General applications at NPL including work on test-stick technology

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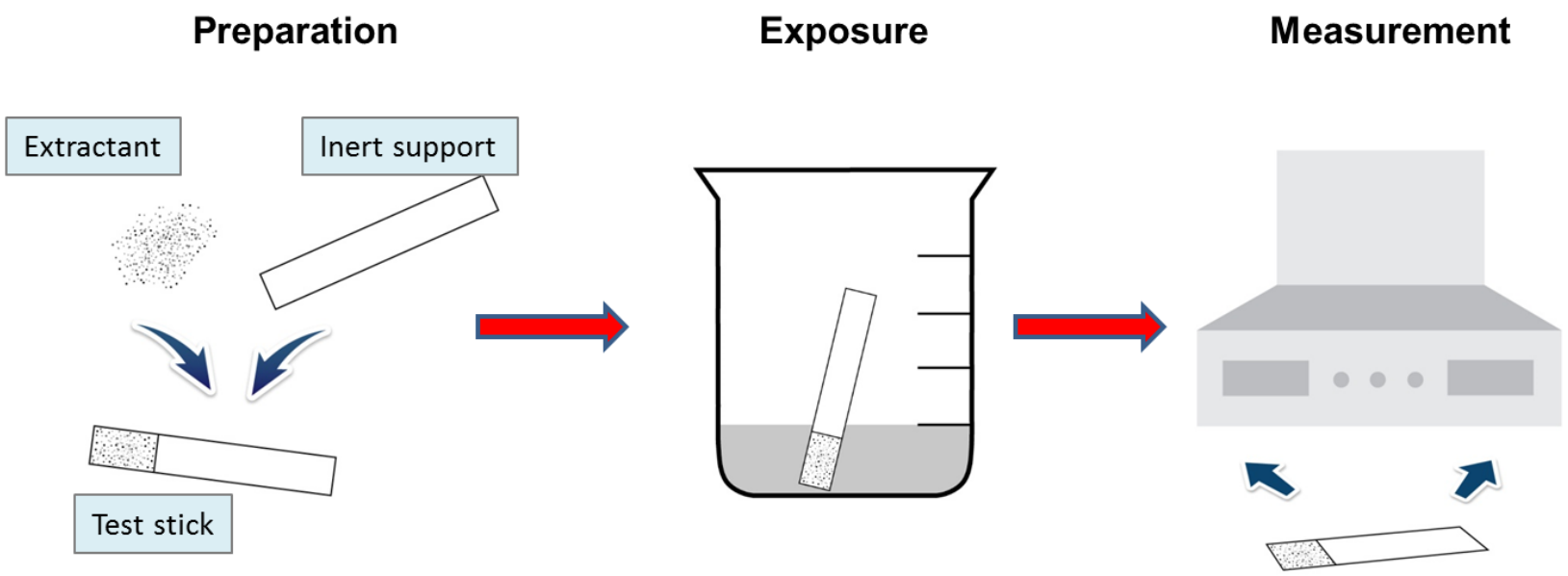
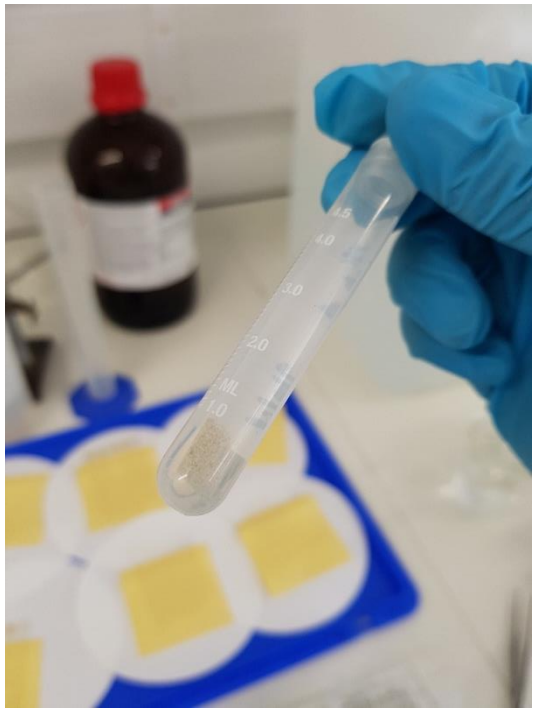
Test-stick technology

Past, Present and Future

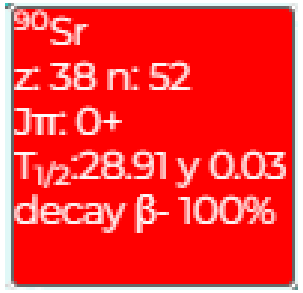
Test-stick technology: Methodology

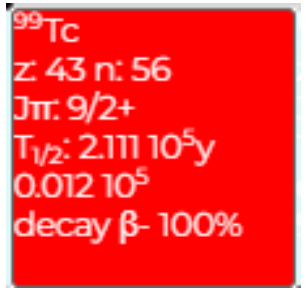
- Test-stick technology presents a rapid screening method for difficult-to-measure (DTM) radionuclide uptake on-site. This method can be organised into 3 phases – preparation, sample exposure and measurement.





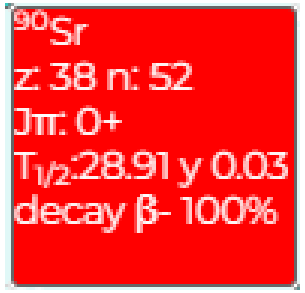
Test-stick technology: target radionuclides

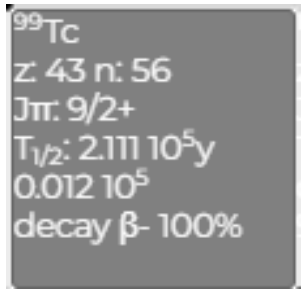




- Key factors:
  - Difficult-to-measure (DTM) radionuclides due to 100% β^- emission resulting in chemical work-up often required.
  - High fission yields (>5%) and good mobility in the environment makes these nuclides problematic and prevalent in the environment if not accounted for and treated.

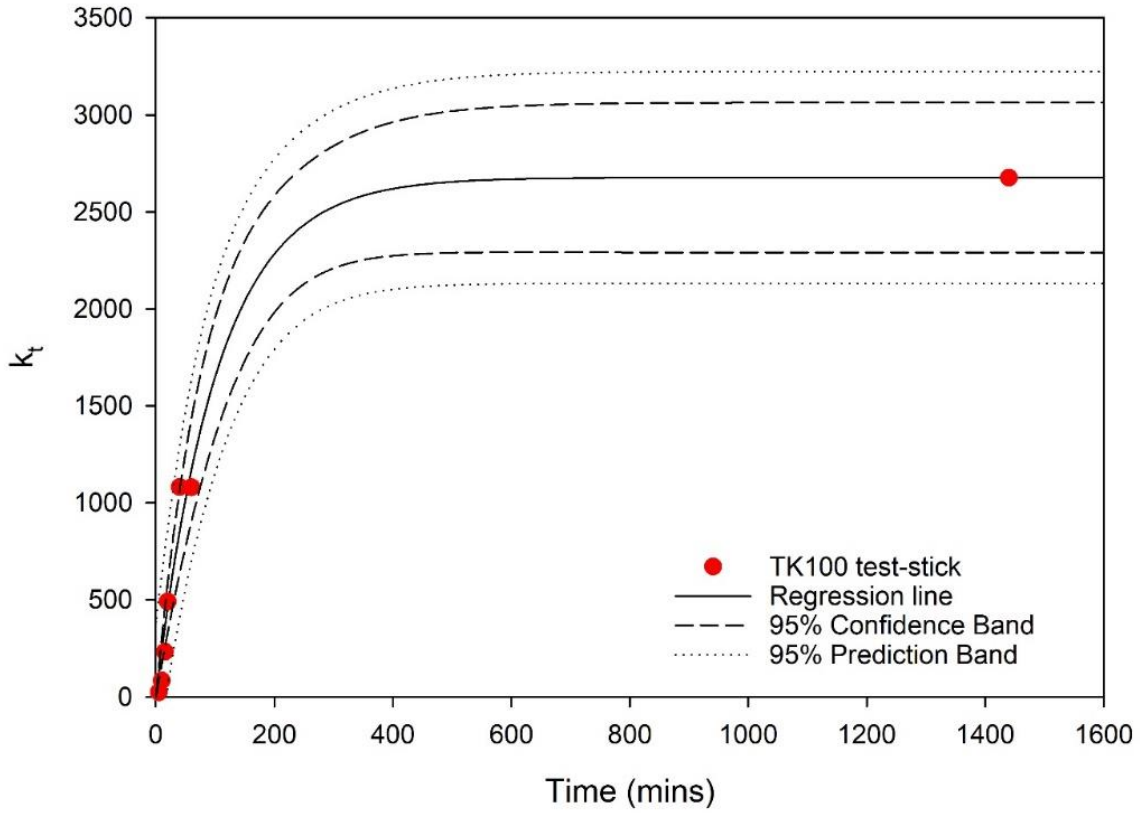
Test-stick technology: target radionuclides





- Test-stick:
  - TK100 extractant the preferred candidate for test-sticks due to selective extraction of ^{90}Sr possible.

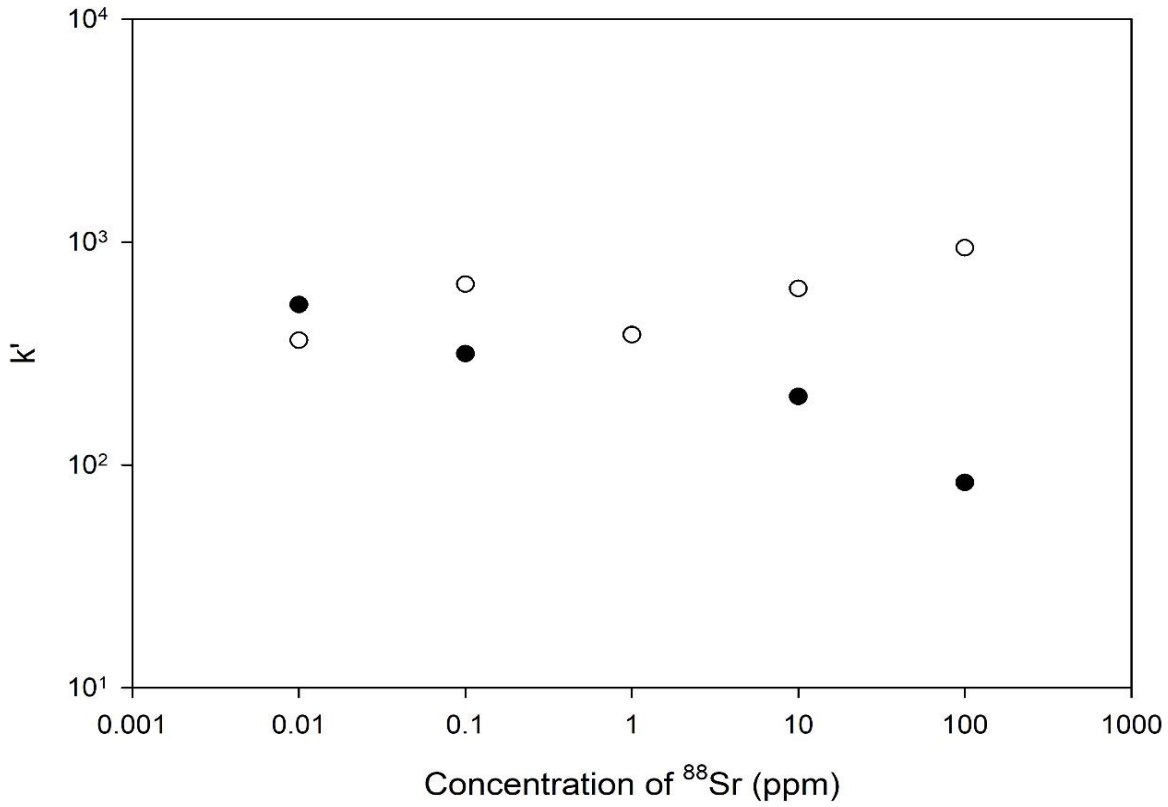
Test-stick technology: Kinetics

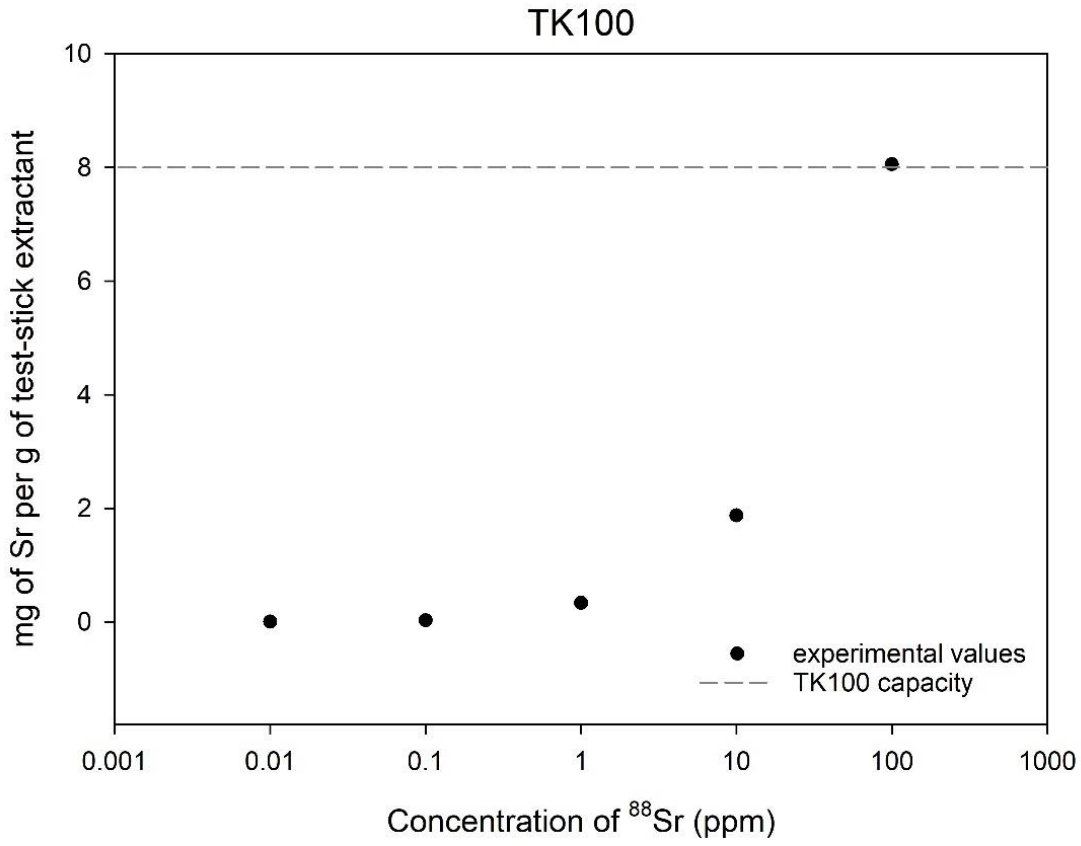


$$k_t = \left(\frac{A_{stick}}{[A_{aq}]_t \times M_s}\right)$$

- TK100 test-sticks were found to reach kinetic equilibrium within 40-to-60-minute sampling times.

Test-stick technology: ^{90}Sr





- TK100-test-sticks were found to saturate from 10 ppm onwards with loading calculations on test-sticks showing that in 100 ppm ^{88}Sr solutions the resin capacity is being reached.
- These results show that the TK100-test-sticks are performing as expected and the 2-D uptake geometry of the test-sticks is not affecting the performance of the bound resin.

Test-stick technology: proportional mechanism

- Effectiveness of test-stick technology is dependent on the proportionality of uptake.

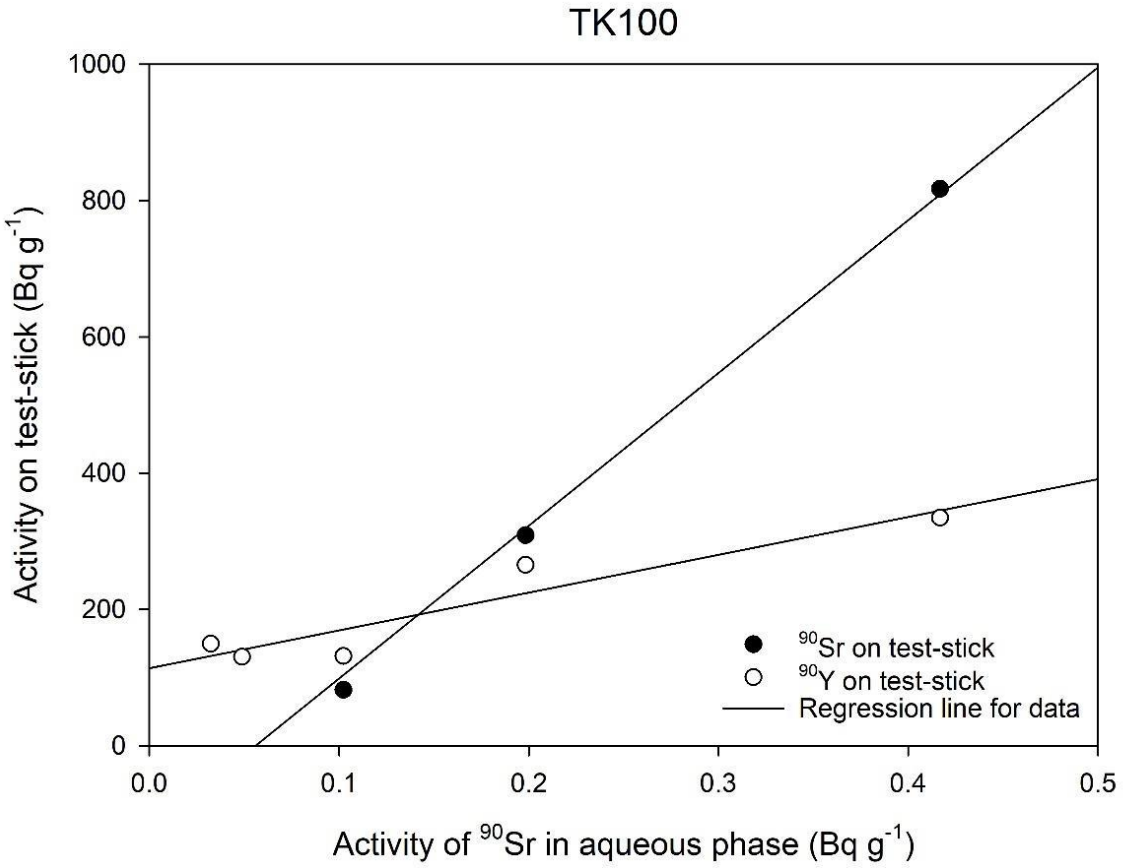
$$A_{stick} \propto A_{aq}$$

- This means that with increasing activity of ^{99}Tc in the aqueous phase (groundwater), the uptake of ^{99}Tc onto the test-stick will also increase…

$$A_{stick} = b_t \cdot [A_{aq}]_0$$

…proportionally, hopefully.

Test-stick technology: ^{90}Sr



- Spiked ^{90}Sr activities: approximately 0.4, 0.8, 2.0, 4.0 and 8.8 Bq
- Proportional mechanism (R^2 = *0.998,* b_t = 1.709 Bq mL Bq^{-1}) in place but ^{90}Y contribution must be considered.
- Why is ^{90}Y here and how do we deal with this?

Test-stick technology: ^{90}Y crisis

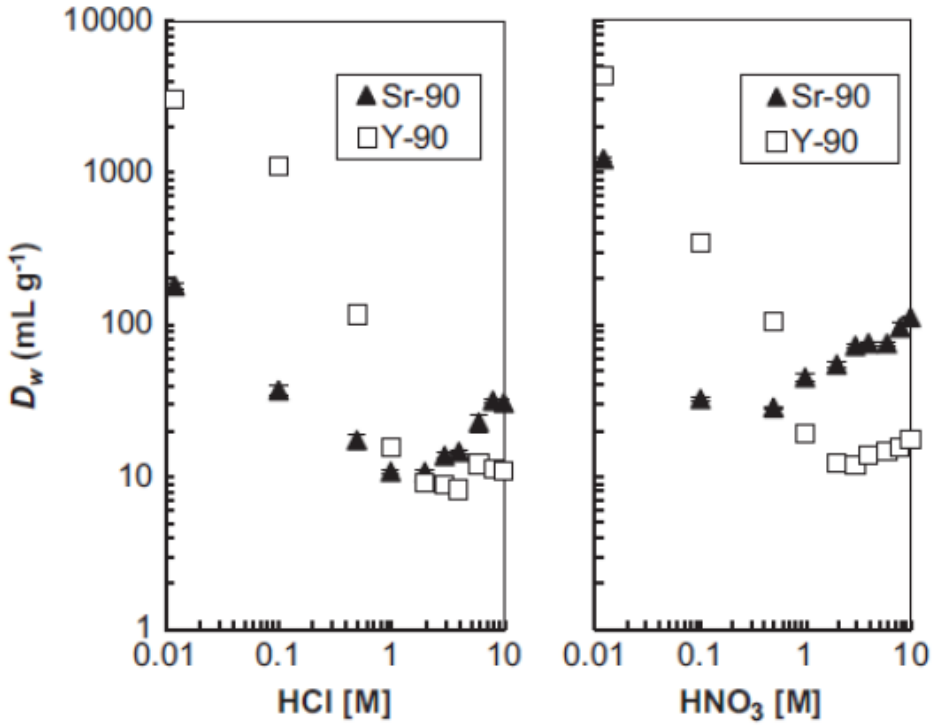


Figure 4: D_W values Sr and Y on TK100 Resin, varying HNO_3 and HCl concentrations[2]

- Reviewing TK100 product sheet showed that Y uptake is high on TK100 in low acid conditions – this may also be happening in DI water which is why we're seeing contributions of ^{90}Y even a couple hours post sampling.
- How do we correct for this?

Test-stick technology: solving for ^{90}Y

Derivation for the simultaneous equations, to solve for the activity of both ^{90}Sr and ^{90}Y, are shown below:

$$c_1 = k_1 A_{Sr-90} + k_2 A_{Y-90}$$

$$c_2 = k_3 A_{Sr-90} + k_4 A_{Y-90}$$

Rearranging to give A_Y,

$$c_2 - k_3 A_{Sr-90} = k_4 A_{Y-90}$$

$$A_{Y-90} = \frac{c_2}{k_4} - \frac{k_3}{k_4} A_{Sr-90}$$

Substituting into equation for c_1,

$$c_1 = k_1 A_{Sr-90} + k_2 A_{Y-90}$$

$$c_1 = k_1 A_{Sr-90} + k_2 \left(\frac{c_2}{k_4} - \frac{k_3}{k_4} A_{Sr-90}\right)$$

$$c_1 = k_1 A_{Sr-90} + \frac{c_2 k_2}{k_4} - \frac{k_2 k_3}{k_4} A_{Sr-90}$$

Grouping terms for $A_{Sr\text{-}90}$,

$$c_1 = \left(k_1 - \frac{k_2 k_3}{k_4}\right) A_{Sr-90} + \frac{c_2 k_2}{k_4}$$

$$c_1 - \frac{c_2 k_2}{k_4} = \left(k_1 - \frac{k_2 k_3}{k_4}\right)$$

$$\frac{\left(c_1 - \frac{c_2 k_2}{k_4}\right)}{\left(k_1 - \frac{k_2 k_3}{k_4}\right)} = A_{Sr-90}$$

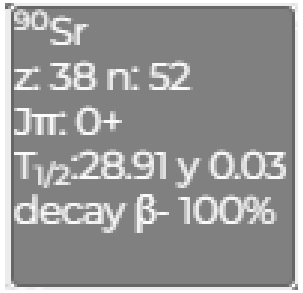
Solving for ^{90}Y,

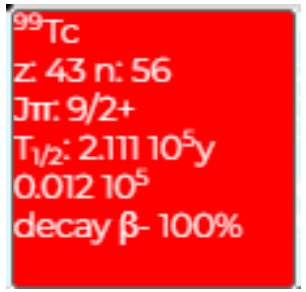
$$c_1 = k_1 A_{Sr-90} + k_2 A_{Y-90}$$

$$c_1 - k_1 A_{Sr-90} = k_2 A_{Y-90}$$

$$A_{Y-90} = \frac{c_1 - k_1 A_{Sr-90}}{k_2}$$

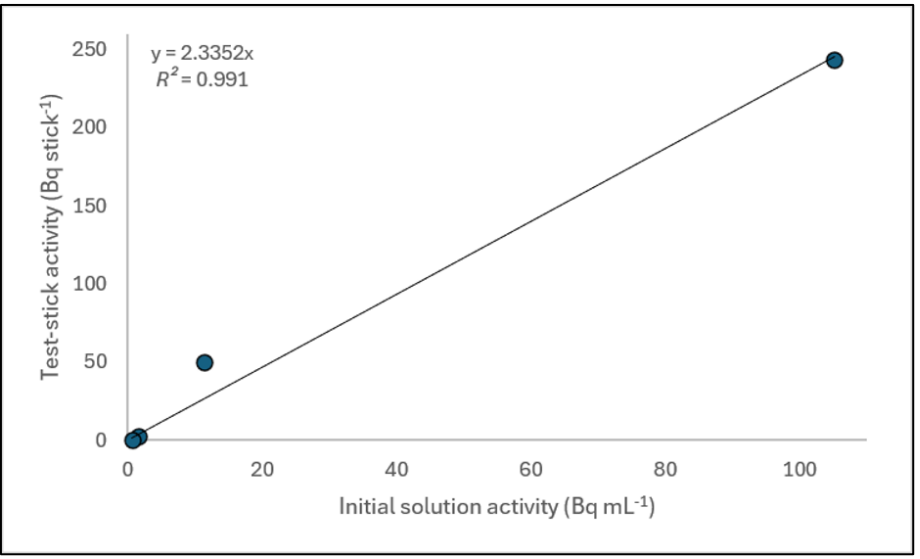
Test-stick technology: target radionuclides



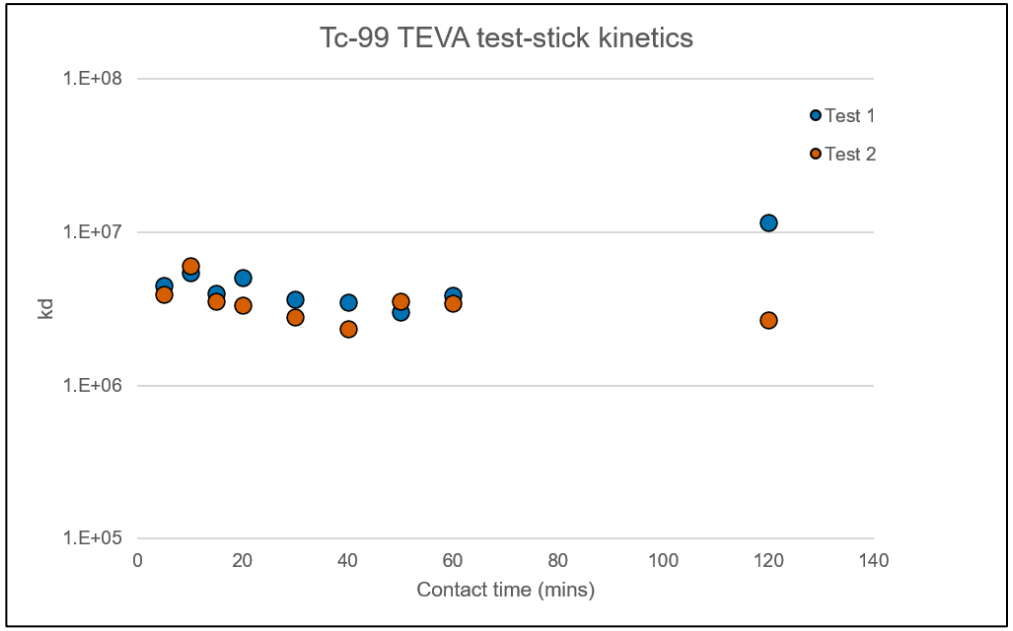


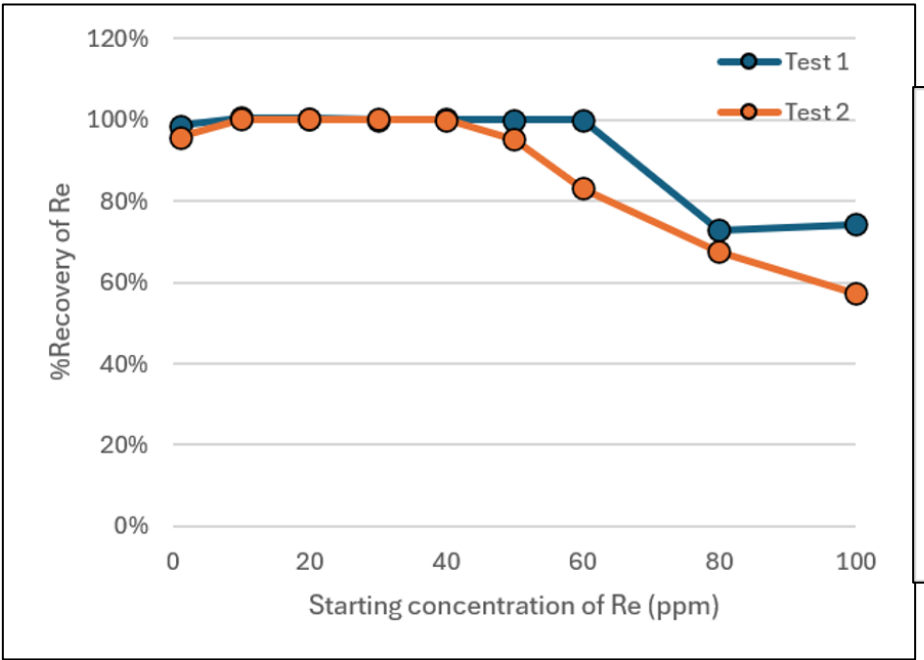
- Test-stick:
  - TEVA extractant the preferred candidate for test-sticks due to selective extraction of ^{99}Tc possible.

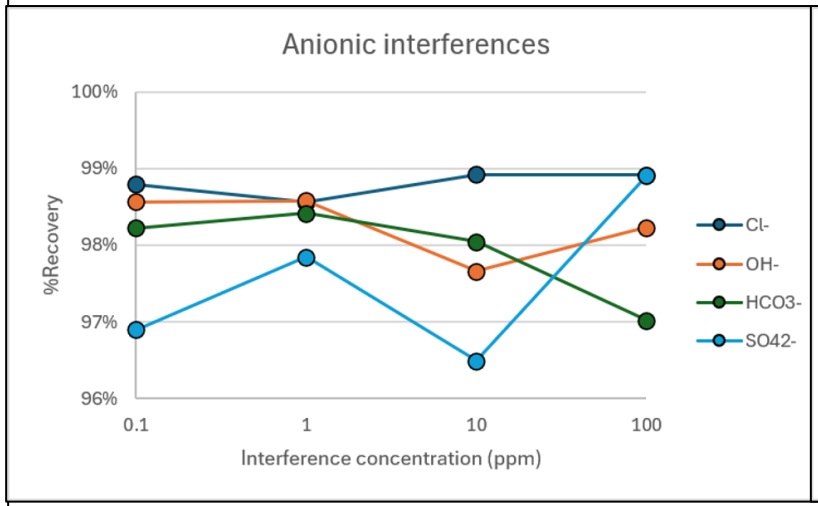
Test-stick technology: ^{99}Tc

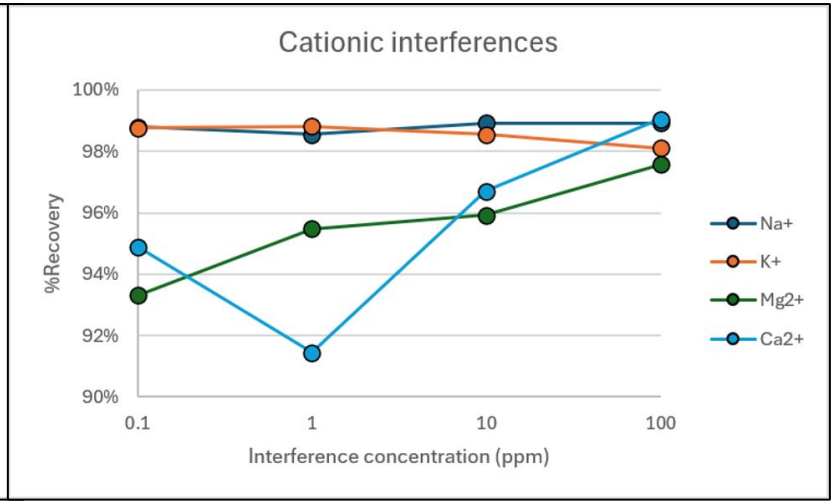


$$K_d = \left[\frac{A_s \cdot M_{aq}}{A_{aq} \cdot M_s}\right]$$









Conclusion

- TEVA-test-stick has been shown to have fast kinetics with ^{99}Tc uptake equilibrium reached within 5 mins and able to demonstrate strong ^{99}Tc recoveries even in the presence of variable concentrations of ionic interferences.
- Proportional uptake mechanism demonstrated which is crucial to test-stick operation.
- TEVA test-sticks also perform well even in high activity concentrations which makes it suitable for waste segregation and environmental monitoring including potentially emergency response.
- Ionic interferences had some impact on ^{99}Tc uptake, but recoveries were still above 91%.
- Shelf-life studies show test-stick retain their performance post-manufacture for up to a month.

Test-stick technology: The Future

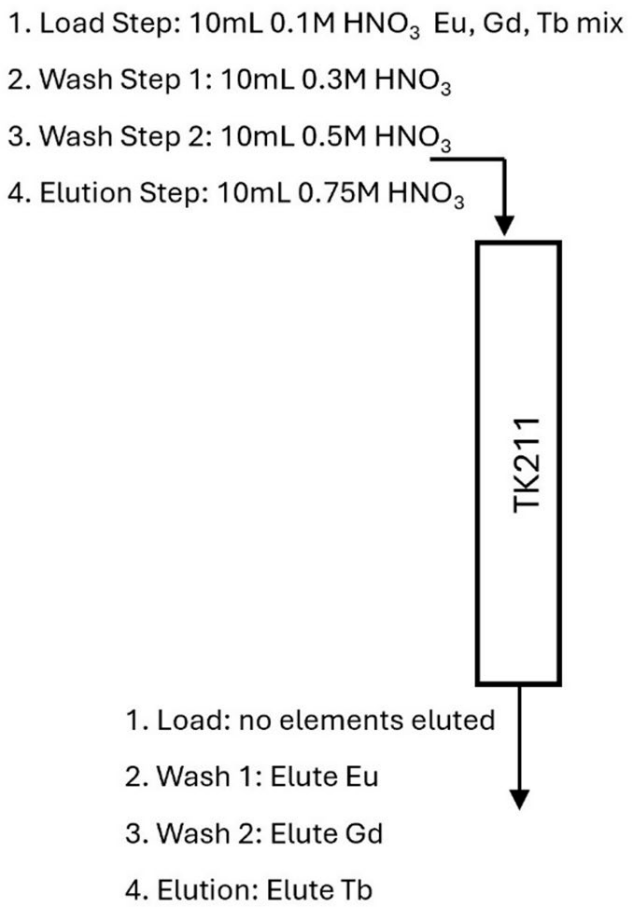
- Next steps include applying TEVA-test-sticks onto real decommissioning samples to validate the test-stick performance.
- Further tests including extending shelf-life tests to 3-6 months, and potentially beyond, can provide confidence in the test-stick performance and that no degradation of the test-stick is occurring over this time scale.
- Begin developing new test-sticks focussing on other challenging radionuclides such as actinides.
- Start investigating methods into reliably manufacturing test-stick technology whilst minimising costs and time and maintaining the extractant integrity of the resins.
- Test-sticks provide a flexible and effective platform to screen problematic radionuclide in numerous settings such as nuclear decommissioning, environmental monitoring and emergency response. But may also be developed new challenges and calls. Please let us know

General Applications at NPL

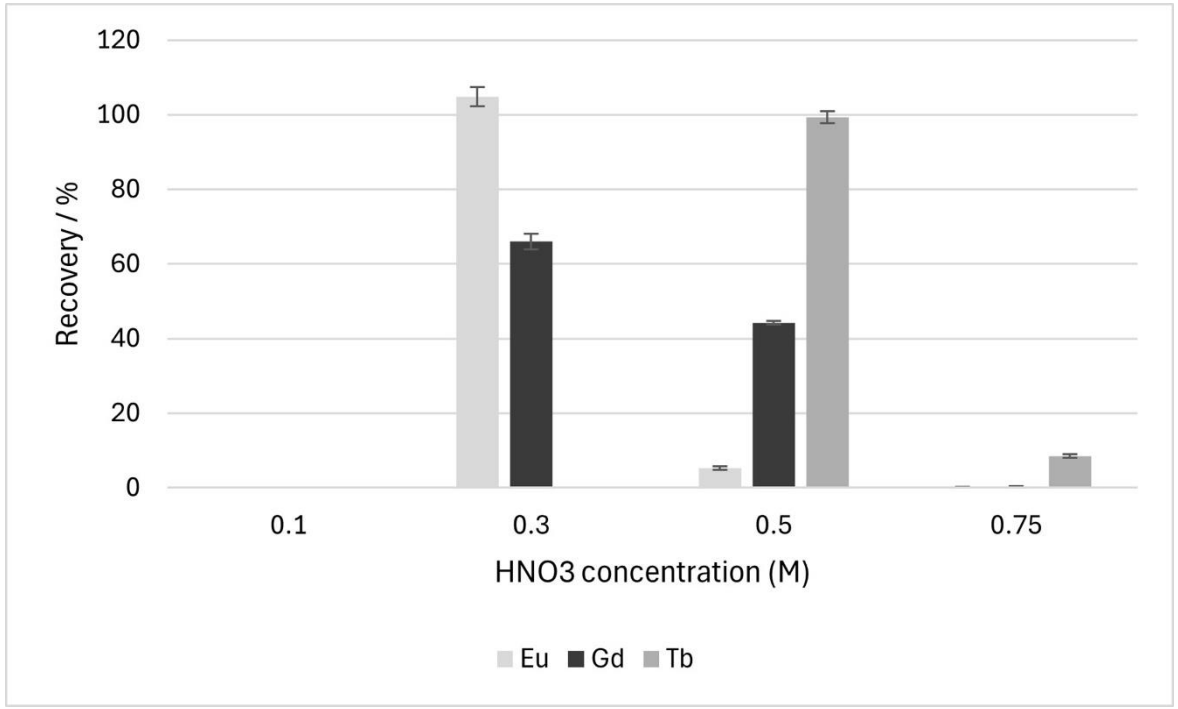
A small overview of what we've worked on recently

TK211 separation

- TK211 is a development of the LN resin introducing aromatic groups to improve radiolysis stability of the resin.
- A method was tested with TK211 on the Hidex Q-ARE50 to separate an Eu/Gd/Tb mix.
- This provided a test to evaluate the performance of the TK211 resin and implementing this system on a commercial automated separator.

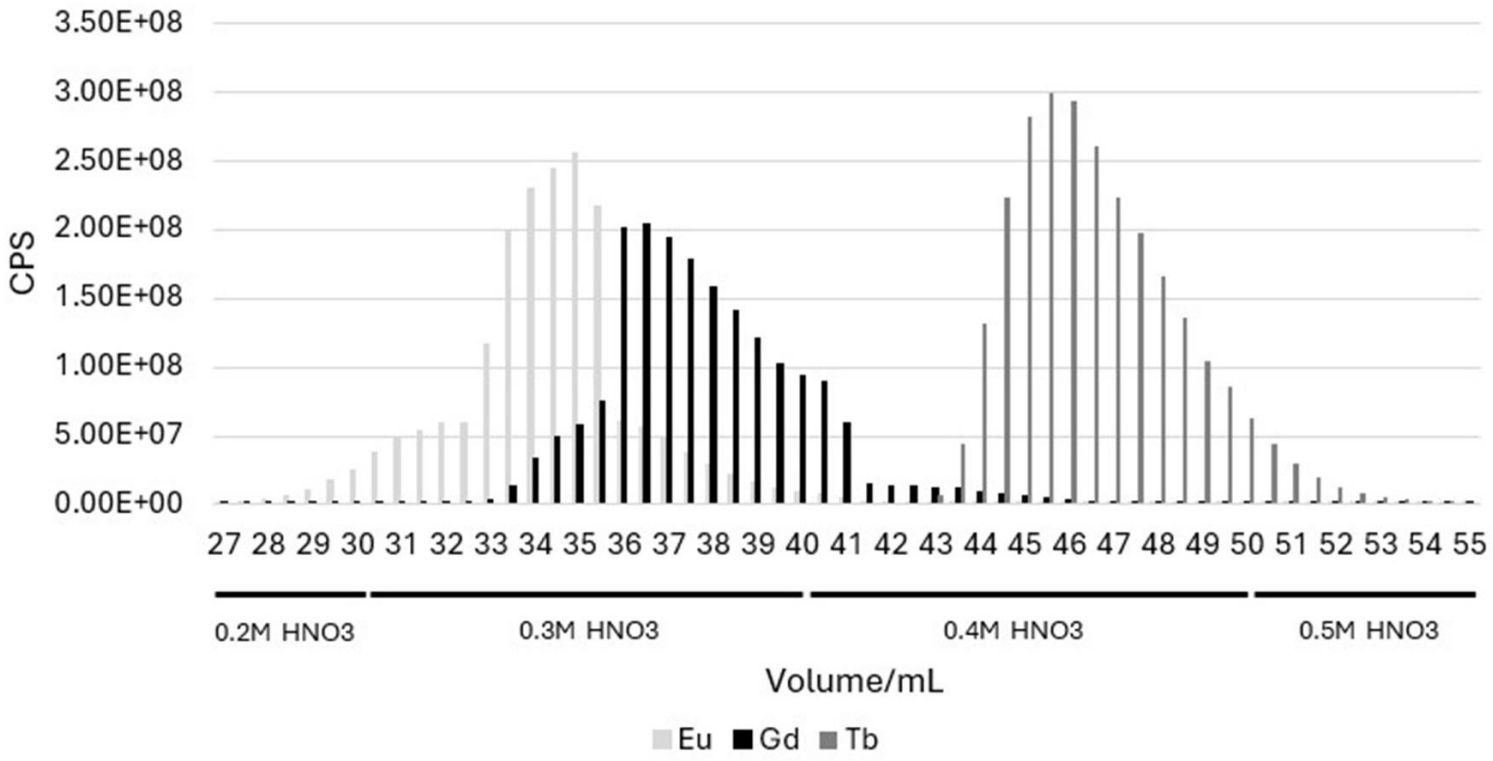


TK211 separation of Eu/Gd/Tb



- TK211 showed 100% recovery of Eu in the 0.3 M HNO3 fraction, whilst Gd had recoveries of 66% in the 0.3 M HNO3 fraction (Kd = 100) and the remainder of the Gd (44%) was recovered in the 0.5 M HNO3 fraction (Kd = 10).
- Tb recovery was 99% in the 0.5 M HNO3 fraction (Kd = 100) with trace (0.75%) residual recovery in the 0.75 M HNO3 Fraction (Kd = 10).
- These results agreed with TrisKem data (product sheet), which used larger column volumes (29 mL vs. 2 mL) and higher loadings (500 µg Tb + Gd vs. 0.1 µg Tb + Gd).

TK211 separation: Coupling



Purification of ^{93}Zr

- Existing inventory of ^{93}Zr but last measured in 2018 – requires re-analysing and highly likely for the need to be re-purified.
- Removal of ^{93m}Nb key due to being an isobaric interference in mass spec analysis.
- Nb removal can be tricky but a few options available:
- TEVA
- TK221
- TK400

Zr/Nb separation: TEVA

- Option 1
- Load – 1 x 5 mL of 12M HCl
- Wash – 3 x 5 mL of 12M HCl
- Elution – 2 x 5 mL of 6M HCl

- Option 2
- Load – 1 x 5 mL of 12M HCl
- Wash – 3 x 5 mL of 12M HCl
- Elution – 2 x 5 mL of 9M HCl/0.1M HF (or NH_4F)

Shimada, A. *et al.* (2014) 'Development of a separation method for molybdenum from zirconium, niobium, and major elements of rubble samples', *Journal of Chromatography A*, 1371, pp. 163–167. doi:10.1016/j.chroma.2014.10.053.

Zr/Nb separation: TK221

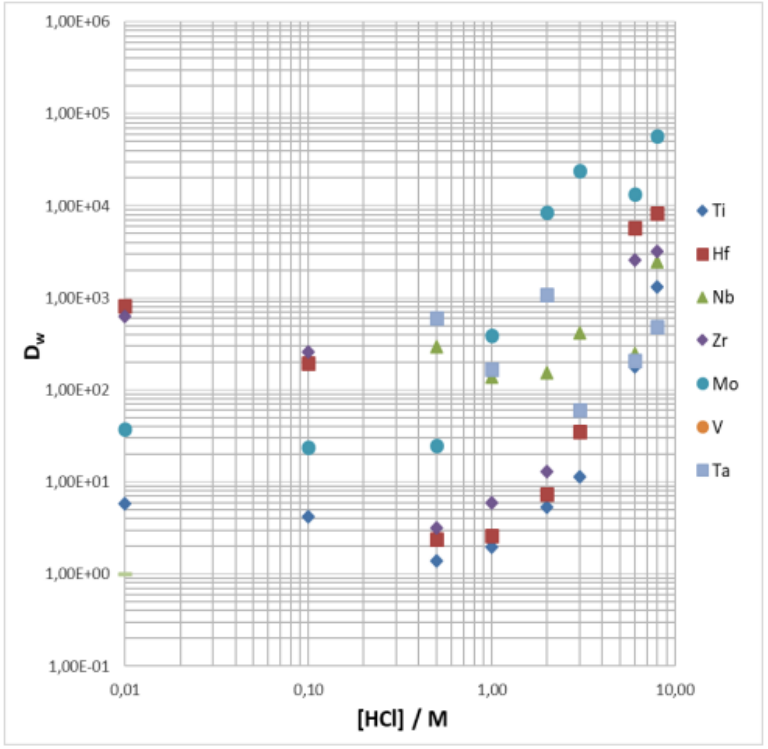


Figure 8: Dw values of selected elements on TK221 in HCl

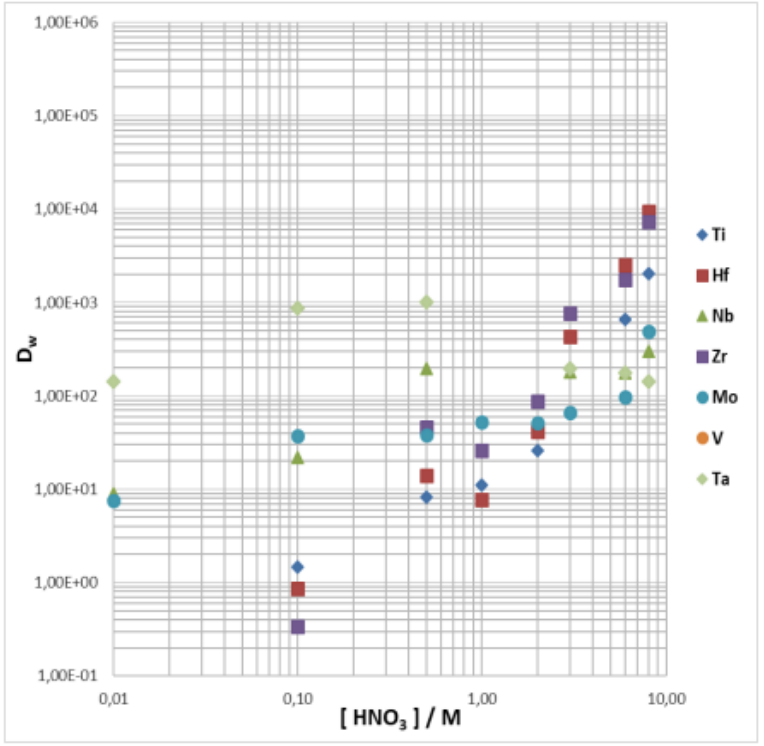


Figure 3: Dw values of selected elements on TK221 in HNO_3

- Loading – 1 x 5 mL of 0.1M HNO_3
- Wash – 5 x 5 mL of 0.1M HNO_3

Zr/Nb separation: TK400

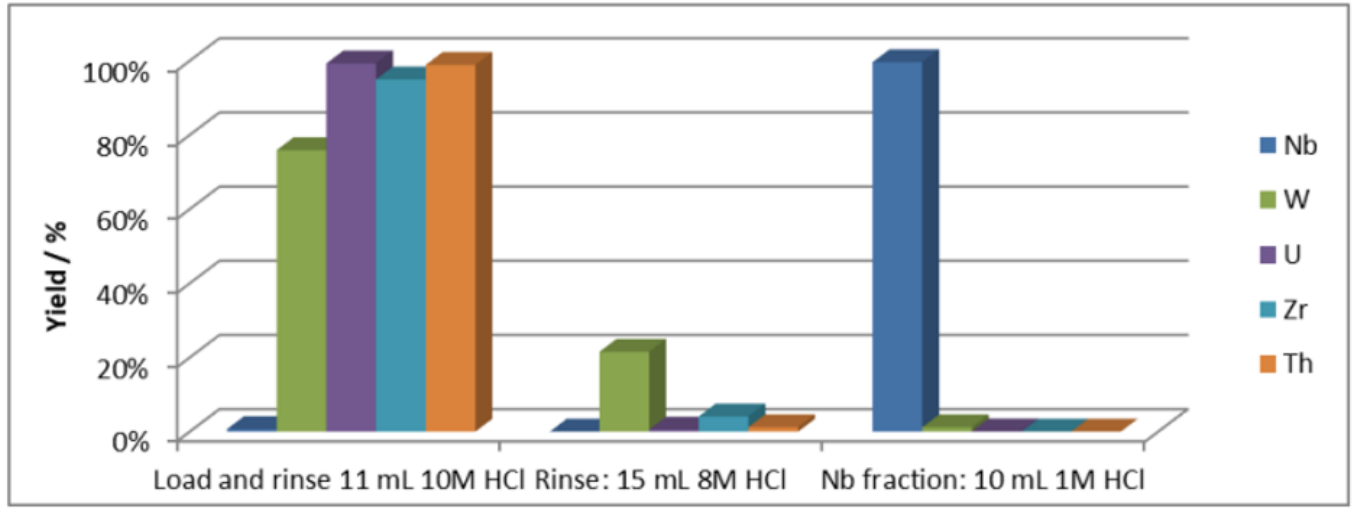


Figure 2: Elution study, Nb separation from selected cations, 2 mL TK400 column

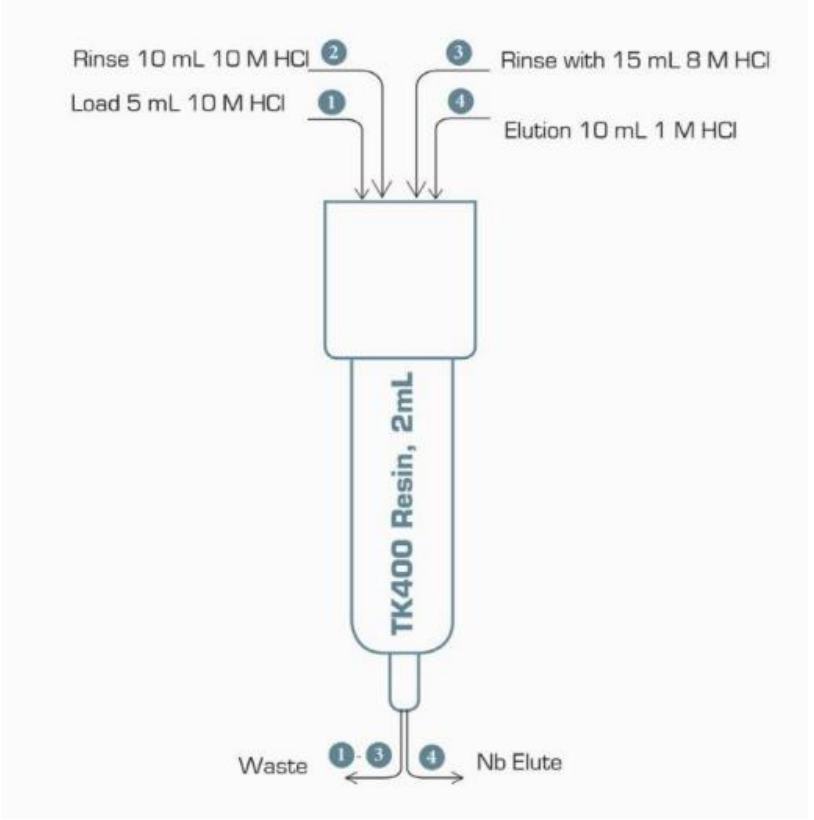


Figure 3: Nb separation on TK400 Resin

- Load – 1 x 5 mL of 10M HCl
- Wash – 2 x 5 mL of 10M HCl
- Wash 2 – 3 x 5 mL of 8M HCl
- Elution – 2 x 5 mL of 1M HCl

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TRISKEM
Expertise in Separation Chemistry

University of Southampton

Thank you for listening

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