New developments 1 – TrisKem

UGM - 21/09/2018

Jesus College - Cambridge (UK)

Aude Bombard

TRISKEM
Expertise in Separation Chemistry

New Developments

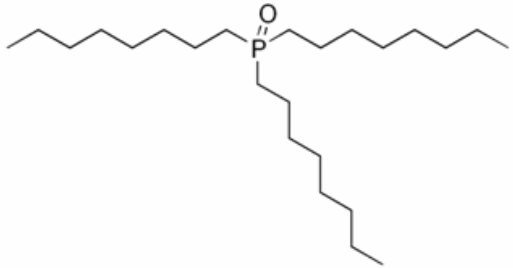
TRISKEM
Expertise in Separation Chemistry

Environmental field

- TK200 Resin
  - Actinides separation
- TK201 – TK202 Resins
  - Tc/Mo separation
- Updates
  - Cs Resins (AMP-PAN/KNiFC-PAN)
  - TK100 resin
  - TK400 resin

TK200 Resin

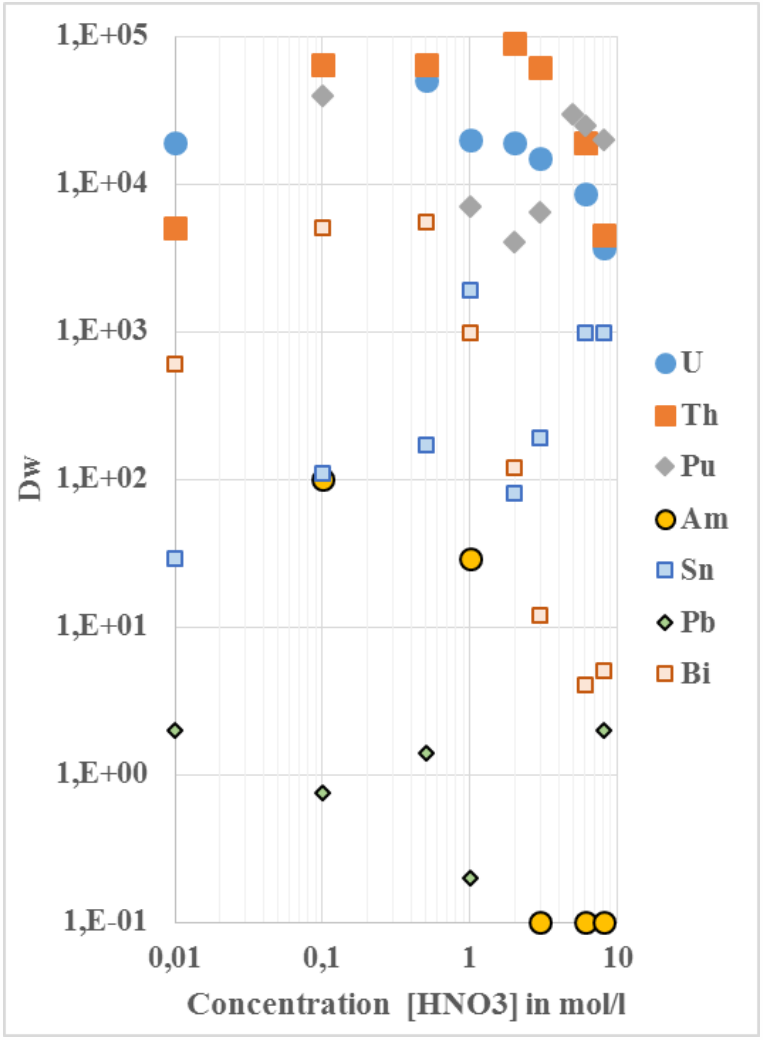
- TOPO based Resin
- Impregnated



- Well studied in Liquid-liquid systems for various metals
- Use in nuclear industry and radiotoxicology for actinides extraction[1]
- Preconcentration and sequential separation of actinides from pH2 solutions
- RadioPharma use show in TKI's afternoon presentation

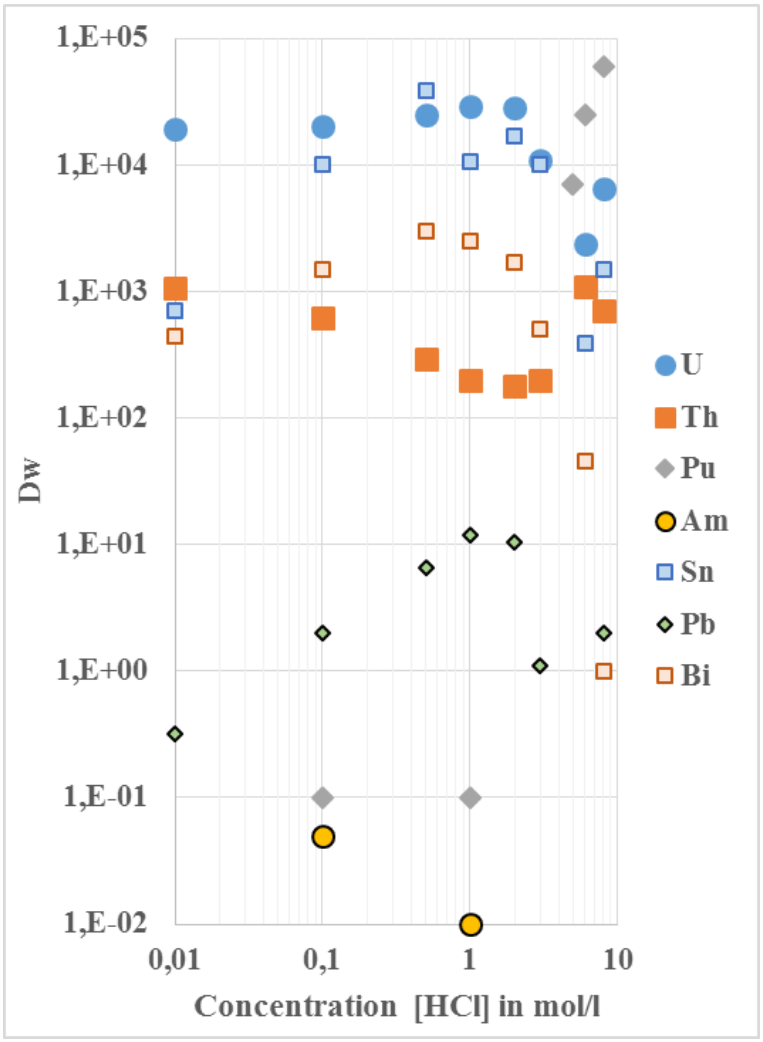
Braun T. et al.,Extraction Chromatography, Journal of Chromatography Library (vol2), Elsevier Scientific Publishing Company – 1975, pp.279-303

TK200 Resin – Dw studies HNO_3



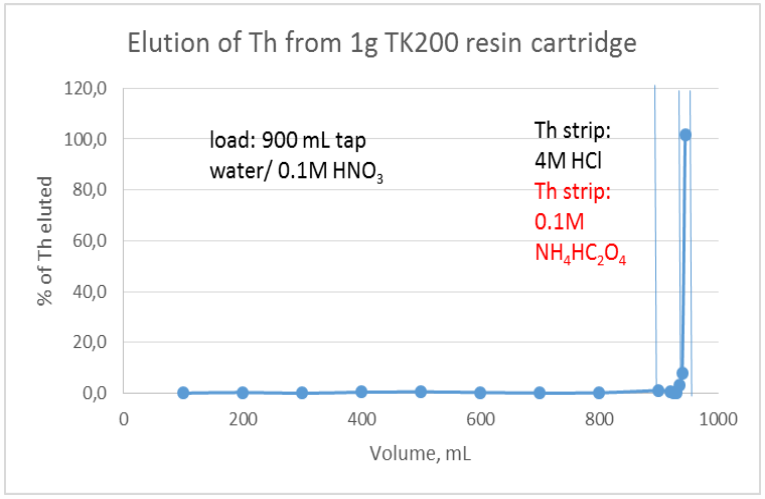
- Retention of Am < 0,1M HNO_3;
- U/Th/Pu uptake over the whole acidity range studied;
- High uptake of Bi from 0,01 – 2M HNO_3 => possibility to separate from Pb in case of MS measurement;
- Uptake of Sn from 0,1 – 10M HNO_3 (alternative to TBP Resin).

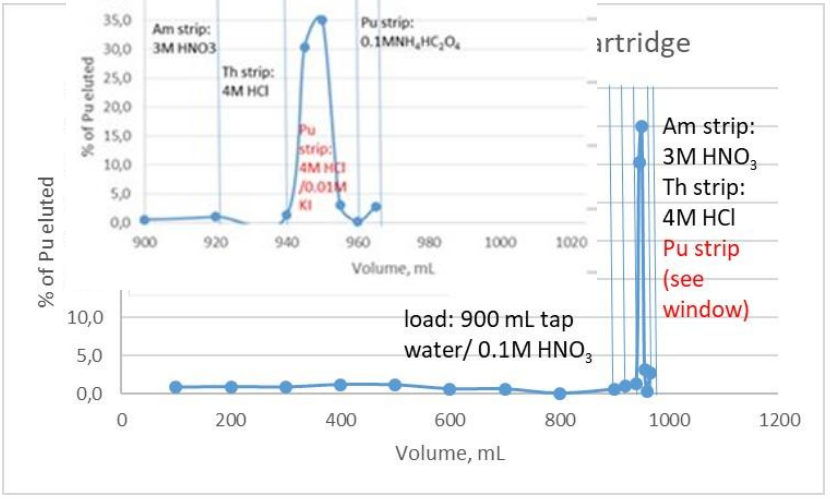
TK200 Resin – Dw studies HCl

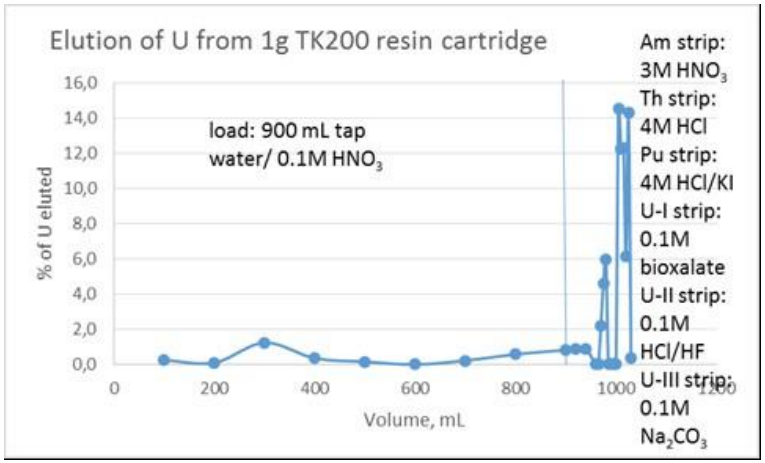


- No retention of Am ;
- U/Th uptake over the whole acidity range studied;
- Pu uptake from 3-10M HCl – no retention below 3M HCl;
- High uptake of Bi from 0,01 – 3M HCl => possibility to separate from Pb in case of MS measurement;
- High uptake of Sn over the whole acidity range studied (alternative to TBP Resin)

Actinides on TK200 – Application





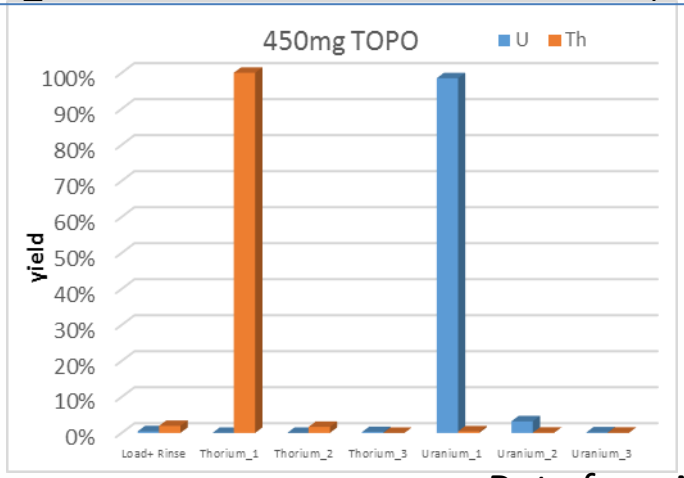


- Method development on-going
- Aim, direct load of actinides from acidified water
- Sequential separation

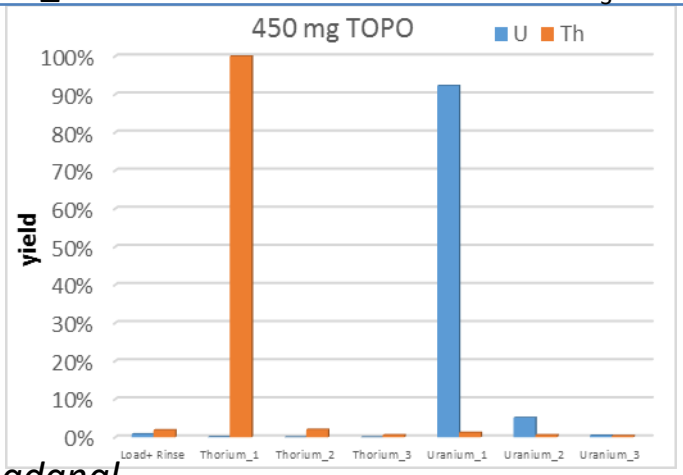
Data from N. Vajda - Radanal

TK200 Resin – Elution studies for U/Th separation from acidic solutions

Load+ Rinse	5mL Load 3 M HNO_3 + 5mL 3 M HNO_3
Th_1	10 mL 0.1 M HCl-0.1 M oxalic acid
Th_2	5 mL 0.1 M HCl-0.1 M oxalic acid
Th_3	5 mL 0.1 M HCl-0.1 M oxalic acid
U_1	10 mL 0.1 M Ammoniumoxalate pH 9
U_2	5 mL 0.1 M Ammoniumoxalate pH 9
U_3	5 mL 0.1 M Ammoniumoxalate pH 9



Load+ Rinse	5mL Load 3 m HNO_3 + 5mL 3 m HNO_3
Th_1	10mL 0.1 m HCl-0.1 m oxalic acid
Th_2	5 mL 0.1 m HCl-0.1 m oxalic acid
Th_3	5 mL 0.1 m HCl-0.1 m oxalic acid
U_1	10 mL 0.1 m $NaHCO_3$
U_2	5 mL 0.1 m $NaHCO_3$
U_3	5 mL 0.1 m $NaHCO_3$



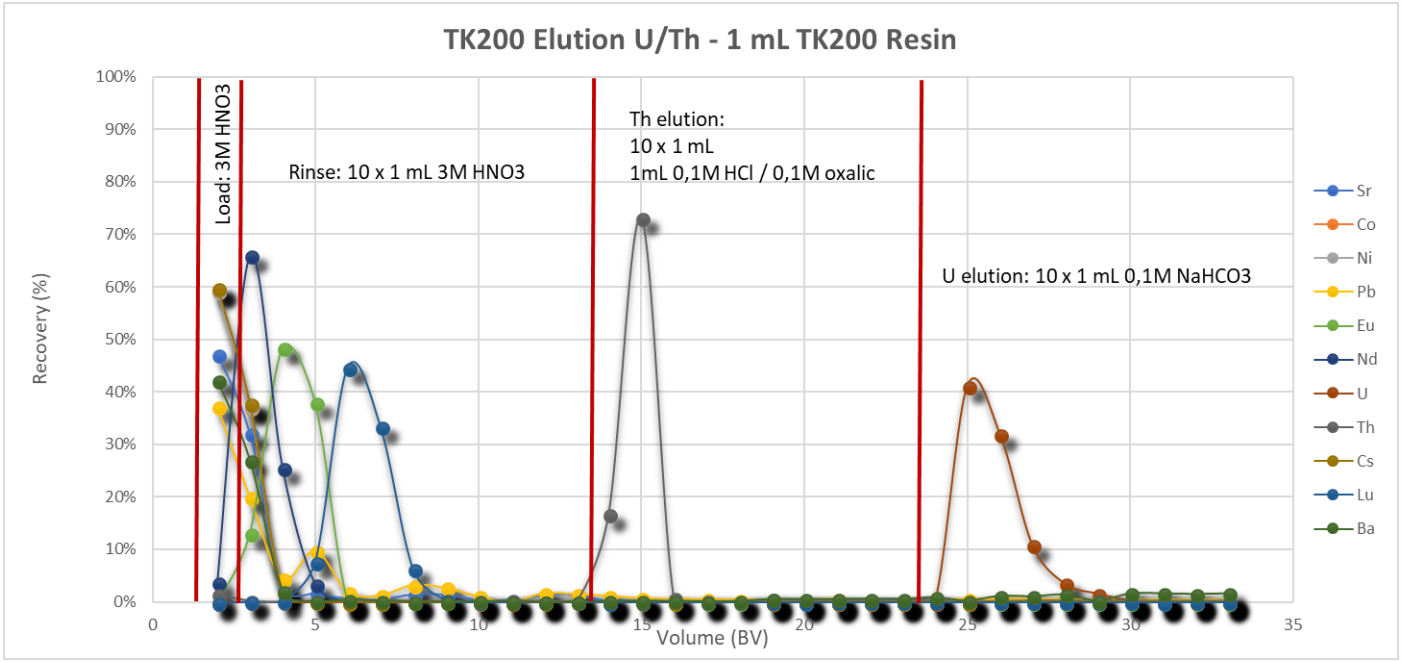
Data from N. Vajda - Radanal

Th selectively separated from U and recovered quantitatively

U quantitatively recovered with 15mL of various solutions depending on needs

=> Good alternative resin to UTEVA resin

U/Th separation on TK200



- Load: 3M HNO_3 or ≥ 1L pH2 (HNO_3)
- Very clean U/Th separation

TK200 Resin – Conclusions

- Preconcentration of actinides from pH1-2 solutions => medium usually used to preserve samples for storage and prior to analysis
- Alternative to UTEVA Resin for Th/U separation from acidic conditions
- Possibility to extract/concentrate Sn and Cd in HCl and elute in low HNO_3 concentration.
- Zr/Hf are well extracted in HCl (1-10M) and HNO_3 (whole studied range)

Developments for Tc-99 separation

- Tc-99 (difficult to measure – DTM Radionuclide) – 100% beta emitter
- Interest in decommissioning and radioactive waste management and in Nuclear medecine
- TEVA resin allows for Tc separation but quantitative elution needs highly acidic medium

➢ 2 new resins developped for load with both acidic or alkaline media and specific elution in slightly alkaline or water

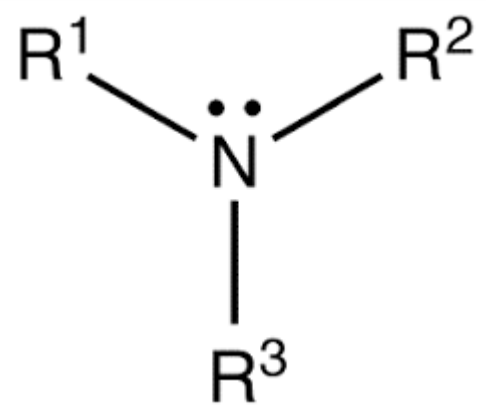
TK201 Resin

- Based on tertiary amine (weak Anion Exchanger) impregnated on inert support

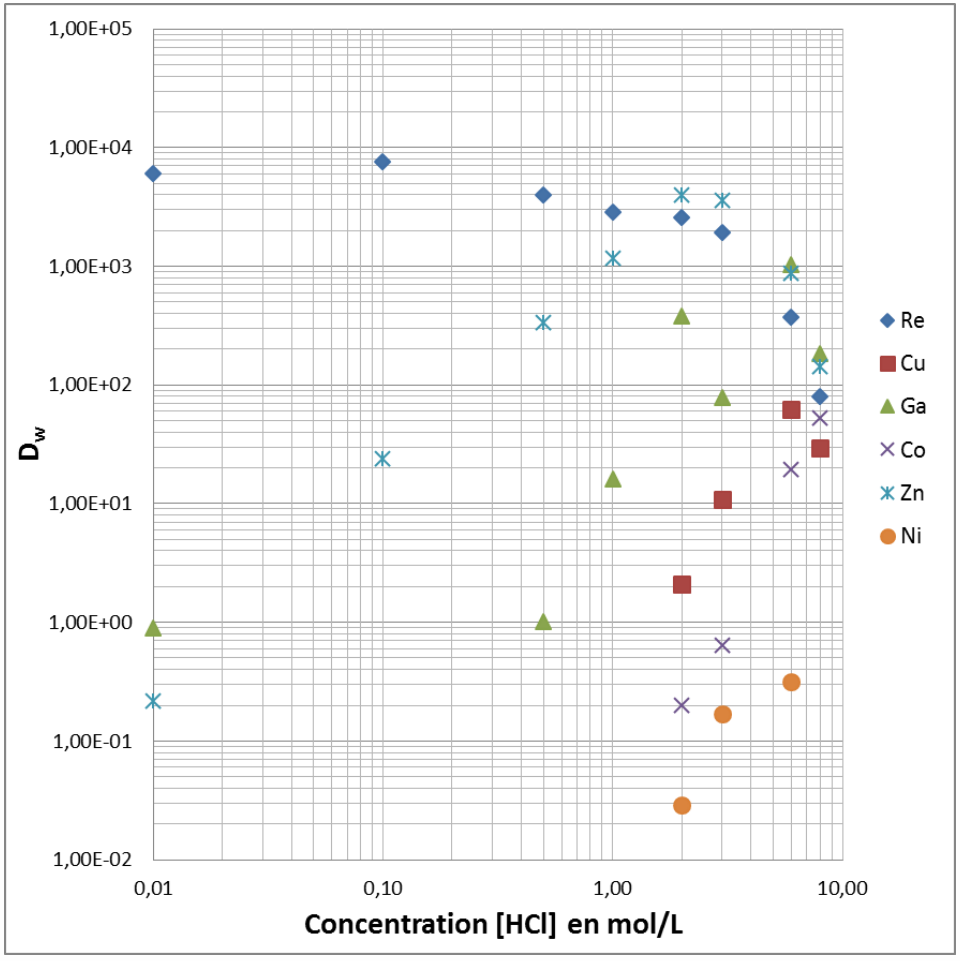
- In acidic medium,

  $R1(R2)(R3)\text{-}N^{+}H\ Cl^{-}$

  Exchange of the counter anion



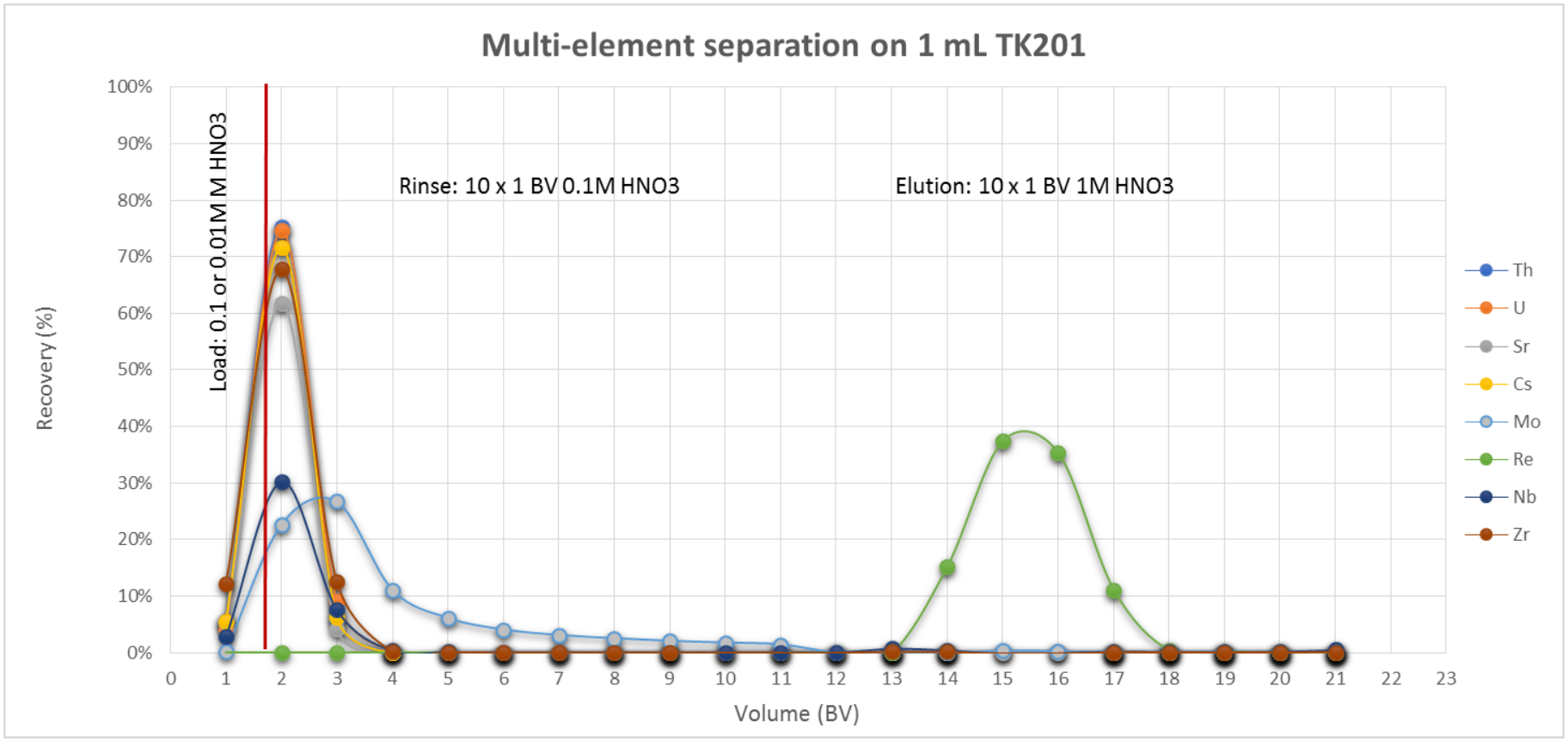
TK201 – Dw in HCl



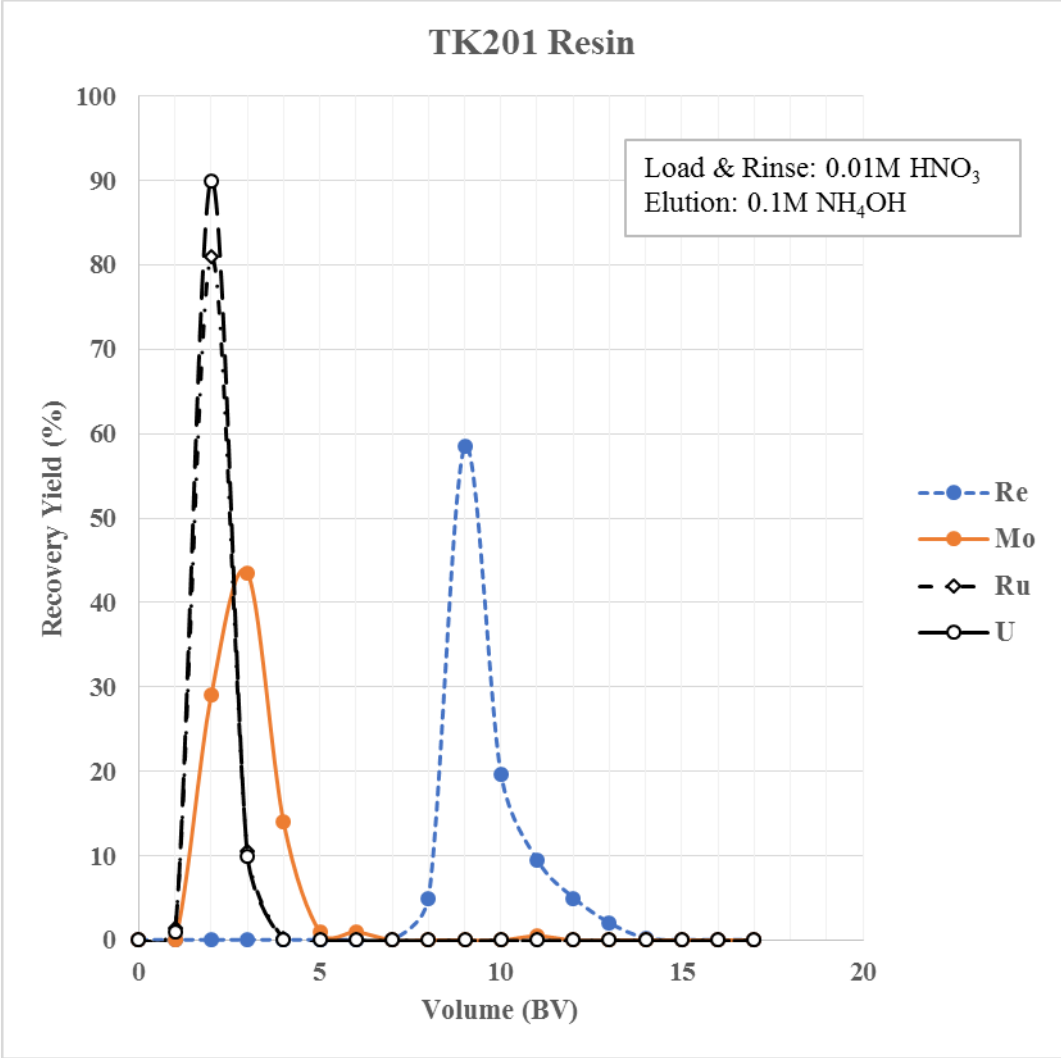
- Re uptake between pH 2 – 5M HCl
- In HNO_3 medium, Re fixed at pH 1-2

TK201 Resin – Elution curve

- Load of sample at pH 1-2 to fix Re(Tc)
- Elution of Re @ 1M HNO3



TK201 Resin – Elution curve Separation Re(Tc)/Mo

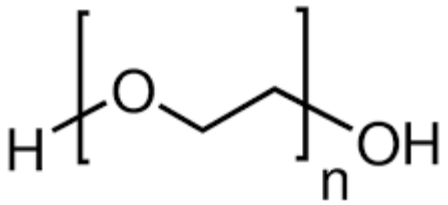


- Clean separation of Re in 6BV 0,1M NH_4OH
- Elution of Re also possible with 1M HNO_3
- No retention of other elements studied

TK202 Resin

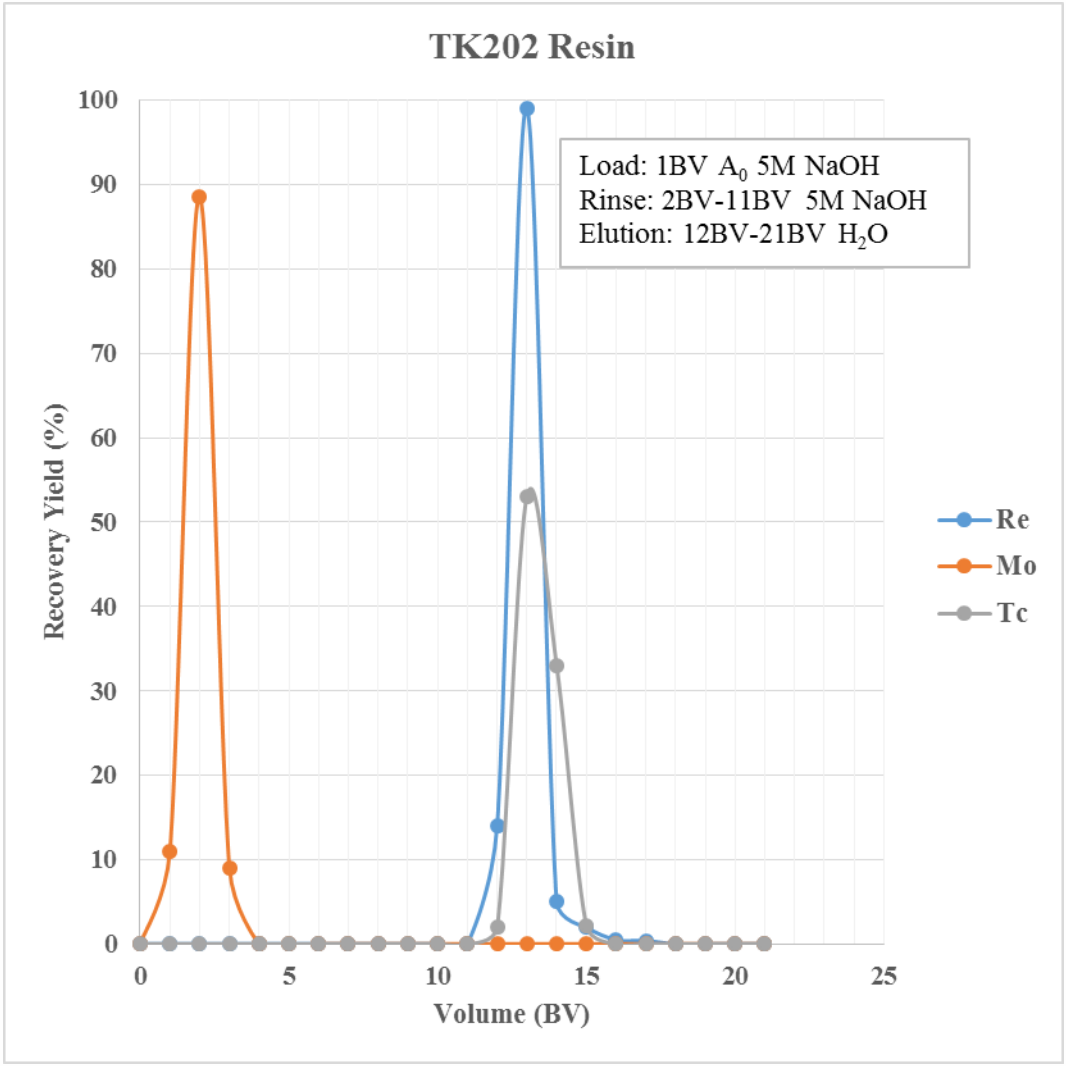
- Based on Polyethylene Glycol

(PEG) grafted on inert support



- Exchange from rich PEG phase to poor PEG phase based on
  - salting out effect due to 5M NaOH medium in our case
  - ability of salt to easily dissociates and break hydrogen bonds

TK202 Resin – Elution curves



- Tests show Re-Tc have similar behaviour in tested conditions
- Clean separation of Re-Tc and recovery in 5BV H2O

TK201/TK202 Resins - Conclusion

- 2 resins allowing for the separation of Tc either from starting acidic or alkaline media (liquid wastes/ alkaline dissolutions of concretes for analysis in decommissioning)
- Elution with much less acidic solution (compared to TEVA) or water in case of TK202 Resin
- Further testing going-on with real samples for resins robustness for Tc/Mo separation
- Use in MS for isobars elimination prior to analysis

Updates: CS Resins

- Two resins:
  - AMP-PAN (acidic samples)
  - KNiFC-PAN (slightly acidic to neutral samples)
  - 70 – 85% active componant, fast kinetics
- Both resins efficiently remove Cs, very difficult to regenerate
- Typical applications:
  - Low level Cs-134/7 determination of water samples by gamma spectrometry => bulk, columns, cartridges
  - Removal of high levels of Cs-137 before MS => safeguards
  - Cs-137 decontamination of contaminated effluents => bulk, large quantities and particle sizes

Cs measurements in Seawater [8][9]

- Procedure:
  - Seawater Sample volumes: 100L,
  - Acidified (pH 1-2) and raw samples,
  - Column bed 25ml of AMP-PAN or KNiFC-PAN,
  - Flowrate: maximum at 300ml.min^{-1},
  - Gamma spectrometry measurement

➢ Results: Yield > 90% Cs retention

[8] Pike et al., Extraction of Cesium from Seawater off Japan using AMP-PAN Resin and Quantification via Gamma Spectrometry and Inductively Coulped Mass Spectrometry, J. Radioanal. Nucl. Chem, DOI 10.1007/s10967-012-2014-5, 2012

[9] Kamenik J. et al., Fast Concentration of Dissolved forms of Cesium Radioisotopes from Large Seawater Samples, J. Radioanal. Nucl. Chem, DOI 10.1007/s10967-012-207-4, 2012

Updates: TK100 Resin

- Development for measurement of ^{90}Sr and ^{226}Ra by Russel and Van Es from NPL

Rapid Analysis of Radium-226 in Water Samples by ICP-QQQ

Application Note

Nuclear, environmental

Authors

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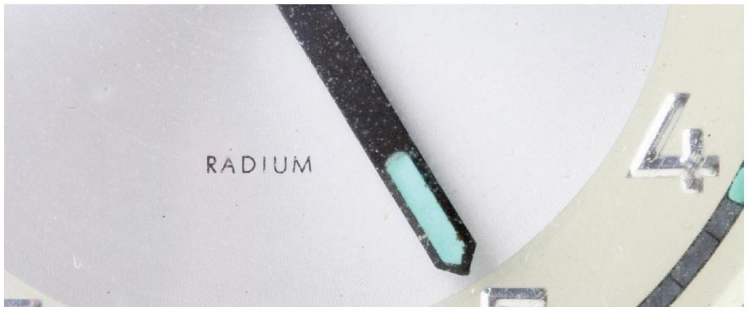

https://www.agilent.com/cs/library/applications/8800_ICP-MS_5991-8324EN_radium_analysis.pdf

TK400 Resin

Results and applications to be presented by

- Peter Ivanov
- Chris Gilligan

Later during this meeting

Thank you for your attention!

New website @ www.triskem.com

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