National Physical Laboratory

Studies on the use of TK400 resin for the separation of ^{231}Pa from actinide elements and decay products

Peter Ivanov
National Physical Laboratory, UK
peter.ivanov@npl.co.uk

TrisKem UGM, 21 September 2018, Cambridge

Overview

- Motivation
- Challenges in Pa chemistry
- IX and EC separation schemes
- TK400 resin
- Results
- Conclusions

Protactinium

- One of the rarer elements…
  - Discovered in 1913
  - Element 91
  - Occurs with uranium

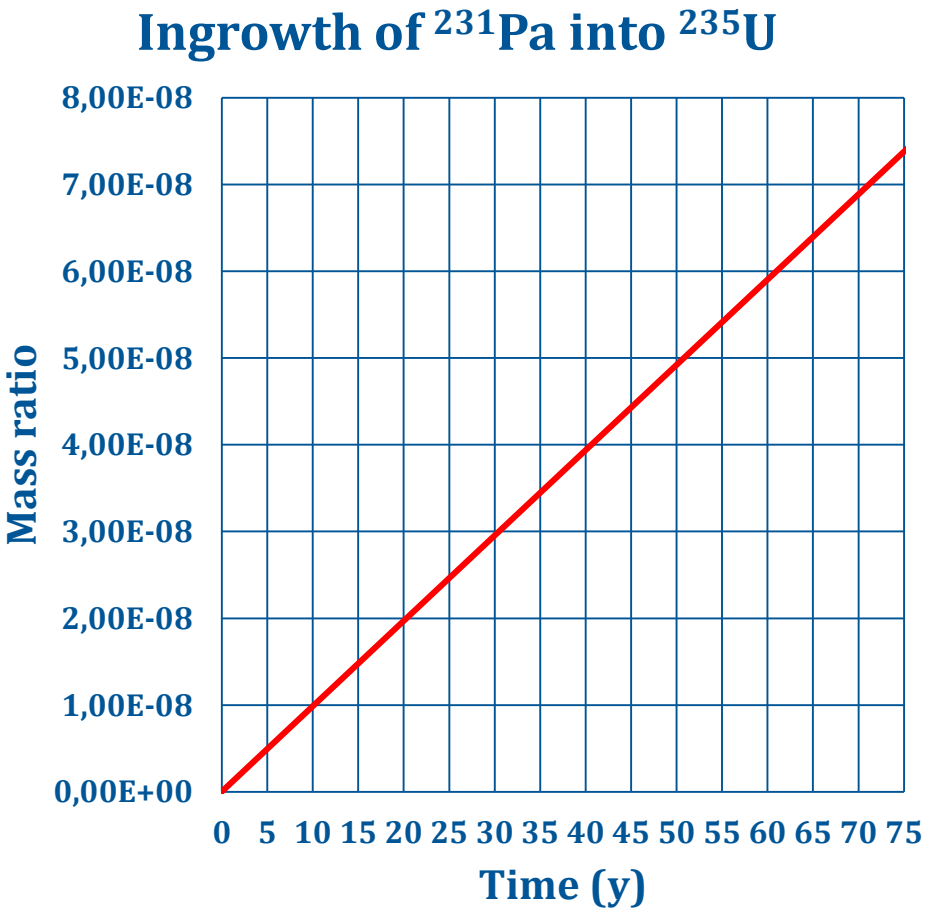
    Concentration: ~330 ng/g uranium

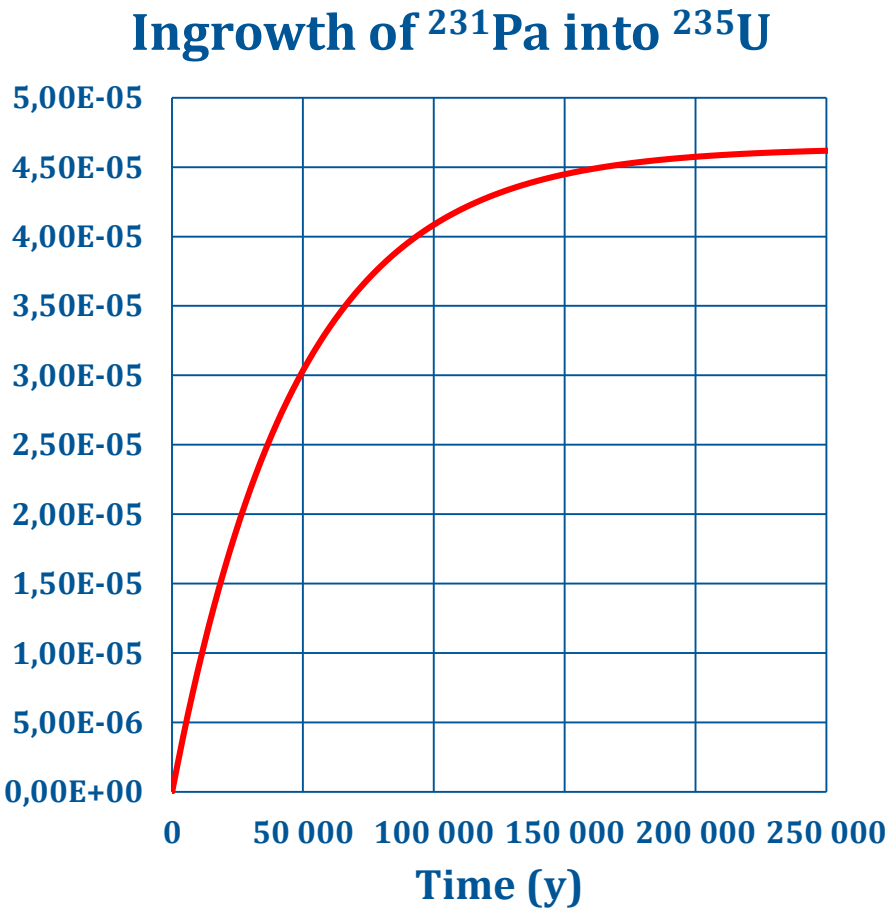
    Mass ratio ^{231}Pa:^{226}Ra: 0.961 ± 0.018 (*k=2*)
- Naturally occurring isotopes
  - Protactinium-231: $T_{½}$ = 32670 (± 260) y — 576 Bq/g U
  - Protactinium-234m: $T_{½}$ = 1.159 (± 0.011) m — 12350 Bq/g U
  - Protactinium-234: $T_{½}$ = 6.70 (± 0.5) h — 18 Bq/g U

    Branching ratio 0.15 (± 0.01)
- Neptunium (4n+1) series
  - Protactinium-233: $T_{½}$ = 26.98 (± 0.02) d

Forensics and sedimentation

- Protactinium-231
  - Long half-life means it is suitable for dating





Chemistry

- Approach is mainly limited by protactinium chemistry
- Analogous to niobium and tantalum
- Chemistry dominated by chloro- or fluoro- complexes
- Hydrolyses and precipitates easily
- Behaviour exacerbated at trace (<10-8 M) levels
- Solubilised by oxalate, citrate and tartrate
- Most knowledge from UKAEA work in 1950s and 1960s

  ~125 g (~220 GBq) recovered from uranium waste in UK nuclear programme *(finally located as mainly being at JRC Karlsruhe – former ITU)*

- Studied in hydrochloric acid

Separation

NPL National Physical Laboratory

- Needed to recover material from NPL solutions with questionable chemistry
  - Legacy material from early 1990s

    Dissolved solid source…solution is >8M HCl, contains HF traces, Fe, U, Th
  - Aims:

    Separation of protactinium in high yield
    Recovery of ^{227}Ac daughter, ^{227}Th and ^{223}Ra for data measurements
    High purity ^{231}Pa required for standardisation
  - Chemical issues

    Neither ion exchange, nor existing extraction chromatography were giving the consistent yields and purities required
    Tantalum carrier interferes with mass spectrometry work
  - Solvent extraction?

    No! Solvent extraction is not favoured…
    But long chain alcohols and ketones are effective and specific for protactinium

Cation exchange with HCl

National Physical Laboratory

- Few indications in the literature what was possible
  - Strategy: Absorb neptunium on the resin
  - Use the anionic nature of protactinium in solution to separate

Column:	AG50-X8	(1g)
Load solution:	0.2 M HCl	
Pa wash solution:	0.2 M HCl	(10 mL)

^{233}Pa washes through the resin

^{237}Np is retained

Np wash solution:	0.2 M HCl/1 M HF	(10 mL)

^{237}Np is removed

- Results
  - Protactinium-233 yield: 89%
  - Neptunium-237 yield: ~36%

Cation exchange with HNO_3

NPL National Physical Laboratory

- Few indications in the literature what was possible
  - Strategy: Absorb neptunium on the resin
  - Use the anionic nature of protactinium in solution to separate

Column:	AG50-X8	(1g)
Load solution:	1 M HNO_3	
Pa wash solution:	1 M HNO_3	(10 mL)
^{233}Pa washes through the resin		
^{237}Np is retained		
Np wash solution:	1 M HNO_3/1 M NH_4F	(10 mL)
^{237}Np is removed		

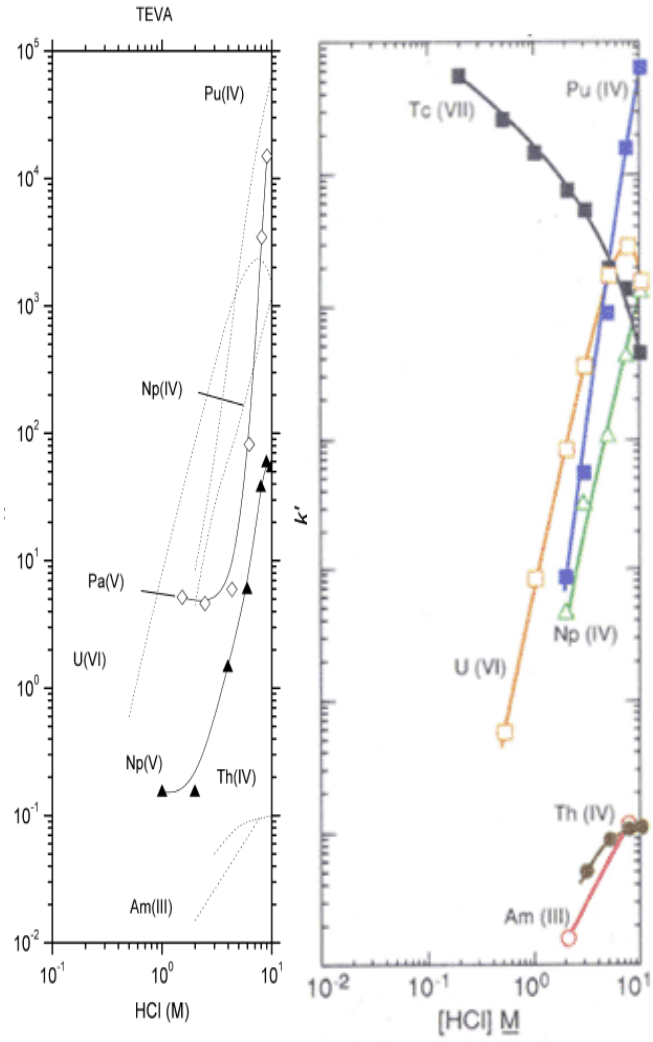
- Results
  - Protactinium-233 yield: 83%
  - Neptunium-237 yield: ~9%

TEVA with HCl

- Published data suggests that Pa is bound weakly by HCl on TEVA
  - To separate

    Column: TEVA (1g)
    Load solution: 2 M HCl
    Pa wash solution: 2 M HCl (10 mL)
    ^{233}Pa washes through the resin
    ^{237}Np is retained
    Np wash solution: 0.1 M HCl (10 mL)
    ^{237}Np is removed

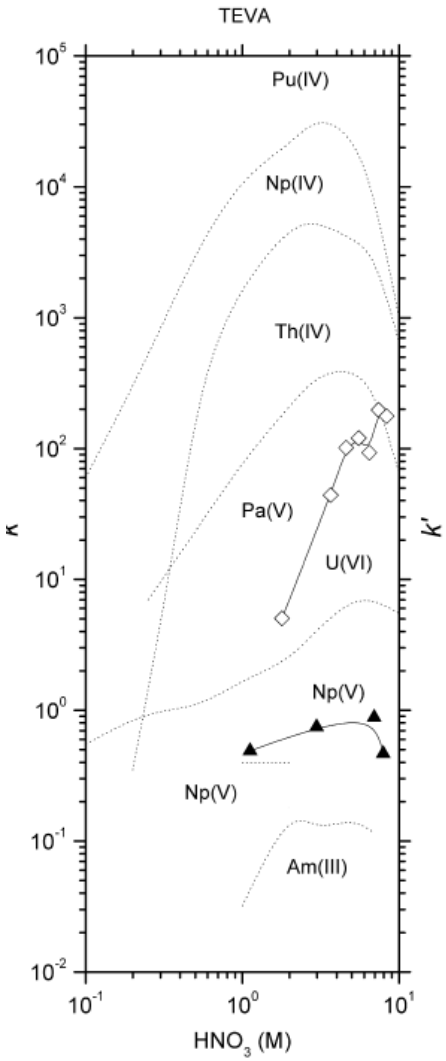
- Results
  - Protactinium-233 yield: 83%
  - Neptunium-237 yield: ~11%



TEVA with HNO_3

- Published data suggests that Pa is bound strongly by HNO_3 on TEVA
  - To separate

    Column: TEVA (1g)
    Load solution: 8 M HNO_3
    Pa wash solution: 8 M HNO_3 (10 mL)
    ^{233}Pa washes through the resin
    ^{237}Np is retained
    Np wash solution: 1 M HNO_3 (10 mL)
    ^{237}Np is removed
- Results
  - Protactinium-233 yield: ~100%
  - Neptunium-237 yield: ~30
    (in Pa fraction)

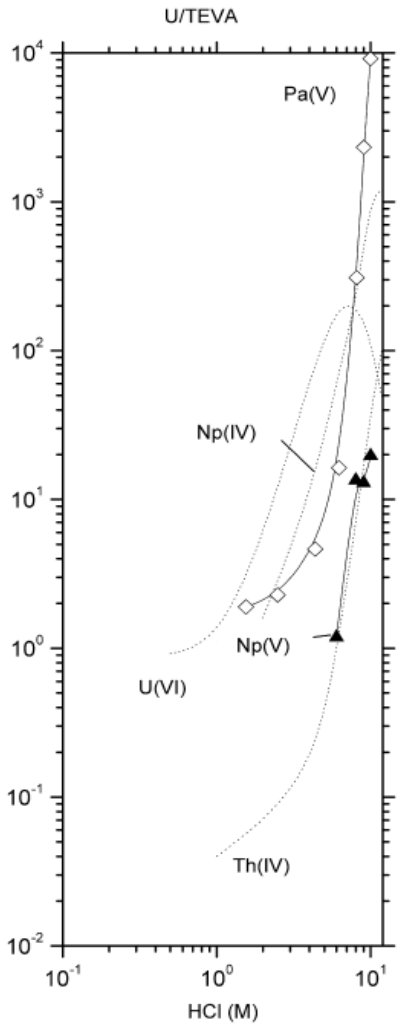


UTEVA with HCl

- Published data suggests that Pa is bound strongly by HCl on UTEVA with strong acid
  - To separate

Column:	UTEVA	(1g)
Load solution:	9 M HCl	
Th wash solution:	4.5 M HCl	(10 mL)
^{229}Th washes through the resin		
Pa wash solution:	4.5 M HCl/0.1 M HF	(10 mL)
^{233}Pa washes through the resin		
U wash solution:	0.1 M HCl	(10 mL)
^{232}U is removed		

- Results
  - Protactinium-233 yield: ~40%
  - Thorium-229 yield: ~80%
  - Uranium-232 yield: ~80%



Results

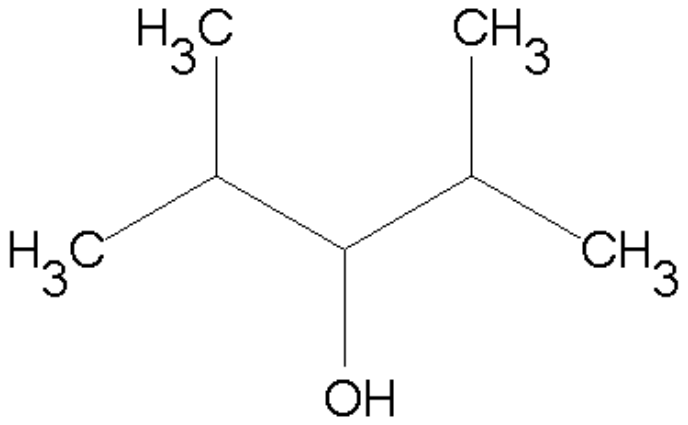
NPL National Physical Laboratory

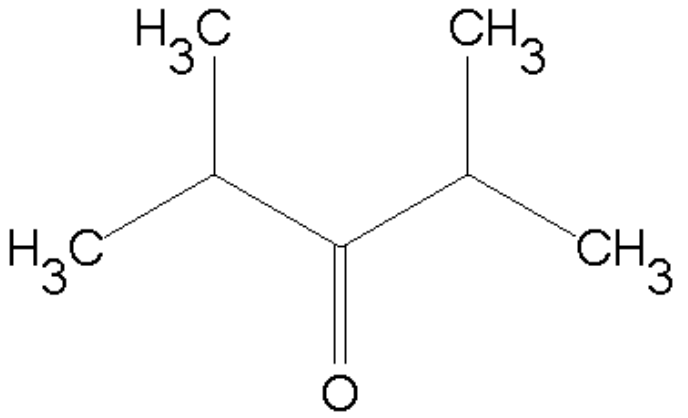
Resin	Eluant	Pa	Np	U	Th	Comments
AG50	HCl	89%	Nil	Nil	Nil	Pa in good yield, separation from Np is effective
	HNO_3	83%	Nil	n/a	n/a	Pa in good yield, separation from Np is effective
TEVA	HCl	83%	~30%	Nil	Nil	Pa in good yield, separation from Np is not very effective
	HNO_3	~100%	~30%	n/a	n/a	Pa in good yield, separation from Np is not very effective
TBP	*HCl*	*~39%*	*Nil*	*n/a*	*n/a*	*Pa in poor yield, separation from Th, U and Np is effective*
UTEVA	HCl	*40%*	Nil	Nil	Nil	Pa in poor yield, separation from Th, U and Np is effective

Alcohols and ketones

- Effective
  - Long been known that alcohols and ketones are effective in extracting protactinium
- Needs
  - Limited solubility in water
  - Good k_d for extraction for protactinium
  - Low toxicity and volatility
- Safety
  - In general, agitation of volatile solvents containing α-emitters makes people uncomfortable

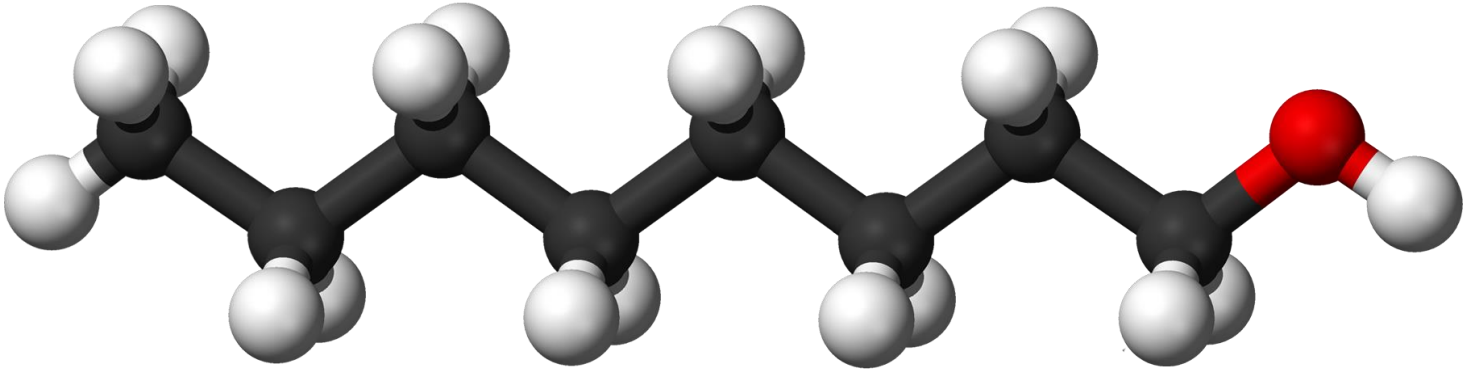
    Very uncomfortable





TrisKem TK-400 resin

- Developed by Knight, *et al*
  - Extractant is octan-1ol adsorbed onto a support
  - Octan-1-ol is selective for protactinium
  - Was used successfully for ^{233}Pa separation
  - Great! But not commercially available at that time



Knight, A.W., Nelson, A.W., Eitrheim, E.S., Forbes, T.Z. and Schultz, M.K., 2016. A chromatographic separation of neptunium and protactinium using 1-octanol impregnated onto a solid phase support. Journal of Radioanalytical and Nuclear Chemistry, 307, 59–67 **(DOI 10.1007/s10967-015-4124-3)**

Resin tests

- Worked with TrisKem
  - Developing TK-400 as a product.
  - Knight's work aimed at neptunium/protactinium separation
- Separations needed
  - Resolution of mixture into:

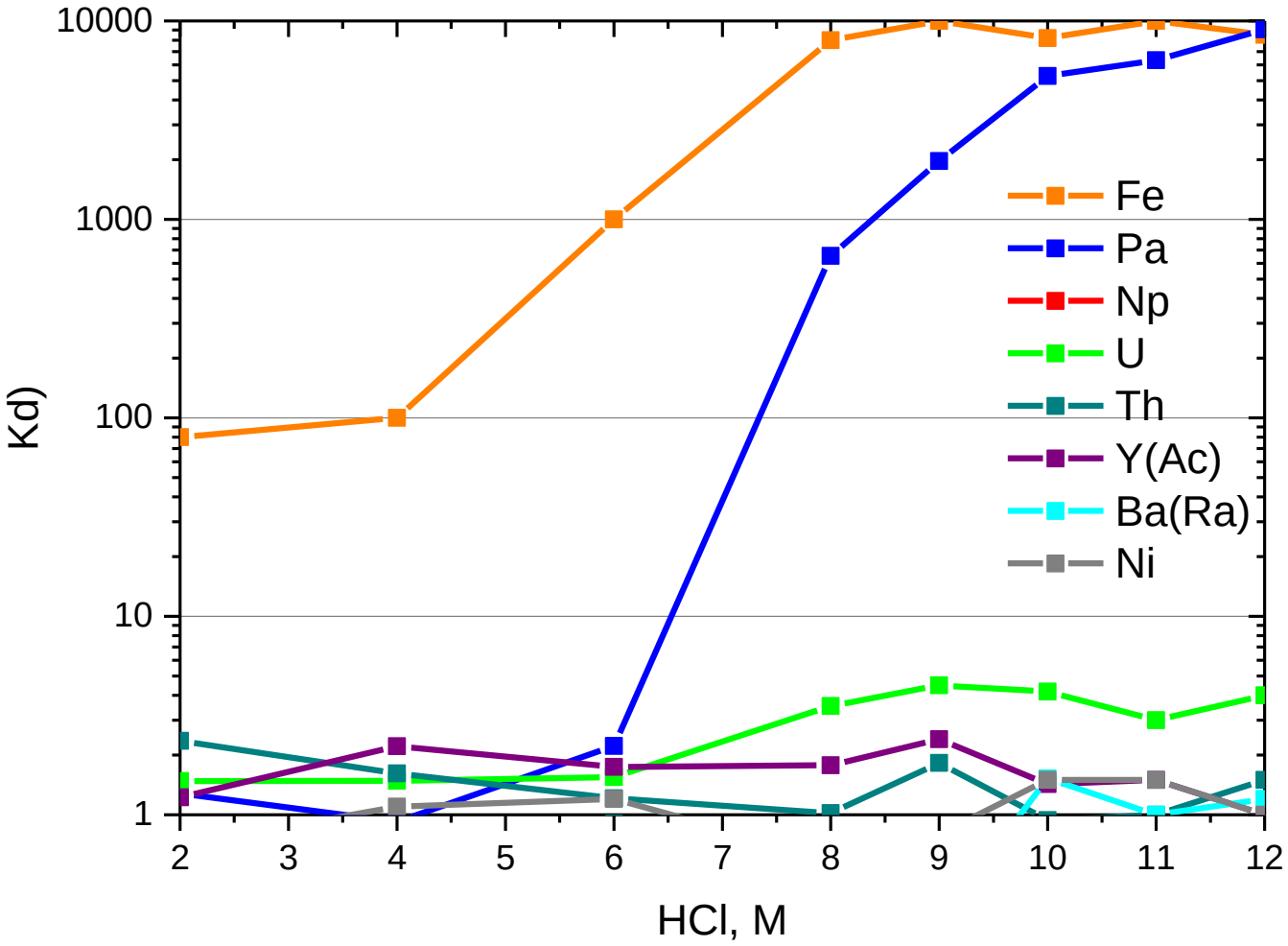
Protactinium fraction:	Standardisation and decay data
Actinium fraction:	Half-life
Thorium fraction:	Ongoing studies of ^{227}Th
Radium fraction:	Supporting work on Xofigo

  - Separation from thorium, uranium, neptunium and plutonium
- Extending scope of current knowledge
- Extractable species $[PaOCl_6]^{3-}$

Mass spectrometry

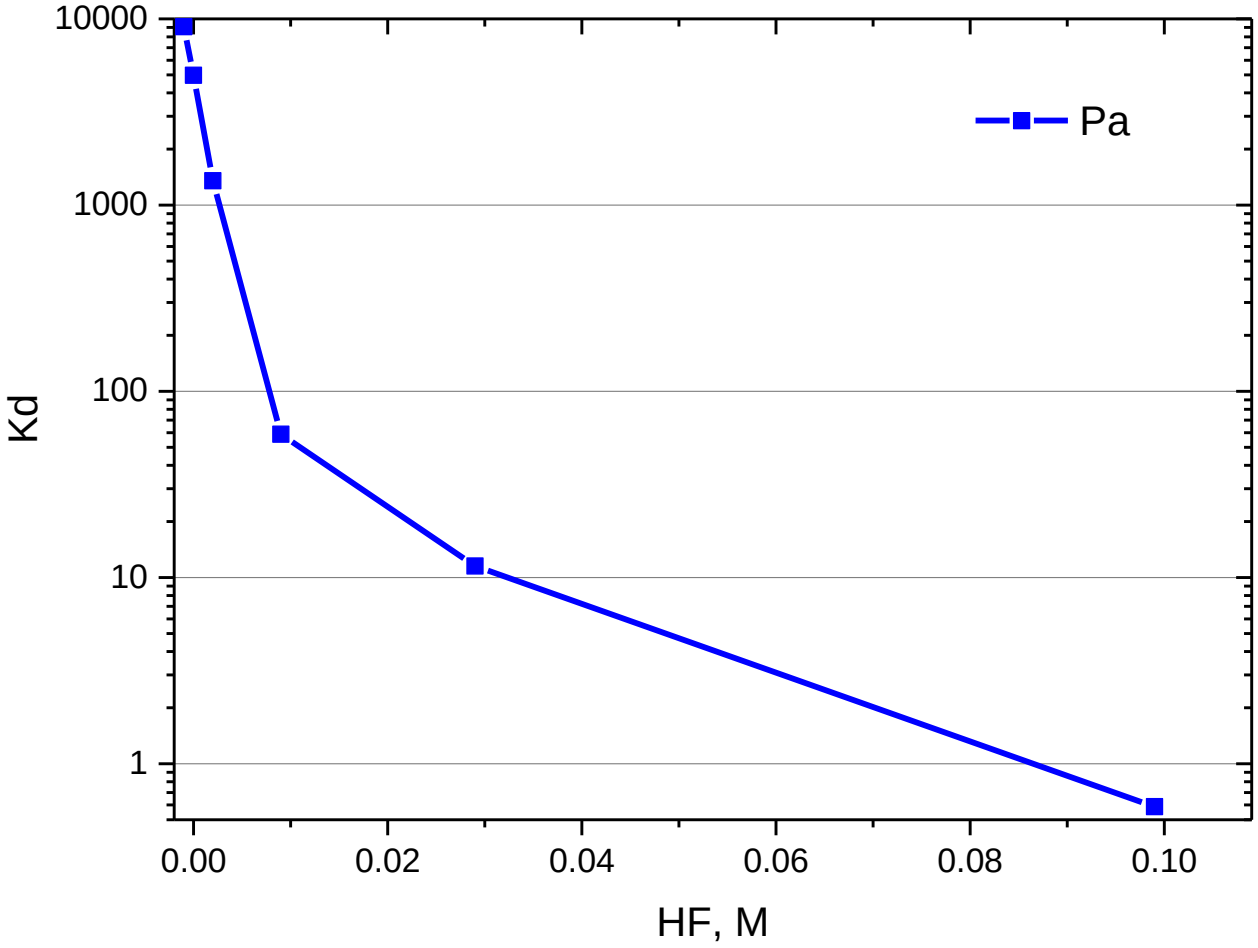
- Flexible and quick
  - Can measure Y, Ba, Th and U at the same time…
  - …and we have got one!
- Triple quadrupole ICP-MS (ICP-QQQ-MS)
  - HEPA-filtered lab under positive pressure
  - Fume cupboard
  - Deionised water unit

Results: Distribution coefficients



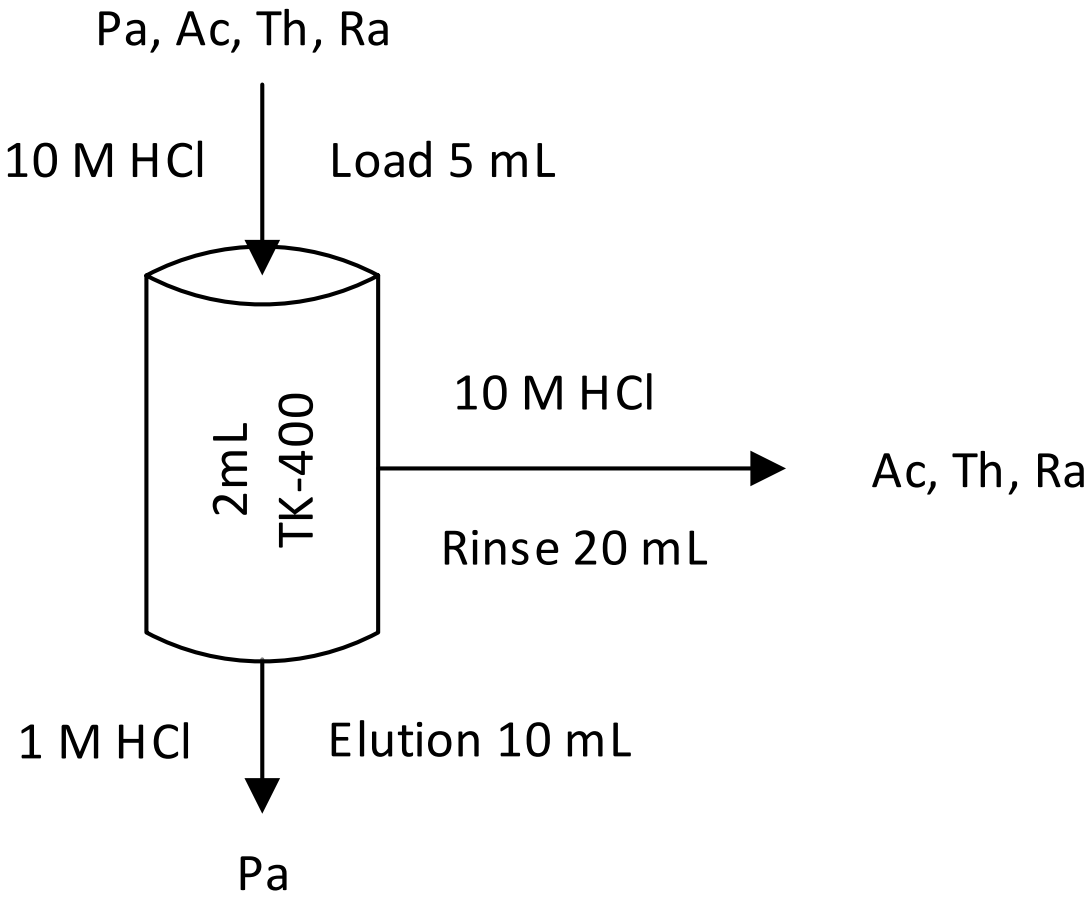
Distribution coefficients of Pa, Np, U, Th, Y(Ac), Ba(Ra), Fe and Ni on TK-400 resin as a function of HCl molarity

Results: The effect of HF



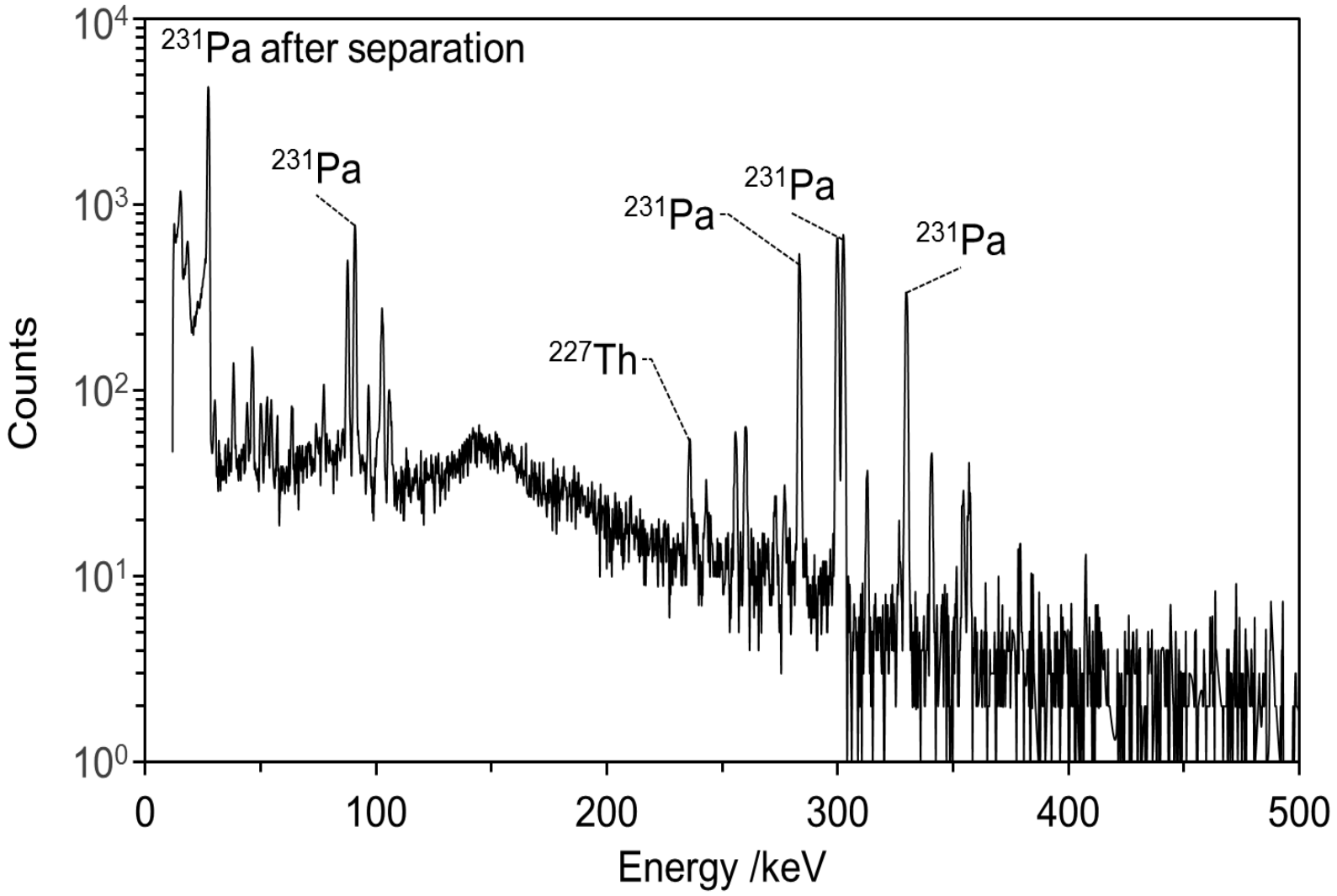
The effect of HF molarity on Pa distribution coefficient for TK-400 in 12 M HCl

Separation scheme



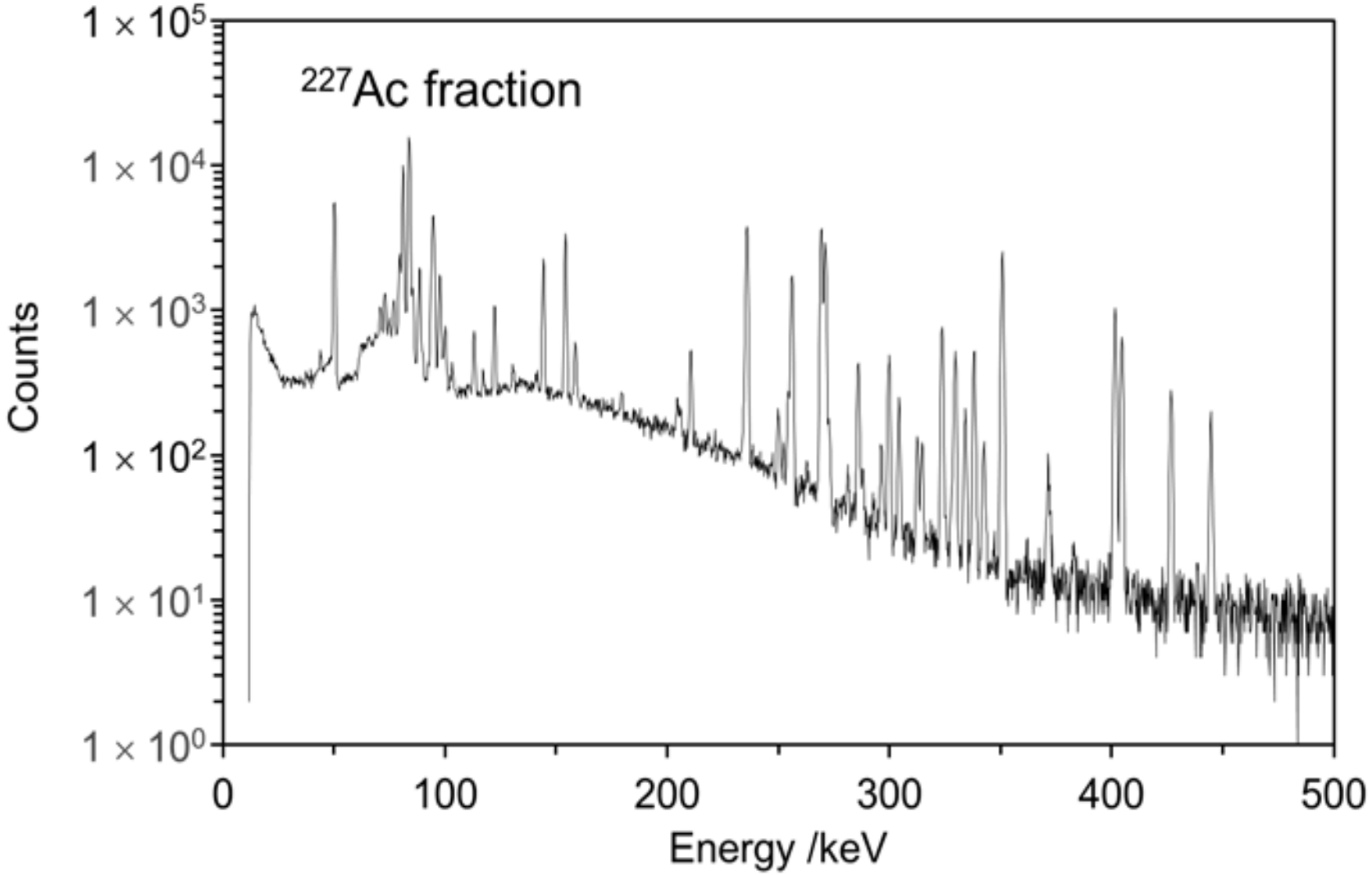
Flowchart representing separation of Pa from its progeny using TK-400

Results: Gamma-spectra



HPGe γ-ray spectrum of ^{231}Pa fraction collected after radiochemical separation using TK-400 resin

Results: Gamma-spectra



HPGe γ-ray spectrum of separated ^{227}Ac fraction

Conclusions

- The separation of protactinium is favourable on TK400
  - At >10 M hydrochloric acid, k_d ~9000
- Other elements (Ra, Ac, Th, U, Np)
  - At >10 M hydrochloric acid, k_d <5

    Remove from the column by rinsing with conc HCl
- Measurements by γ-spectrometry
  - Actinium fraction (10 M hydrochloric acid)

    Contains vast majority of ^{227}Ac, ^{227}Th and ^{223}Ra

    No evidence of ^{231}Pa
  - Protactinium fraction (removed with 6 M hydrochloric acid)

    Contains vast majority of ^{231}Pa

    No evidence of ^{227}Ac or ^{223}Ra, trace ^{227}Th consistent with the ingrowth
- Ongoing primary standardisation measurements

Acknowledgement

Chemistry team

Simon Jerome, Ben Russel

Gamma-spectrometry

Sean Collins

Primary standardisation

Arzu Arinc, John Keightley

TrisKem:

Aude Bombard, Steffen Happel

Thank you!

Department for Business, Energy & Industrial Strategy

FUNDED BY BEIS

The National Physical Laboratory is operated by NPL Management Ltd, a wholly-owned company of the Department for Business, Energy and Industrial Strategy (BEIS).