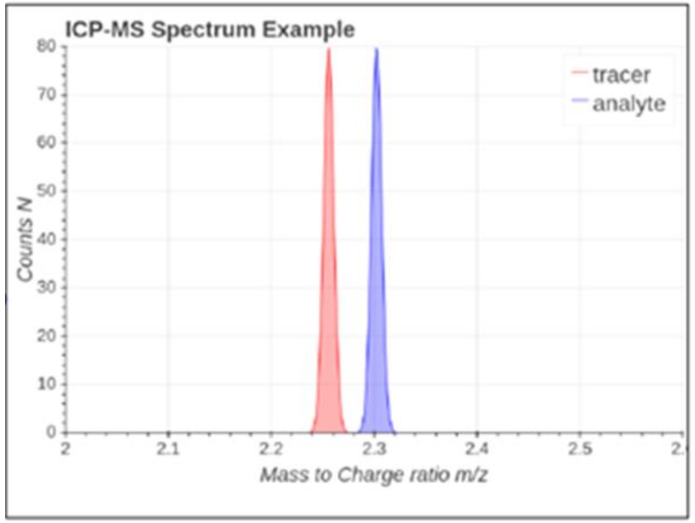
Sample
(+interferences)



Tracer-spiked
sample



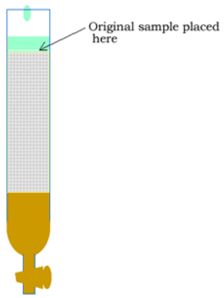




Tracer

- Chemically identical to analyte
- Discrete physical characteristic
- Does not contain analyte

Separation



Measurement

- Remove interference
- Retain tracer and analyte for measurement

^{99}Tc Measurement – ICP-MS

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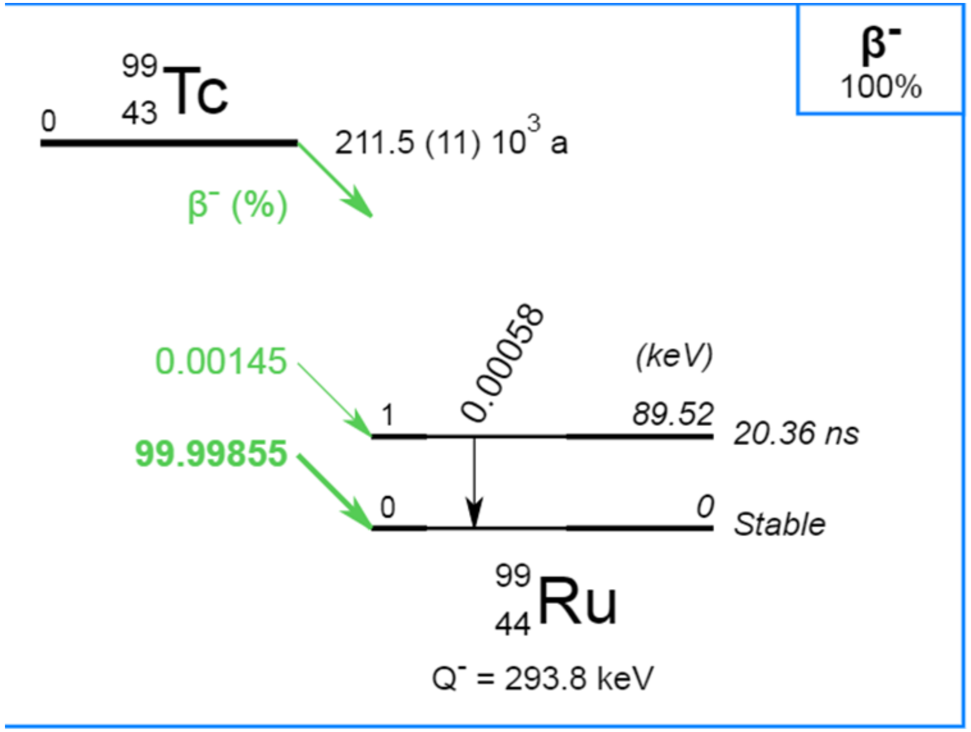
Reference	Matrix	Separation	Measurement	LOD
Kabai et al. 2013	Milk	TEVA	LSC	0.2 Bq/L
Temba et al. 2016	Filters	TEVA	LSC	3.15 Bq/L
Guerin et al. 2017	Water	TRU	LSC	5 Bq/L
Su et al. 2017	Cement	TEVA	ICP-MS	8.5 Bq/kg
Sahli et al. 2017	Sediment	TEVA	ICP-MS	0.03 Bq/kg
Matsueda et al., 2021	Water	TK201	SPE-ICP-MS	0.0059 Bq/L

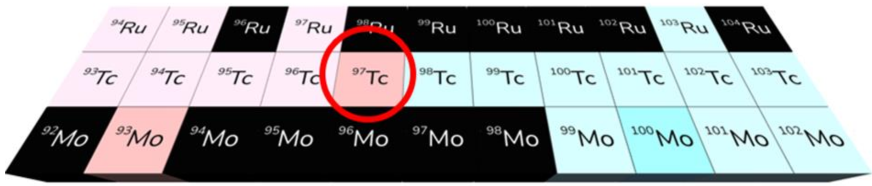


http://www.lnhb.fr/nuclear-data/module-lara/

Increase in ICP-MS being used for ^{99}Tc measurement

^{99}Tc Separation and Measurement – Existing Radiotracers

^{99}Tc Measurement	Tracer Used	Reference
ICP-MS	^{95m}Tc: $T_{1/2}$ - 61.96 ± 0.24 d (measured by gamma spectrometry)	McCartney et al., 1999
		Tagami and Uchida., 2005
	^{97}Tc: $T_{1/2}$= 4.21 x 10^6(16) y (measured by isotope dilution ICP-MS)	Beals et al., 1997
LSC ICP-MS	Stable Re*	Butterworth et al., 1995

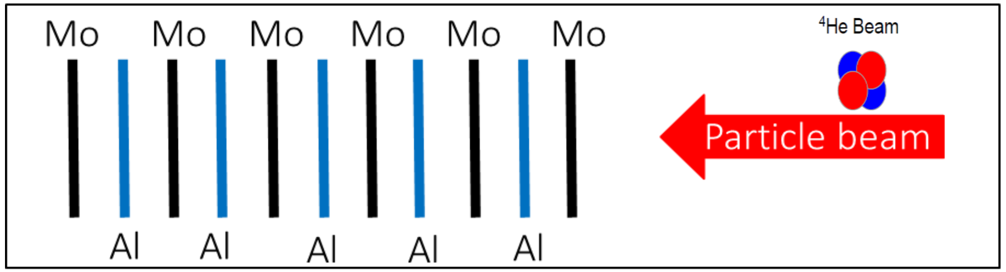


Tracer most suited for ICP-MS is ^{97}Tc. However, it is currently not widely supplied by industry.

^{97}Tc Tracer - Production Route

Cyclotron Irradiation at University of Birmingham:

- A stack of 6x 1µm ^{nat}Mo foil target irradiated with a ^{4}He charged particle beam for 6 hours at 40 MeV



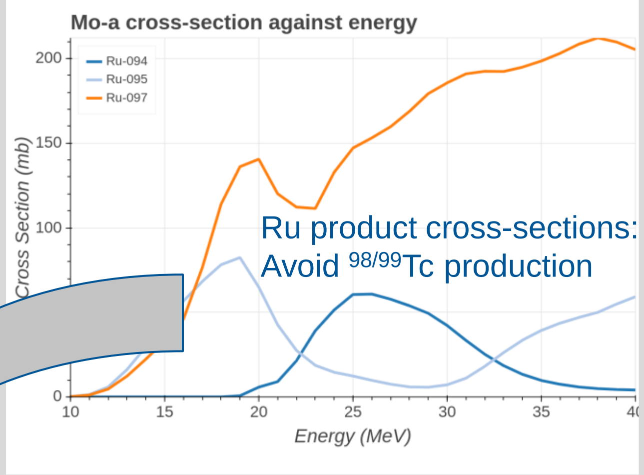
$$^{nat}\mathrm{Mo}(^{4}\mathrm{He}, xn)^{97}\mathrm{Ru}$$

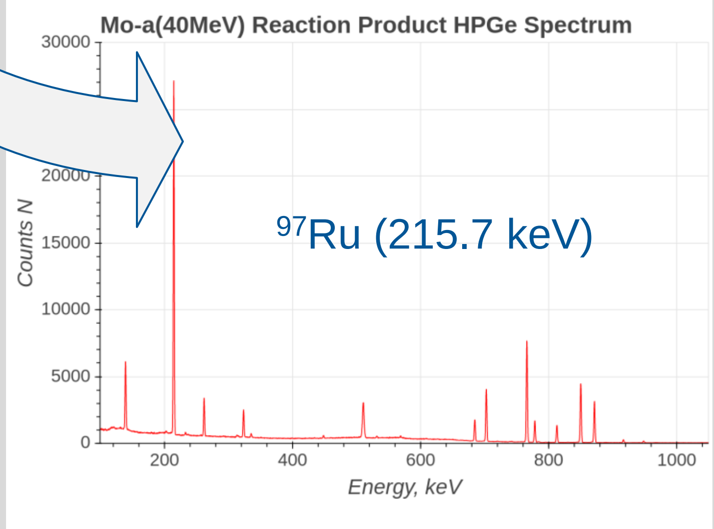
$$^{97}\mathrm{Ru} + ^{-} e \rightarrow ^{97}\mathrm{Tc} + \nu_e$$

- Initial gamma spectrometry analysis at University of Birmingham showed the successful production of ^{97}Ru (E(γ) = 215.7 keV)

Next, radiochemistry required to produce ^{97}Tc from ^{97}Ru

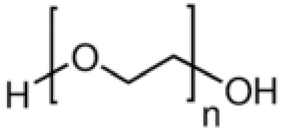
Nuclear Reaction Modelling





Technetium Separation with TK202 Resin

Extractant system: polyethylene glycol (PEG)



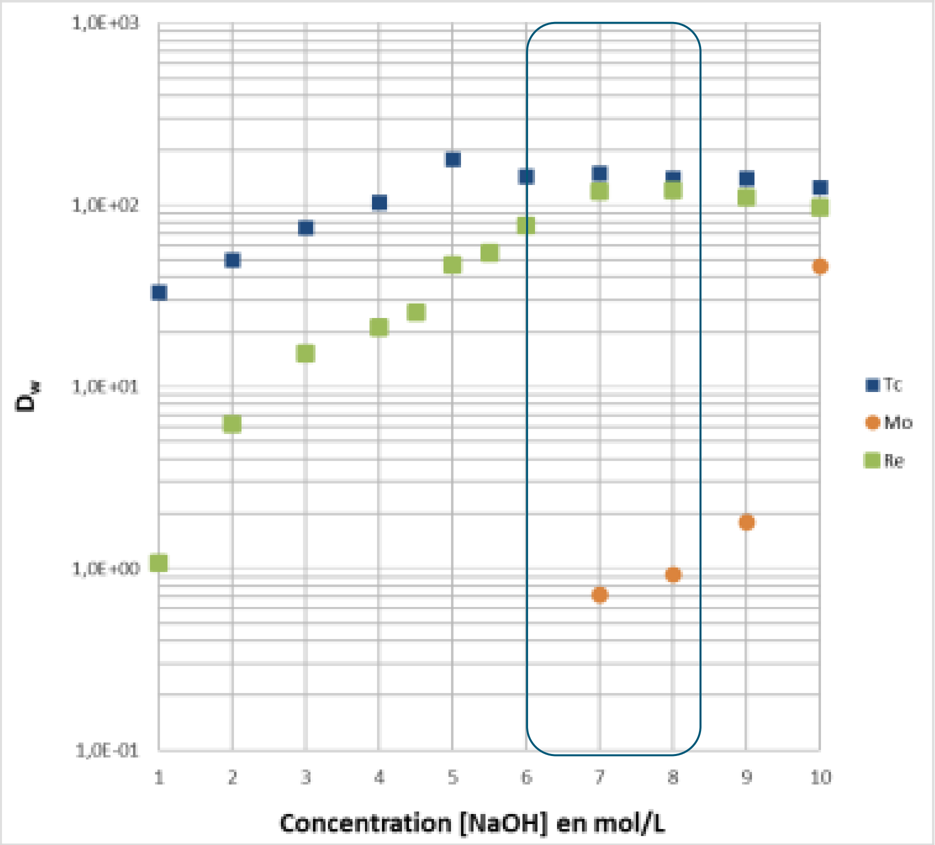
Separation of **Technetium(VII) from alkaline samples**

- e.g. Tc from Mo foil target
- Load sample in 7-9 M NaOH
- Ru behaviour unclear

Tc can be eluted directly using dilute acid or deionised water → expect minimal Mo breakthrough

Well established method for both ^{99}Tc and ^{97}Tc measurement via ICP-MS

TK202 TrisKem Product Sheet



Method Development – TK202 Resin

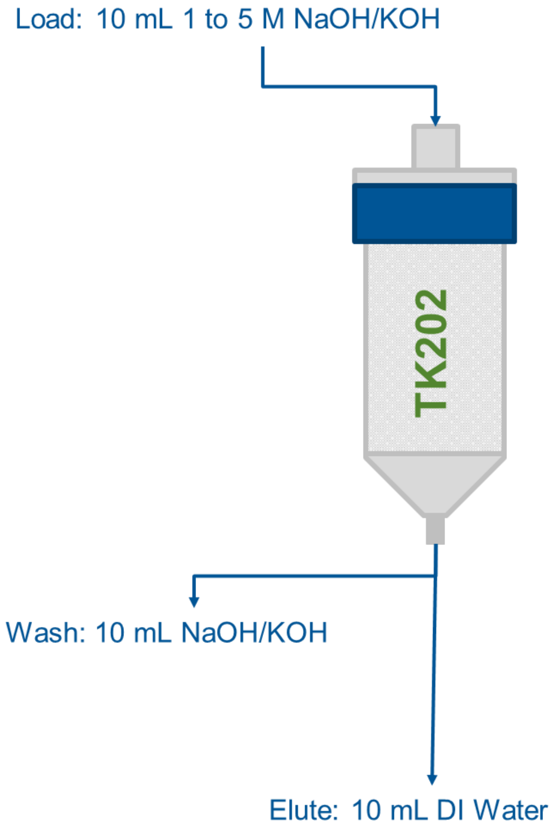
Radiochemistry Requirements:
- Resin capable of handling > 100 mg of Mo foil target and alkaline conditions
- Low Mo breakthrough for both Ru and Tc fraction collected.

$$^{nat}\mathrm{Mo}(^{4}\mathrm{He}, xn)^{97}\mathrm{Ru}$$

$$^{97}\mathrm{Ru} + ^{-}e \rightarrow ^{97}\mathrm{Tc} + \nu_e$$

Mo Target Dissolution
1. Alkaline foil dissolution with 30% or 50% hot hydrogen peroxide.
2. Dissolve the resulting precipitate in either NaOH or KOH (1 to 5 M) for direct loading onto TK202 resin (method outlined by Pawlak et al., 2016 used)

TK202 Separation – Inactive Test
1. Spike alkaline Mo sample with Ru and Re (analogue of Tc used for initial testing)
2. Load sample (NaOH or KOH) directly to 2 mL TK202 resin → collect Ru
3. Elute Re using DI water
4. Collect load, wash and eluted fraction and measure by ICP-MS to determine optimal method – assess which method leads to **low Mo breakthrough, high Ru and Re recovery**



Method Development – NaOH and KOH

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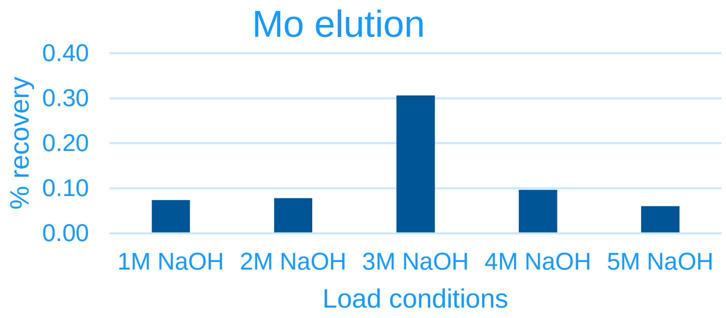
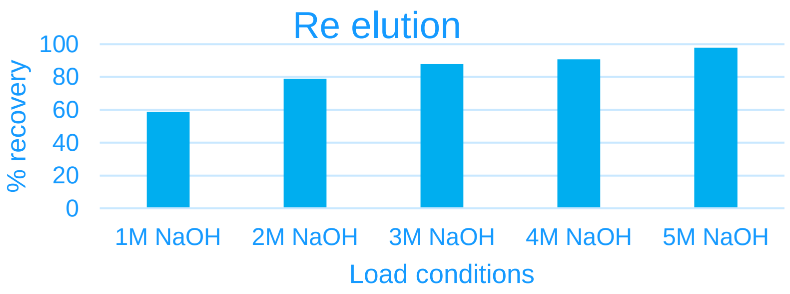
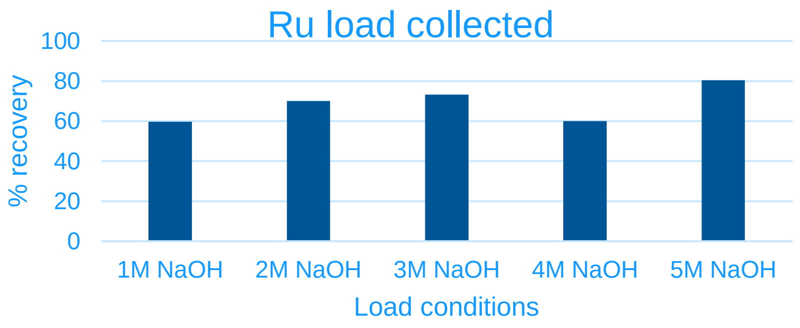
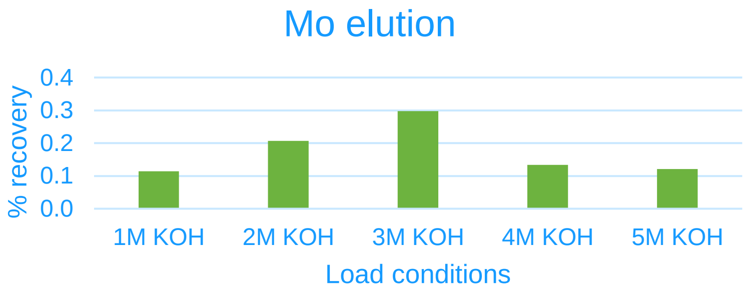
NaOH - TK202 Resin

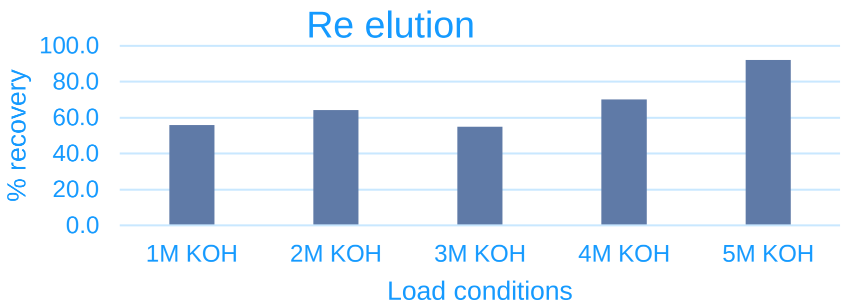


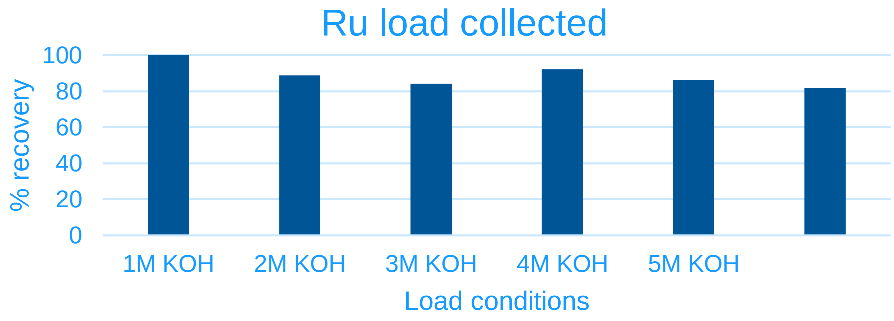




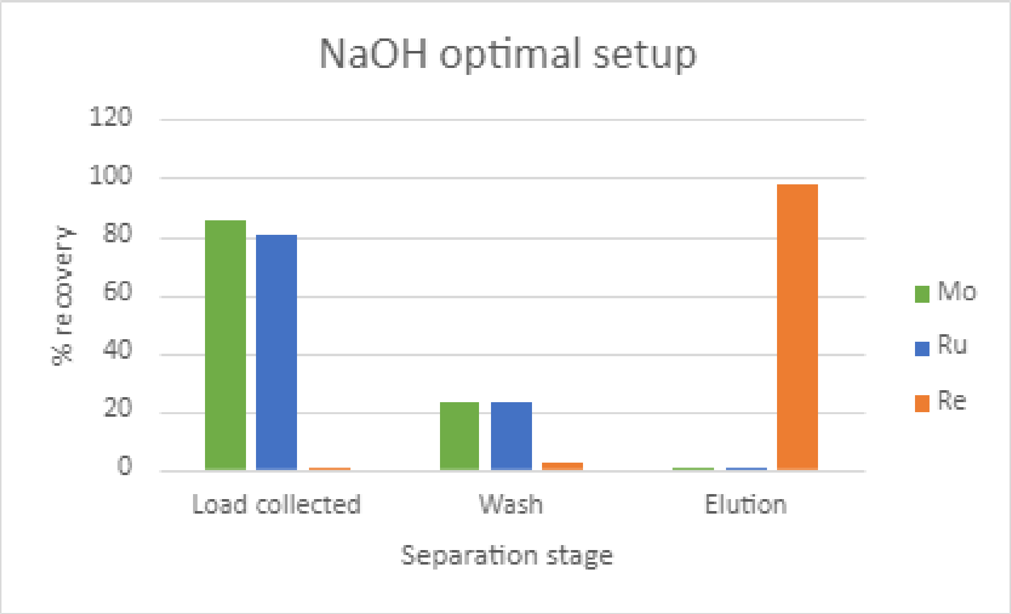
KOH - TK202 Resin

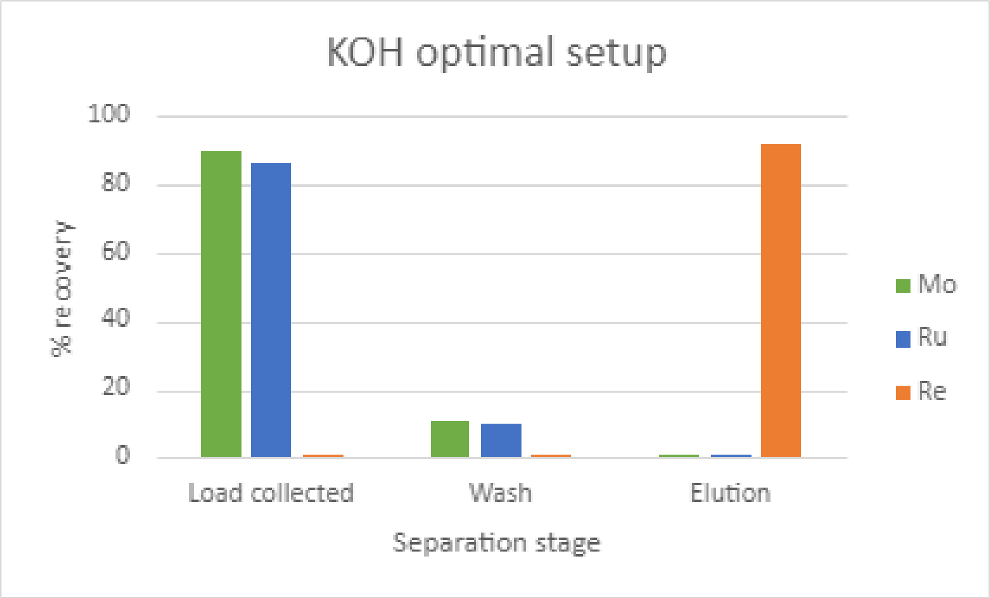






Method Development – Optimal Method





Low Mo breakthrough and high Ru (load) and Re (eluent) recovery observed with 5 M NaOH

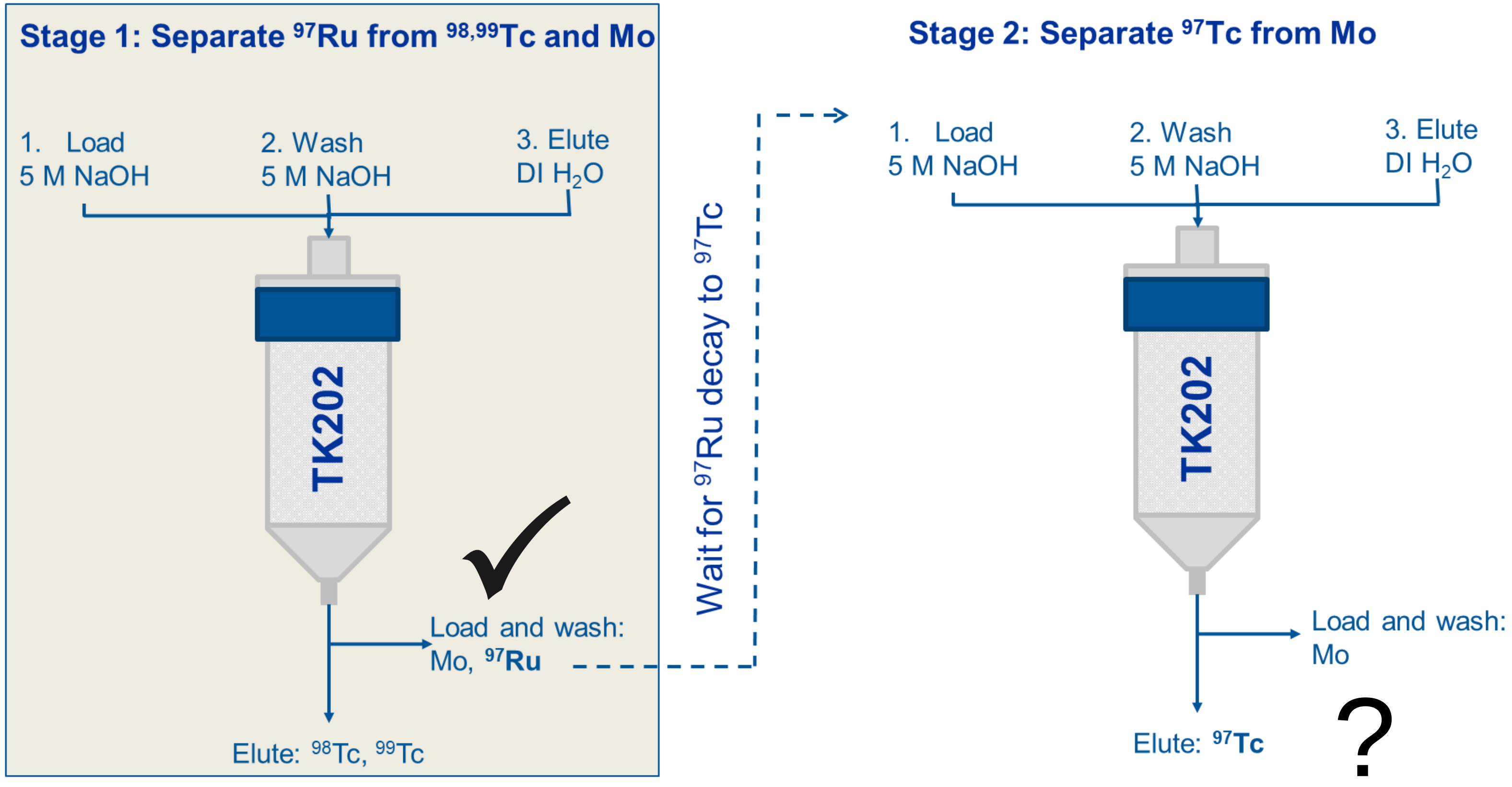
Method Validation – Separation Scheme

Experimental Methodology
Mo Target Dissolution

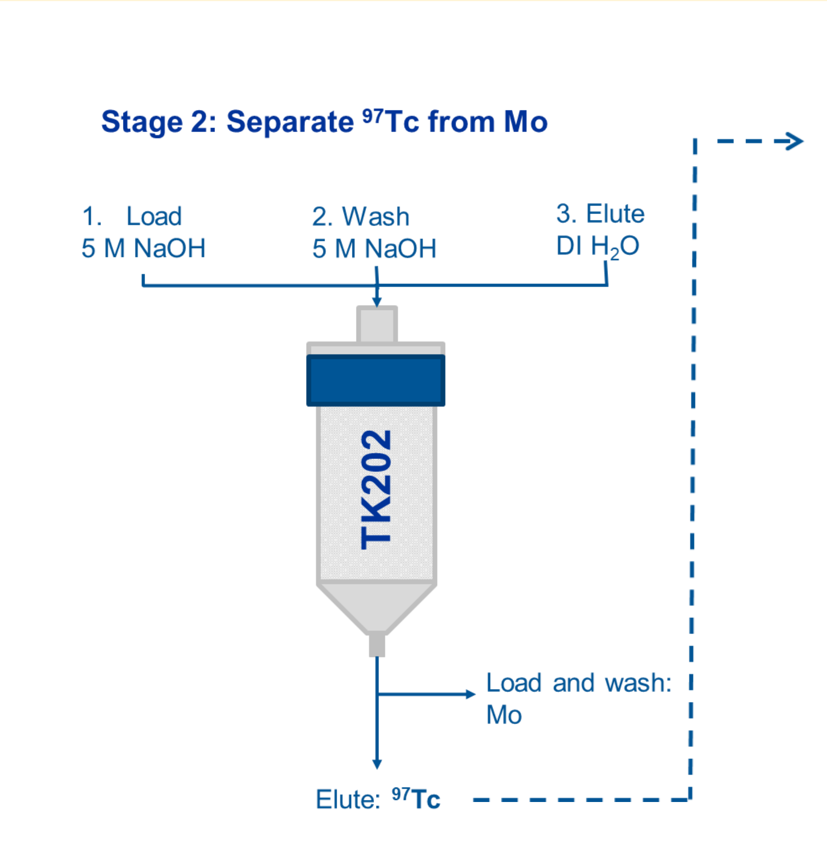
1. Add hydrogen peroxide and heat Mo target to 80ºC for 5 minutes
2. Re-prepare sample in 5 M NaOH for direct loading onto TK202

TK202 Resin

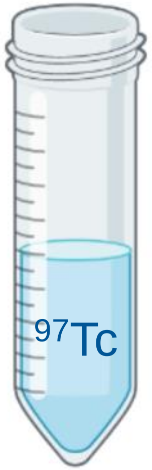
3. Stage 1 - ^{97}Ru collection
   - Initial sample screening of load and wash sample via gamma spectrometry to confirm production of ^{97}Ru
   - Impurities removed: ^{95}Tc, ^{98}Tc or ^{99}Tc
4. Stage 2 – High purity ^{97}Tc collection
   - Eluent collected and measured via ICP-MS to confirm if ^{97}Tc is present

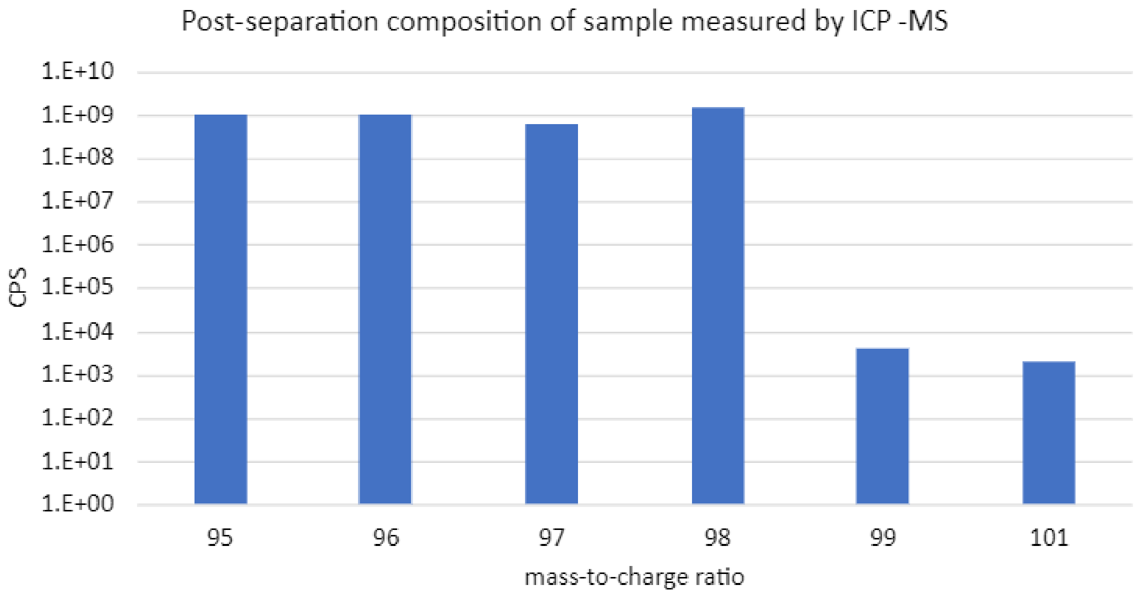


Results – Initial Screening of Stage 2: ^{97}Tc



Eluent measured by ICP-MS: confirmed Mo breakthrough requires further clean-up.





Summary

- Mo decontamination of 1.4×10^{6} in final fraction compared to dissolved Mo target
- High counts observed at m/z 95 to 98 indicating presence of large Mo contamination in eluent fraction → further separation required to remove Mo contribution at m/z 97.

Conclusions and next steps

- ^{97}Tc tracer is an industry-relevant tracer, which is an ideal candidate to be used by radioanalytical laboratories to asses the chemical yield for Tc separation.
- First target sent to NPL from a cyclotron-irradiation completed at the University of Birmingham.
- TK202 resin characterised for effective Mo, Tc and Ru separation.
  - Radiochemistry at NPL used to separate ^{97}Ru from Mo target.
  - Following ^{97}Ru decay, ^{97}Tc was separated and analysed via ICP-MS.
- ICP-MS measurement of ^{97}Tc shows additional Mo removal is required to remove ICP-MS interferences: mainly isobaric ^{97}Mo and ^{98}Mo tailing
  - Future work: investigate the use of tandem TK202 cartridges or alumina to improve Mo removal.