Preparation of a ^{233}Pa standard for uranium age dating measurements by MC-ICP-MS. (using TK400 resin)

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(Radiochemistry)

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(Isotope Mass Spectrometry)

TRISKEM User Forum, Cambridge
Friday 21 September 2018

Contents

- Uranium age dating ($^{230}Th/^{234}U$ and $^{231}Pa/^{235}U$
- Tracers for ^{231}Pa
- Protactinium separations (ANX/TK400)
- Standardization / measurement of ^{233}Pa

- Summary /Future work
- Questions

Uranium age dating

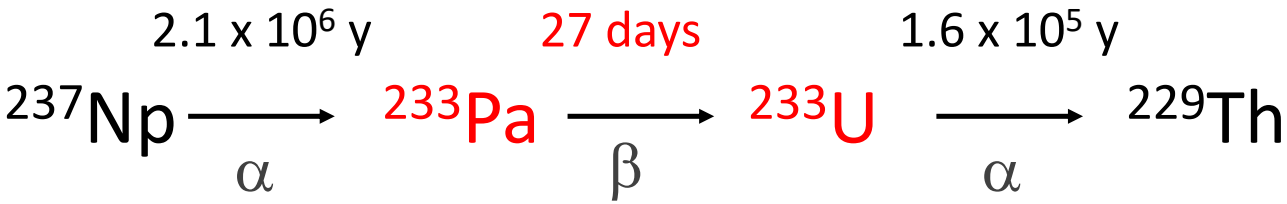
$$^{235}U \xrightarrow{7.0 \times 10^8\ y} {}^{231}Th \xrightarrow{1.06\ d} {}^{231}Pa \xrightarrow{3.3 \times 10^4\ y} {}^{227}Ac$$

$$^{238}U \xrightarrow{4.4 \times 10^9\ y} {}^{234}U \xrightarrow{2.5 \times 10^5\ y} {}^{230}Th \xrightarrow{7.5 \times 10^4\ y} {}^{226}Ra$$

232U 68.9 Y α: 100.00% 24Ne: 9E-10%	233U 1.592E+5 Y α: 100.00% 24Ne: 9E-10%	234U 2.455E+5 Y 0.0054% α: 100.00% SF: 1.6E-9%	235U 7.04E+8 Y 0.7204% α: 100.00% SF: 7.0E-9%	236U 2.342E7 Y α: 100.00% SF: 9.4E-8%	237U 6.75 D β-: 100.00%	238U 4.468E9 Y 99.2742% α: 100.00% SF: 5.4E-5%
231Pa 3.276E+4 Y α: 100.00% SF < 3E-10%	232Pa 1.32 D β-: 100.00% ε	233Pa 26.975 D β-: 100.00%	234Pa 6.70 H β-: 100.00%	235Pa 24.4 M β-: 100.00%	236Pa 9.1 M β-: 100.00%	237Pa 8.7 M β-: 100.00%
230Th 7.54E+4 Y α: 100.00% 24Ne: 6E-11 0%	231Th 25.52 H β-: 100.00% α= 4E-11%	232Th 1.40E+10 Y 100% α: 100.00% SF: 1.1E-9%	233Th 21.83 M β-: 100.00%	234Th 24.10 D β-: 100.00%	235Th 7.1 M β-: 100.00%	236Th 37.3 M β-: 100.00%

^{233}Pa Radiochemical Tracer:

- ^{233}Pa next longest lived protactinium isotope after ^{231}Pa



- Separate and standardise ‘in-house’
- Protactinium hydrolyses & adsorbs to glass

- Rapid separation from of ^{237}Np required
  (40kBq 1.5mg ^{237}Np contains 40kBq 52pg ^{233}Pa)

Atom ratio 3 x 10^7 ^{237}Np:^{233}Pa

Separation of $^{237}Np/^{233}Pa$

- Glass wool X
- Silica gel X
- Solvent extract X

- Anion Exchange (HCl:HF or HBr)
- Extraction chromatography
  -TK400 Octanol

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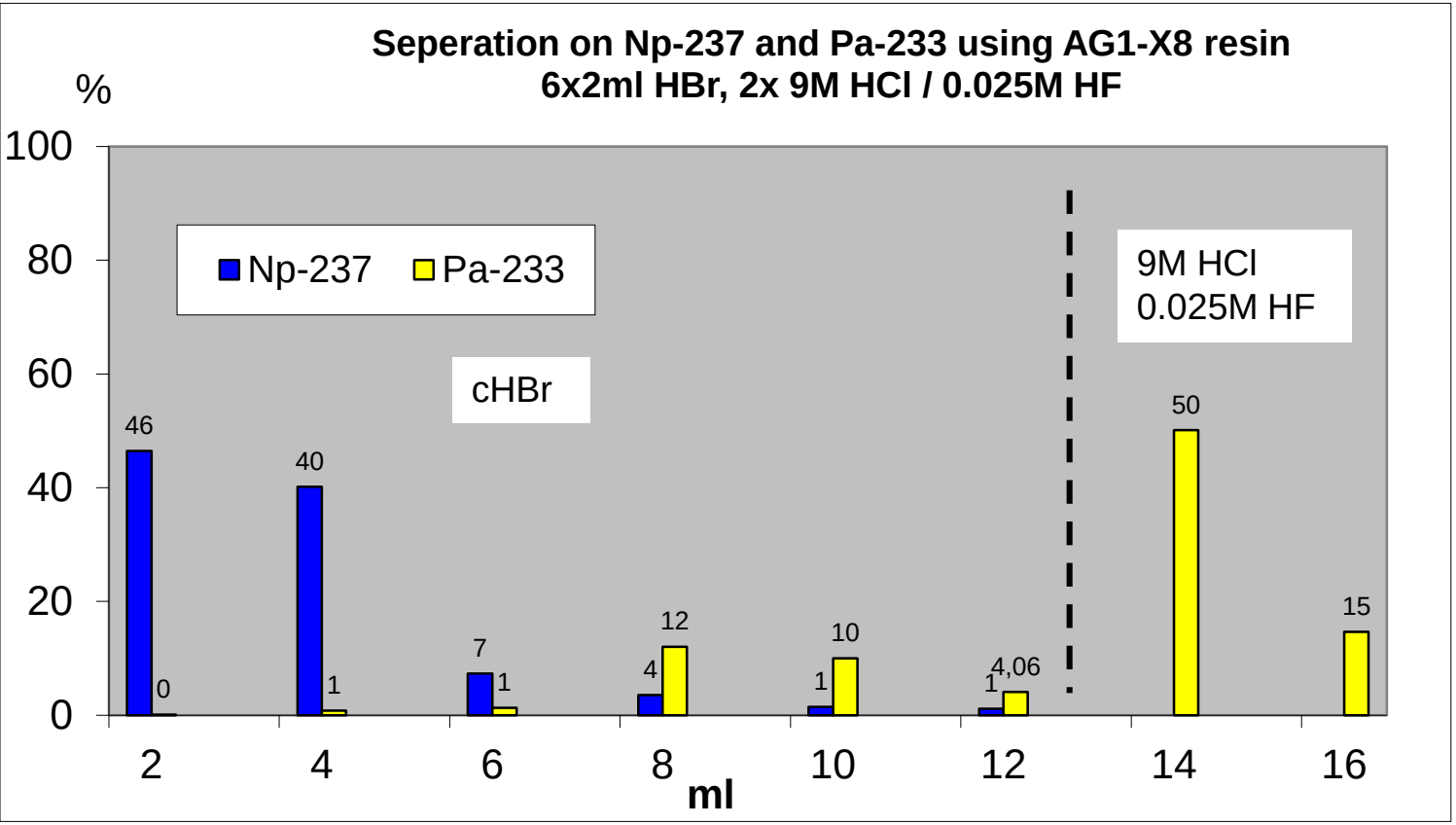
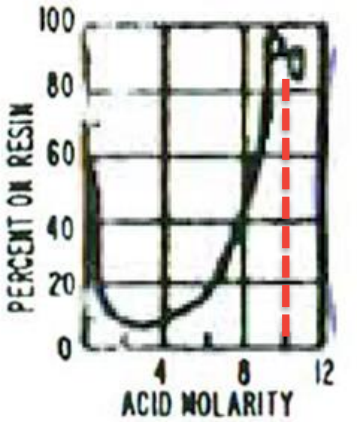
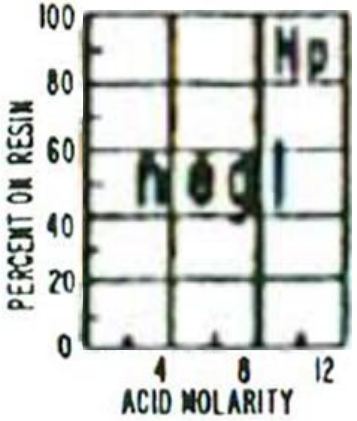
Separation of ^{233}Pa from ^{237}Np

- Anion Exchange –HBr







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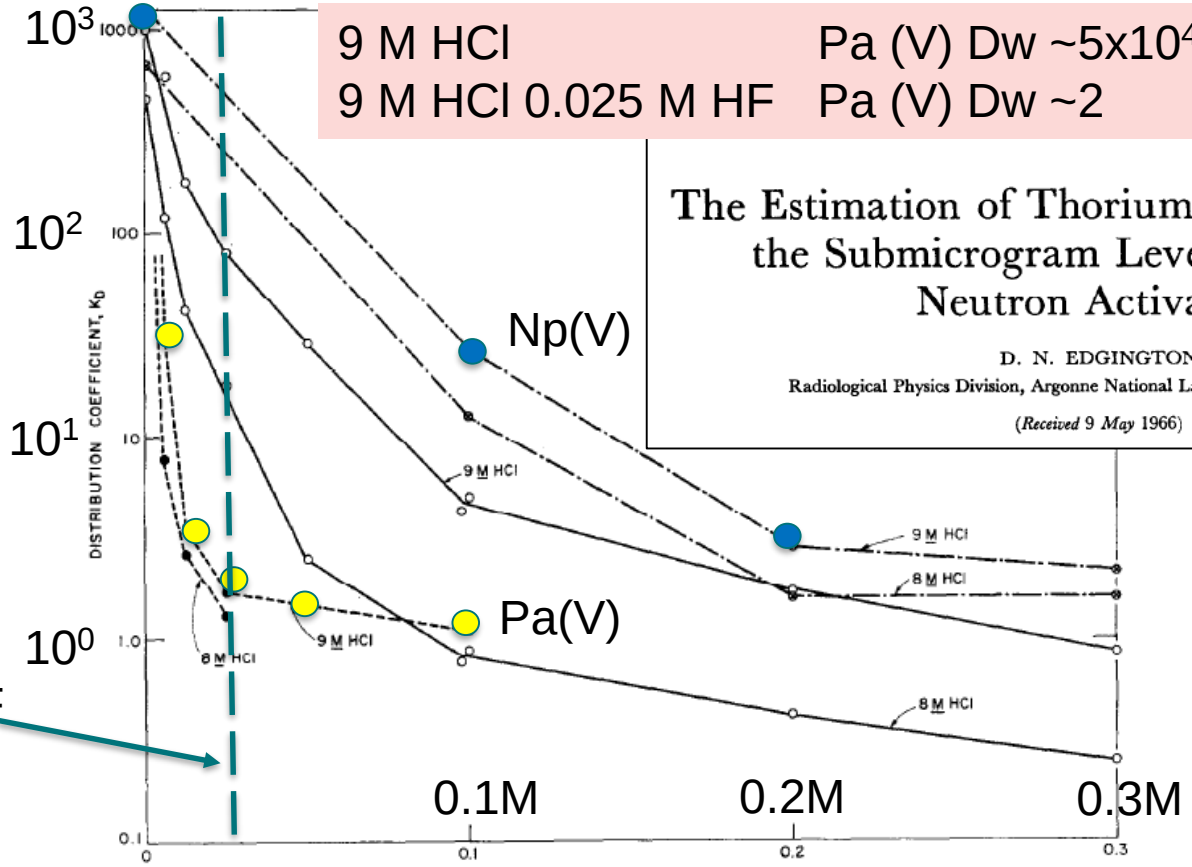
Separation of ^{233}Pa from ^{237}Np

- Anion Exchange. HCl:HF mixes

9 M HCl	Pa (V) Dw ~$5x10^4$	Np(V) Dw ~10^3
9 M HCl 0.025 M HF	Pa (V) Dw ~2	Np(V) Dw ~100



The Estimation of Thorium and Uranium at the Submicrogram Level in Bone by Neutron Activation*

D. N. EDGINGTON
Radiological Physics Division, Argonne National Laboratory, Argonne, Illinois

(*Received* 9 *May* 1966)

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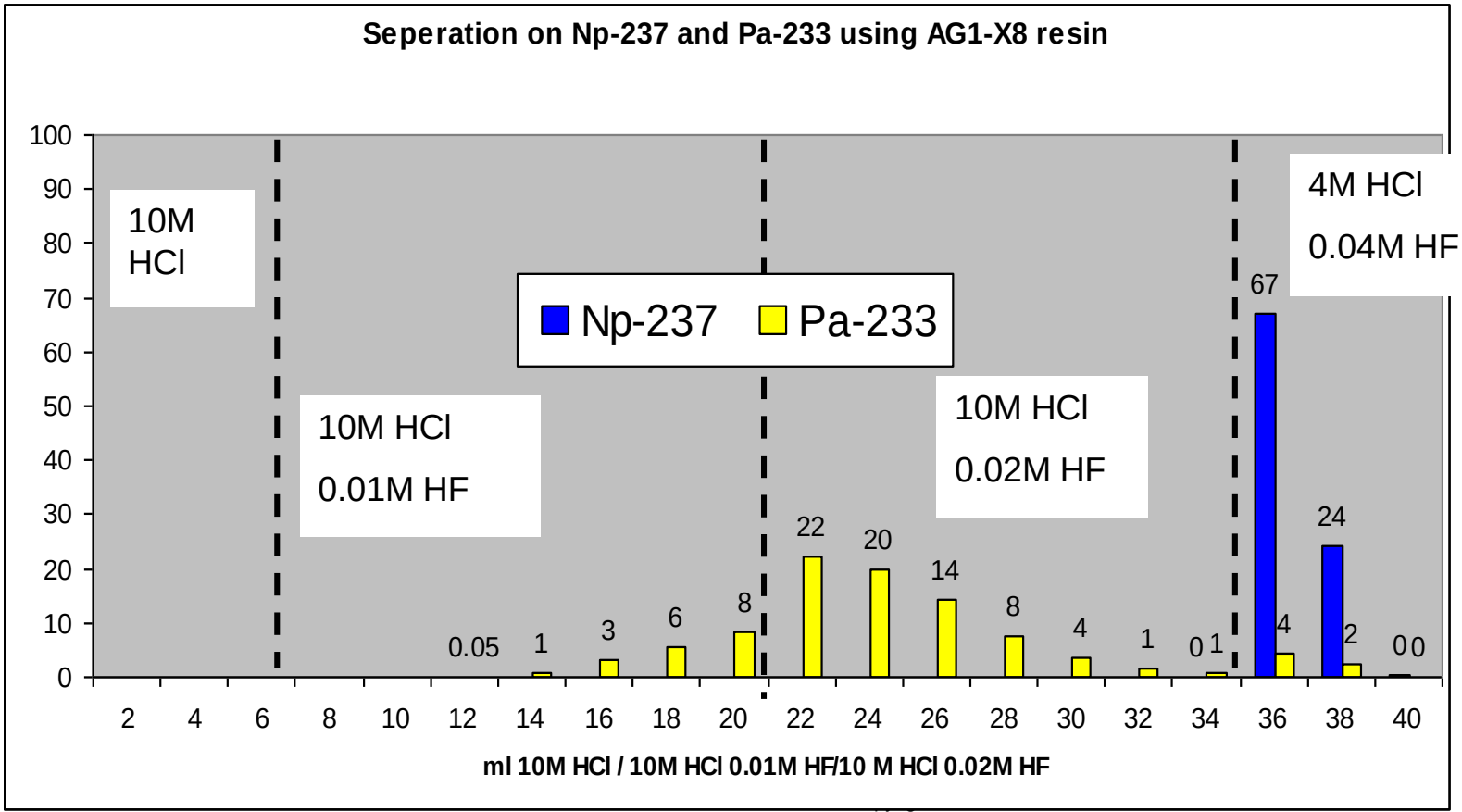
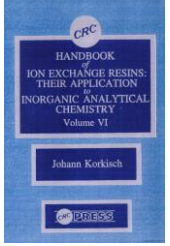
Separation of ^{233}Pa from ^{237}Np

- Anion Exchange. HCl:HF mixes



Separation of ^{233}Pa from ^{237}Np

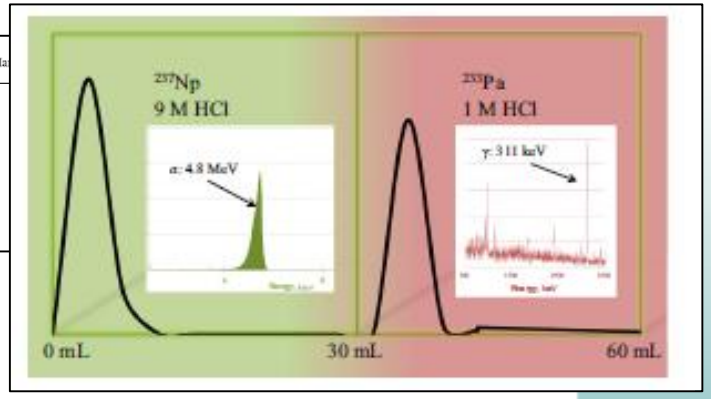


- 6-9M HCl $PaCl_6^-$, 9-12M HCl $PaCl_7^{2-}$ $[Pa(OH)_2Cl_4]^-$
- Protactinium adsorbs to TK400 (Octanol) resin in HCl (A. Knight 2016)
  -Protactinium eluted with dilute HCl

J Radioanal Nucl Chem (2016) 307:59–67
DOI 10.1007/s10967-015-4124-3

A chromatographic separation of neptunium and protactinium using 1-octanol impregnated onto a solid phase support

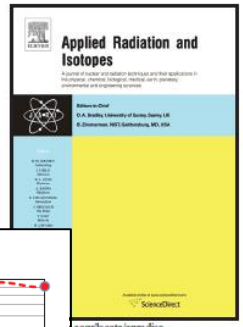
Andrew W. Knight[1] · Andrew W. Nelson[2] · Eric S. Eitrheim[1] · Tori Z. Forbes[1] · Michael K. Schultz[2,3]



Author's Accepted Manuscript

Isolation and Purification of Protactinium-231

S.M. Jerome, S.M. Collins, S. Happel, P. Ivanov, B.C. Russell



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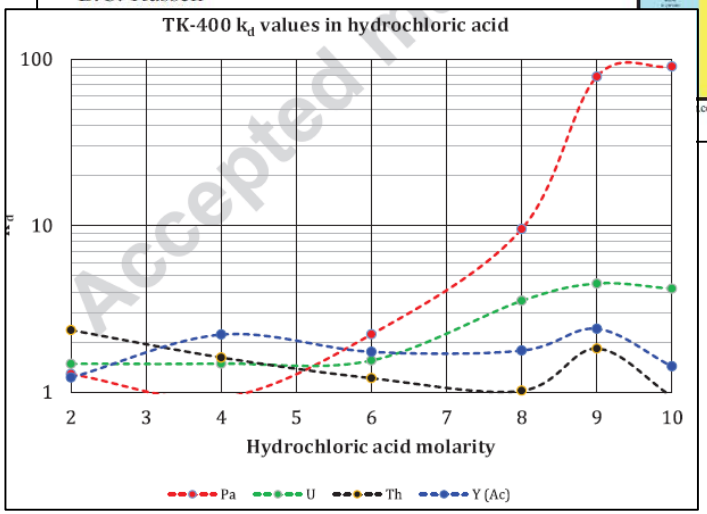

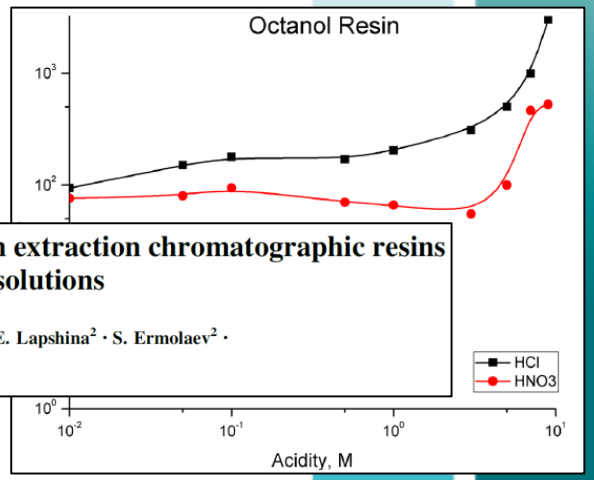

Sorption of protactinium(V) on extraction chromatographic resins from nitric and hydrochloric solutions

V. Ostapenko[1,2] · I. Sinenko[1] · E. Arefyeva[1] · E. Lapshina[2] · S. Ermolaev[2] · B. Zhuikov[2] · S. Kalmykov[1,3]

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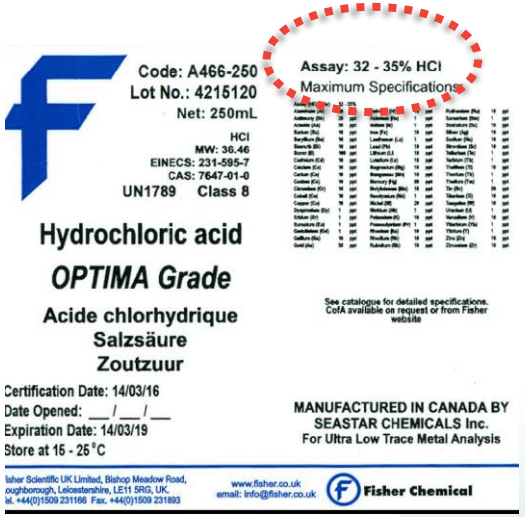
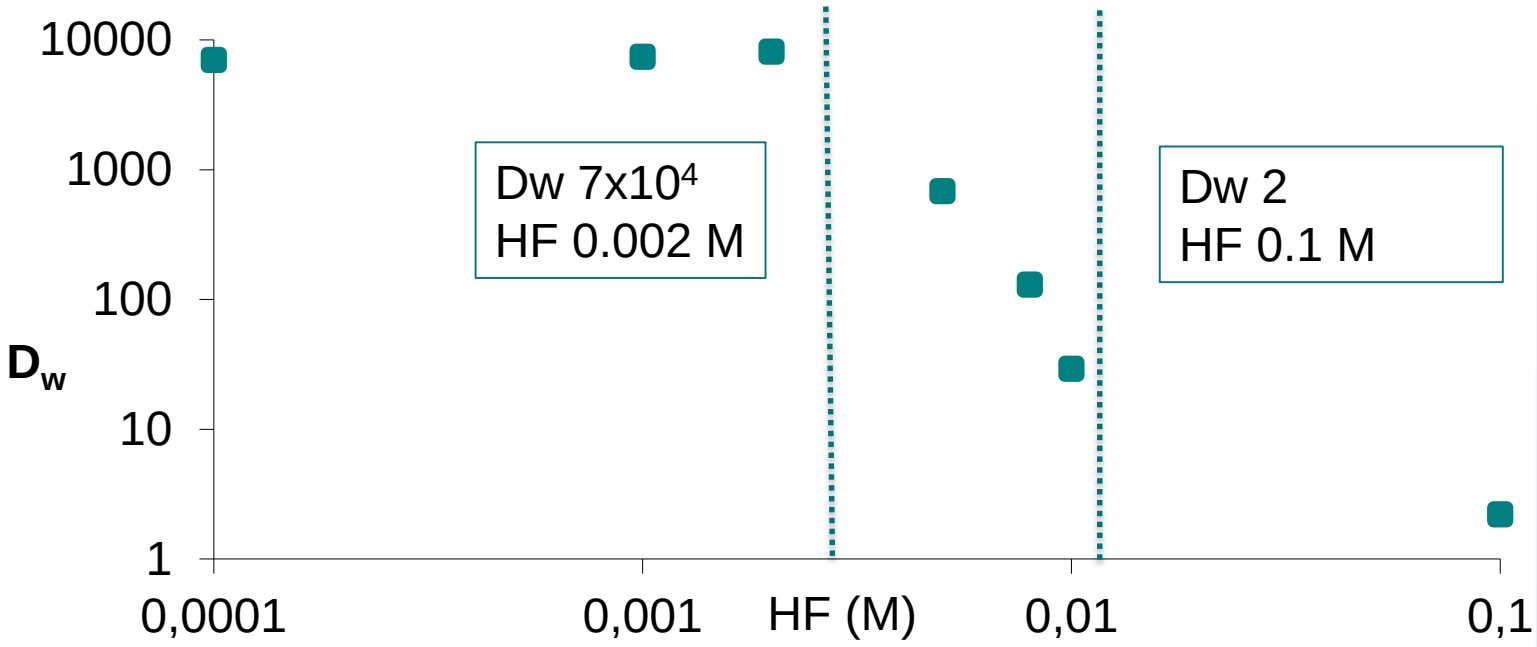
Protactinium & Thorium Separation from Uranium
Extraction chromatography –TK400

- Extraction chromatography TK400 -hydrochloric acid



Dw	10.5M HCl	10.5M HCl 0.001M HF	10.5M HCl 0.01M HF	10.5M HCl 0.1M HF
Pa(V)	$7x10^3$	$7x10^3$	30	2

Adsorption of Pa(V) on TK400 from 10.5M HCl decrease with hydrofluoric acid concentration



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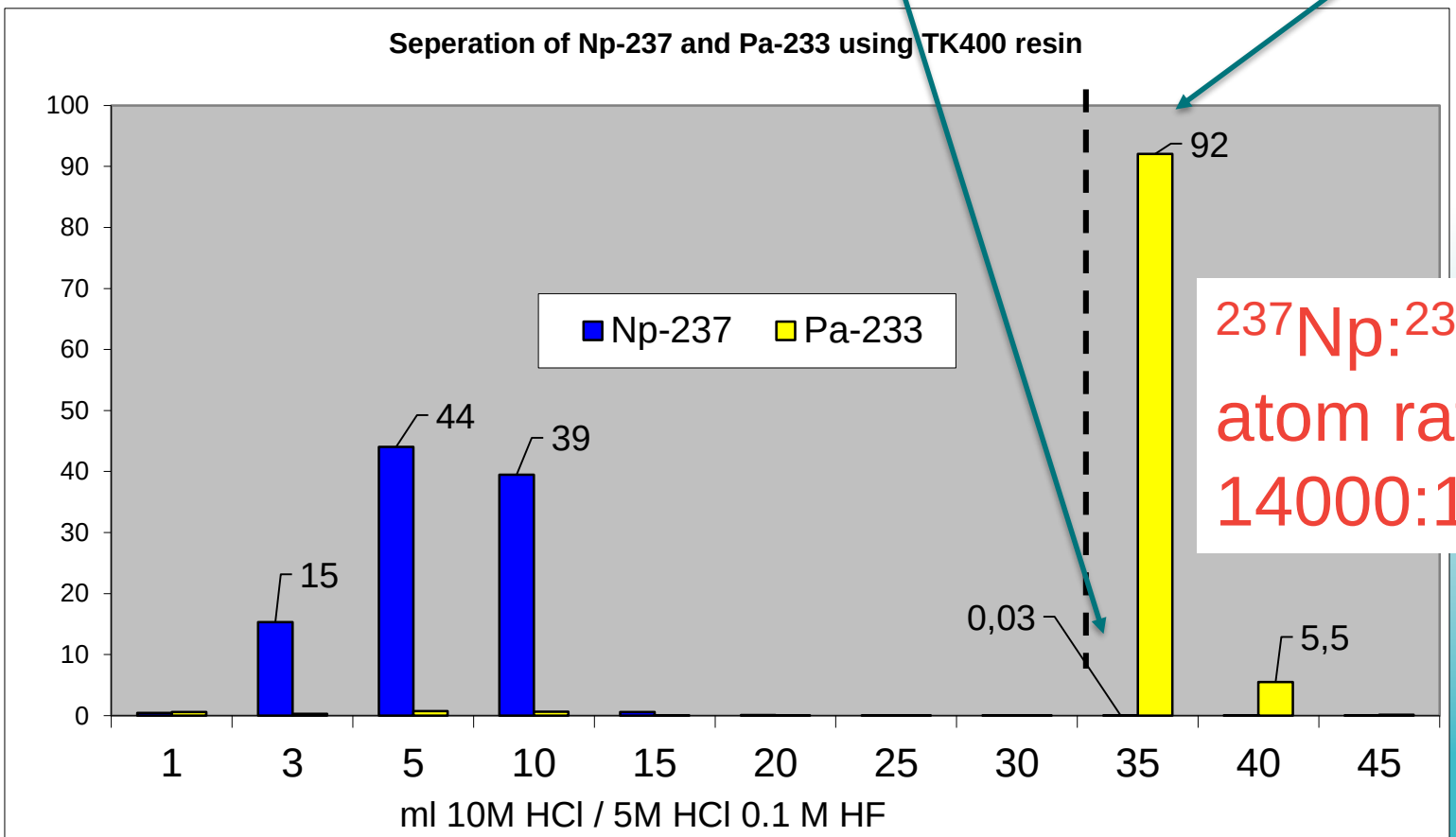
Separation of ^{233}Pa from ^{237}Np

- Neptunium adsorbed??? (VI > IV > V in solvent extraction)

0.03% ^{237}Np ~70 ppb 1Bq/g

92% ^{233}Pa ~5ppt 4 kBq/g



^{237}Np:^{233}Pa atom ratio 14000:1

ThermoNeptune *Plus* multi-collector-ICPMS

- Nuclear package
- Reserved for ultra-trace work
- Multi-collection vs peak-jumping

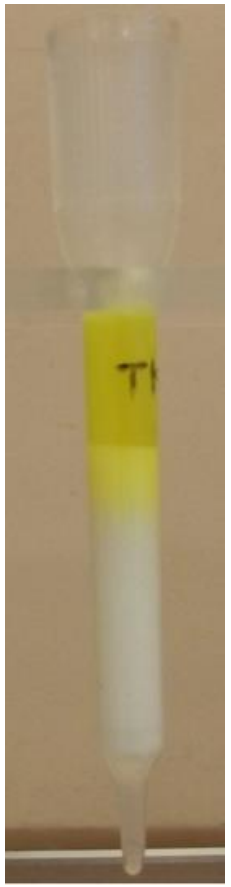
	Off-axis array of ion counters						Detectors on "typical" focal plane						
Detector	IC4	IC3B	IC2	IC1B	L4	IC5	L3	L2	L1	C/IC1C	H1	H2	H3
Detector type	CDD	SEM	SEM	SEM	FAR	CDD	FAR	FAR	FAR	FAR/SEM	FAR	FAR	FAR
RPQ	×	✓	×	✓	×	×	×	×	×	✓	×	×	×

Improve ^{237}Np: ^{233}Pa: Separation

- Separation factor ~3x10^3
  (3x10^7 to get 1:1 ^{237}Np:^{233}Pa atoms)

- Dw values of Np (IV, V, VI) on TK400 resin

Reagent	Dw	Np?
Fe^{2+}	4	IV
H_2O_2	5	V,VI
HCl	8	IV, V,VI
Asorbic Acid	10	IV
Nitrite	11	V



- Decrease resin volume?
- Increase wash volume?
- Repeat the separation? Careful drying down Pa!
- Np(VI)? Using BrO_3^-

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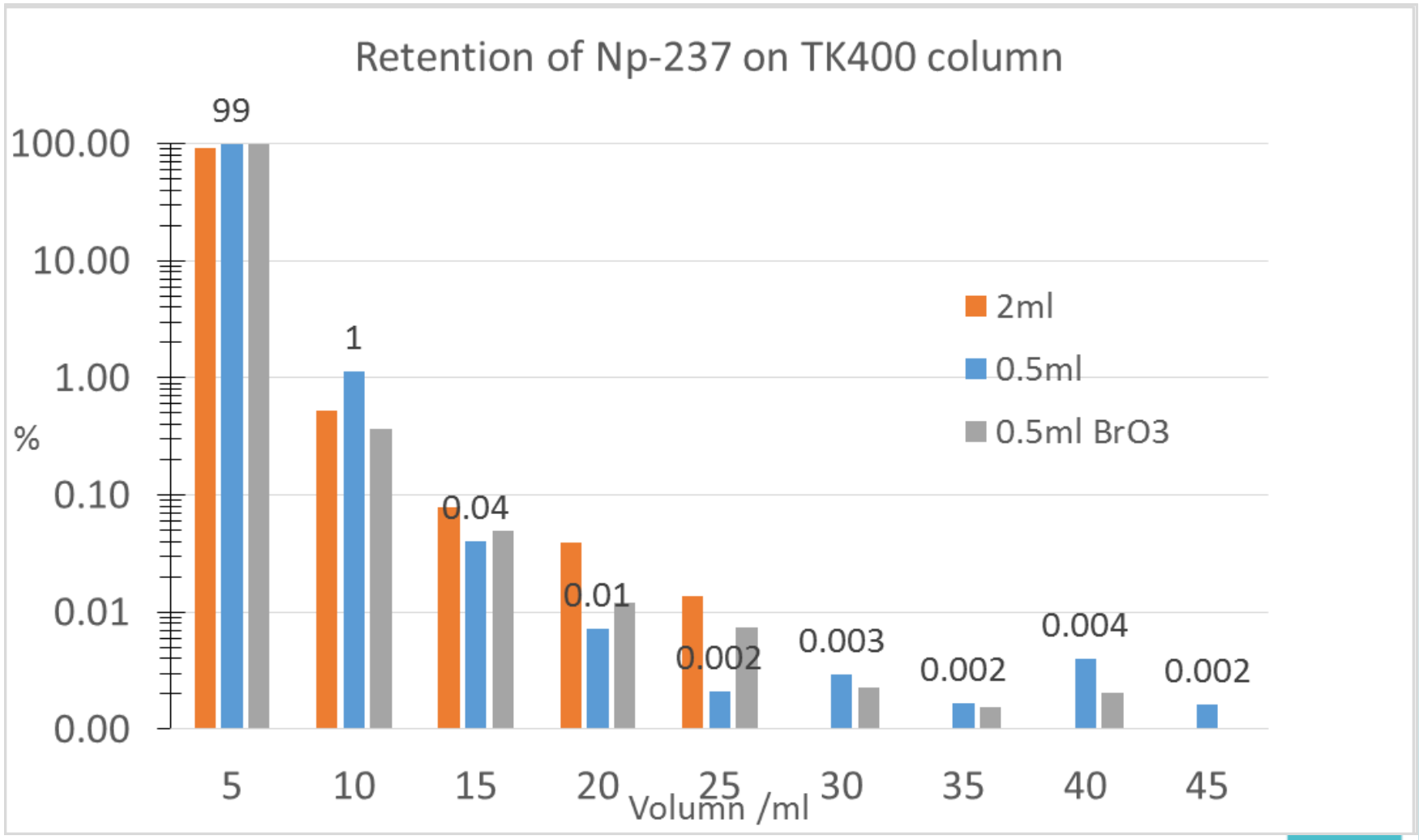
Improve ^{237}Np: ^{233}Pa: Separation



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Standardization of ^{233}Pa

- ^{233}Pa (87 keV + 311 keV gamma)
- ^{237}Np (88 keV + 143 keV gamma)
  -Measure ^{237}Np with ICP-Q-MS

- ICP-MC-MS ^{231}Pa:^{233}Pa
  –requires ^{231}Pa standard
  ^{233}U isobaric inference with ^{233}Pa

- Standardise ^{233}Pa using Ciemat NIST (98%-99% counting efficiency)

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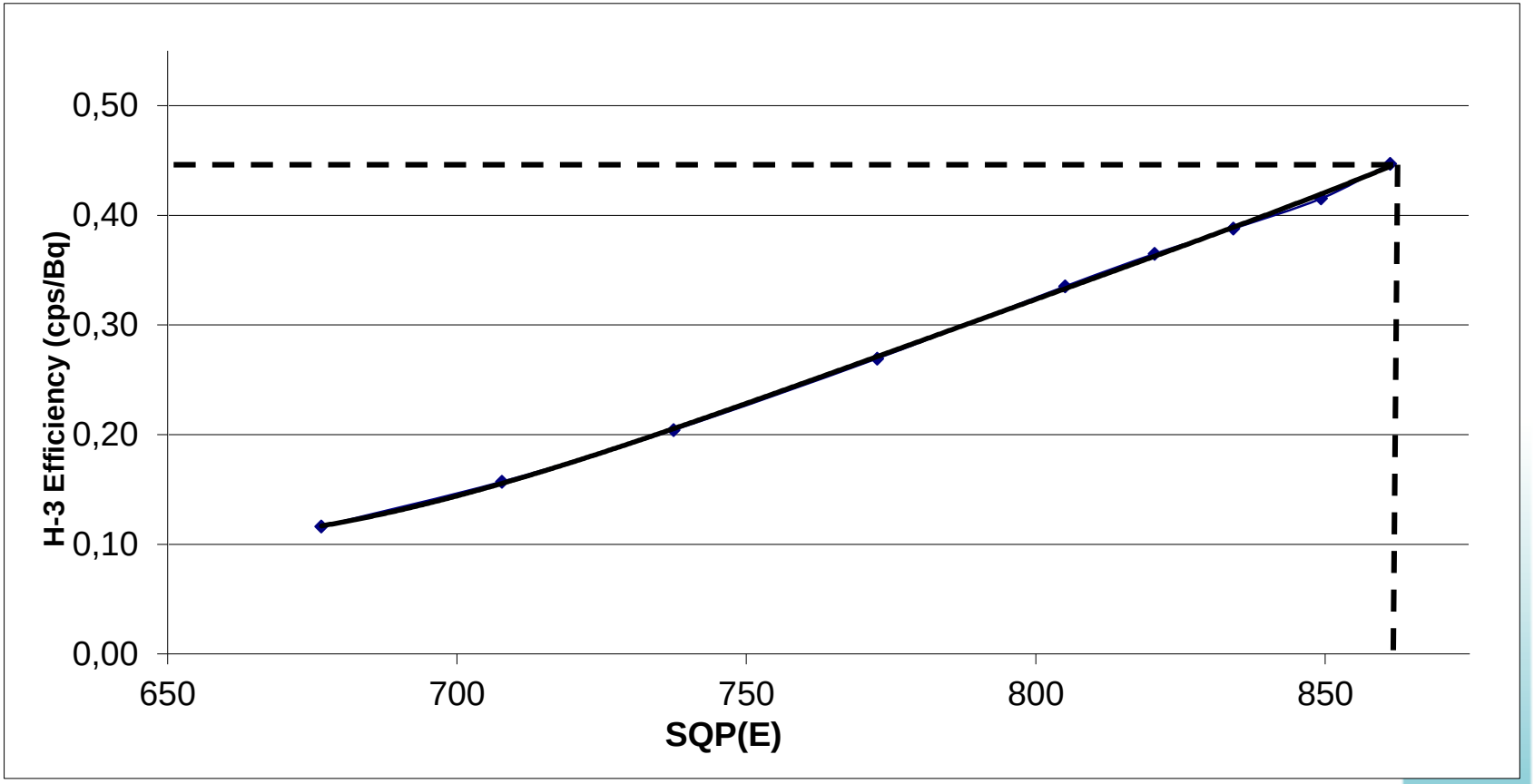
Standardise ^{233}Pa using Ciemat NIST

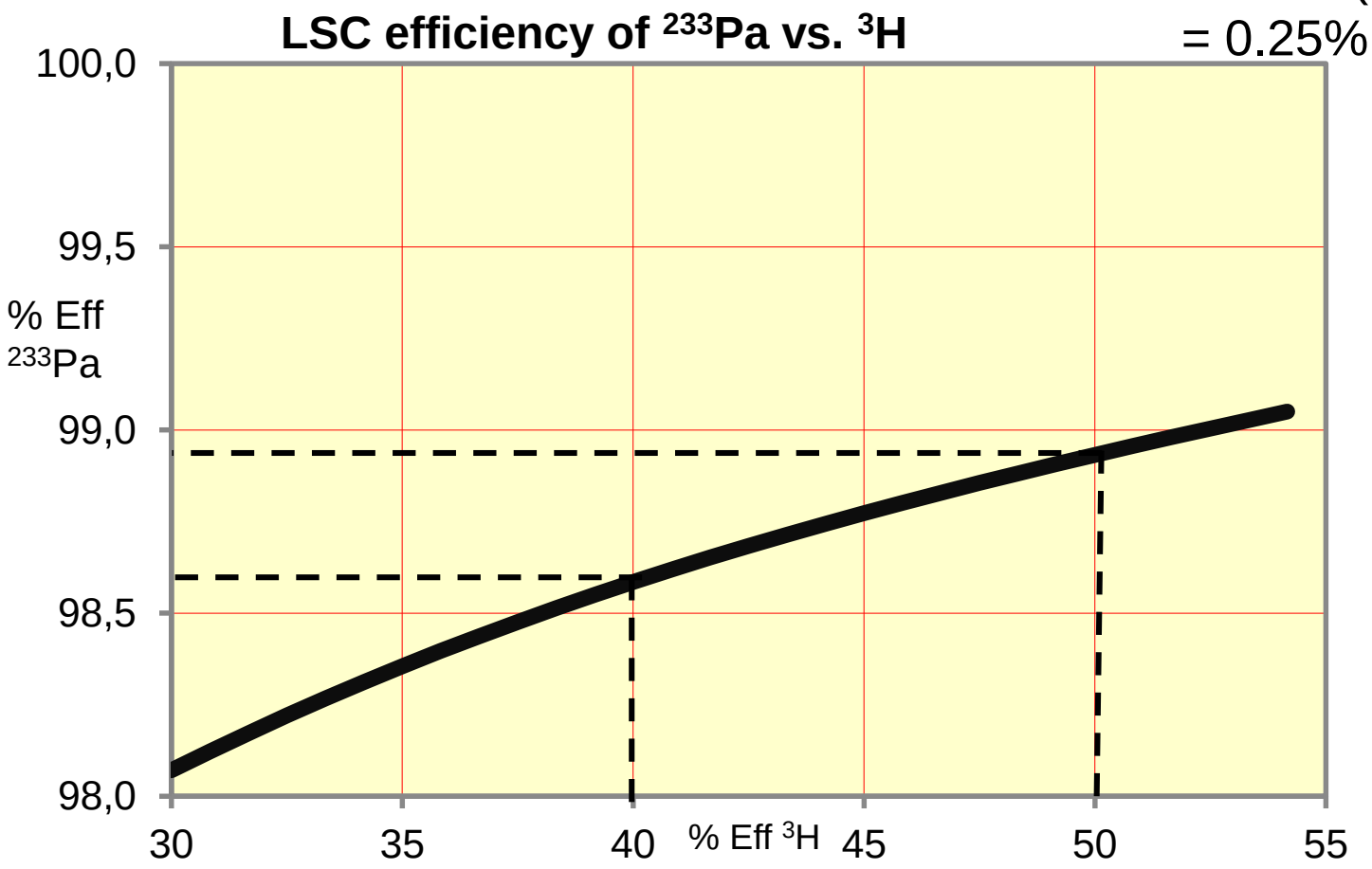


^{3}H=45% for SQP(E) 860

Standardise ^{233}Pa using Ciemat NIST

^{3}H=45(5)% ^{231}Pa=98.6

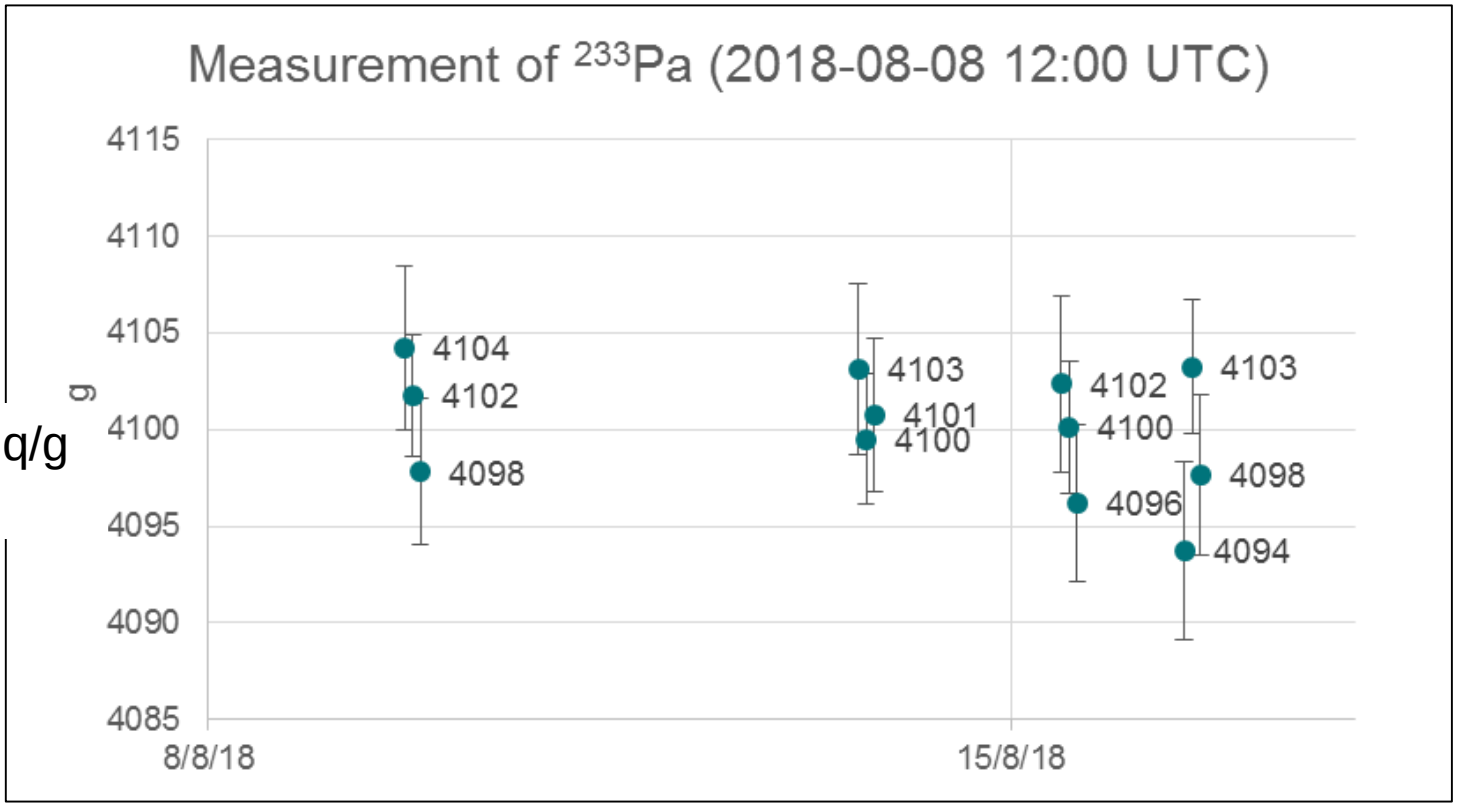
^{233}Pa = 98.75(25)
= 0.25% U



Standardise ^{233}Pa using Ciemat NIST

^{233}Pa 4.07(2) kBq/g	^{237}Np 0.3 Bq/g	Ratio $1:7x10^{-5}$

^{233}Pa 5ppt	^{237}Np 10ppb	Ratio $1:2x10^{3}$

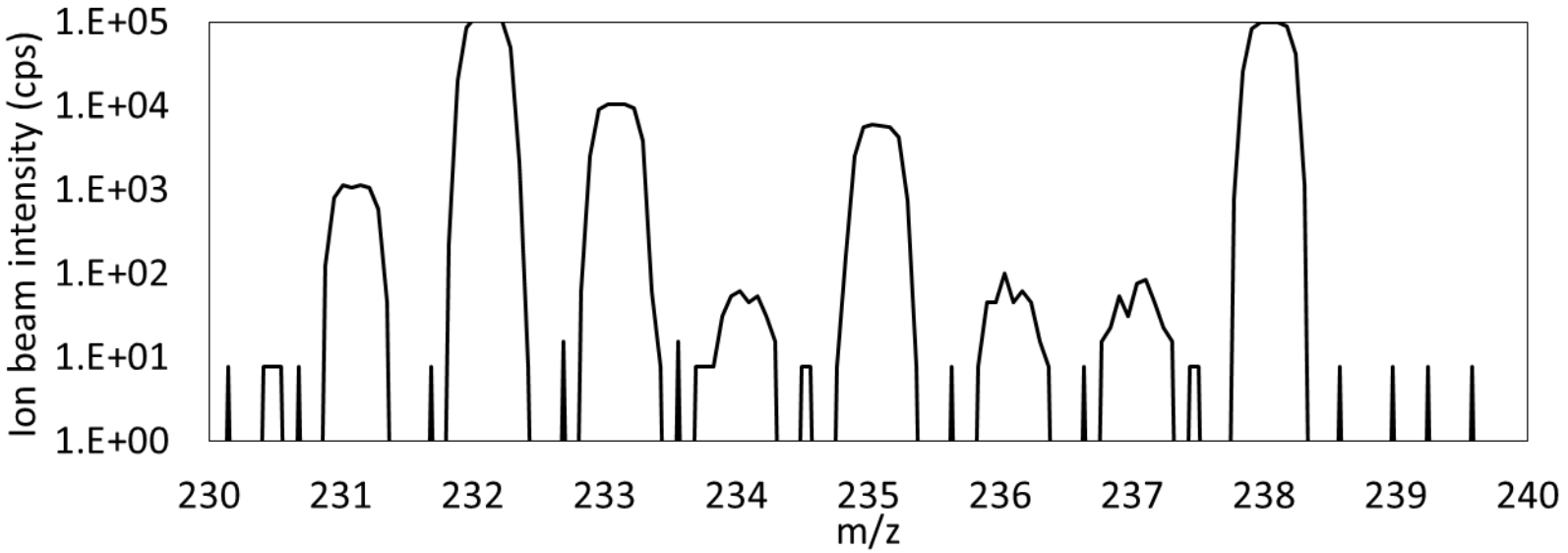


Standardise ^{233}Pa using ^{231}Pa

ICP-MC-MS ^{231}Pa:^{233}Pa

- –requires ^{231}Pa standard
- – ^{233}U isobaric inference with ^{233}Pa
- – ^{233}Pa/^{237}Np separation >3x10^{7}
- – 3 x TK400 column

^{231}Pa	0.02 ppt	^{233}Pa	0.2ppt
^{237}Np	0.002ppt (0.5μBq/g)	^{238}U	2ppt (10μBq/g)



Summary

- ^{233}Pa prepared from ^{237}Np; tracer to measure ^{231}Pa (U age dating)
- 1x TK400 column for ^{233}Pa standardisation via LSC (<0.5%)
- 3x TK400 columns for standardisation of ^{233}Pa by MC-ICP-MS
- Future work to obtain ^{231}Pa standard

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Thanks to

Steffen Happel	Triskem
Peter Ivanov & Andy Pearce	NPL

Questions?

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