Developments in Technetium separation for environmental monitoring, nuclear medicine and tracer production

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2023 Triskem User Group Meeting, 22nd February

Overview

Nuclear Metrology Group

Research Motivation

- Measurement of Technetium
- Importance of Tracers

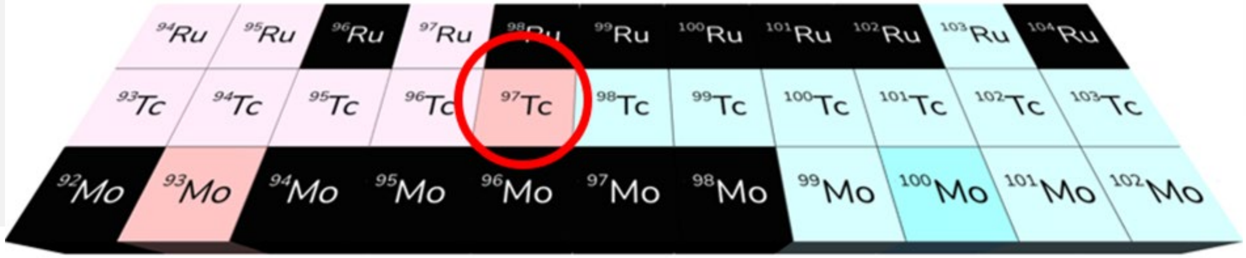
Separation of Technetium

- Current Separation Methods

Applications

- Environmental Monitoring
- Nuclear Medicine
- Tracer Production

Summary



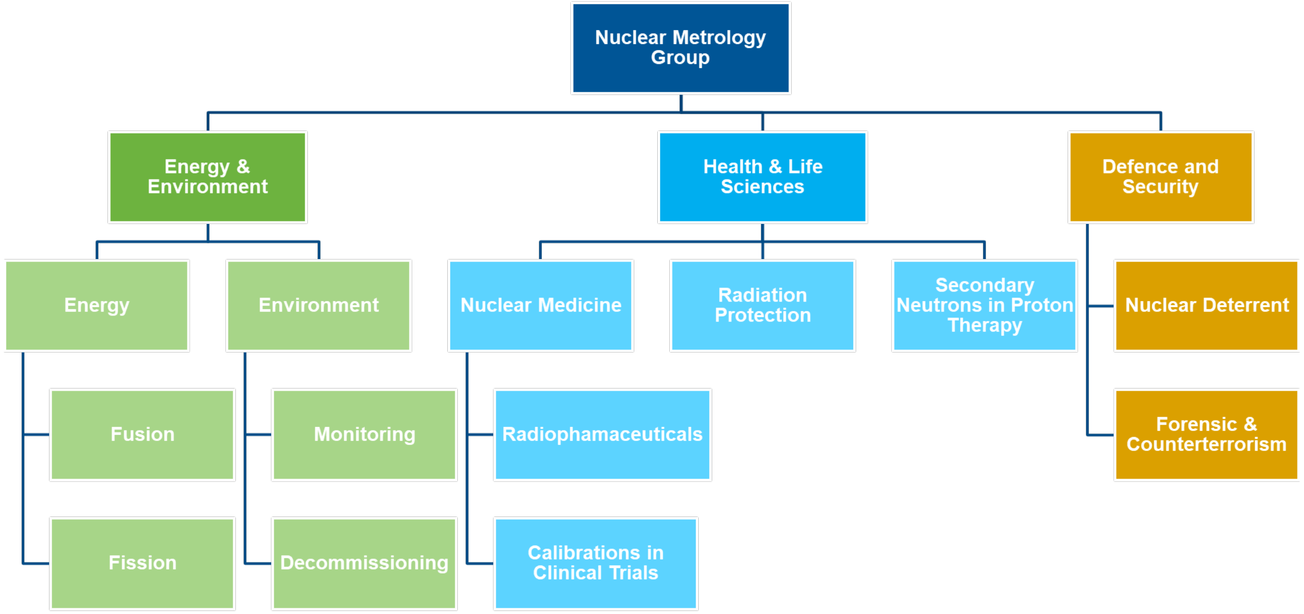
NMG: Radiochemistry

Capabilities:

1. Development of separation schemes for radionuclides of interest for nuclear medicine, decommissioning or environmental monitoring applications

2. Expanding the use of tandem inductively coupled plasma-mass spectrometry (ICP-MS/MS) for accurate long-lived radionuclide measurement

3. Support supply of radionuclide standards and tracers to end users



Research Motivation – Technetium

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

- Prevalent in the environment- reprocessing sites, weapons test fallout, nuclear accidents
- Forms highly mobile ions: Tc(VII)O^{4-} (under oxidising conditions)
- Long half-life ($T_{1/2}$: 2.111x10^5(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

^{99m}Tc: radiopharmacy and nuclear medicine applications

- Widely used medical radionuclide with supply significantly dependent on the availability of fission-produced ^{99}Mo
- Alternative methods for production investigated with a need for optimised approaches with a high capacity for ^{99}Mo removal

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TYPE Review
PUBLISHED 22 July 2022
DOI 10.3389/fchem.2022.926258

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OPEN ACCESS

EDITED BY
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New strategies for a sustainable ^{99m}Tc supply to meet increasing medical demands: Promising solutions for current problems

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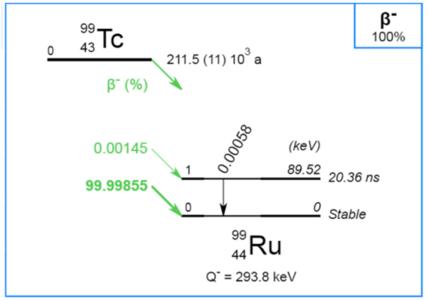
Department of Chemistry, Biochemistry, and Pharmaceutical Sciences (DCBP), Faculty of Science, University of Bern, Bern, Switzerland

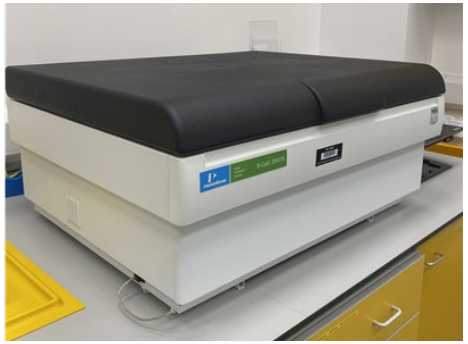
Research Motivation – Measurement of ^{99}Tc

LSC Measurement

- Beta emitter- radiometric interferences (other beta-emitting radionuclides) need to be removed prior to LSC

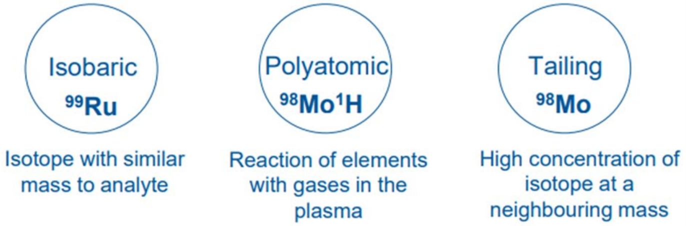


http://www.lnhb.fr/nuclear-data/module-lara/



ICP-MS Measurement

- Determination of ^{99}Tc by mass spectrometry requires the reduction and/or removal of isobaric interferences prior to measurement



Measurement of ^{99}Tc – Importance of Tracers

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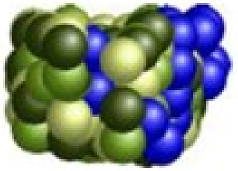
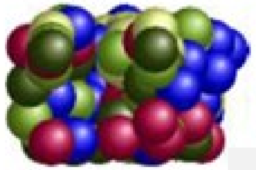
Tracers are required to determine the chemical yield of a process e.g., separation scheme.
No stable isotopes of technetium exist ∴ need for a supply of radiotracers to support analysis of ^{99}Tc.

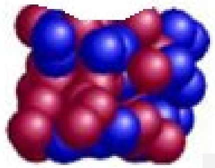
Sample
(+interferences)



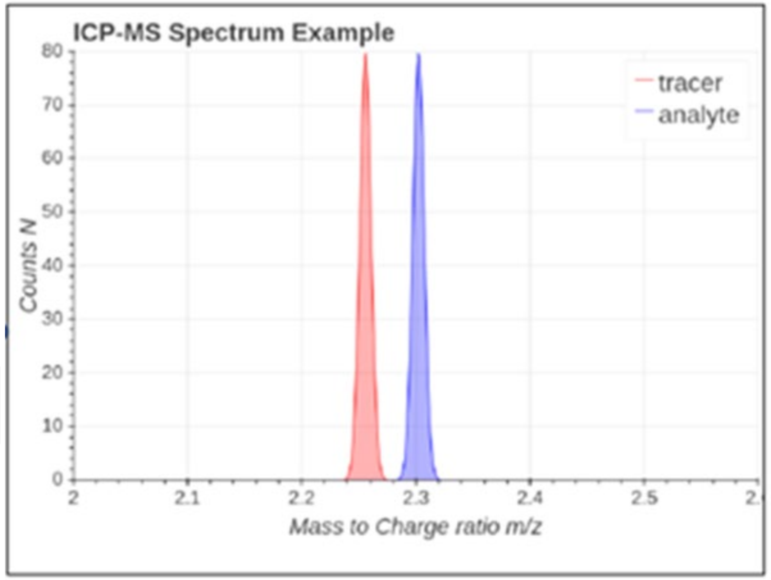
Tracer-spiked sample



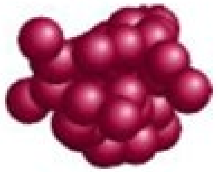
Separation



Measurement



- Remove interference
- Retain tracer and analyte for measurement



Tracer

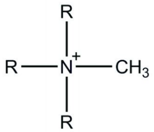
- Chemically identical to analyte
- Discrete physical characteristic
- Does not contain analyte

Separation of Technetium

- Current Separation Methods

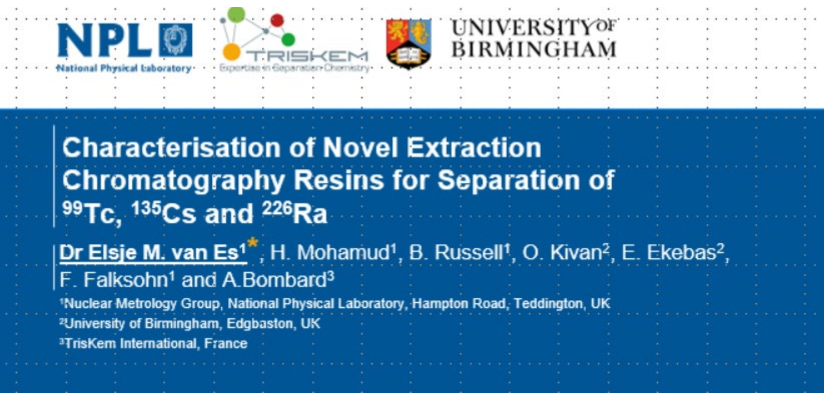
Current Separation Methods - TEVA Resin

Extractant system: Trialkyl-methylammonium nitrate/chloride



For Tc analysis, sample can be loaded in 0.01 - 1 M HCl and HNO_3 (both retain Tc(VII))

Tc may be eluted in 8 M HNO_3 → for both LSC and ICP-MS elution in dilute nitric or alkaline medium preferred

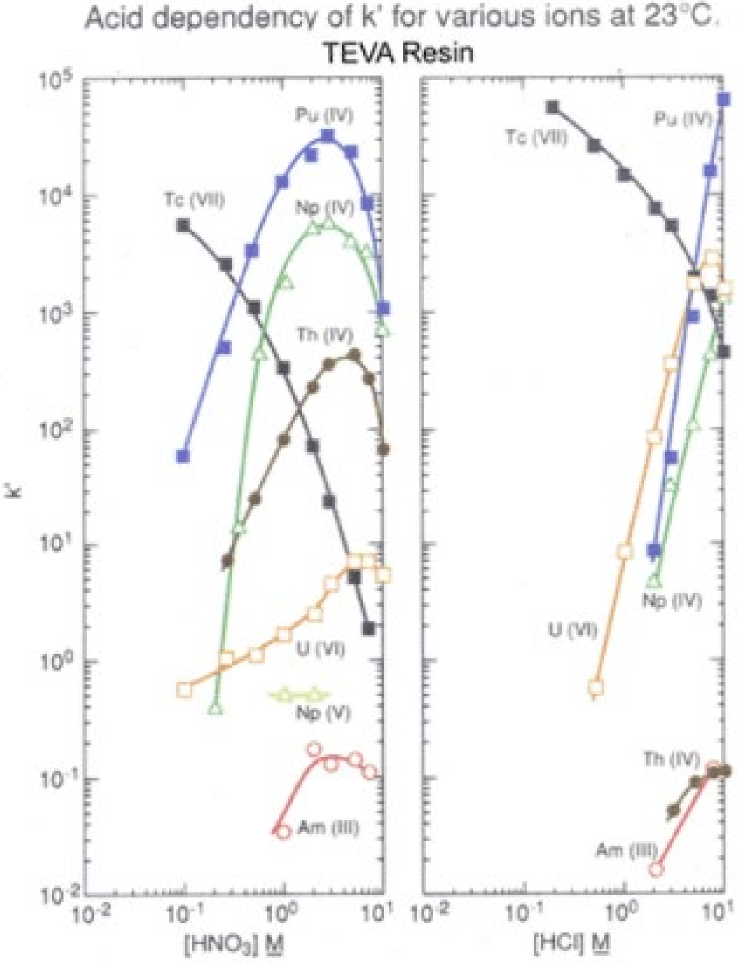

Characterisation of Novel Extraction Chromatography Resins for Separation of ^{99}Tc, ^{135}Cs and ^{226}Ra

Dr Elsje M. van Es[1*], H. Mohamud[1], B. Russell[1], O. Kivan[2], E. Ekebas[2], F. Falksohn[1] and A.Bombard[3]

[1]Nuclear Metrology Group, National Physical Laboratory, Hampton Road, Teddington, UK
[2]University of Birmingham, Edgbaston, UK
[3]TrisKem International, France

Previous 2019 UGM showed that TK201 resin was a good alternative to TEVA resin with elution of Tc possible with dilute NH_4OH

[TEVA Resin Product Sheet]



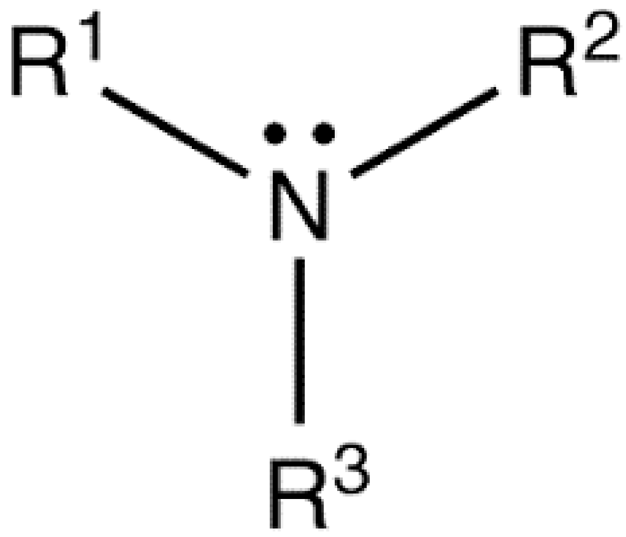
Application – Environmental Monitoring and Nuclear Medicine

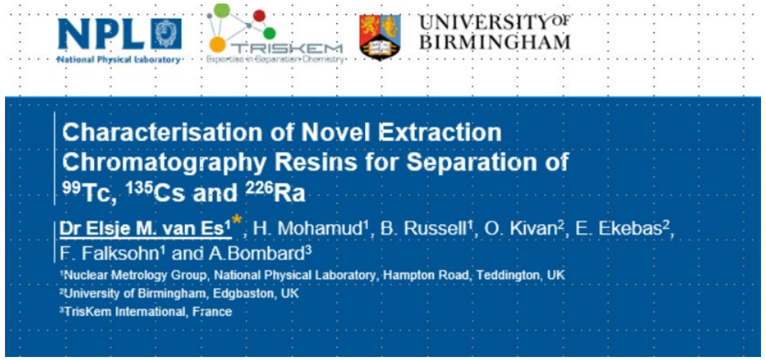
- TK201 Characterisation
- TK201 Elution Profile

TK201 Resin

TK201 Resin

- Based on a tertiary amine
- Also contains a small amount of a long-chained alcohol (radical scavenger) to increase its radiolysis stability.
- Can use dilute HNO_3 or alkaline conditions to elute Tc





Characterisation of Novel Extraction Chromatography Resins for Separation of ^{99}Tc, ^{135}Cs and ^{226}Ra

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Characterisation of TK201 Resin

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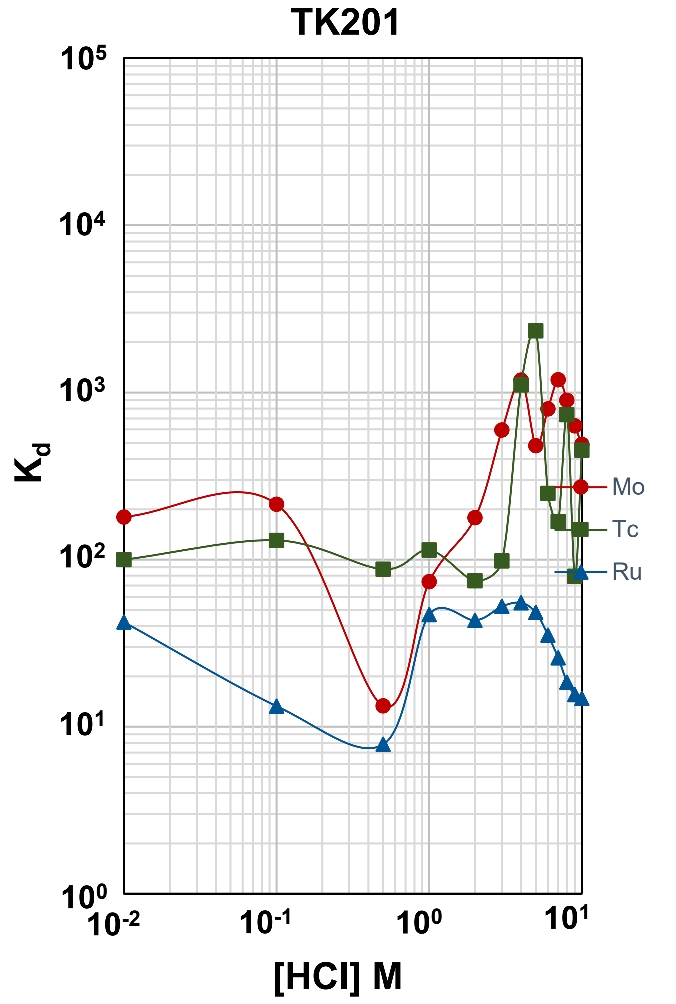
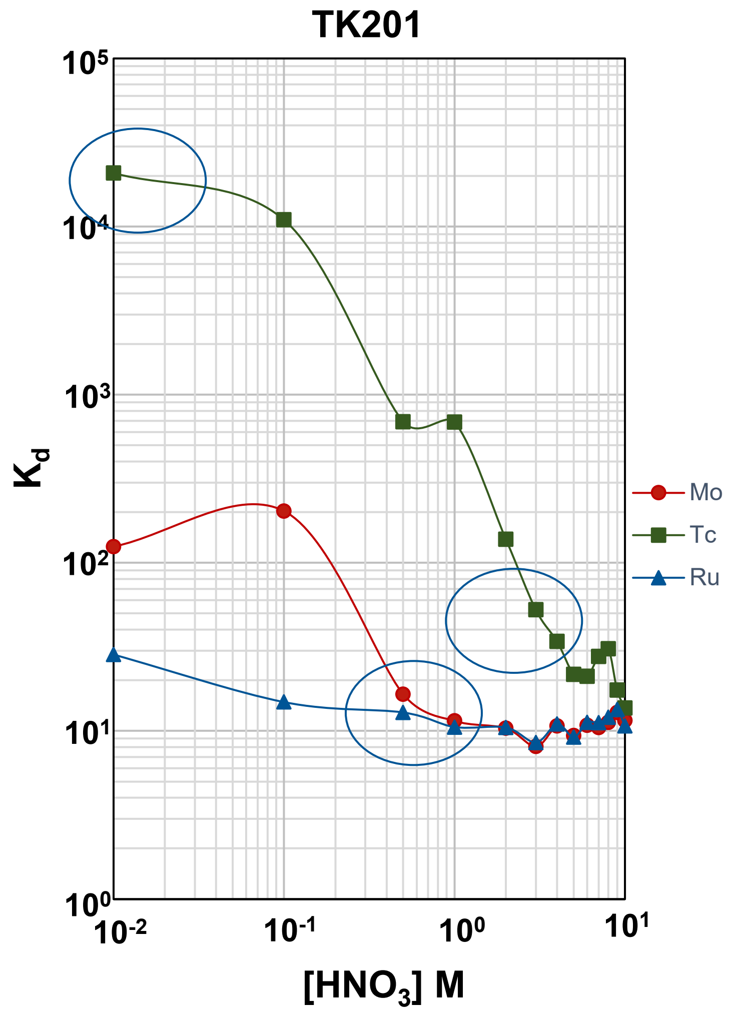
Varying HCl conditions (0.01 to 10 M)



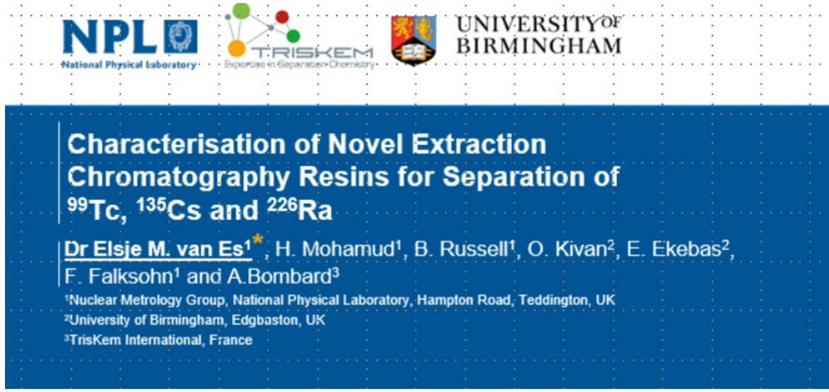
Varying HNO_3 conditions (0.01 to 10 M)



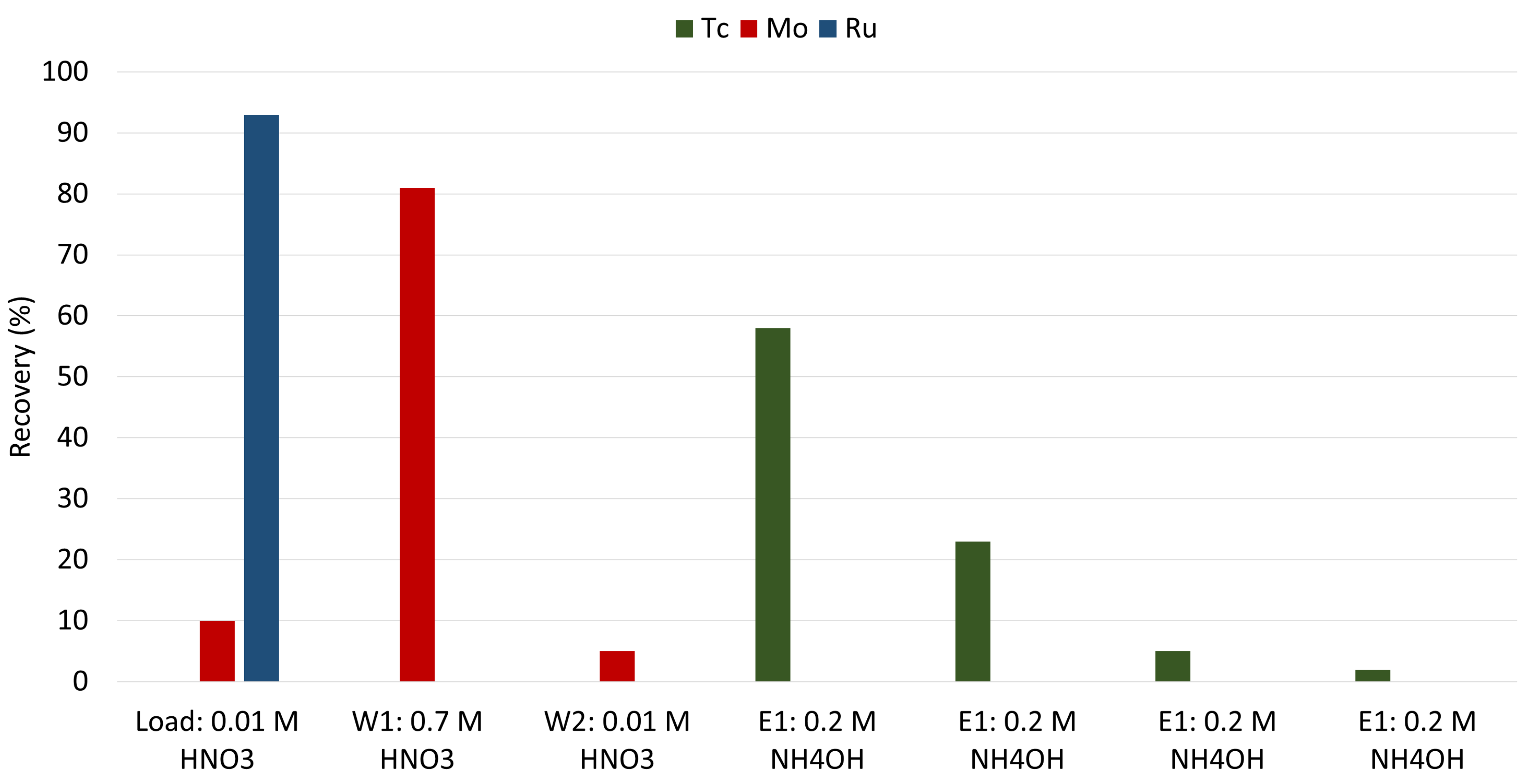
High Tc retention using 0.01 M HNO_3

Use of <1 M HNO_3 to remove Ru and Mo

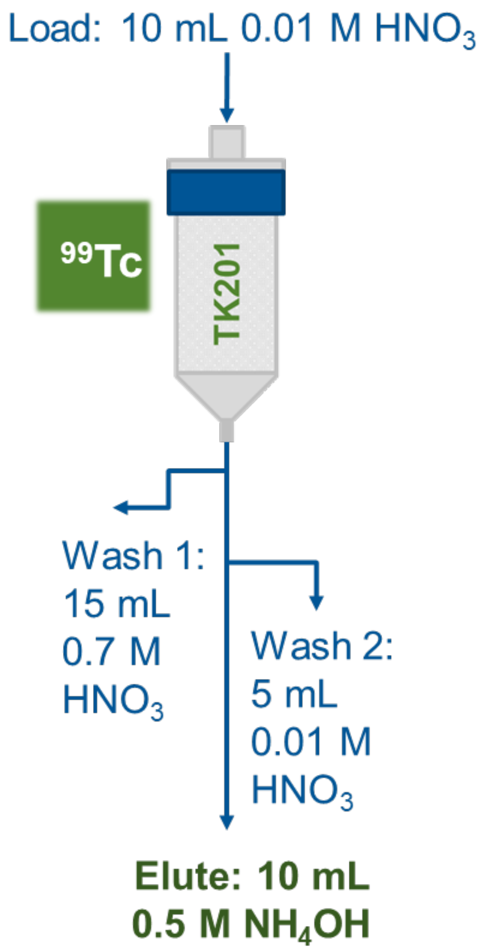
Can elute Tc using ≥ 2 M HNO_3



Elution Profile for TK201 Resin



Elution of ^{99}Tc with 0.2 M NH_4OH enables for > 90 % recovery

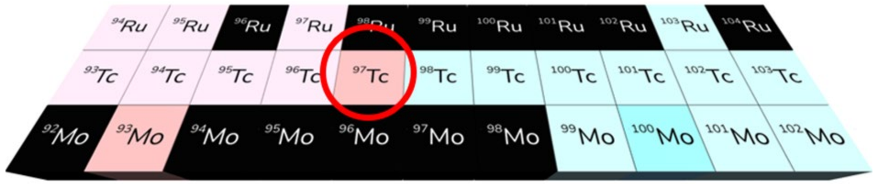


Application – Tracer Production

- Existing Radiotracers
- Method Development - TK202 Resin
- Method Validation – irradiated Mo target

^{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	McCartney et al., 1999
		Tagami and Uchida., 2005
	^{97}Tc: $T_{1/2}$= 4.21 x 10^6(16) y	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

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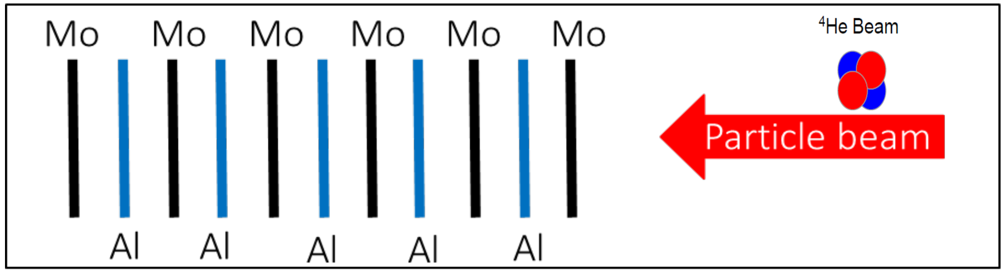
Cyclotron Irradiation at University of Birmingham:

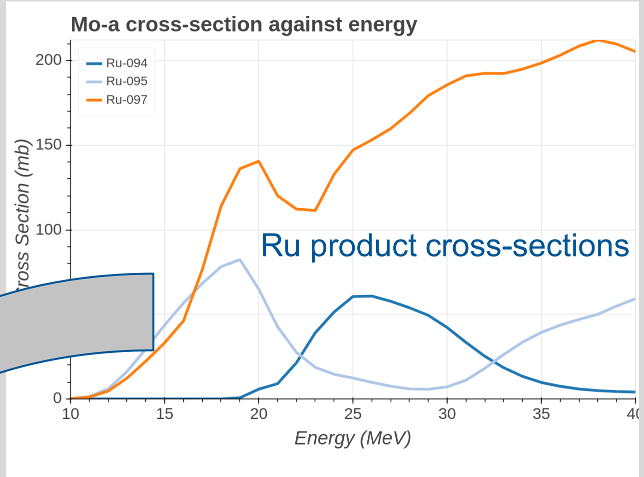
- Stack of 6x 1μm ^{nat}Mo foil target irradiated with a ^{4}He charged particle beam for 6 hours at 40 MeV

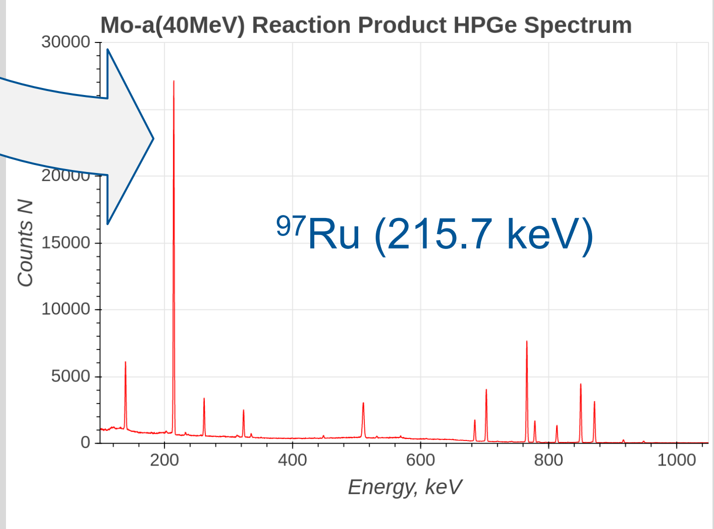


$$^{nat}\mathrm{Mo}(^{4}\mathrm{He}, xn)^{97}\mathrm{Ru}$$

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

Nuclear Reaction Modelling



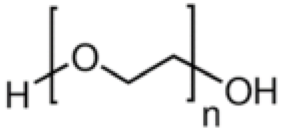


- Initial gamma spectrometry analysis at University of Birmingham showed the successful production of ^{97}Ru (E(γ) = 215.7 keV)

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

Technetium Separation with TK202 Resin

Extractant system: polyethylene glycol (PEG)



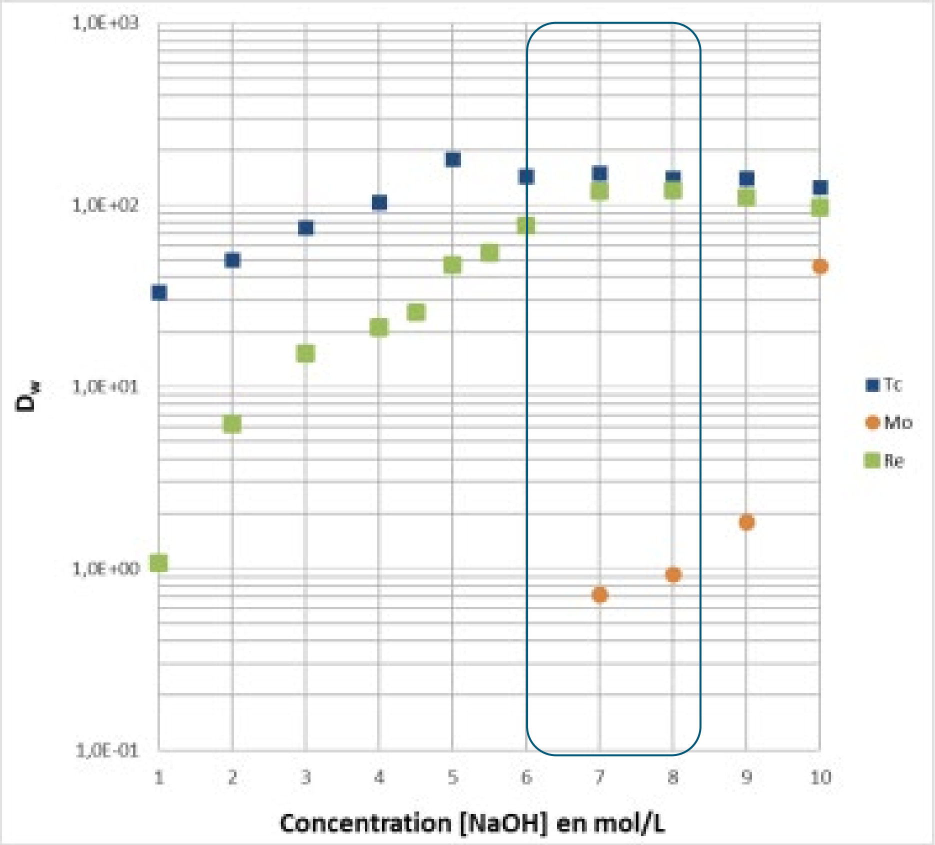
Separation of **Technetium(VII) from alkaline samples**

- e.g. Tc from Mo foil target
- Load sample in 7-9 M NaOH
- Ru behaviour unclear for ICP-MS applications?

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

Aim to develop method for both ^{99}Tc and ^{97}Tc measurement via ICP-MS

TK202 TrisKem Product Sheet



Method Development – TK202 Resin

National Physical Laboratory

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

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

Radiochemistry Requirements:

- Resin capable of handling > ppm levels of Mo foil target and alkaline conditions
- Low Mo breakthrough for both Ru and Tc fraction collected.

Initial Testing

Mo Target Dissolution

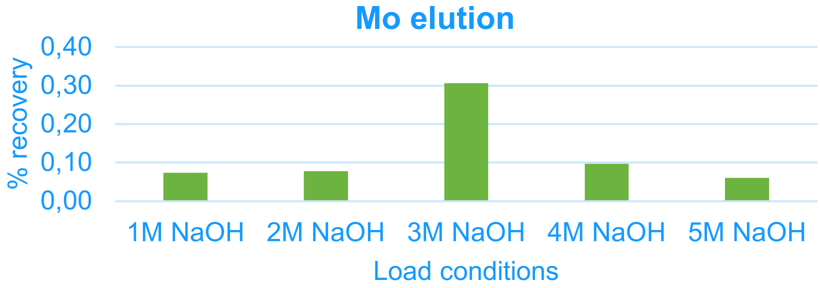
1. Alkaline foil dissolution with 30% or 50% hot hydrogen peroxide and then dissolving the resulting precipitate in either NaOH or KOH (1 to 5 M) for direct loading onto TK202 resin

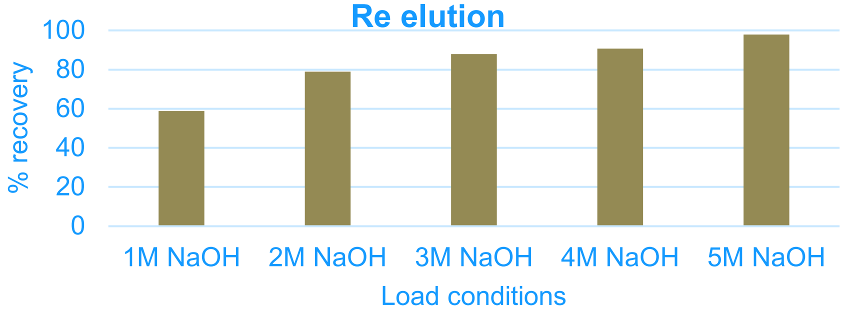
TK202 Separation

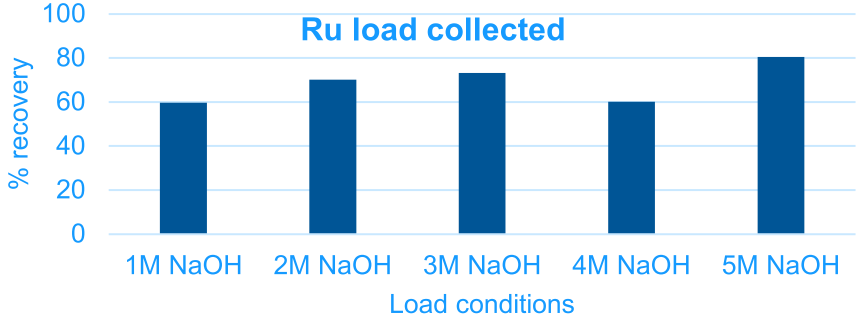
1. Spike alkaline Mo sample with Ru and Re (analogue of Tc used for initial testing)
2. Load sample (NaOH or KOH) directly to TK202 resin → collect Ru
3. Elute Re using DI water
4. Collect load, wash and eluted fraction and measure by ICP-MS to determine optimal method – assess which method leads to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

Method Development – Optimal Method

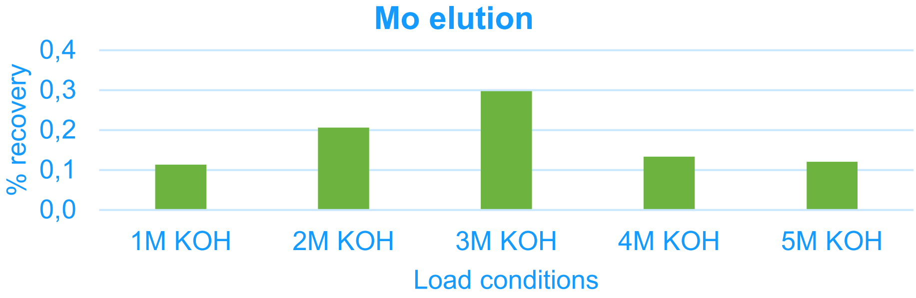
NaOH - TK202 Resin

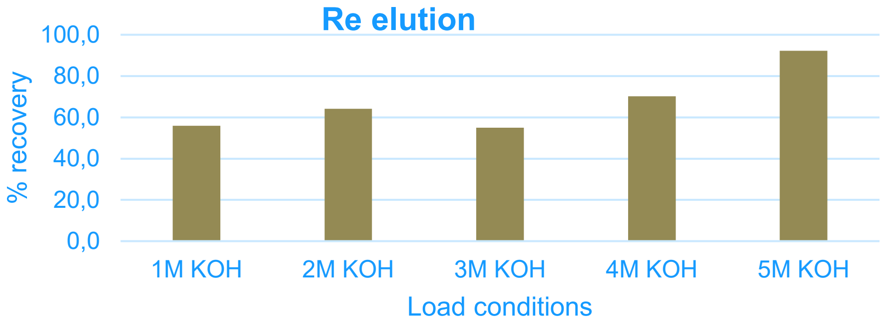


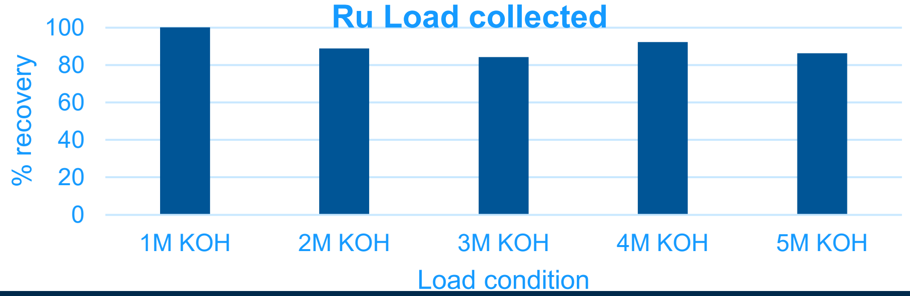




KOH - TK202 Resin







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

Method Validation – Separation Scheme

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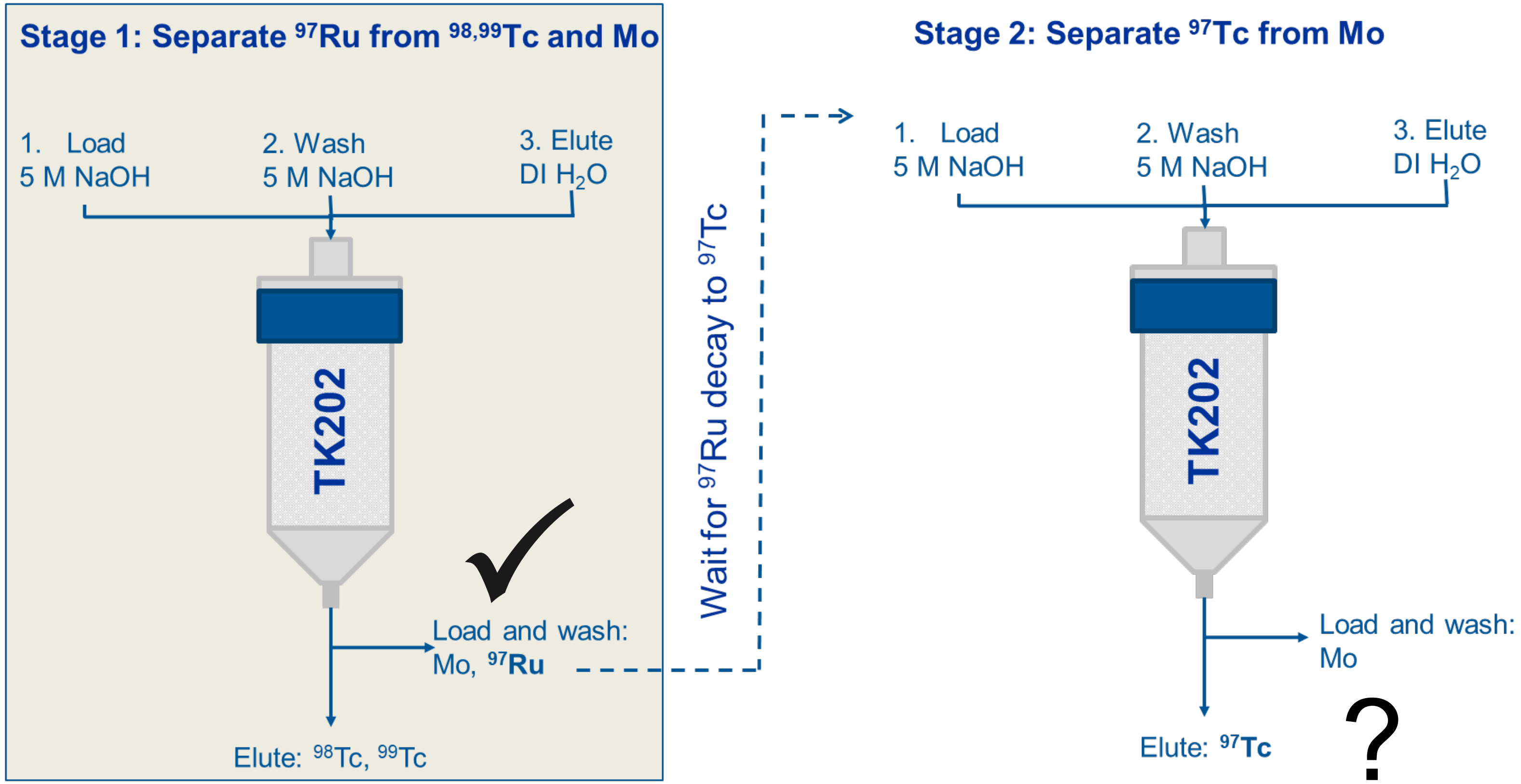
Experimental Methodology
Mo Target Dissolution

1. Add hydrogen peroxide and heat Mo target to 80^{o}C 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
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

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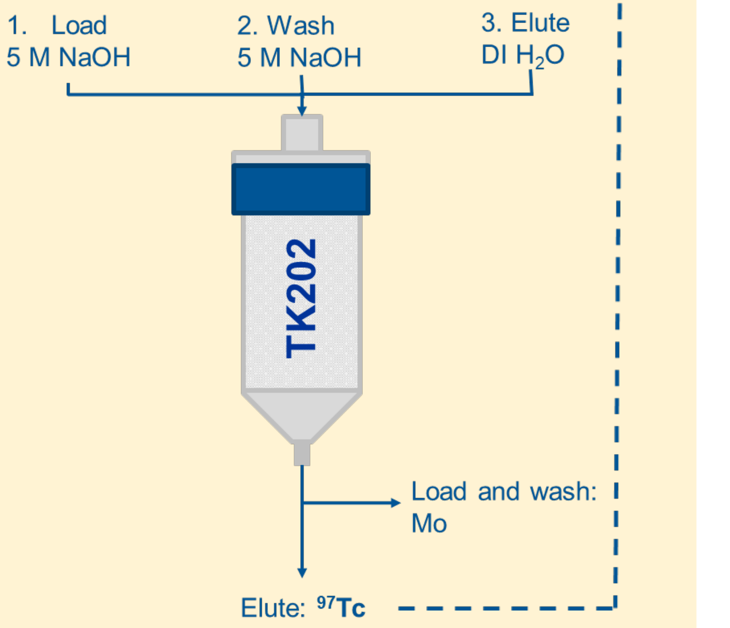
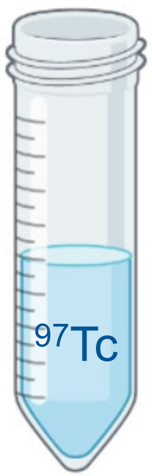
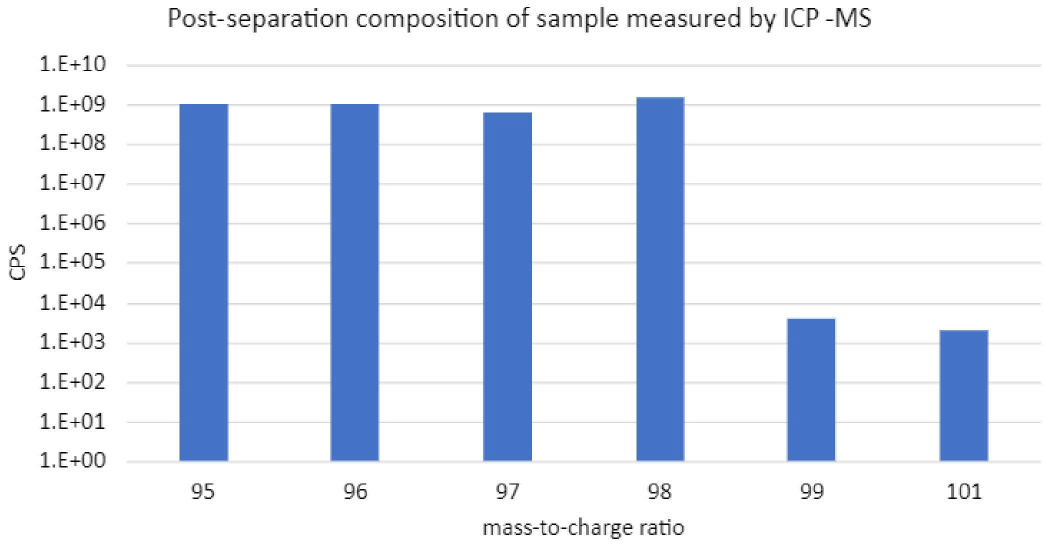
Stage 2: Separate ^{97}Tc from Mo



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





Summary

- Mo decontamination of $1.4x10^6$ 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 – TK202 Resin

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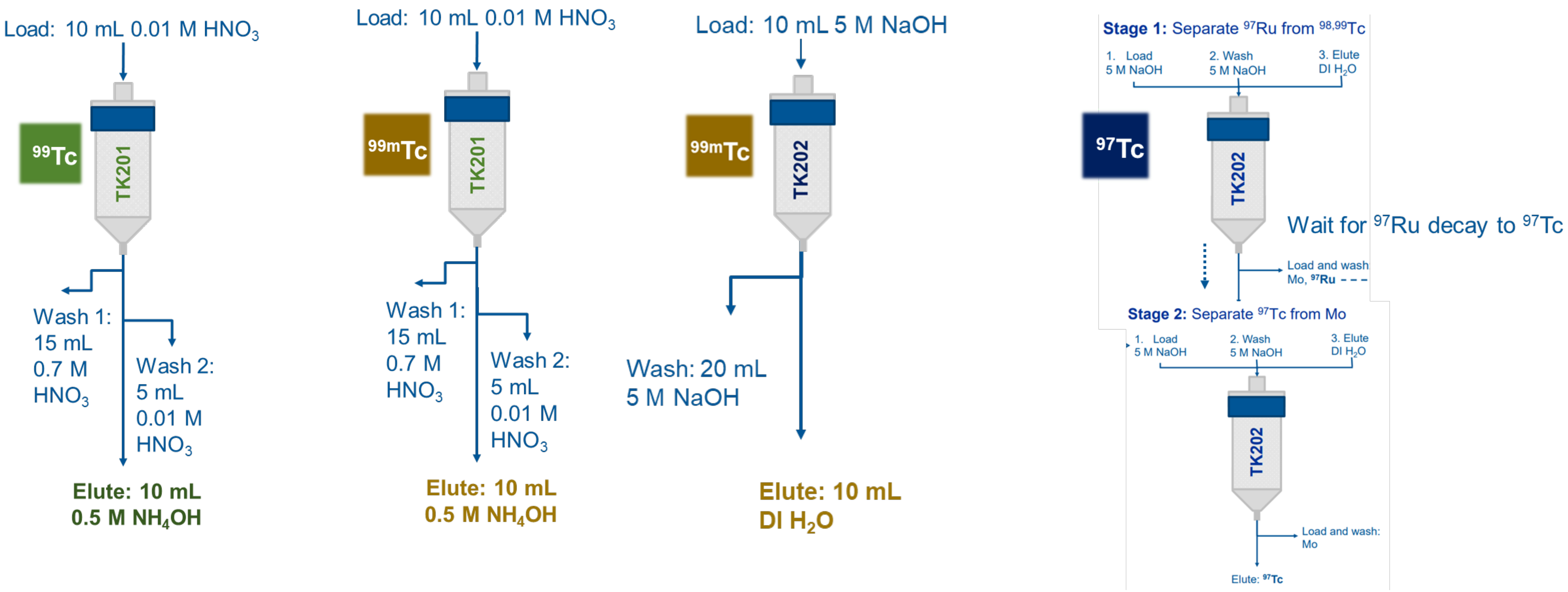
- ^{97}Tc tracer is an industry-relevant tracer, which is an ideal candidate to be used by radioanalytical laboratories to asses the chemical yield for Tc separation.
- First target sent to NPL from a cyclotron-irradiation completed at the University of Birmingham.
- Radiochemistry at NPL used to prepare a ^{97}Ru generator from Mo target.
- TK202 resin allowed for effective Mo and Ru separation.
  - Initial ICP-MS measurement of ^{97}Tc requires shows further Mo removal is required to remove ICP-MS interferences: mainly ^{98}Mo tailing.
  - Future work: investigate the use of tandem TK202 cartridges and CEX resins to improve Mo removal.
- Additional application is measurement of ^{99}Tc in solid samples following alkali dissolution.

Summary: Developed Tc Separation Methods

TRISKEM Expertise in Separation Chemistry — NPL National Physical Laboratory

Environmental	Nuclear Medicine	Tracer Production



Next steps- automated separation

National Physical Laboratory

- Hidex Q-ARE 50
- Aim to transfer existing separation schemes to this instrument
- Applicable to all Tc separation methods described
- Additional applications:
  - Environmental applications: High volume ^{226}Ra, ^{210}Pb and ^{90}Sr separations (TK100, TK101)
  - Nuclear Medicine: Lanthanide separations (LN resin)

Acknowledgments

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Many Thanks for Listening!
Any Questions?

Department for
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TRISKEM
Expertise in Separation Chemistry

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