Applications of Triskem resins for Actinide Analysis

Triskem User Group – York 2022

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Actinide Analysis

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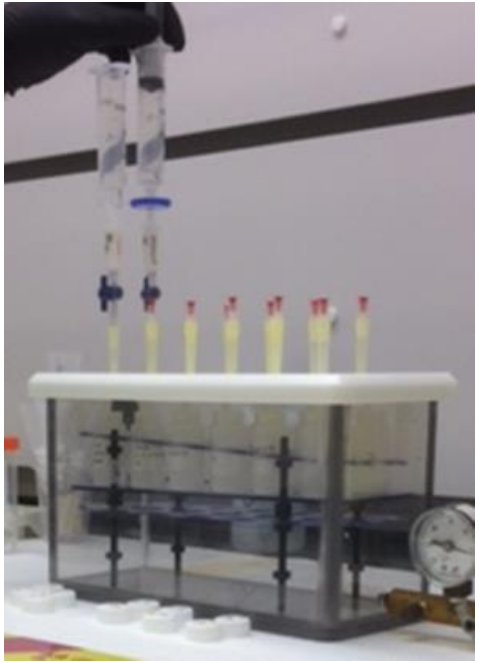
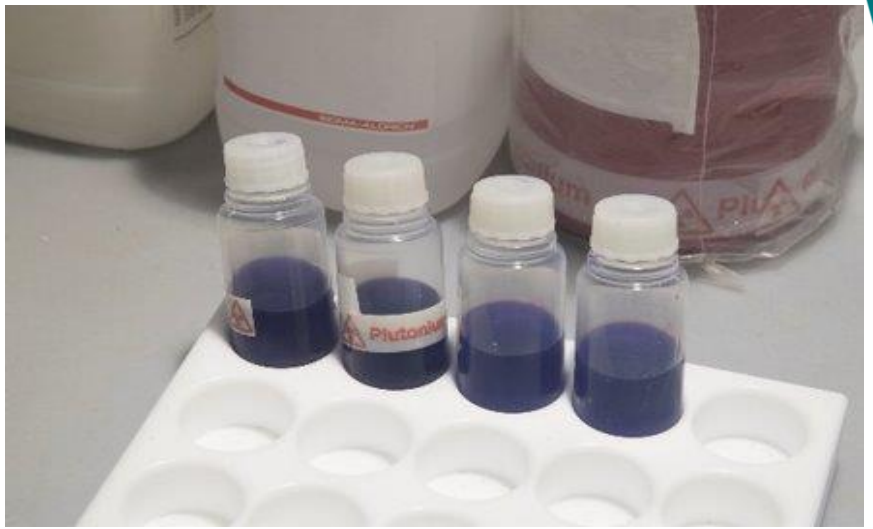


Agenda

- Actinide Analysis at AWE
- Drivers for improved processes
- TK400 Resin
- Applications
  - Pa Tracer
  - U Radiochronometry (+Zr Resin)
  - Major elements in Pu by WD-XRF
- Summary



Pu (III) in HCl

Mission

Diverse Research Portfolio

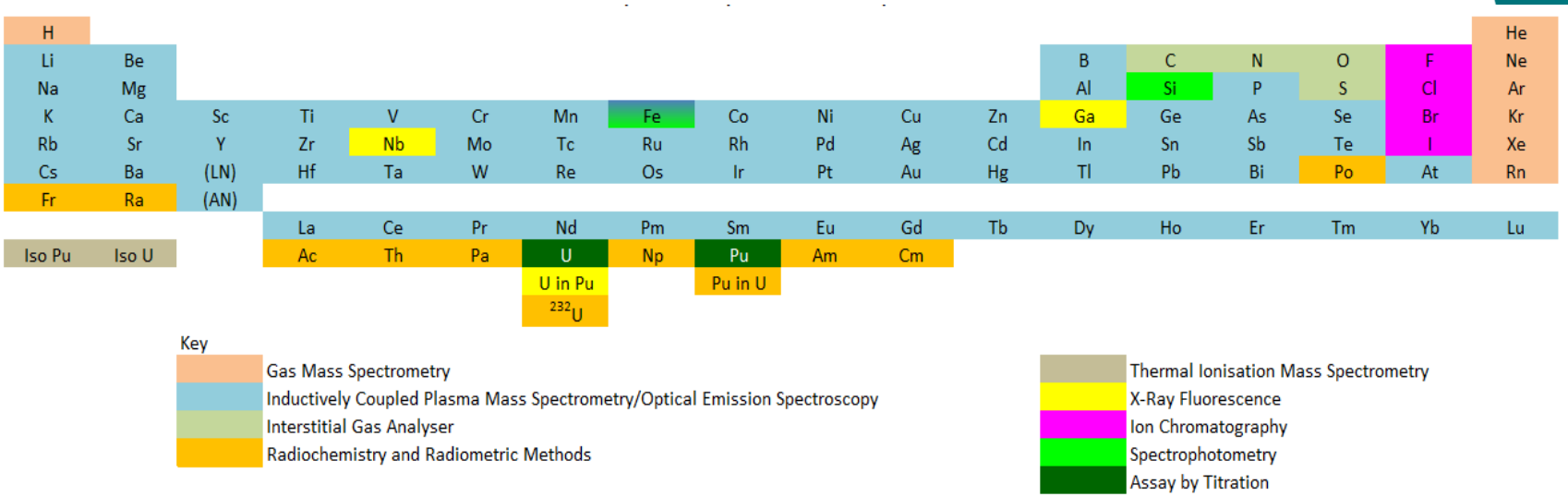
- Process control and stockpile stewardship
- Material recycle operations
- Actinide materials research
- Nuclear forensic analysis capability
- Measurements for waste sentencing

Current State

- Pu & U metals, alloys, compounds and oxides
- Mainly wet, acidic chemistry in gloveboxes
- Safety case requires ongoing consideration of methods of risk reduction

Example instrumentation for actinide analysis

Actinide Analytical Chemistry



- **Analysis of virtually any element in actinide materials**
- **Accurate and precise analysis covering orders of magnitude i.e. major (%), minor (%-10^{-3}) and trace (10^{-3}-10^{-15})**
- **Chemical and instrumental processes for removal of analytical interferences**

Driver for change

- R&D programme tailored to meet future challenges and demand
- New laboratory project underway
- Driving the reassessment of safer and more efficient analytical processes

Recent R&D Highlights

- Automation and robotics

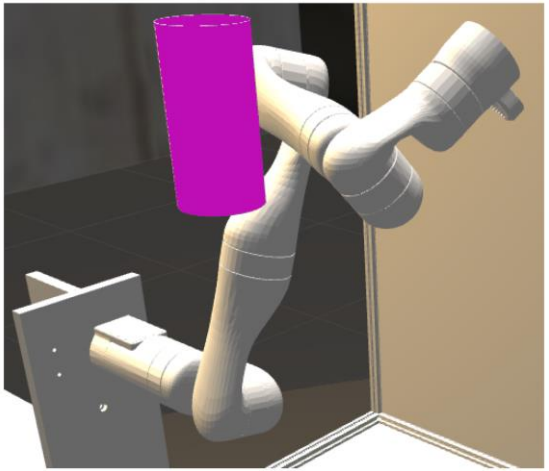
Higginson, M. et al. *J Radioanal Nucl Chem* 320, 689–698

- Smaller scale techniques

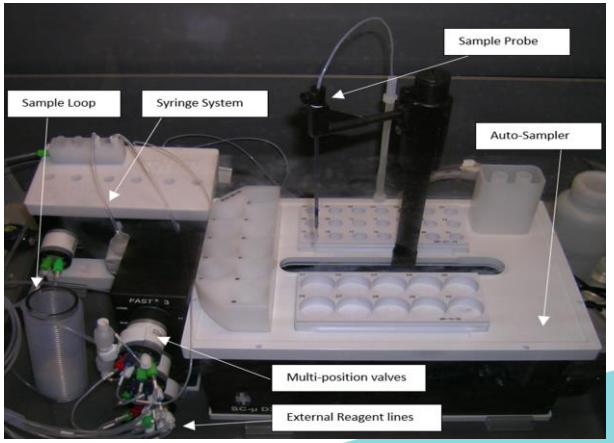
Higginson, M. et al. *J Radioanal Nucl Chem* (2022), https://doi.org/10.1007/s10967-022-08411-0

- Direct analysis approaches

Higginson, M. *et al*. *J Radioanal Nucl Chem* 330, 901–911 (2021).



Tokatli and Burroughes et al. Robotics 2021, 10(3), 85



Higginson, M. et al. *J Radioanal Nucl Chem* 320, 689–698

TK400 Resin

- Knight et al. demonstrated that long-chained alcohols, especially octanol, show selectivity towards Pa at high HCl concentrations [1]
- Analogous to liquid-liquid behaviour
- Jerome et al. continued this trend looking at the actinide series showing limited retention [2]
- How does this expand the radiochemists toolkit?
- Many specific applications developed since by colleagues e.g. Zr/Nb etc.
- How can it be used for actinide analysis applications?

Example U/Np/Pa separation on TK400 resin [3]

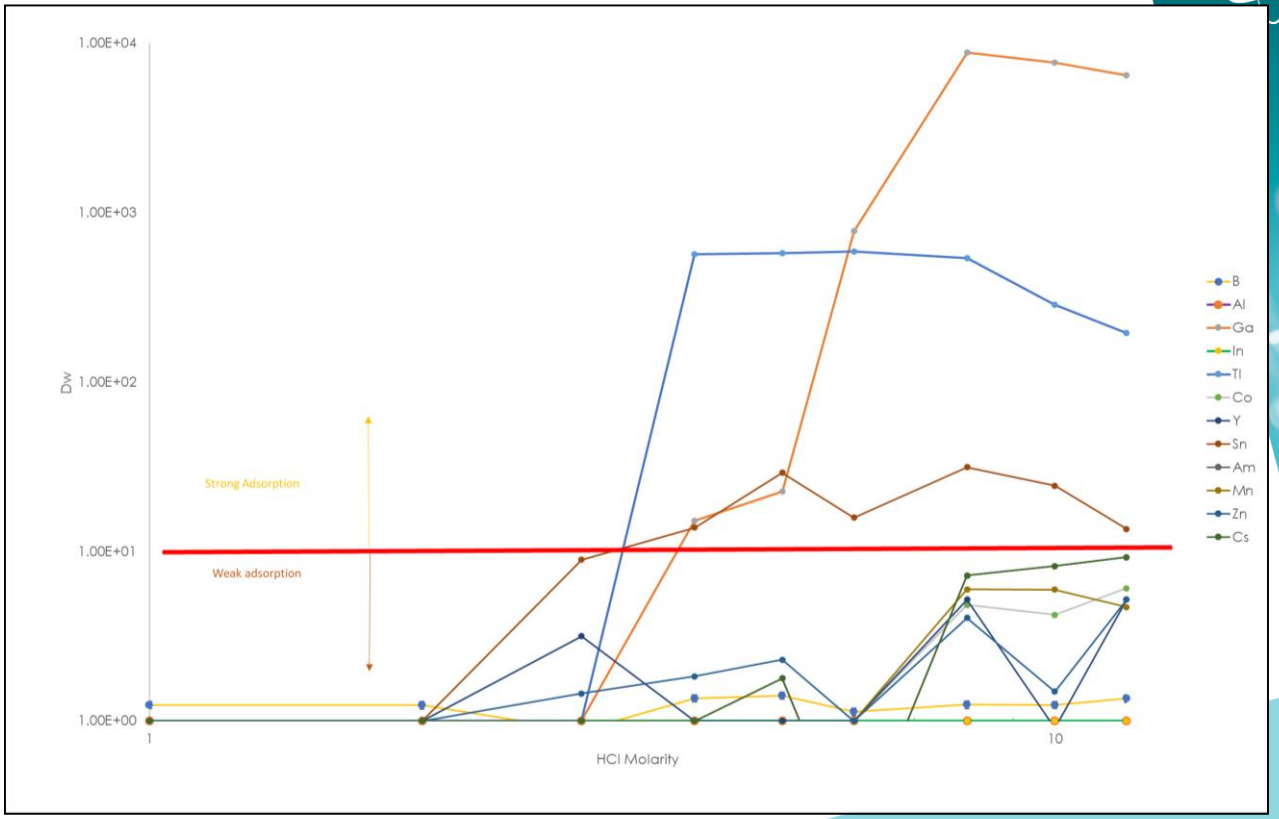
[1] Knight AM *et al*, J Radioanal Nucl Chem (2016) 307:59–67 (2)
[2] Jerome SM, *et al*, Appl Radiat. Isot. (2018), 134:18-22.
[3] Higginson M *et al. J Radioanal Nucl Chem* 318:157–164 (2018).

Example TK400 Dw values in HCl

- Recalling Cambridge UM in 2018
- Limited actinide interaction in HCl
- Dw <1 for Pu, Th, Am, Cm, U….

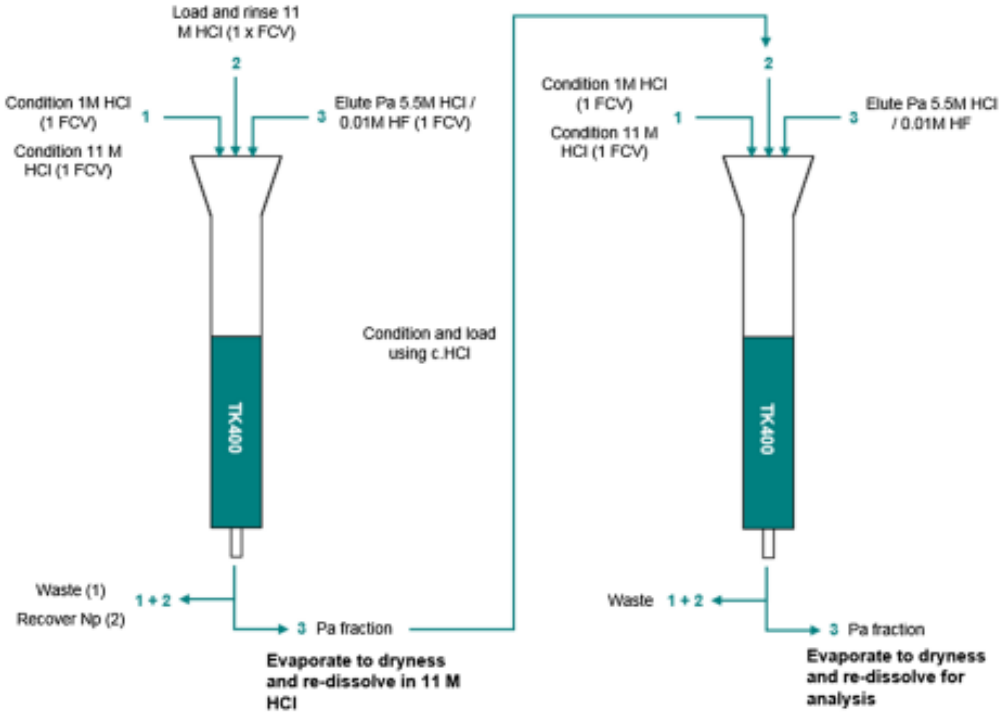
Applications

- Decay products in actinides
- Selectivity for Pa
- Np/Pa tracer



Example Dw values for TK400 in HCl

Application – ^{233}Pa Tracer Preparation



- Minimal to no dry downs (Pa hydrolysis)
- One step >10^3 SF – vacuum box
- More robust than classical approaches e.g. anion exchange and silica gel
- Standardise with CIEMAT-NIST or ID-MS

Higginson, M., *et al., J Radioanal Nucl Chem* **318**, 157–164 (2018).

Application – Uranium Age Dating

2003 ^{230}Th-^{234}U model ages assisted the investigation of stolen U fuel pellets

"All the News That's Fit to Print" **The New York Times** Late Edition

NEW YORK, SUNDAY, NOVEMBER 15, 1992

Lithuania's Dangerous Orphans: 2 Huge Reactors

U fuel pellet analyzed at the Institute for Transuranium Elements (ITU), Germany. (Wallenius et al., 2006)

IGNALINA, Lithuania, Nov. 9 — With the dissolution of the former Soviet Union, the two most powerful nuclear reactors in the world have been cast adrift by their creator. And if the foster parents of these formidable orphans fail to resolve some big problems, a devastating accident could occur.

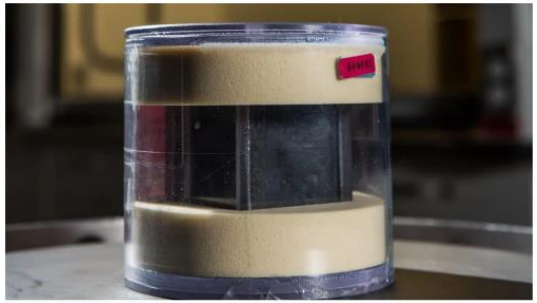
The New York Times

2021 Model ages used to confirm origins of materials of historical significance

The New York Times

Did Nazis Produce These Uranium Cubes? Researchers Look for an Answer.

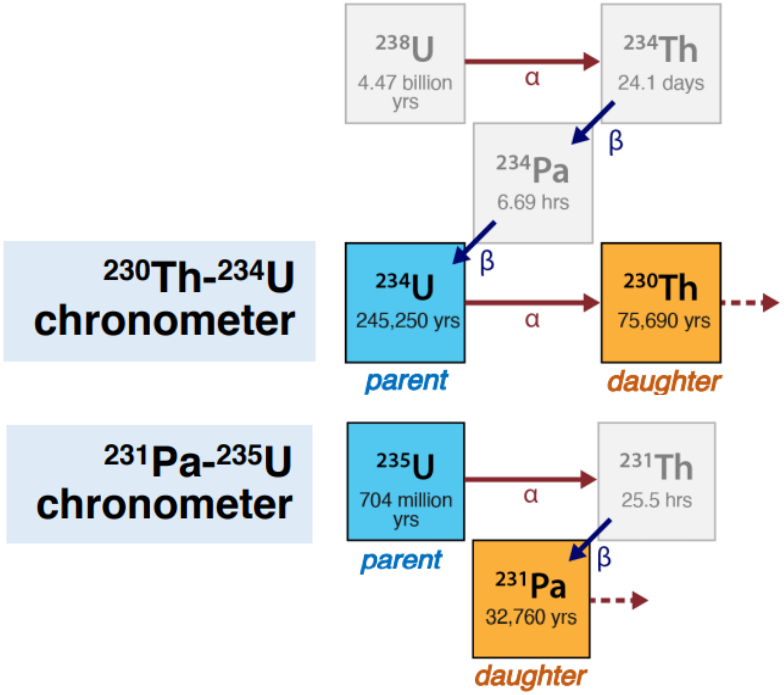
Determining whether the cubes were produced by Nazi Germany could lead to more questions, such as whether the Nazis could have had enough to create a critical reaction.

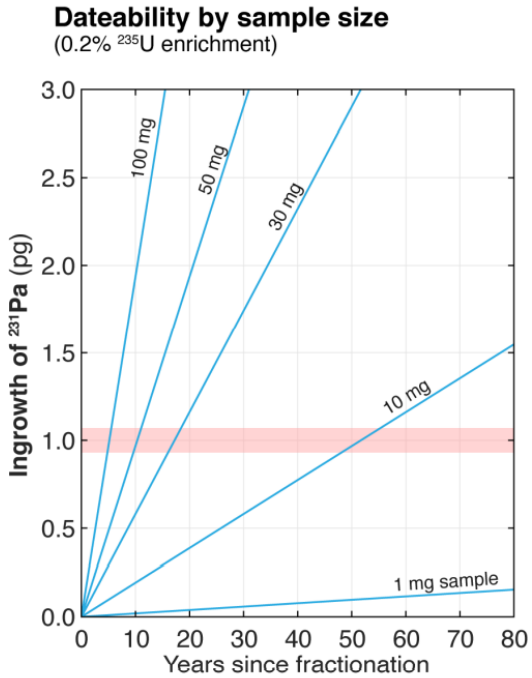


Pacific Northwest National Laboratory's cube, which is enclosed in a protective case.
Andrea Starr/PNLL

Radiochronometry has provided key context for >20 years

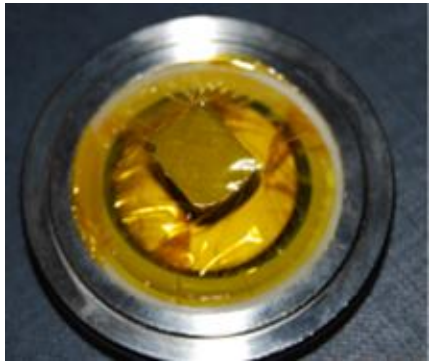
Application – Uranium Age Dating

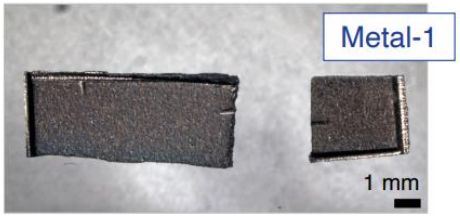


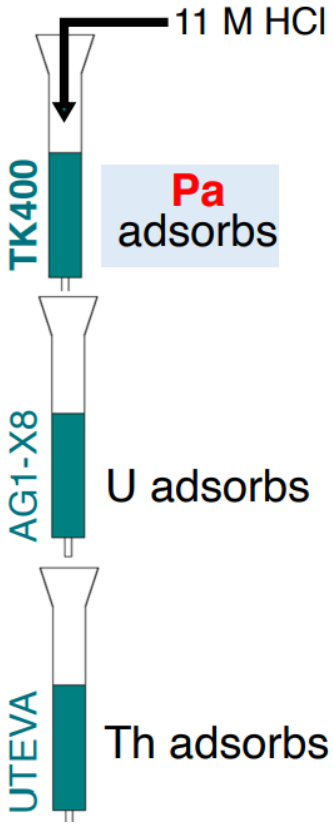


- Have a requirement for highly selective separation
- Ideally combine Th, U and Pa separation

U/Th and U/Pa Age Dating







- Bulk samples – TK400 combined methodology
- $^{231}Pa/^{235}U$ low due to enrichment (0.2% ^{235}U)
- Decay products <pg if young

Higginson, M., *et al., J Radioanal Nucl Chem* **318**, 157–164 (2018).

U/Th and U/Pa Age Dating

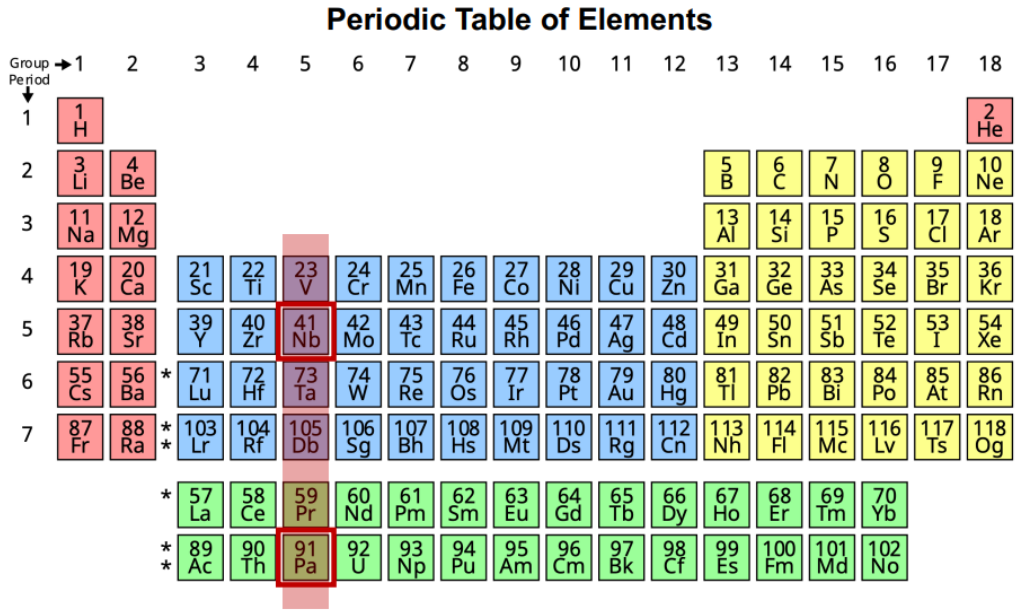
- CMX-6 international forensics exercise
- Depleted uranium metal provided in 2019 to 26 laboratories
- Only two made this measurement - agreement
- Produced in April 2018 at PNNL for the exercise [1]
- Measured using published method [2]
- ^{231}Pa <LOD using sub sample
- Youngest forensic measurement?

Sample ID	CMX-6 U metal
Chosen isotope pair	^{234}U /^{230}Th
Time since last processing (years)	1.37
Model Age at Reference Date	11-Apr-18
Uncertainty (years)	0.13

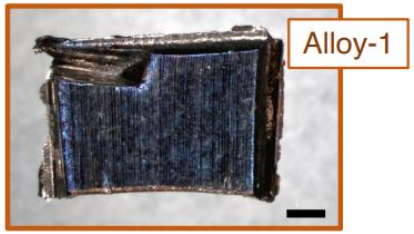
Example radiochronometry measurement of CMX-6 exercise sample using TK400 method from bulk uranium (4 gram)

[1] Schwantes, J et al. - Twenty Years of Collaborative Materials Exercises by the Nuclear Forensics International Technical Working Group. United States: N. p., 2020. Web.
[2] Higginson, M., *et al., J Radioanal Nucl Chem* **318**, 157–164 (2018).

Application – U alloy age dating



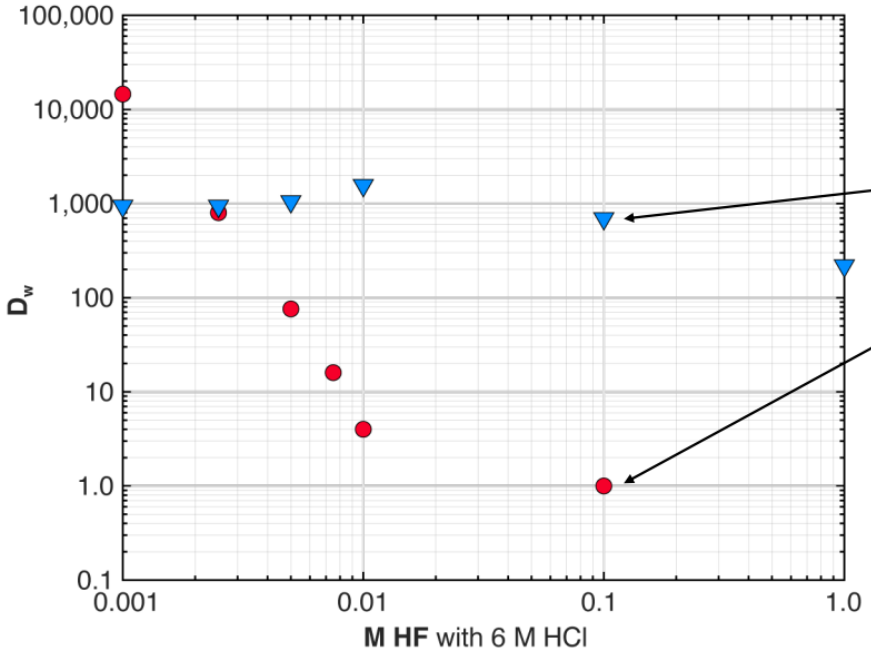
Pa and **Nb** are ***homologues***, meaning they have near-identical chemistry — separating the two will be difficult.



A real challenge! Nb is present in large quantities, whereas Pa is in ultratrace-level quantities.

Application – U alloy age dating (+ZR resin)

Distribution coefficient (D_w) of Nb and Pa for ZR resin in 6 M HCl with HF



$$D_W = \frac{[\text{solid phase}]}{[\text{aqueous phase}]}$$

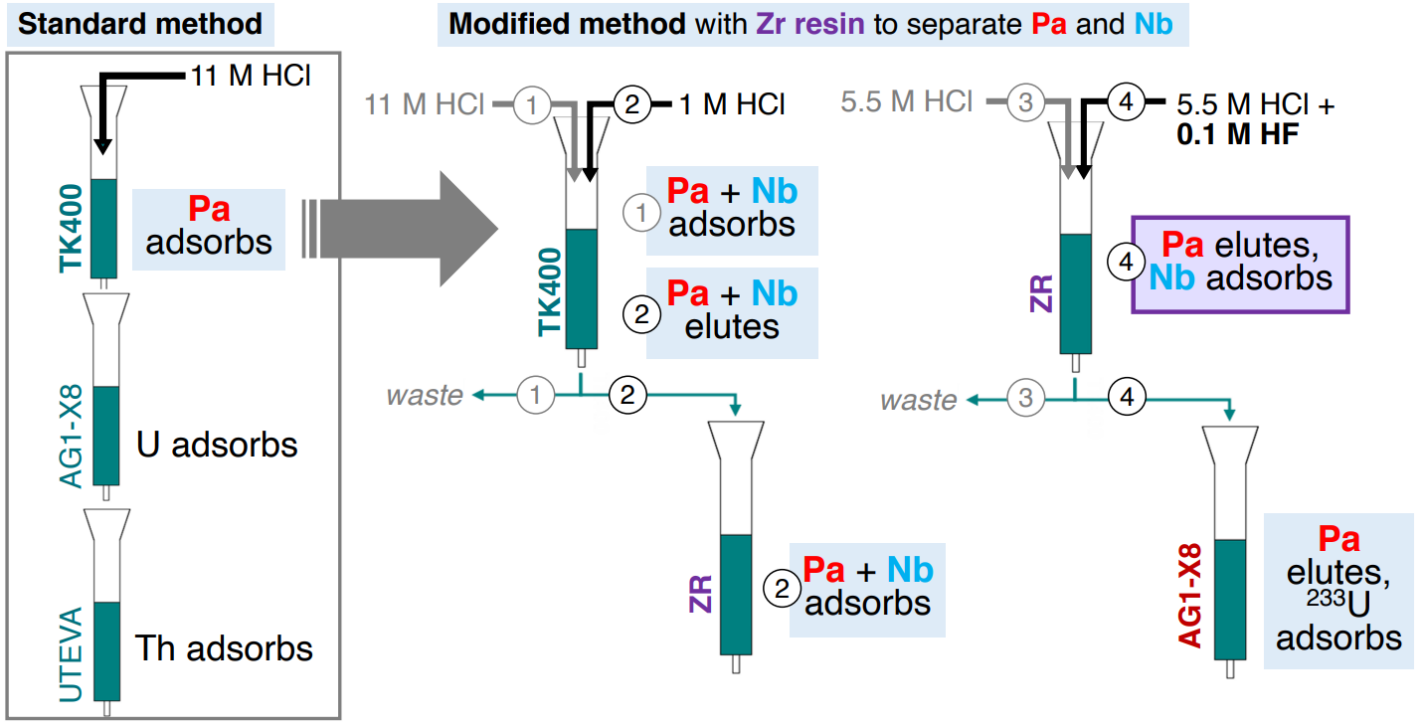
Nb strongly ***adsorbs*** to Zr resin in 6 M HCl + 0.01 M HF.

Pa is ***stripped*** from Zr resin in 6 M HCl + 0.01 M HF.

Imperfect Pa recovery, but is sufficient for mass spectrometry.

- **Wider applicability to Mo/Zr/V U alloys – weak interaction**
- **More robust radiochronometry methods**

Application – U/Nb alloy age dating



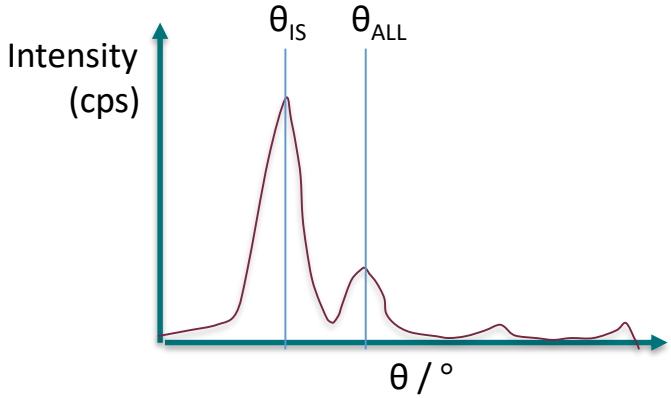
Higginson, M.A et al. *J Radioanal Nucl Chem* (2022).
https://doi.org/10.1007/s10967-022-08428-5

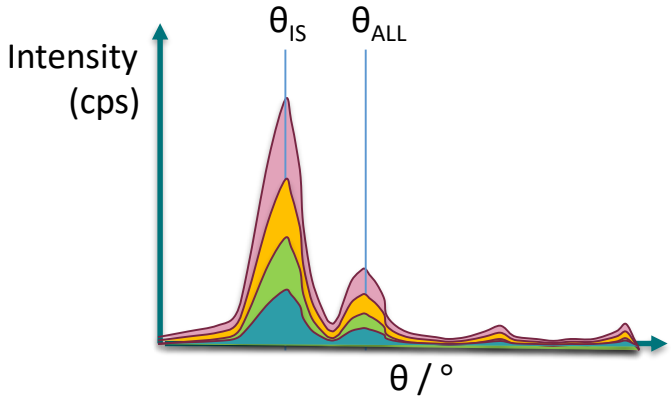
Drivers

- Ga is required in actinide samples for a variety of customers with quick turnaround times over a wide concentration range
- WD-XRF and ID-MS methods maintained
- Improve process safety:
  - Latest injected wound dose hazard assessment for chemistry is >Sv
  - Apply ERICPD principles
- Develop efficient laboratory workflows – automated method not easily achieved on anion exchange due to redox control
- Reduce nuclear material accountancy & control burden
- Minimise waste

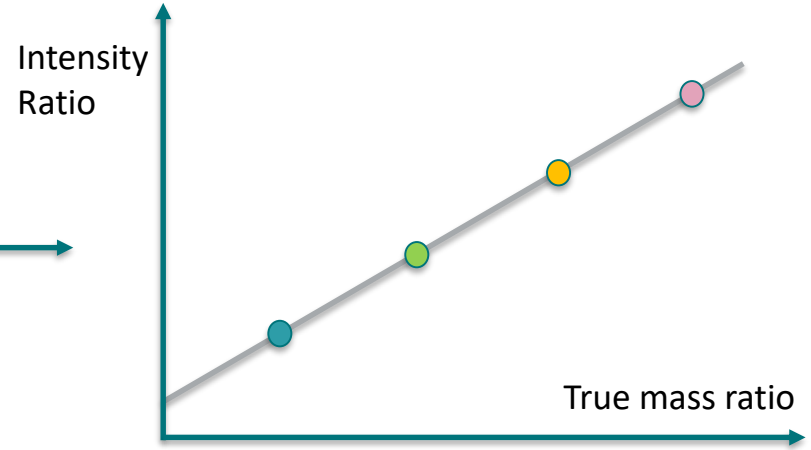
Higginson, M.A *et al. J Radioanal Nucl Chem* (2022).
https://doi.org/10.1007/s10967-022-08411-0

Principles of X-ray Fluorescence Spectroscopy



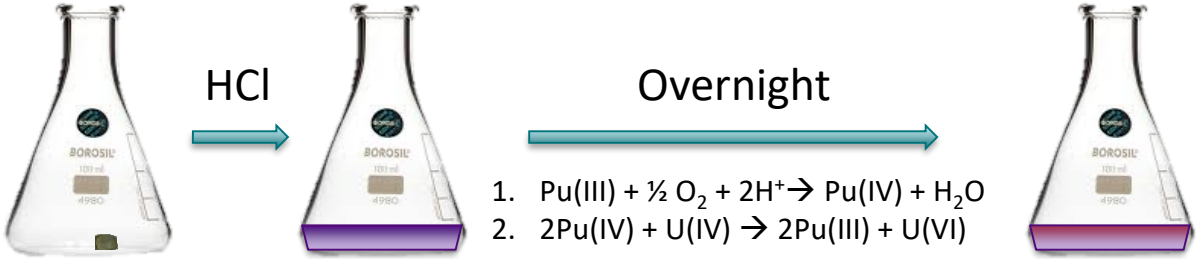


$$\frac{I_{ALL}}{I_{IS}} \propto \frac{m_{ALL}}{m_{IS}}$$



Classic method for Ga/U/Np quantification

- Step 1: Cut, move, dissolve
  - 1 g metal dissolved in heavy duty glassware

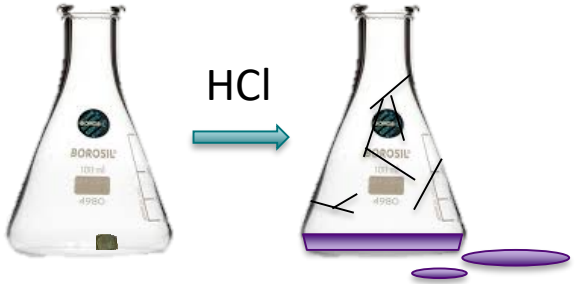


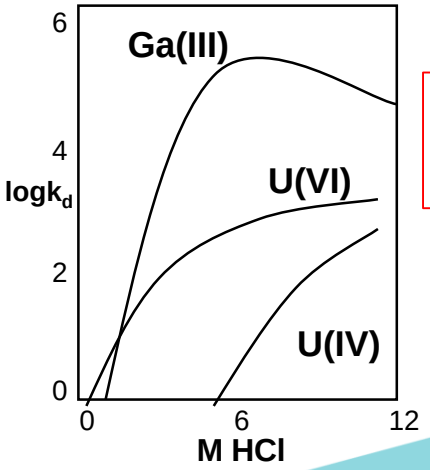
Use of anion exchange resins since 1960 have been continuously improved [1] [2]

[1] Tandon L et al. (2008) J Radioanal Nucl Chem, 276(2):467–473
[2] Worley, C et al. (2002). X-Ray Anal. AXRAAA 45, 421–426.

Classic method for quantification

- Step 2: Separation on AG1-X4 anion exchange resin
  - Reduction of residual Pu(IV)
  - Resin selectivity negligible for Pu, selective for Ga/Np/U….
  - Addition of internal standard
  - Elution of Np in 4 M HCl
  - Elution of Ga/U in 0.1 M HCl
- Step 3: Cell preparation and analysis by WD-XRF
  - Box line → fume cupboard transfer
  - Solution cell preparation
  - Transfer to instrument for analysis under helium…
- **ANX solution contains Pu, U, Np and Ga**
- **ANX solution yields approx. 2 MBq activity solutions for WD-XRF**





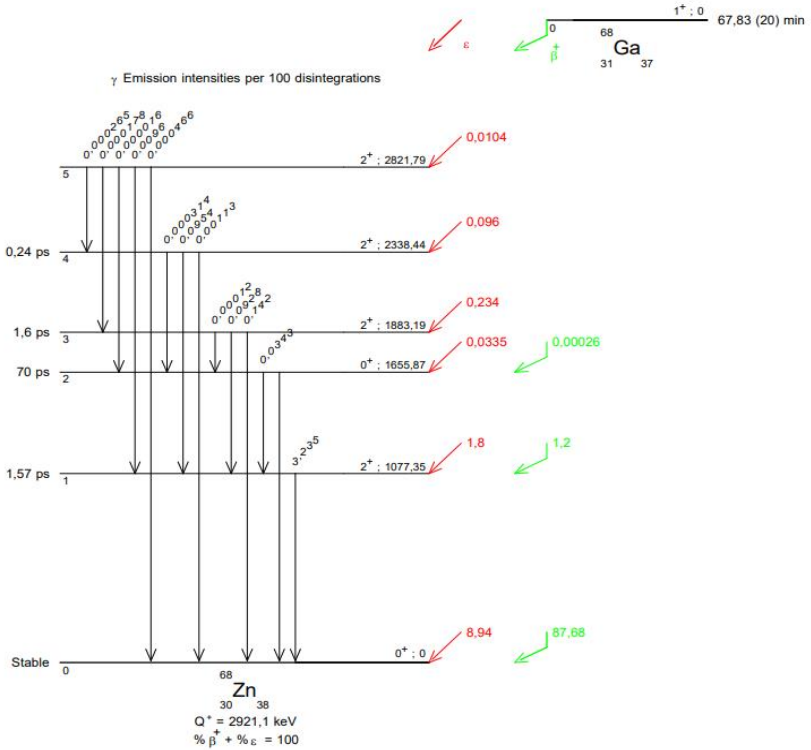
Injected wound dose hazard!

TK400 Trials

- Selectivity identified in trial work using ICP-MS and in literature
- TK200, Zr Resin also tested – retain Ga at >2.5 M HCl – have applications….
- 0.05-1.0 g of Pu solution trialled on TK400
- Ga strongly retained at >5.5 M HCl with little affinity for Pu(III/IV), Np, U, Am….
- Avoids dissolution in glassware
- Pa selectivity allows for indirect Np quantification
- Good results at 50 mg Pu on a CRM:
  - 2%RSD between different solutions
  - 0.2%RSD within same solution

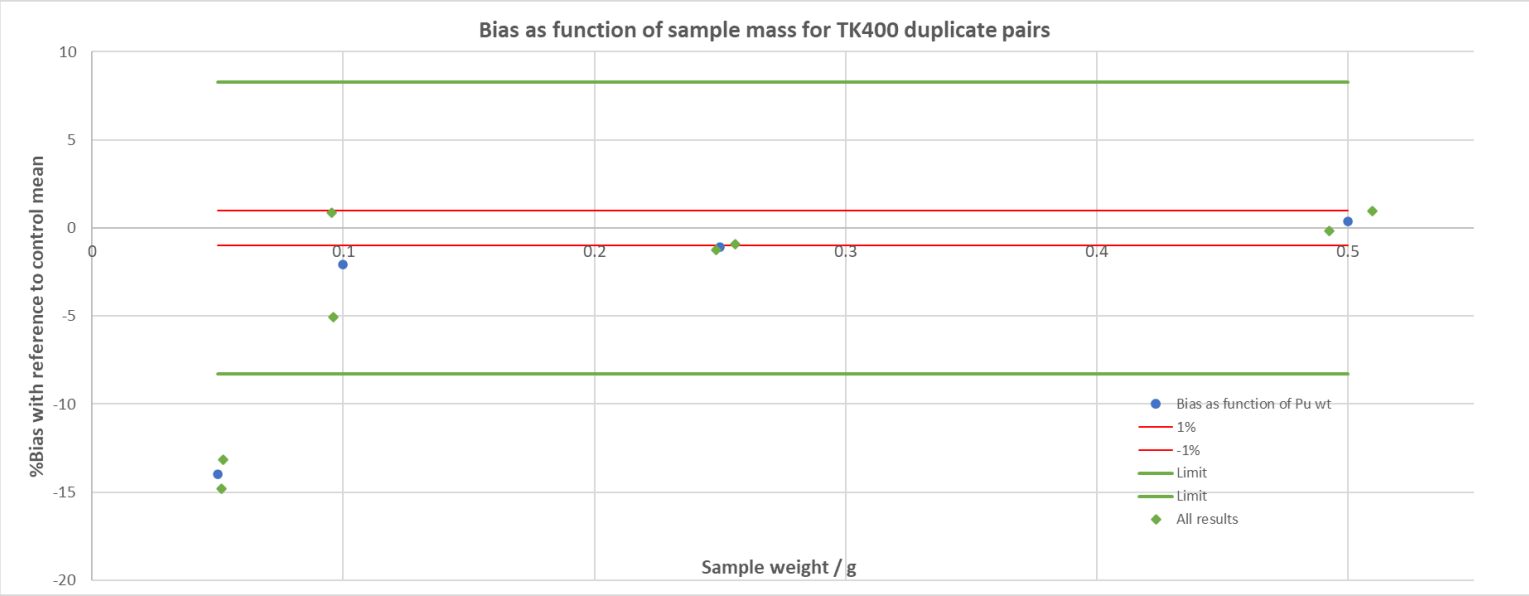
Use of ^{68}Ga Radiotracer

- Commercial generators are **cheap** (3.7 MBq)
- One working day use time (**1.2 h half life**)
- A **TK200/Zr resin system** was developed for Ge/Ga separations
- At 2 M HCl on Zr resin Ge has a Dw >10^3, **no Ga adsorption**
- At 2 M on TK200, trace **Ge is not adsorbed**, and Ga has a Dw >10^2
- Allowing 3.7 MBq to be available on demand
- Quantify with standard to <0.2% on same gamma detector
- Useful for yield correction of TK400 method; low number of atoms for XRF bias



Example decay scheme for ^{68}Ga

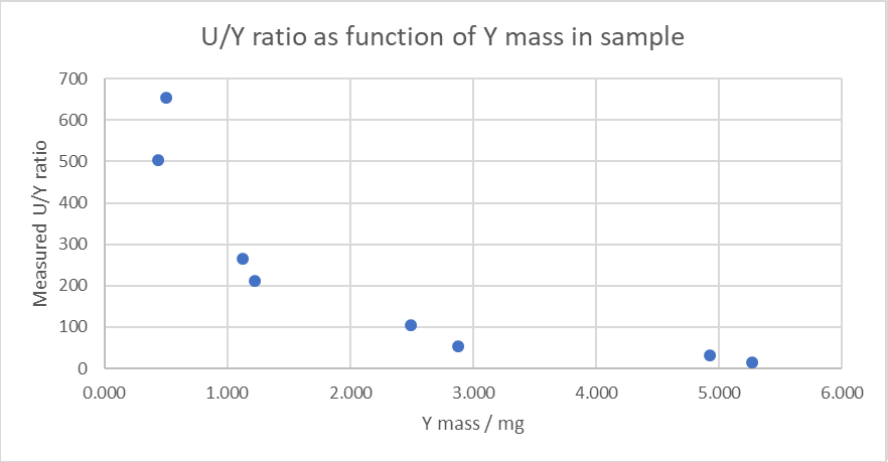
Example trials

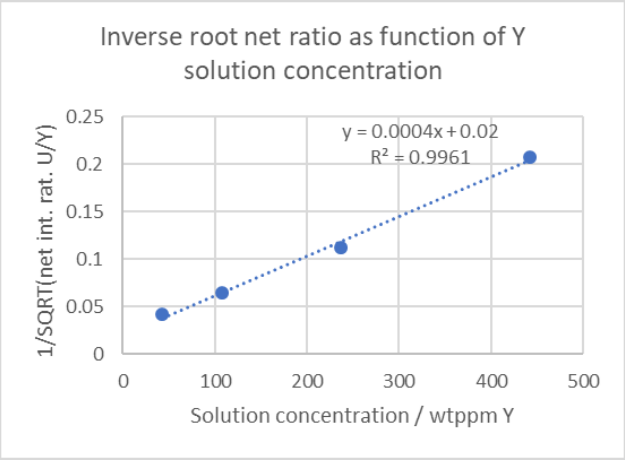


- **100 fold reduction in solution activity – to 2 to 0.02 MBq**
- **Infinite thickness not met**
- **Optimisation of XRF calibration – V reduced, 120 s measurement time, Al at 200 µm to reduce background, common background – S/N increased 60%**

Troubleshooting

- Infinite thickness
  - The thickness, x, at which the sample is considered ‘bulk’
- TK400 expected to show only negligible levels of uranium
- Apparent uranium concentration increase with decreasing sample weight





Infinite thickness

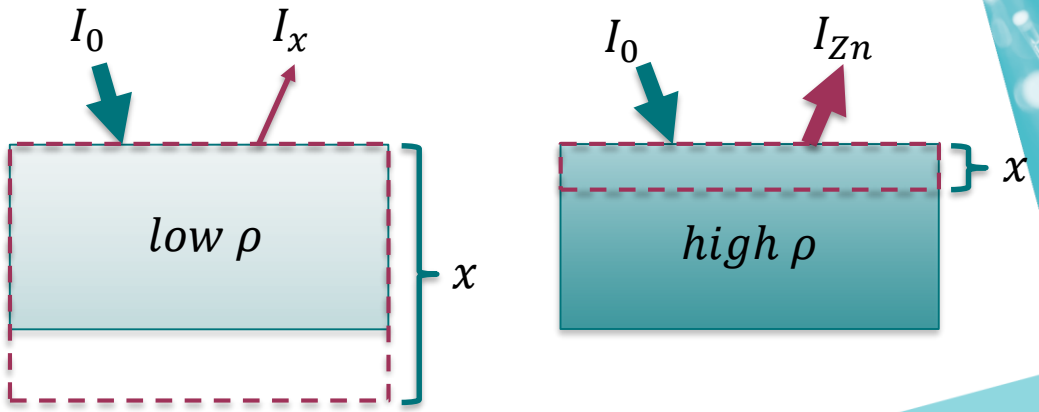
- Infinite thickness

$$I_x = I_0 \exp(-\mu\rho x)$$

- For 1% of X-rays w.r.t I_0

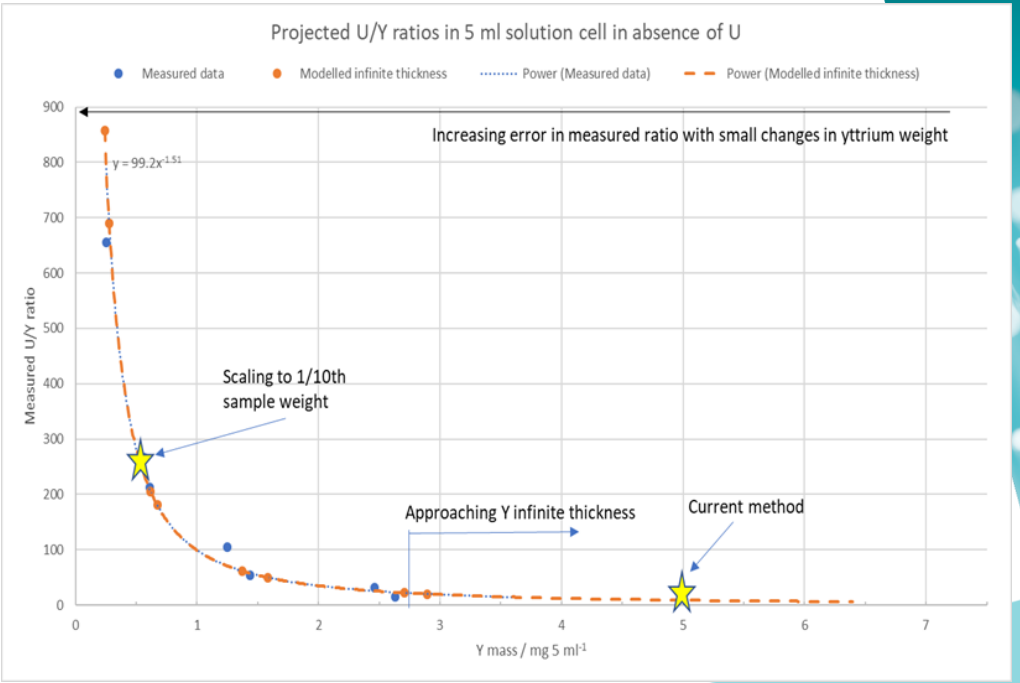
$$x = \frac{4.605}{\mu\rho}$$

Density ≈ solution concentration



XRF Optimisation

- Differences in linear attenuation coefficients between different elements will be exacerbated by increasingly lower solution concentrations
- Cannot simply scale down sample size without optimisation of acquisition parameters and improved internal standardisation



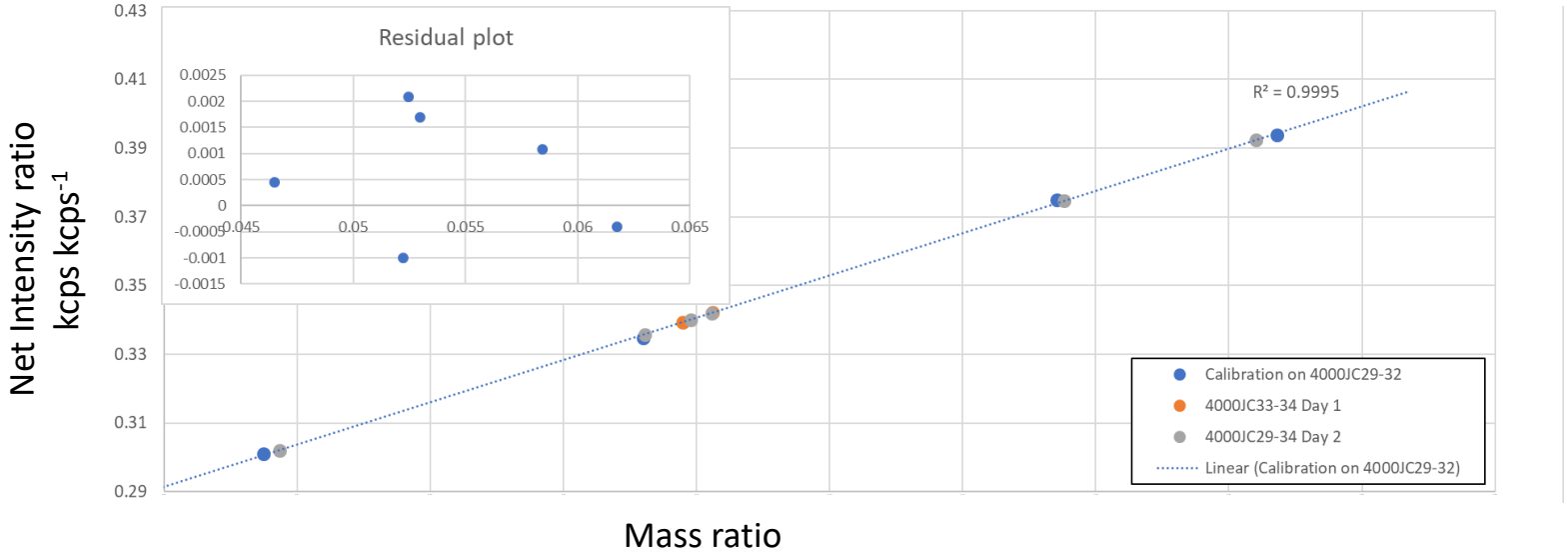
Later trials with optimized XRF method

- Use of optimised acquisition parameters and internal standardisation overcomes infinite thickness issue
- Limited the sample size to 0.1 g
- Pre-packed columns – rapid method (1 day)
- Methodology exercised by different analysts on different days
- Reproducibility for different days

TK400 method in a glovebox

Higginson, M.A *et al. J Radioanal Nucl Chem* (2022). https://doi.org/10.1007/s10967-022-08411-0

Example data at 0.1 g scale



- Excellent performance across calibration range by XRF
- %RSD on all results <0.2% with %Bias <0.05% from CRM

Impact summary

- TK400 method demonstrates:
  1. Possible to eliminate use of glassware from workup routine
     - Reduction in radiological dose consequences
  2. Use of yield tracer
  3. Uses lower concentration and volume of corrosive acids: reduced glovebox maintenance
  4. Higher selectivity over ANX for Actinides
  5. Method amenable to automation
  6. 200 fold reduction in handled solution activities
  7. Enables laboratory workflow design reducing waste and material usage
  8. No compromise on analytical performance
     - Assure method robustness – infinite thickness, calibration, chloride concentration

Conclusions

- Triskem Zr and TK400 resin have showed useful application for measurement of trace progeny and major elements in actinide materials
- Low selectivity for actinides in most oxidation states is useful for a pre-filter selective stages
- Useful for ^{233}Pa isotope separation which can be used for indirect measurements of ^{237}Np in actinide materials or for use as a tracer for ^{231}Pa
- Rationalisation, automation and reduced scale methods using instrumental advances allow for more efficient and safer methods

Acknowledgements

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