Applications of novel resins for Technetium separation from environmental and target samples

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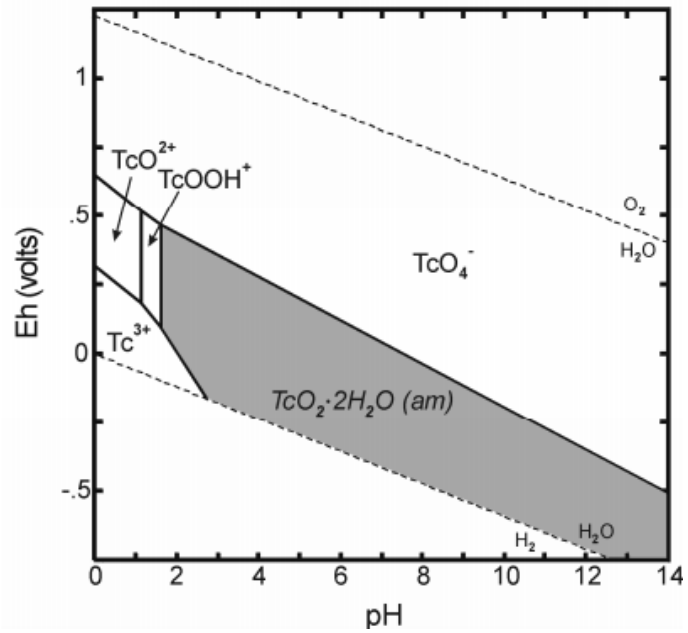
Motivation for ^{99}Tc measurement

- High yield fission product
  - ^{235}U thermal yield: 6.132(92) %
- Long lived radionuclide
  - $T_{1/2}$: 2.111(12) x 10^5y
- Environmental concern
  - Forms mobile ions: Tc(VII)O^{4-}
  - Sellafield (UK) has discharged 1720 TBq over the period of 1952-2008
- Complex analysis
  - Beta emitter
  - Separation from interferences required
- Analysis Techniques
  - Liquid Scintillation Counting
  - **Inductively Coupled Plasma Mass Spectrometry**



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

ICP-MS measurement of ^{99}Tc

- Increasingly applied to ^{99}Tc measurement
- Measurement requires removal of interferences by offline separation

Isobaric
^{99}Ru
Isotope with similar mass to analyte

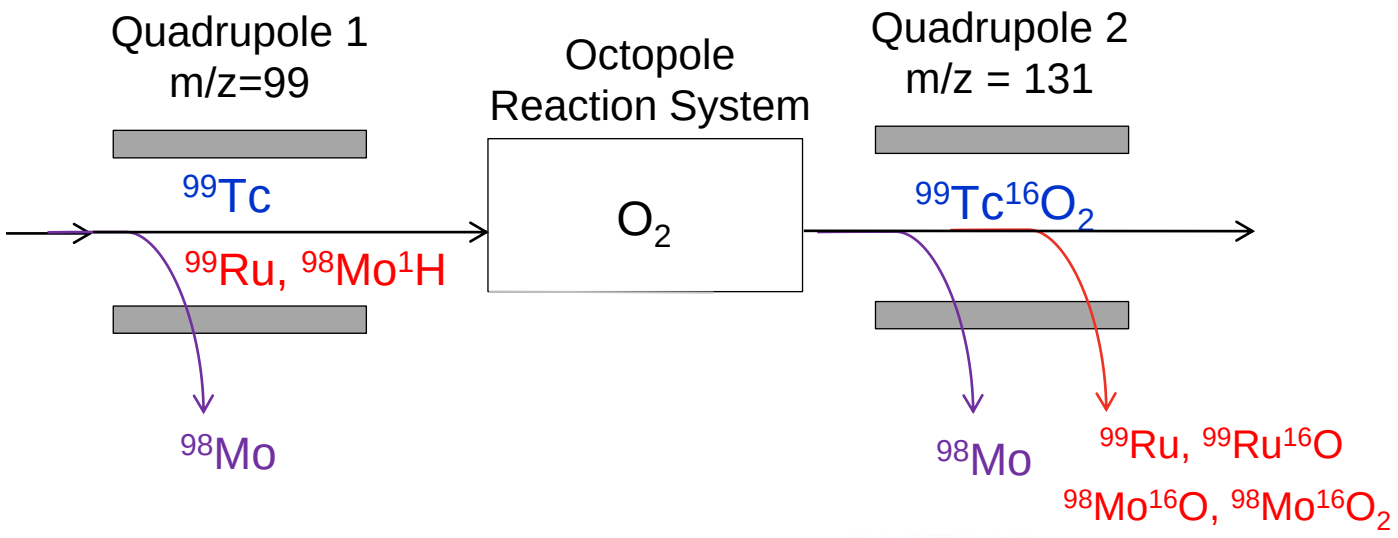
Polyatomic
$^{98}Mo^{1}H$
Reaction of elements with gases in the plasma

Tailing
^{98}Mo
High concentration of isotope at a neighbouring mass

Reference	Sample	Separation	LoD (mg/kg)	LoD (Bq/kg)
Su et al. (2015)	LLW cement	TEVA	0.795	8.5
Zhang et al. (2017)	Groundwater	TEVA	0.155	0.0002
Sahli et al. (2017)	River sediment	TEVA	0.0028	0.03
Kołacińska et al. (2018)	Reactor coolant water	TEVA	0.00056	0.006

ICP-MS/MS measurement of ^{99}Tc

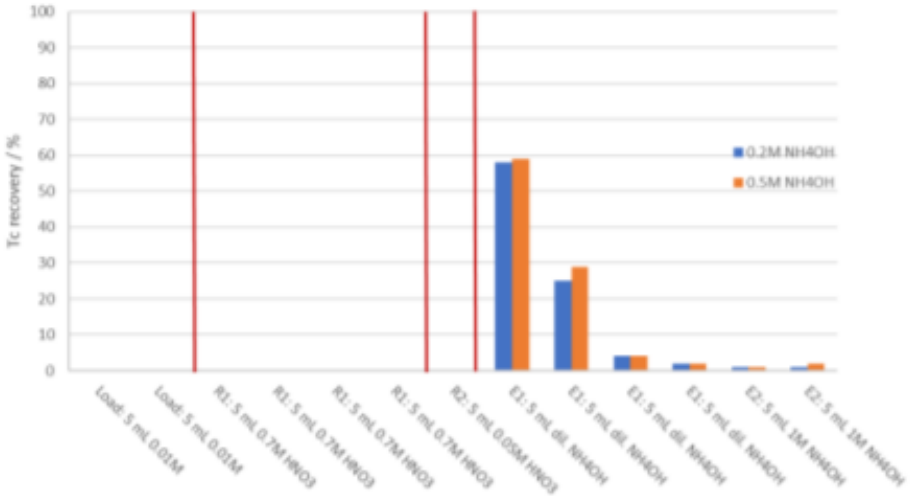
- Improved interference removal
- Oxygen the most promising cell gas ($^{99}Tc^{16}O_2$)
- LOD 0.5 pg g^{-1} (0.3 mBq g^{-1})
- Radiochemical support still required

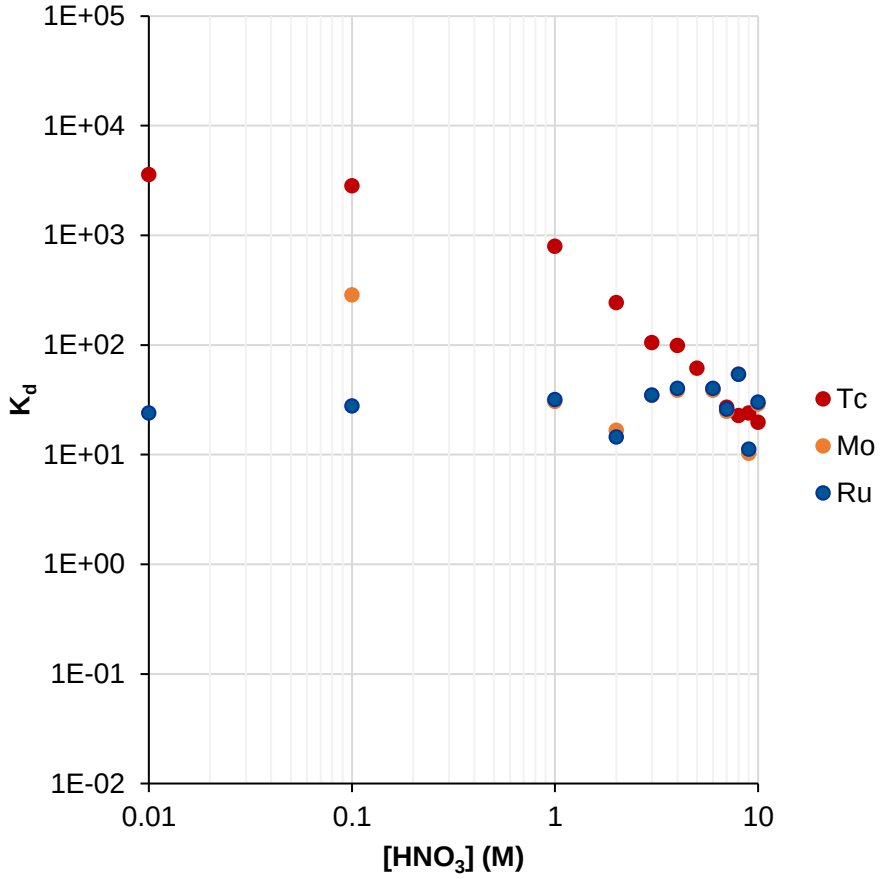


Mode	Q1	Q2	Target CPS per Bq g^{-1} Tc	Target 10 ppb Ru signal (CPS)	1 ppm Mo signal (CPS)
SQ	-	99	450,000	393,000	199.3
MS/MS	99	99	245,000	200,000	95.3
He SQ	-	99	79,000	170,000	4
He MS/MS	99	99	50,000	100,000	4
O_2 standard tune	99	99	126,500*	111,000	196
O_2 (single oxide) standard	99	115	24,500*	15000	36
O_2 (double O) standard	99	131	25,000*	160	4
O_2 custom tune	99	99	223,000	232,000	0
O_2 (single oxide)	99	115	29,000	25,000	4
O_2 (double oxide)	99	131	38,000	500	2
NH_3 standard tune	99	185	900	500	24
NH_3 custom tune	99	185	3,000	40	116

TK201 for environmental samples

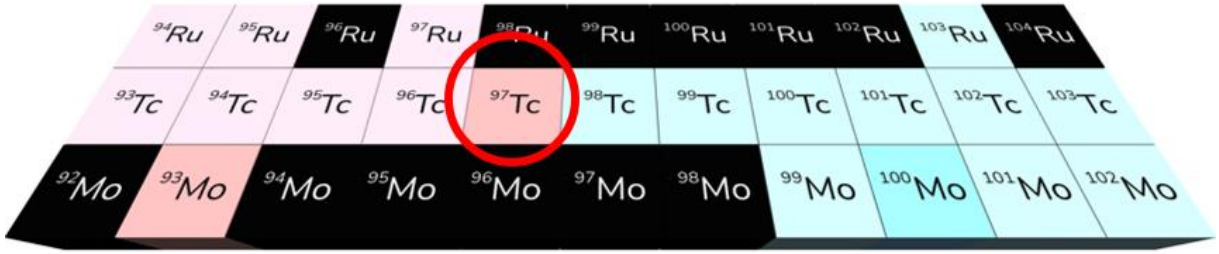
- Load and wash sample in dilute (0.01M) HNO_3
  - ^{99}Tc retained, Mo and Ru eluted
- Elution of 99Tc in dilute (0.1-0.2M) NH_4OH
- Can be directly loaded to ICP-MS
- Tested on water and aqueous waste samples
- How is the chemical yield assessed?





The need for a mass spectrometry ^{99}Tc tracer

- Requirements of a tracer:
- Chemically identical (same element)
- Distinct characteristics (not adjacent mass numbers)
- Long half-life, low specific activity



- **^{97}Tc** a promising candidate
- $T_{1/2}$ = 4.21 x 10^6(16) a

Reference	Sample Matrix	Tc Tracer	Measurement	Recovery (%)
McCartney et al., 1999	Sediment	95m	ICP-MS	50 - 70
Tagami and Uchida., 2005	Plants	95m	ICP-MS	48 - 92
Kaye et al., 1982	Vegetation	97m	β-counting	37 - 96
Beals et al., 1997	Water	97	ICP-MS	90
Wigley et al., 1999	Biota/Sediment	99m	LSC	70 - 95
Chen et al., 1990	Seawater	99m	β-counting	70
Butterworth et al., 1995	Sediment	Re	LSC	98 - 107

Production of ^{97}Tc

- Calculations run using program developed during project

UoB-TIP (University of Birmingham - Tool for Isotope Production): Python based tool for the automation of nuclear reaction modelling and calculation of isotope production yields

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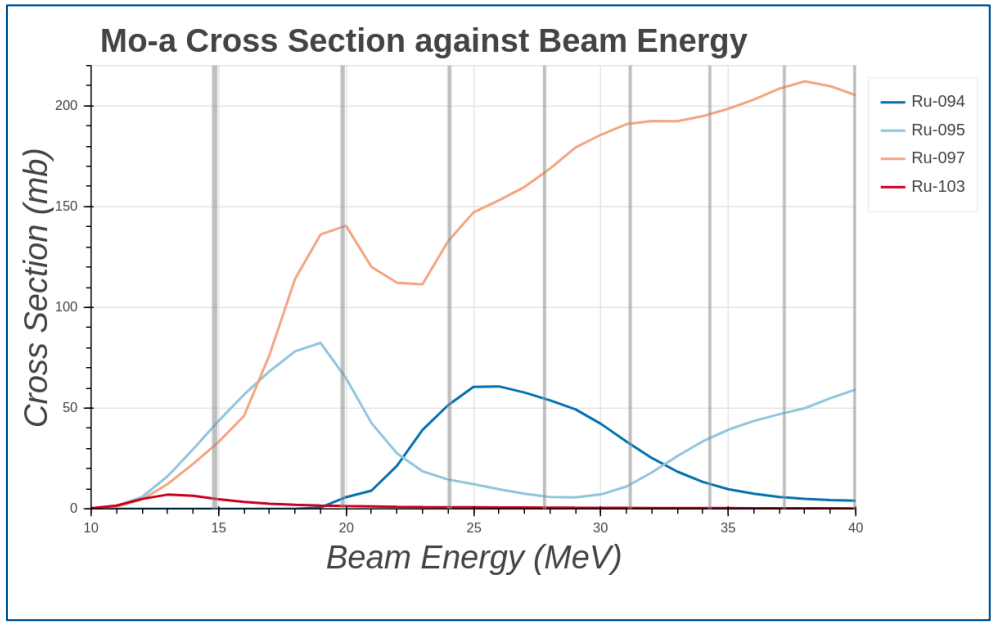
- Cyclotron production
- Stable Mo target
- ^{97}Ru ($T_{1/2}$ 2.83 (23) d) → ^{97}Tc



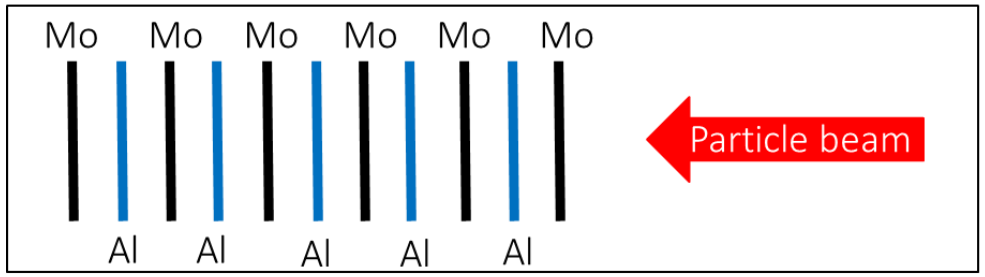
- Predominant reactions:
- 9.15% ^{94}Mo(α, n)^{97}Ru 10-20MeV
- 15.84% ^{95}Mo(α, 2n)^{97}Ru 20-30MeV
- 16.67% ^{96}Mo(α, 3n)^{97}Ru 30-40MeV

Production of ^{97}Tc

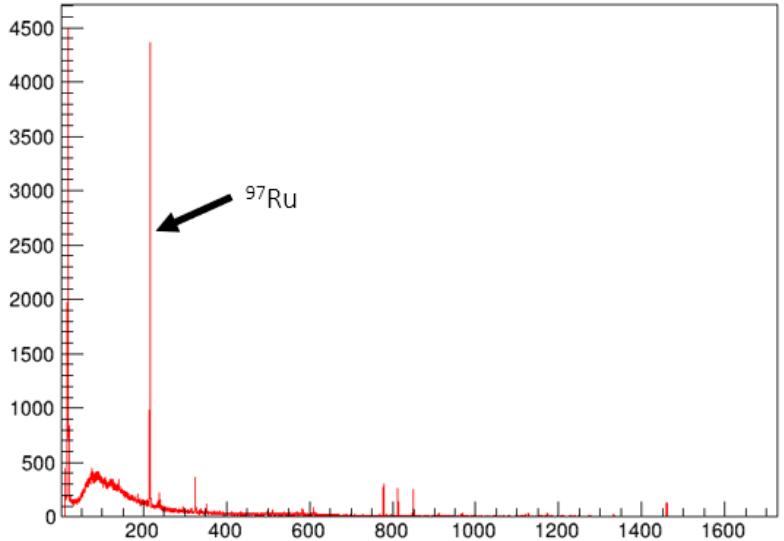
UNIVERSITY OF BIRMINGHAM | CYCLOTRON FACILITY

NPL National Physical Laboratory

- Stack of 6 x 1µm Mo foils, irradiated at a range of energies



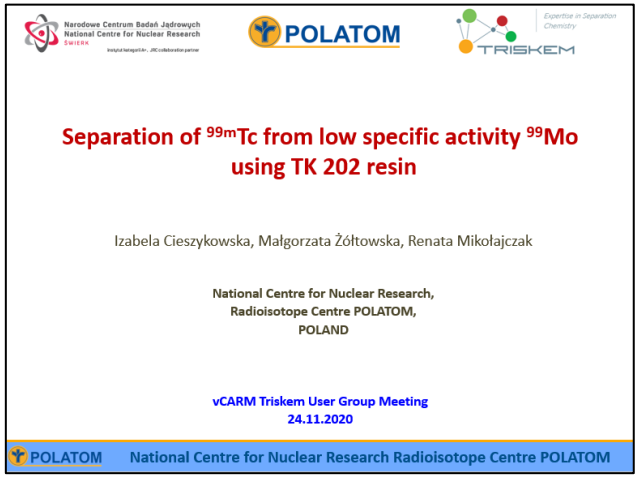
- 10µm Mo foil irradiated at 35MeV
- ^{97}Ru produced
- ^{97}Ru E(γ) = 215 keV
- Separation of target material required…

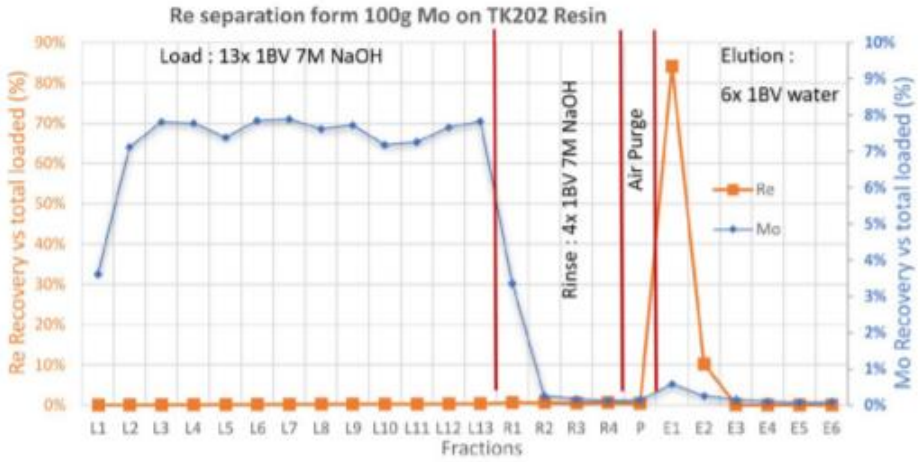


https://www.birmingham.ac.uk/research/activity/nuclear/about-us/facilities/mc40-cyclotron-facility.aspx

Target separation using TK202

- Inspiration from last years Triskem UGM
- TK202 based on Polyethyleneglycol (PEG)
  - Aqueous biphasic (ABS) system
  - In presence of aqueous solutions with high ionic strength and high content of water-structuring (kosmotropic) anions e.g. MoO_4^{2-} extracts chaotropic ions e.g. TcO_4^-
  - **Increasing Mo concentration improves Tc retention**
- Optimal Tc retention in 5-7M NaOH
- Elution in water
- Ru behaviour must be determined



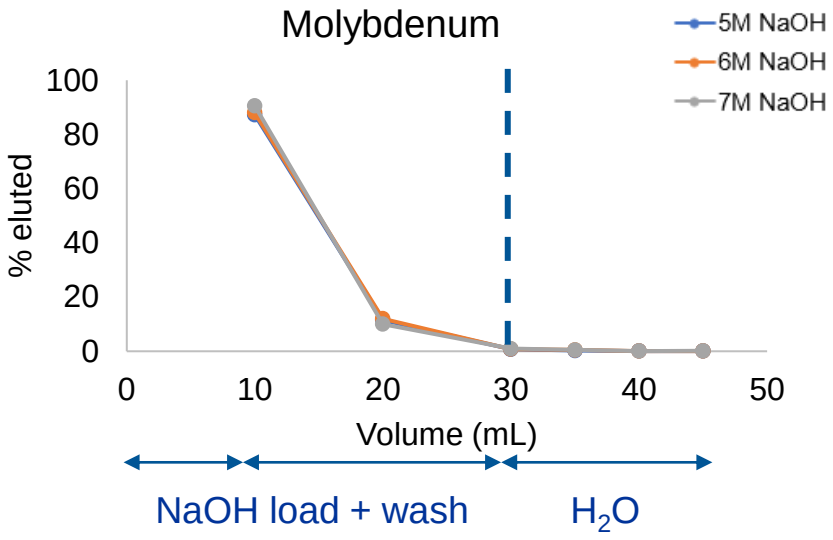


Experimental work

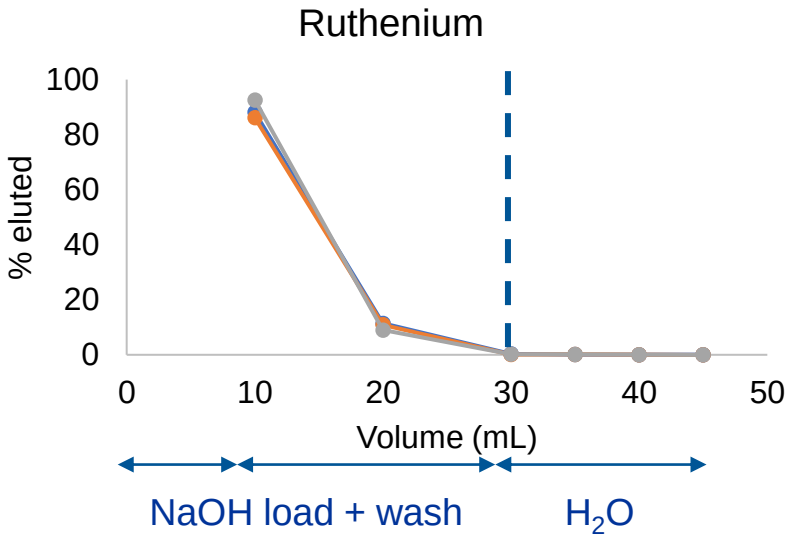
Tested at 5M, 6M and 7M NaOH

- TK202 resin soaked in 0.5M NaOH overnight
- 2 mL cartridge conditioned with 10 mL NaOH
- Mo, Ru, Re loaded in 5 mL
- Wash with 2×10 mL NaOH
- Wash with 3×5 mL DI water
- Vacuum pump run at approximately 0.5 mL/min
- Each fraction measured by ICP-MS

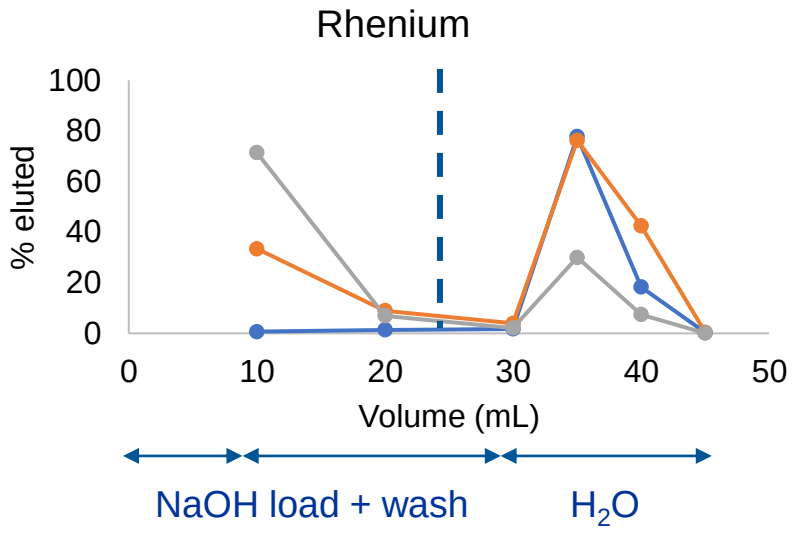
Preliminary results



- Eluted in **5-7M NaOH**
- In agreement with previous studies

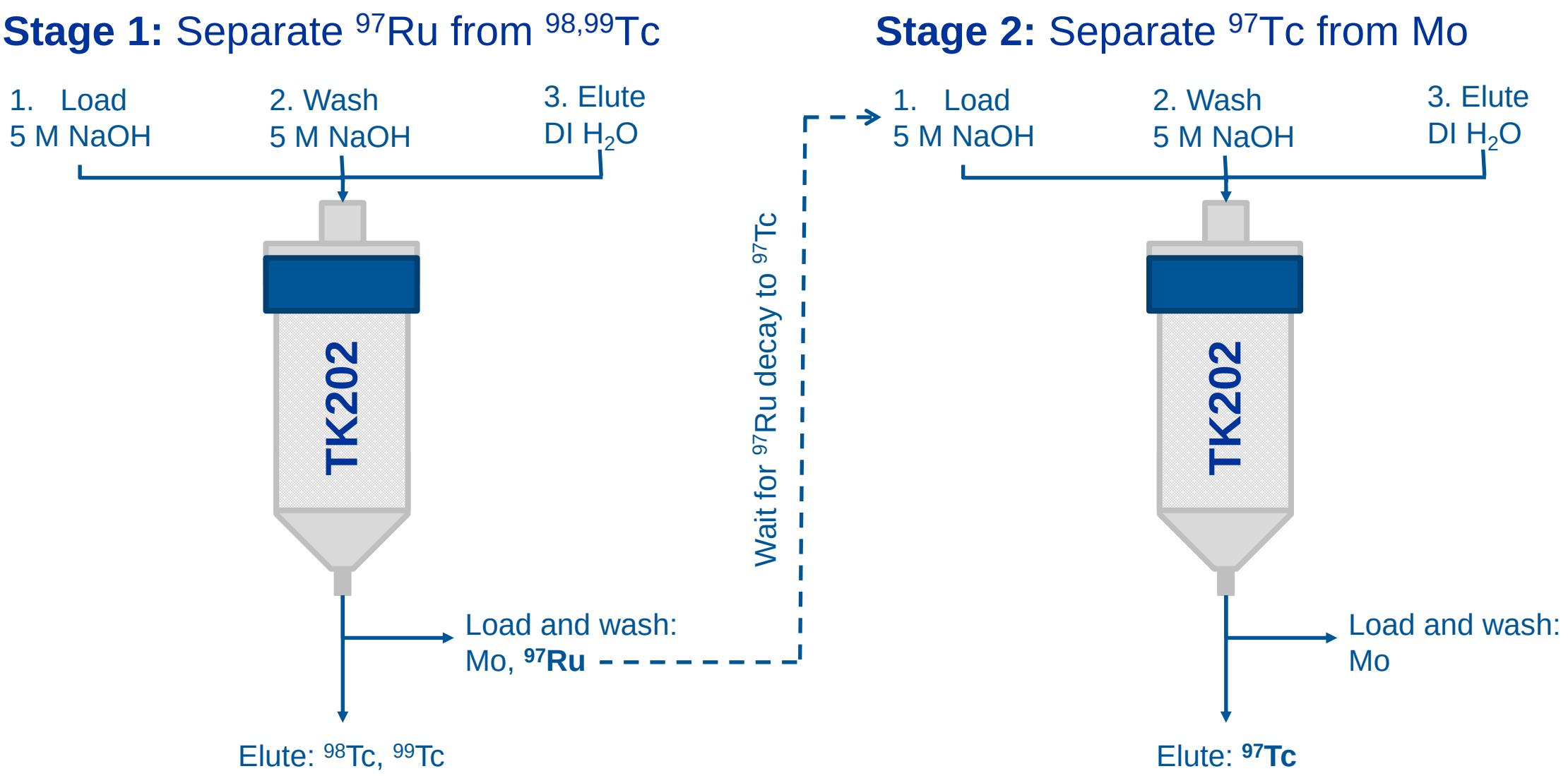


- Eluted in **5-7M NaOH**
- Performance in water unknown; not an issue for proposed separation



- Eluted in **water**
- Potentially more strongly retained in 5M NaOH

Proposed separation scheme



Conclusions and next steps

- New resins offer benefits for ^{99}Tc separation
- Particular focus on Mo and Ru separation for ICP-MS measurement
- TK201 well suited to environmental samples
  - Load in dilute HNO_3
  - Elute in dilute NH_4OH for direct ICP-MS measurement
- Long-lived ^{97}Tc tracer a promising option for assessing yield
  - TK202 offers promising separation from Mo targets
  - Test and real Mo target measurements planned

National Physical Laboratory

Expertise in Separation Chemistry

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