Revisiting Protactinium Chemistry for a Range of New Measurements

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30th October 2015

Scope

- Background
- Uses and reasons to do the work
- Standardisation work
- Column separations
- Summary and conclusions

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Protactinium

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- 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

Protactinium

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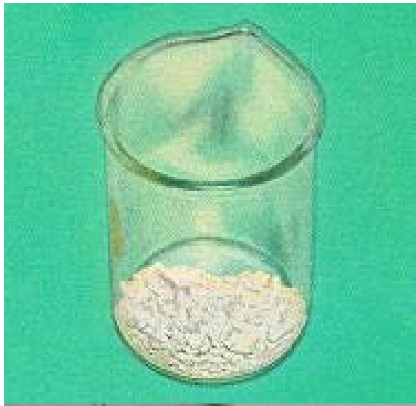
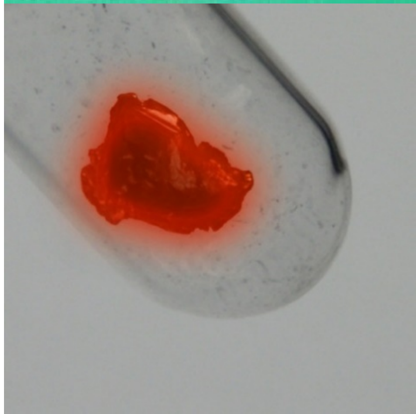
- Has a complicated chemistry
  - Analogous to niobium and tantalum
  - Chemistry dominated by chloro- or fluoro- complexes
  - Hydrolyses and precipitates easily
  - Behaviour exacerbated at trace ($<10^{-8}$ M) levels
  - Solubilised by oxalate, citrate and tartrate

    Also exhibits 4+ oxidation state
  - Most knowledge from UKAEA work in 1950s and 1960s

    ~125 g (~220 GBq) recovered from uranium waste in UK nuclear programme
  - Was considered as a fuel for nuclear weapons

    Fast neutron cross section supposedly similar to ^{239}Pu at neutron energies >1 MeV





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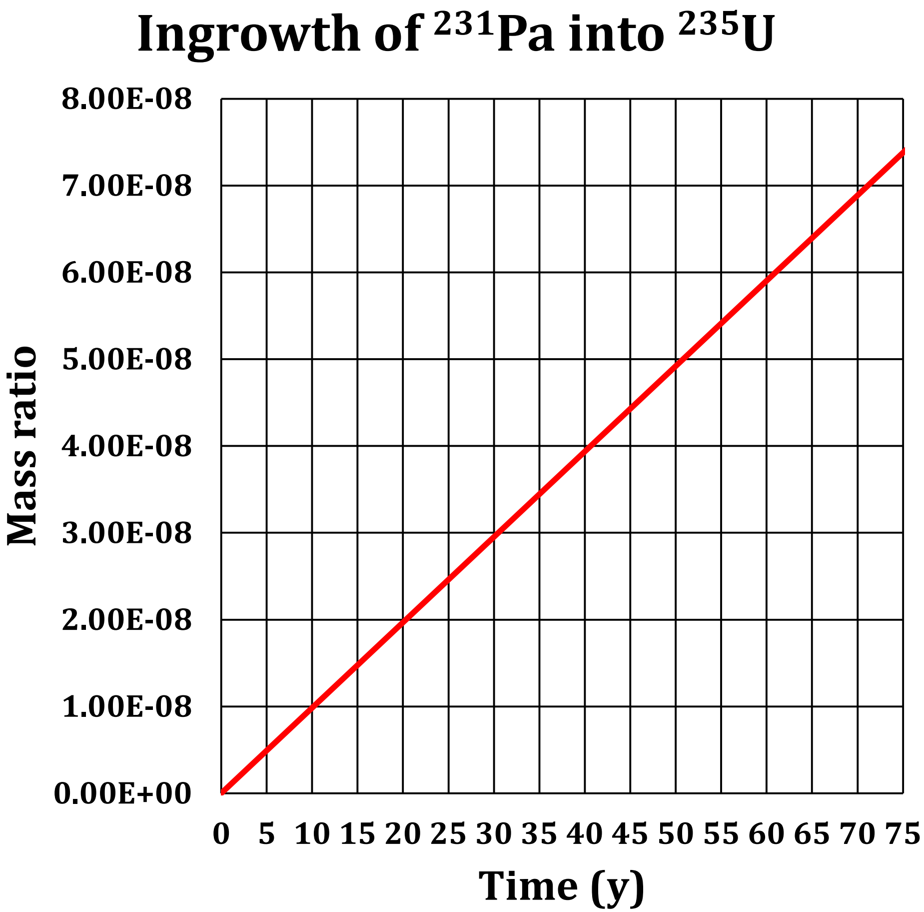
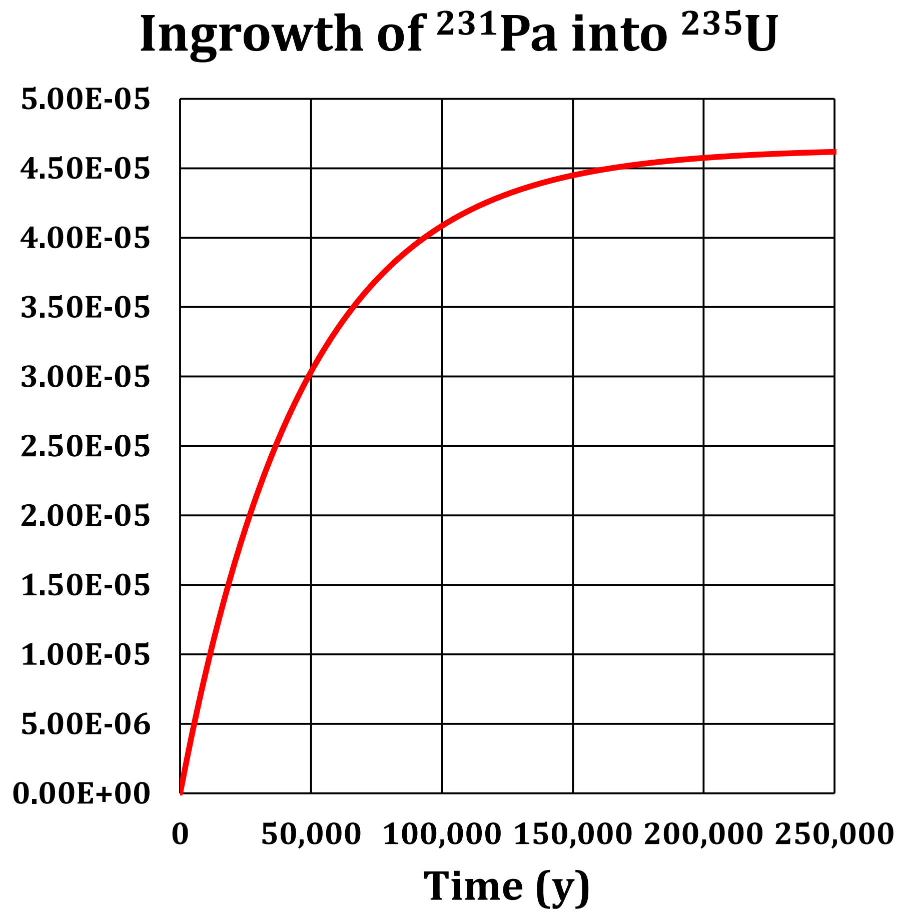
Forensics and sedimentation

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





Uranium measurement by γ-spectrometry

- 20 most abundant photon emissions for $^{234}Th \rightarrow ^{234m}Pa \rightarrow ^{234}Pa$

Nuclide	Energy (keV)	Emission prob. (%)	± Emission prob. (%)	Relative uncertainty
^{234}Th	63.3	3.75	0.08	2.13%
^{234}Th	83.3	0.061	0.005	8.20%
^{234}Th	92.4	2.18	0.19	8.72%
^{234}Th	92.8	2.15	0.19	8.84%
^{234m}Pa	94.7	0.1973	0.0025	1.27%
^{234}Th	95.9	0.021	0.013	61.9%
^{234m}Pa	98.4	0.316	0.004	1.27%
^{234}Pa	98.4	0.0252	0.0022	8.55%
^{234m}Pa	111.2	0.115	0.002	1.74%
^{234}Th	112.8	0.215	0.022	10.2%
^{234m}Pa	114.9	0.0382	0.0005	1.31%
^{234}Pa	131.3	0.0273	0.0019	6.72%
^{234m}Pa	258.2	0.0738	0.0008	1.08%
^{234m}Pa	742.8	0.094	0.003	3.19%
^{234m}Pa	766.4	0.323	0.004	1.24%
^{234m}Pa	786.3	0.0536	0.0007	1.31%
^{234}Pa	946	0.0203	0.0027	13.0%
^{234m}Pa	1001	0.847	0.008	0.94%
^{234m}Pa	1737.8	0.0214	0.0003	1.40%
^{234m}Pa	1831.4	0.01759	0.00023	1.31%

Thorium fuel cycle

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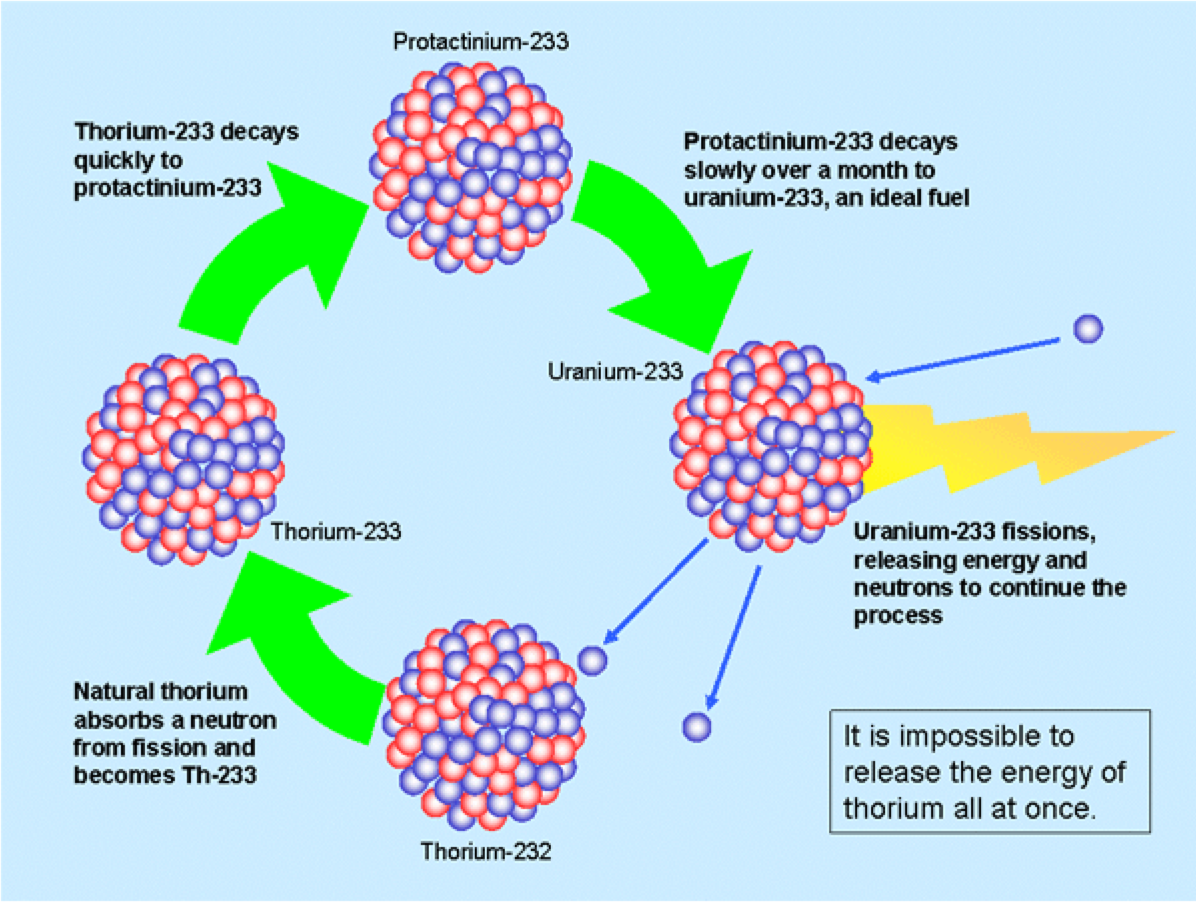
- Alternative fuel cycle
  - Abundance of thorium is at least 4 times that of uranium
- Proceeds via ^{233}Pa

$$^{232}\mathrm{Th}(n,\gamma)^{233}\mathrm{Th}(\beta)^{233}\mathrm{Pa}(\beta)^{233}\mathrm{U}$$

- Important for worker protection



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Work to be done

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- Protactinium-231
  - Produce with defined separation date from daughter nuclides
  - Calibrate by defined solid angle measurements
  - Mass spectrometry for mass measurement
- Protactinium-234m/234
  - Separate 5-10 MBq ^{234}Th from 500-1000g ^{238}U
  - Standardise by 4π β-γ coincidence counting
  - Determine emission probabilities
  - Separate ^{234m}Pa and ^{234}Pa and observe ingrowth
  - Then repeat to measure $^{234m}Pa \rightarrow ^{234}Pa$ branching ratio
  - Iterate calculations to reduce uncertainties and corrections
- Protactinium-233
  - None required

Chemistry required

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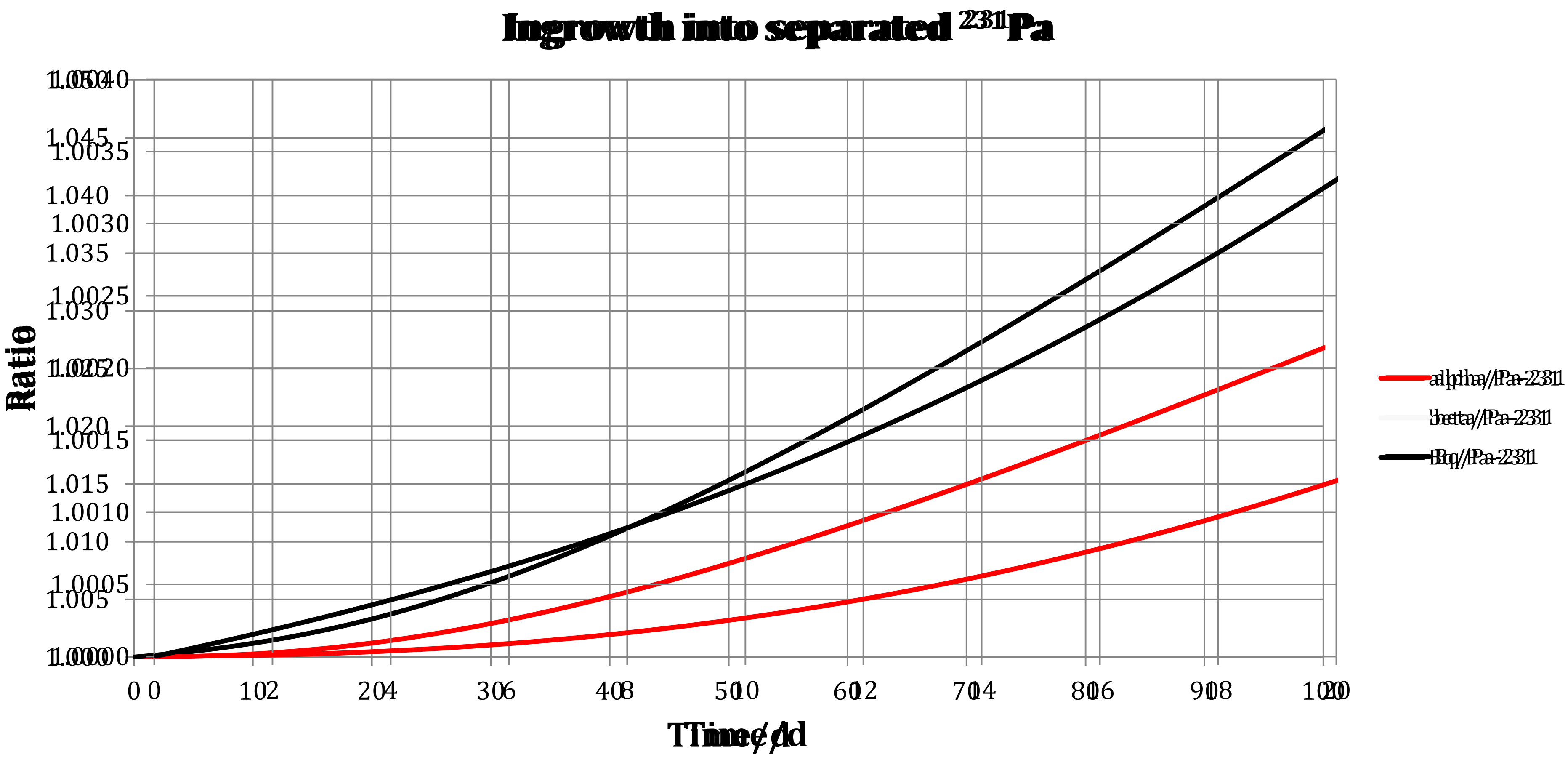
- Protactinium-231
  - Separation of ^{231}Pa from ^{227}Ac, ^{227}Th and ^{223}Ra



More chemistry

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- Protactinium-234
  - Expect to get ~7.5-15 kBq from 5000-10000 kBq ^{234}Th
  - After processing, expect it to have decayed to 6-12 kBq ^{234}Pa
  - Need <0.05% ^{234}Th impurity, ie <3 Bq
  - Decontamination factor needs to be $>3\times10^6$
- Counting technique
  - Liquid scintillation-γ coincidence counting
  - Protactinium needs to be maintained in solution
- Protactinium-233
  - Employed as a tracer for this work
  - Separate from ^{237}Np

    Irradiation of ^{232}Th is not possible (no UK reactors)

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Cation exchange with HCl

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- 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

- 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)

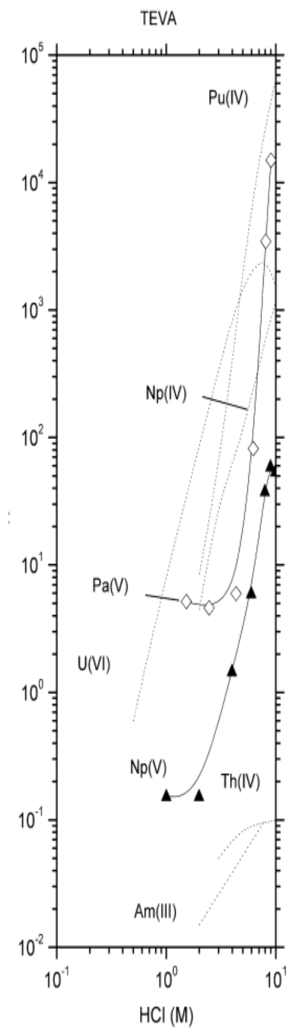
    ^{233}Pa washes through the resin

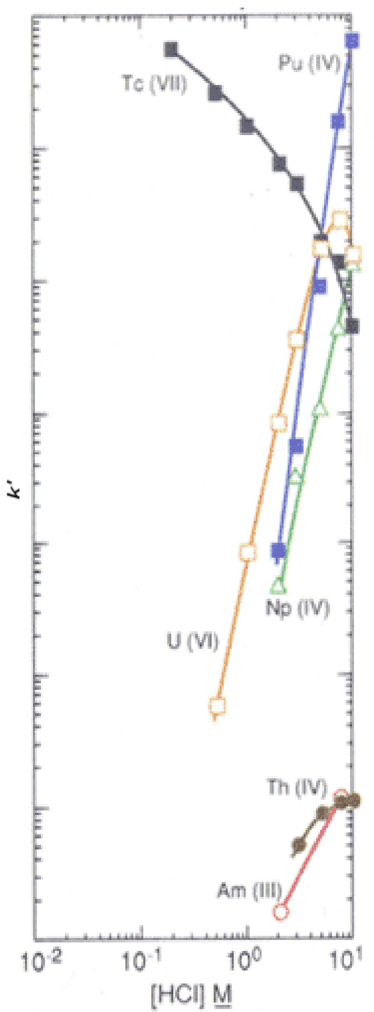
    ^{237}Np is retained

Np wash solution:	0.1 M HCl	(10 mL)

    ^{237}Np is removed

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

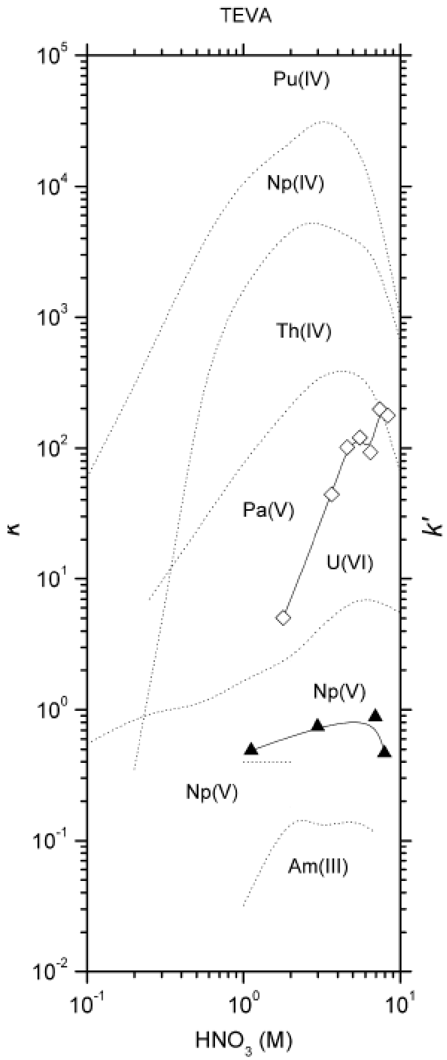




TEVA with HNO_3

- 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

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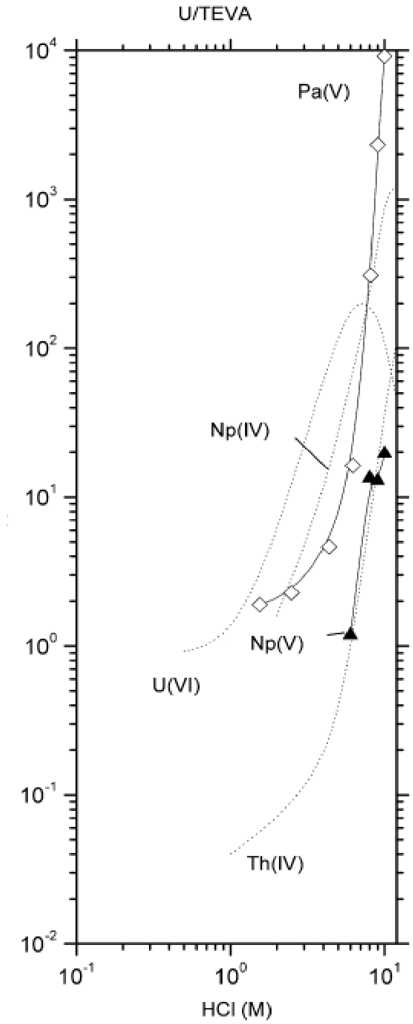
- Published data suggests that Pa is bound strongly by HCl on UTEVA with strong acid
  - To separate

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%



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Summary

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

Conclusions

- Variety of separation media tested
  - AG50 cation resin

    Surprisingly, seems to work well with good separation from Th, U and Np in HCl (HNO_3 only tested for Np).
    Ac to be tested, but predicted to be strongly adsorbed
  - TEVA

    Yield of Pa is good, contaminated by Np, but separation from Th and U is good.
    Ac to be tested, but predicted to be present in Pa fraction
  - TBP resin

    Yield of Pa is poor, but not contaminated by Np (data for Th and Uto be measured).
    Ac to be tested, but predicted to be present in Pa fraction
  - UTEVA

    Yield of Pa is poor, but separation from Th, U and Np is good.
    Ac to be tested, but predicted to be present in Pa fraction

Conclusions

- Choices at this point
  - AG50 cation resin

    Seems to offer the best opportunity for generating clean protactinium

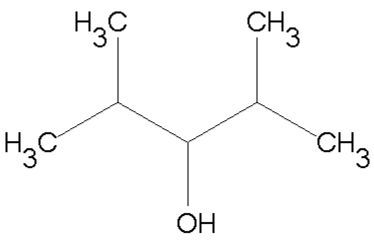
    Thorium and uranium untested in HNO_3

    Actinium and radium also untested but should be strongly retained on the resin
  - Chemical issues

    It is known that tracer levels of protactinium behave poorly and this was observed in some of this work

    Addition of NH_4F (instead of HF) is not recommended – K_2PaF_7 is insoluble, and this is probably true for $(NH_4)_2PaF_7$
  - Solvent extraction work is not complete

Work to be done



- Separations
  - Extend to gaps – mainly actinium and radium
- Solvent extraction
  - Will test 2,4-dimethyl-pentan-3-ol and 2,4-dimethyl-pentan-3-one
- Chemical behaviour
  - Using cerium as an analogue for thorium (in another project) was successful
  - Trying tantalum as an analogue for protactinium ~20 µg/mL or $\sim 10^{-4}$ M
- Standardisations
  - 2016 expected for ^{234}Pa
  - 2016/17 expected for ^{231}Pa BIPM supplementary comparison
  - 2017/18 expected for ^{234}Th/^{234m}Pa BIPM supplementary comparison

Thank you.
Any questions?

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