RAPID DETERMINATION OF ACTINIDES IN WATER SAMPLES USING TEVA AND TK221 RESIN CARTRIDGES

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  Determination of actinides in sea water

Goal

to develop combined procedure for the selective separation of Pu, Am-Cm, U, Np, Th using **chromatographic resins.**

The procedure should be

- adequate for water sample
- adequate for measurement by α spectrometry
- rapid
- robust

to analyse actinides of elevated activities

Analytical applications:

process water

contaminated water (drinking, surface, ground, sea) in emergency situation.

Goal

to develop combined procedure for the selective separation of Pu, Am-Cm, U, Np, Th using **chromatographic resins.**

The procedure should be

- adequate for water sample
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- rapid
- robust

to analyse actinides of elevated activities

Resins of high distribution ratios and selectivities for actinides are needed.

Analytical applications:

process water

contaminated water (drinking, surface, ground, sea) in emergency situation.

Properties of actinides on specific resins

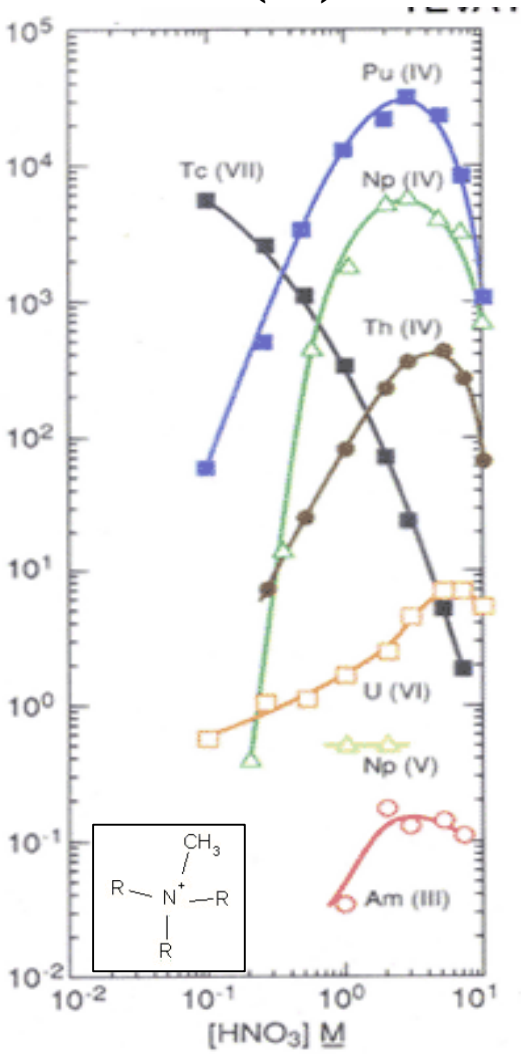
Single column option?	**Multi-column option?**
one resin retains all actinides	resins retain certain actinides
separation is sensitive to the conditions	separation is more robust

® Triskem International homepage: https://www.triskem-international.com/ resins-and-accessories.php

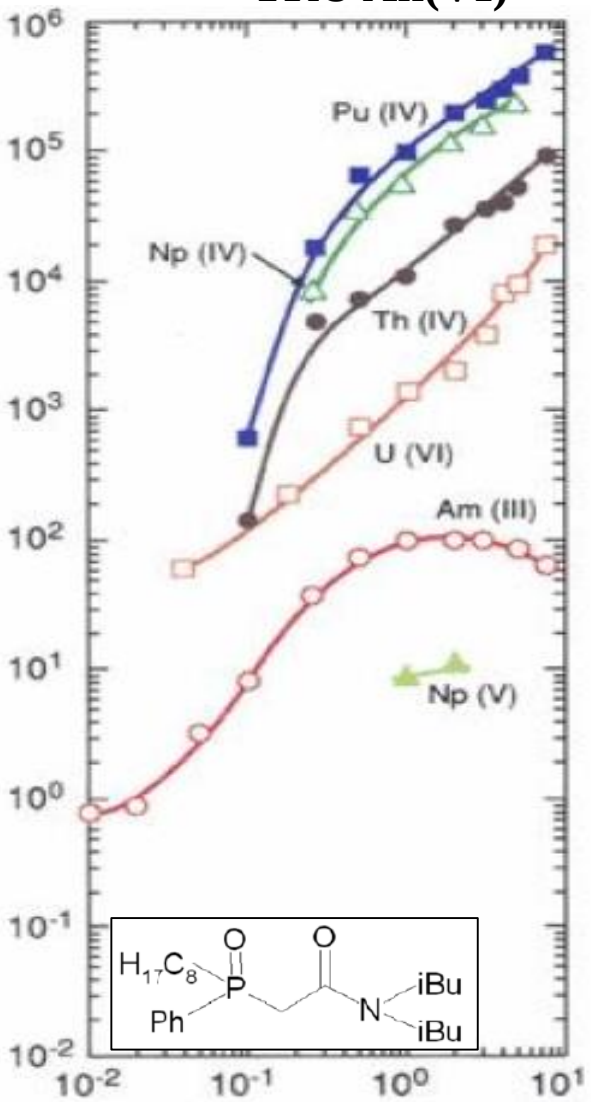
k' capacity factors of An's on EC resins in HNO_3

Pu
Np
Th
Am
U

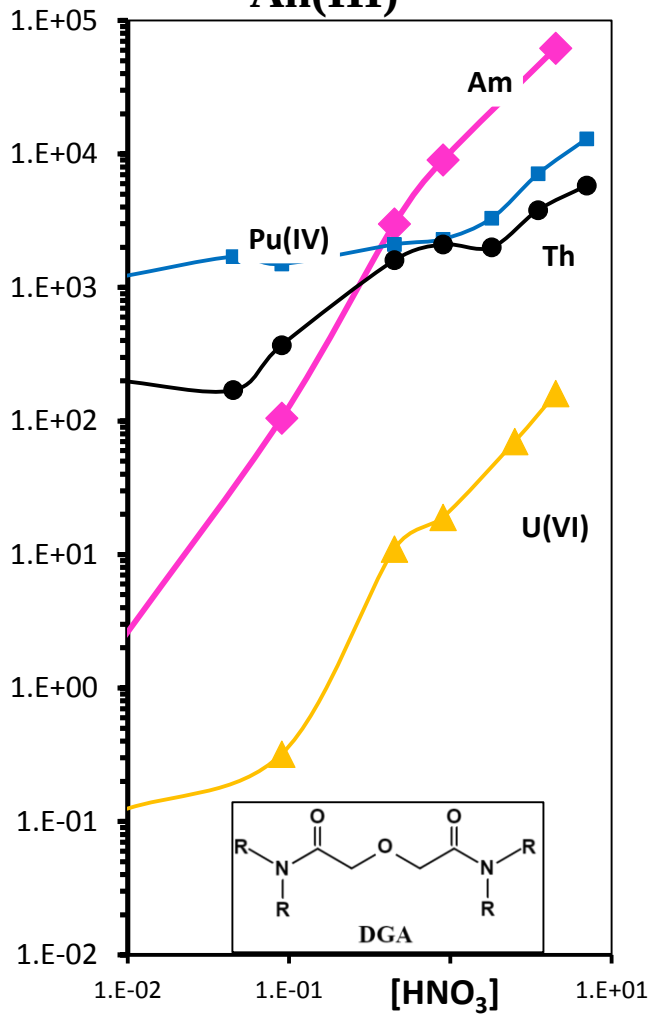
TEVA An(IV)



TRU An(VI)



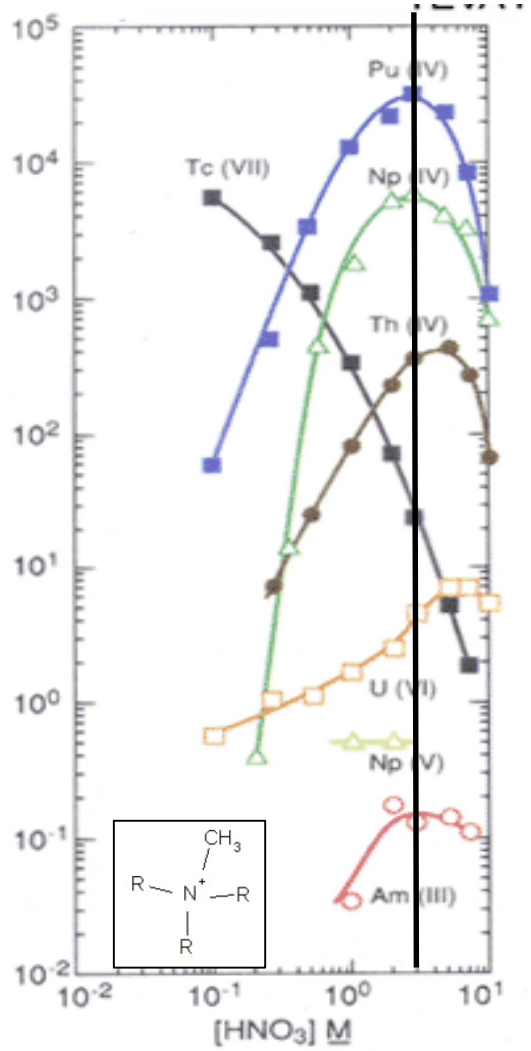
n-DGA An(III)



k' capacity factors of An's on EC resins in 3M HNO_3

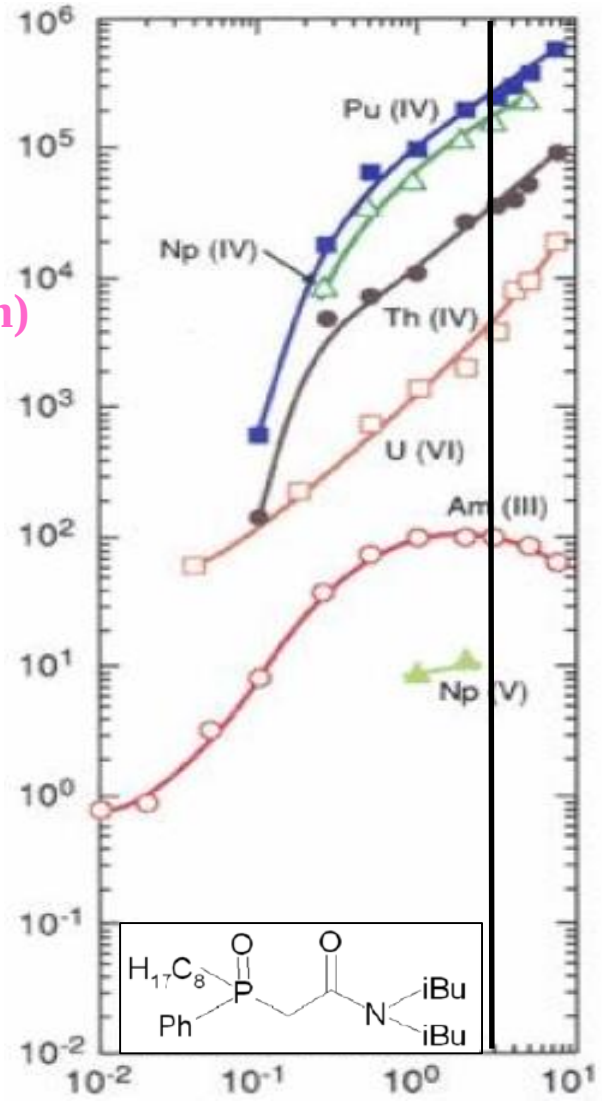
TEVA

Pu
Np
Th



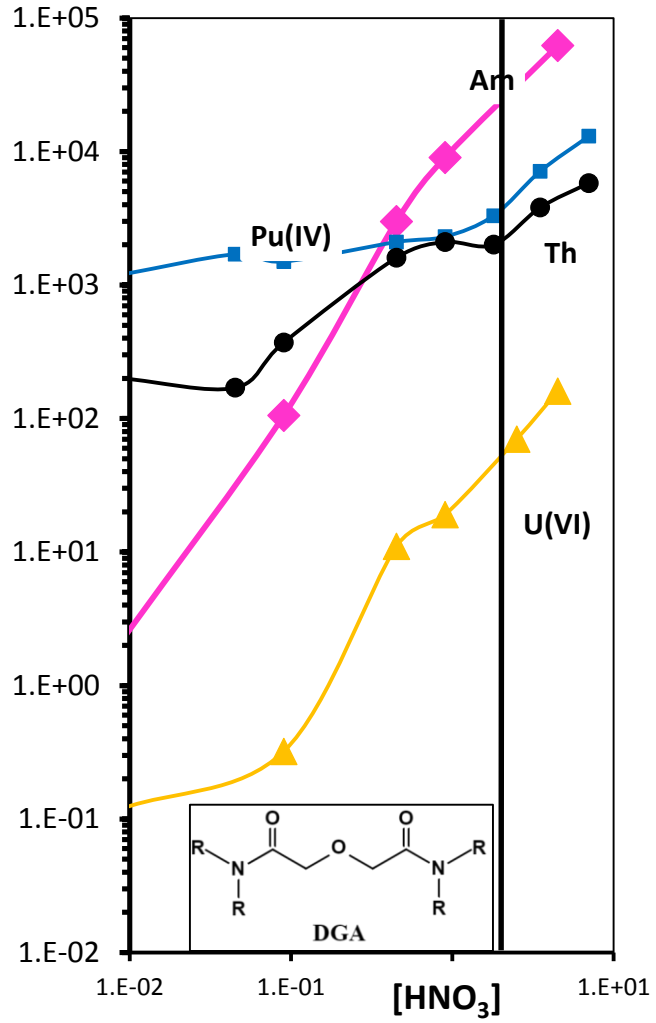
TRU

Pu
Np
Th
(Am)
U



n-DGA

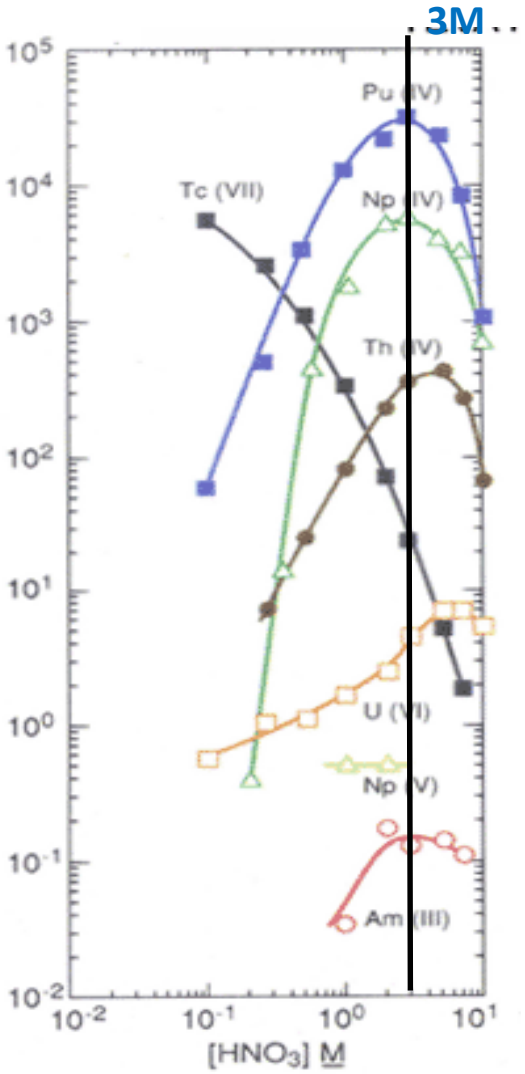
Pu
Np
Th
Am
(U)



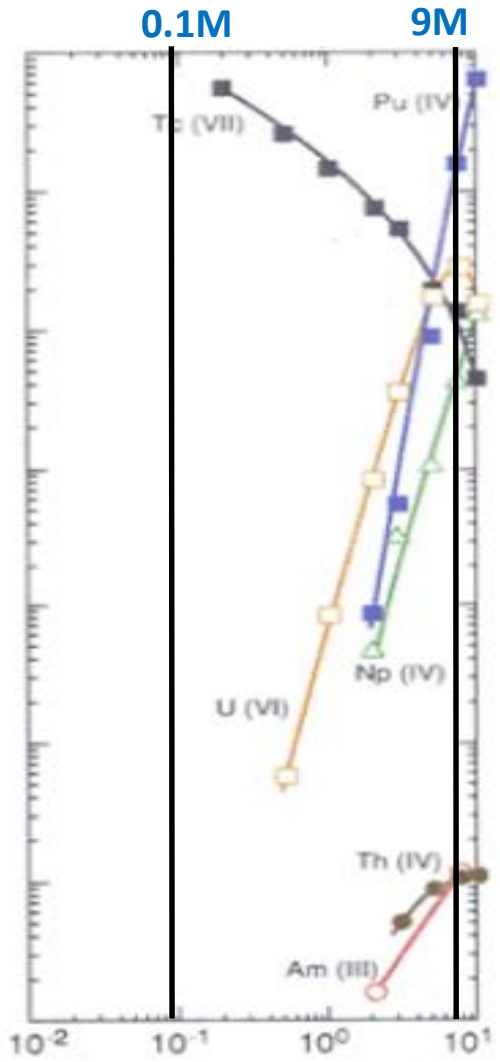
k' capacity factors of An's on TEVA resin in HNO_3 and HCl

Pu
Np
Th

TEVA from HNO_3



TEVA from HCl



Load
from 3M HNO3:
Pu(IV), Np(IV), Th

→ effluent: U(VI), Am(III)

Elution possibilities:
from 9M HCl:
Th

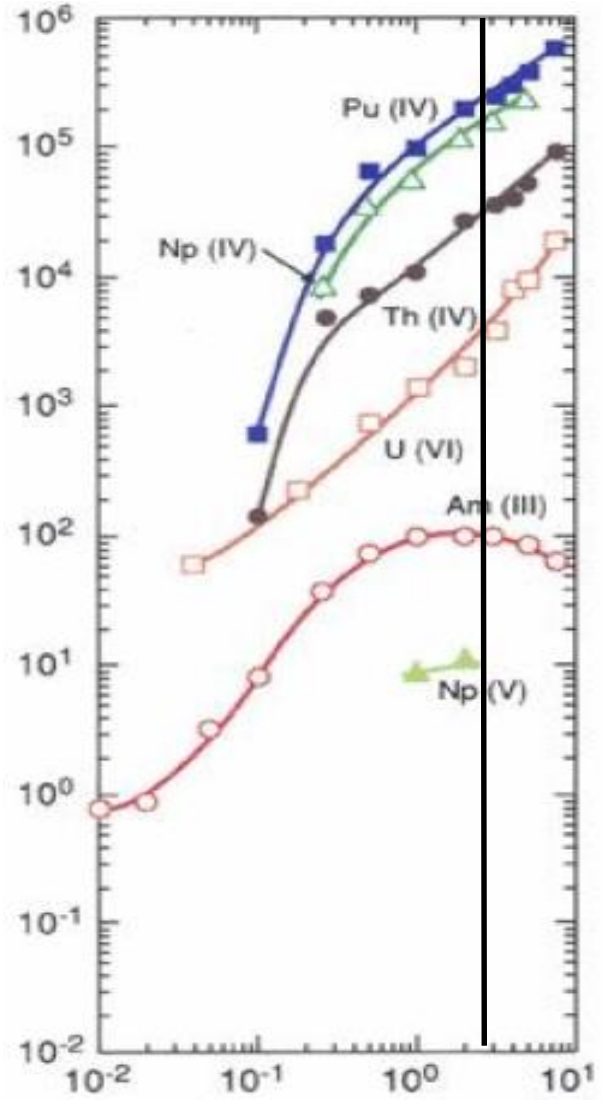
from 0.1M HCl:
Pu(IV), Np(IV)

from 9M HCl/Ti^{3+} :
Pu(III)

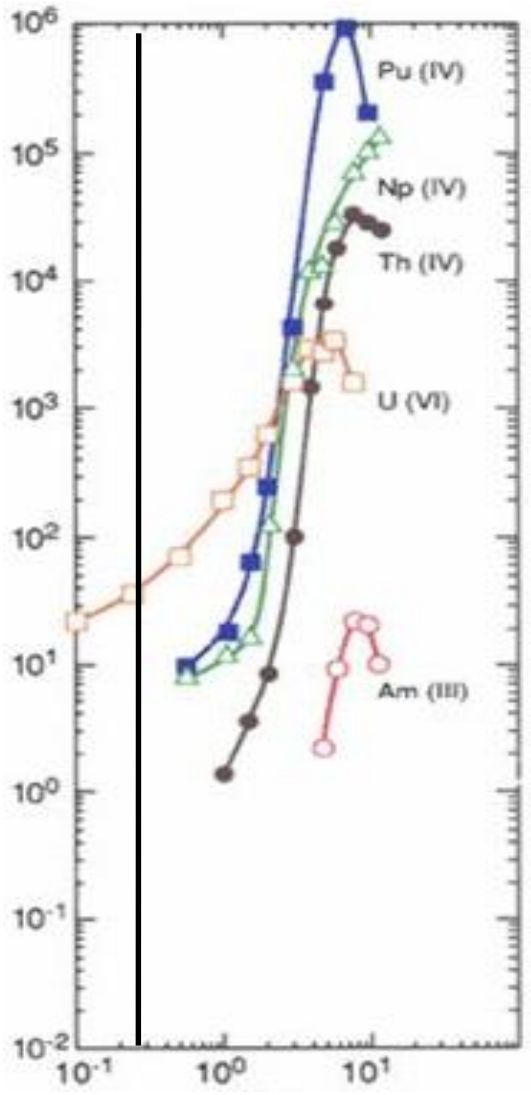
k' capacity factors of An's on TRU resin in HNO_3 and HCl

Pu
Np
Th
(Am)
U

TRU from 3M HNO_3



TRU from HCl



After removal of Pu, Np, Th

Load
from 3M HNO3:
U(VI), (Am)
→ effluent: (Am)

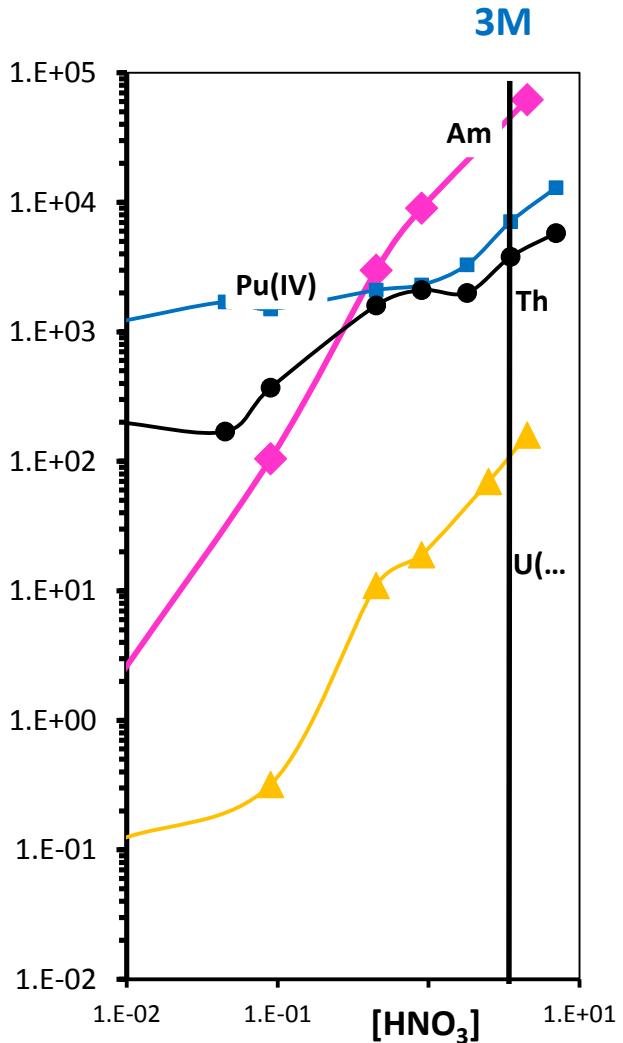
from 0.25M HCl:
Am

Elution possibilities:
from 0.1M $NH_4HC_2O_4$:
U(VI)

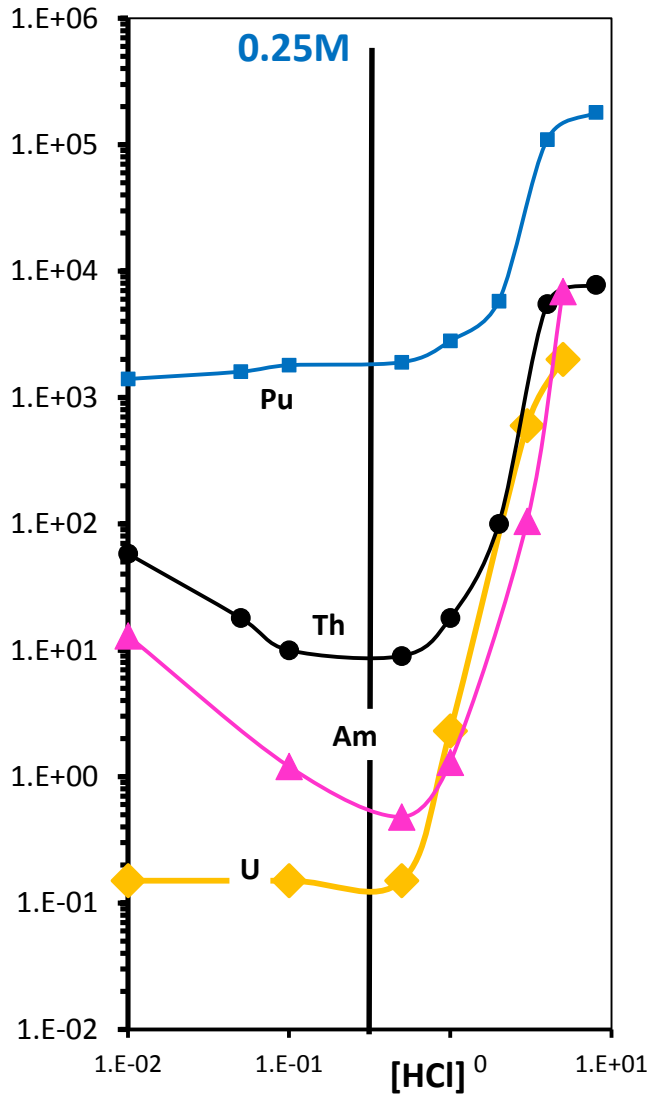
k' capacity factors of An's on DGA resin from HNO_3 and HCl

Pu
Np
Th
Am
U

DGA from HNO_3



DGA from HCl



After removal of Pu, Np, Th, U

Load
from 3M HNO3:
Am(III), (U)
→ effluent: (U)

Elution possibilities:
from 0.25M HCl:
Am

TK221 resin

Combination of TRU resin and DGA resin

Ln's

Designed for

- separation of **lanthanides**, e.g. ^{177}Lu
- separation of **actinides**

Pu
Np
Th
Am
U

Out of natural matrix elements (alkali, alkaline earth, Al) only Ca is slightly retained from HNO_3.
Many III and IV valent elements (e.g. Fe, Zr) are well retained from HNO_3.

Product sheet: TK221 Resin, https://www.triskem-international.com/scripts/files/60cb473fbbe7e8.32187398/PS_TK221-Resin_EN_210607.pdf
S. Happel: "An overview over some new extraction chromatographic resins and their application in radiopharmacy" presented on the 4th of June 2019 at the 102nd Canadian Chemistry Conference and Exhibition (CCCE 2019) in Quebec City, QC
N. Vajda et al. (RadAnal): "Report: Investigation on TEVA/TK221 resins for separation of actinides", Budapest, April 2021

Basic concept

Actinides pre-concentration with Ca phosphate co-precipitation

Load:
15 mL 3M HNO_3/
1M $Al(NO_3)_3$
Oxidation state adjustment

Rinse:
18 mL 3M HNO_3

Rinse:
10 mL 3M HNO_3

Th strip:
15 mL 9M HCl

Pu-Np strip:
15 mL 0.1M HCl/0.05M HF/0.03M Ti^{3+}

Th/NdF_3 **Pu-Np/NdF_3**

Rinse:
10 mL 3M HNO_3

Am strip:
15 mL 0.25M HCl

U strip:
15 mL 0.1M $NH_4HC_2O_4$

Am/NdF_3 **U/NdF_3**

Basic concept – extended for Pu/Np separation

Actinides pre-concentration with Ca phosphate co-precipitation

Load:
15 mL 3M HNO_3/
1M $Al(NO_3)_3$
Oxidation state adjustment

Rinse:
18 mL 3M HNO_3

Rinse:
10 mL 3M HNO_3

Th strip:
15 mL 9M HCl

Pu strip:
15 mL 9M HCl/0.03M Ti^{3+}

Np strip:
20 mL 0.1M HCl/
0.1M HF

Rinse:
10 mL 4M HCl/0.1M HF

Am strip:
15 mL 0.25M HCl

U strip:
15 mL 0.1M $NH_4HC_2O_4$

Th/NdF_3 **Pu/NdF_3** **Np/NdF_3** **Am/NdF_3** **U/NdF_3**

Optimization of the EC separation

Optimization of Am/U separation on TK221

Model
simulating water sample

Ca phosphate co-precip.
Fe and Ca in the load

Oxidation state adjustment:
sulfamic acid/ascorbic acid/
$NaNO_2$

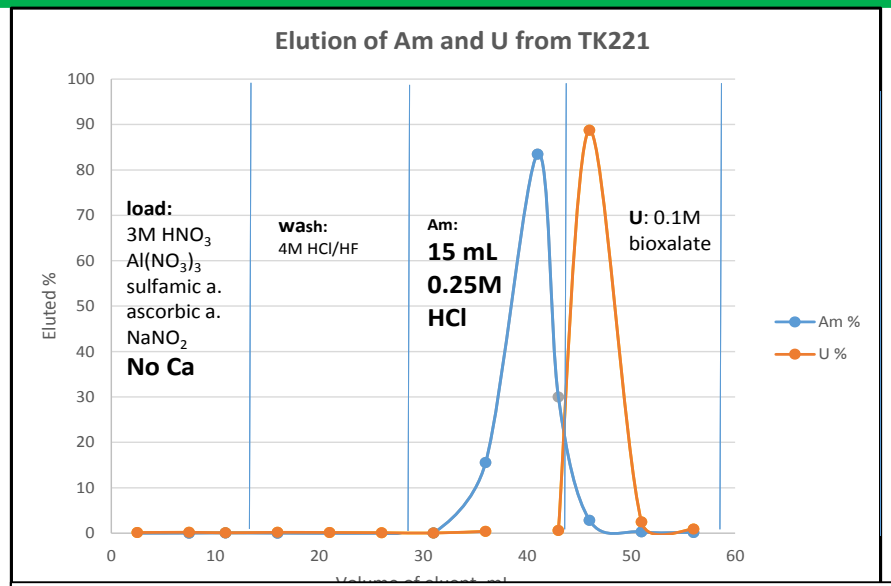
Tracers:
individual: ^{241}Am, ^{233}U
about 50 Bq in each test

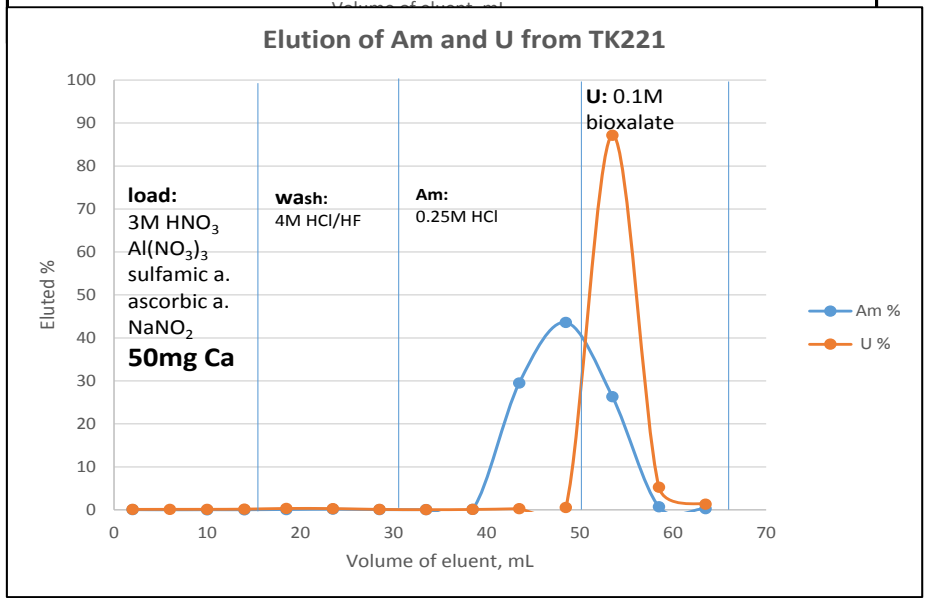
Measurement by LSC

Effect of Ca in load

No Ca

50 mg Ca



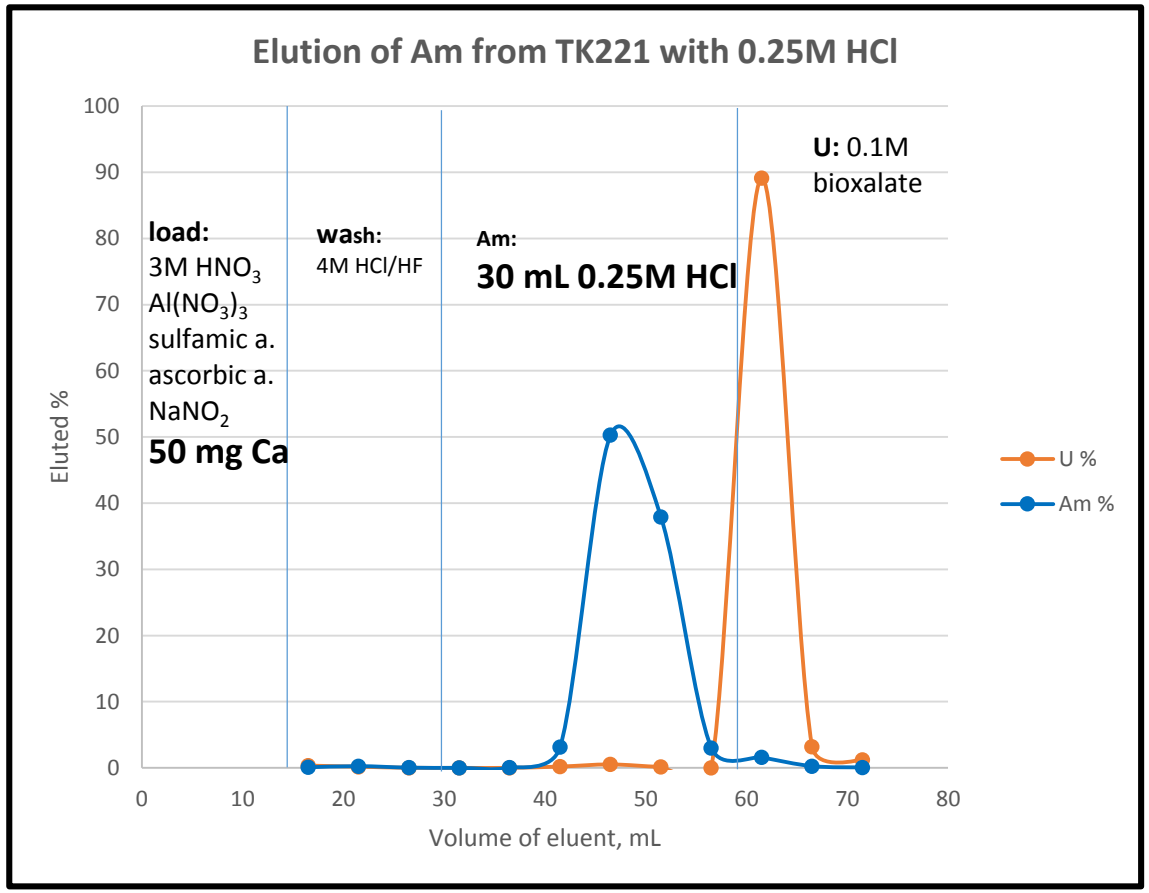


Am
Is hold back

Optimization of Am/U separation on TK221

Model
simulating water sample

Tracers:
individual: ^{241}Am, ^{233}U

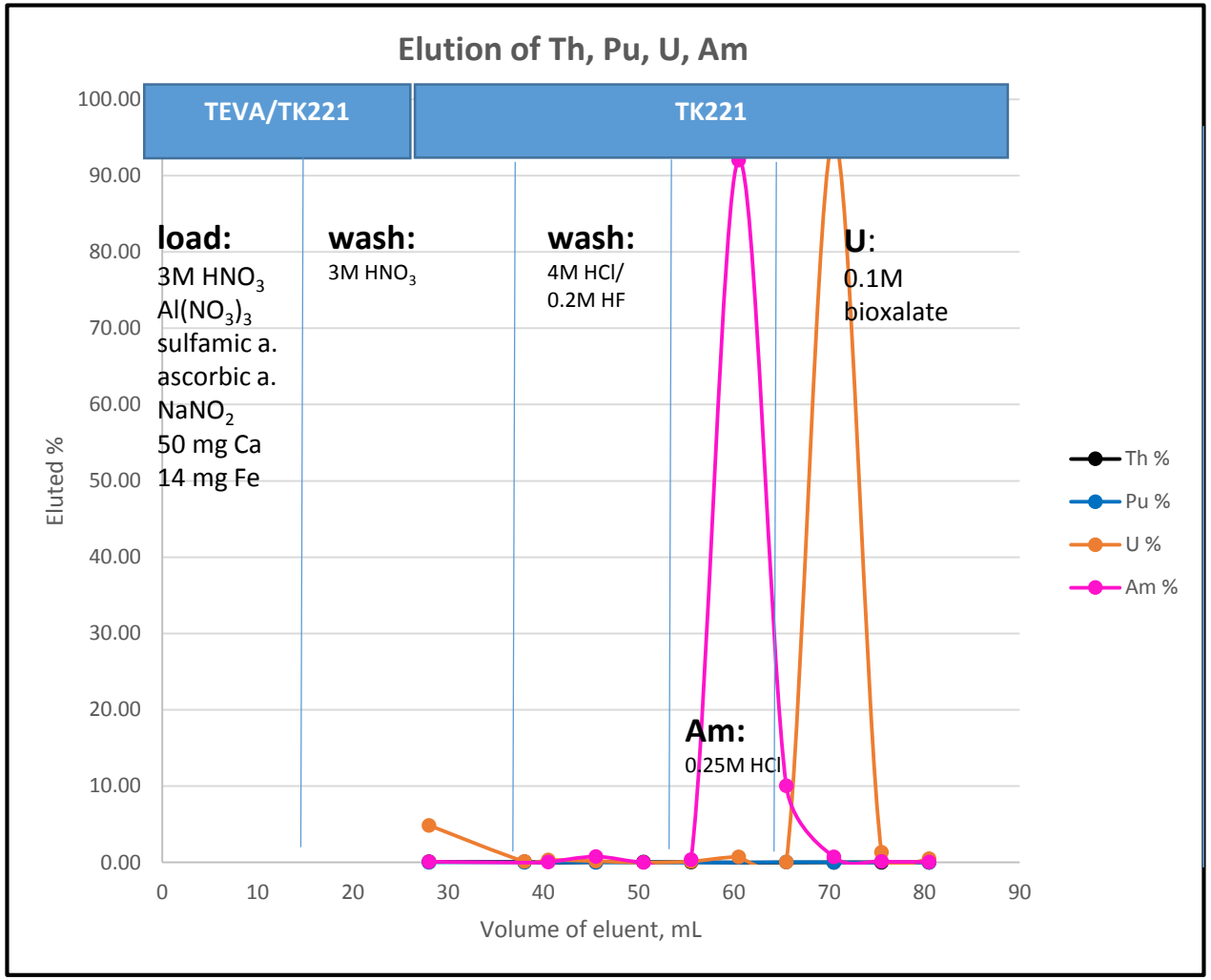


Good Am/U separation by increased eluent volume!

Separation of Am, U, Th, Pu on TEVA/TK221 and TK221

Model
simulating water sample

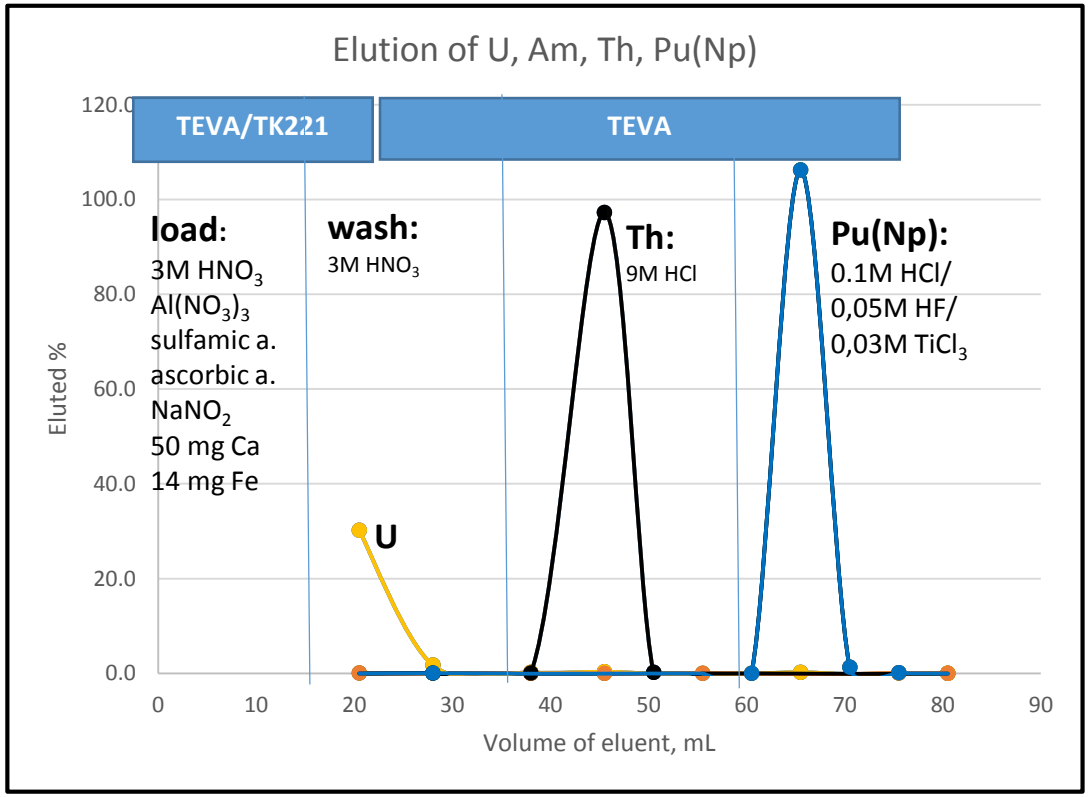
Tracers:
individual:
^{241}Am, ^{233}U
^{230}Th, ^{239}Pu

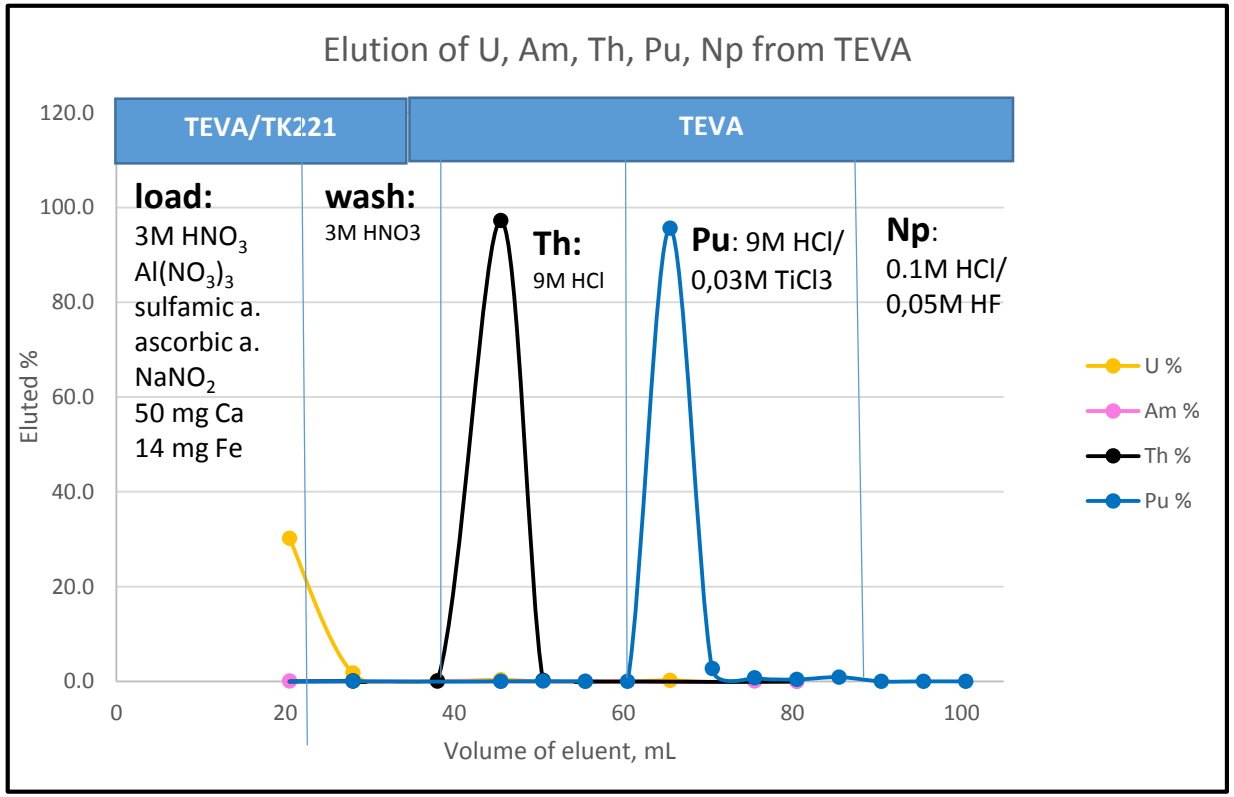


Separation of Th, Pu(Np), Am, U on TEVA/TK221 and TEVA

Model

simulating water sample, Tracers: individual: ^{241}Am, ^{233}U, ^{230}Th, ^{239}Pu





Results of optimization

Model
simulating water sample

Ca phosphate co-precip.
Fe and Ca in the load

Oxidation state adjustment:
sulfamic acid/ascorbic acid/
$NaNO_2$

Tracers:
individual: ^{230}Th, ^{239}Pu,
^{241}Am, ^{233}U
about 50 Bq in each test

Measurement by LSC

Recovery

		U %	Am %	Th %	Pu %
	TEVA/TK221 cartridges				
load	15 mL load				
wash	18 mL 3M HNO_3	2-5	0	0	0
	TEVA cartridge				
wash	10 mL 3M HNO3	0,1-0,2	0	0.1	0
Th strip	15 mL 9M HCl	0.3	0	97	0
Pu strip	15 mL 0.1M HCl/0.05M HF/0.03M $TiCl_3$	0.2	0	0	106
	TK221 cartridge				
wash	15 mL 4M HCl/0.2M HF	0.5	0.7	0	0
Am strip	30 mL 0.25M HCl	0.8	102	0	0
U strip	15 mL 0.1M $NH_4HC_2O_4$	97	0.7	0	0
	SUM %	101-104	103	97	106

High recoveries, some U contamination (<1%) is possible!

Determination of actinides in water samples

Determination of actinides in water samples

800 mL water:

TAP or SEA

spiked with mixed tracers:

^{241}Am, ^{233}U, ^{230}Th, ^{239}Pu, ^{237}Np

of 0.1-0.5 Bq

Ca phosphate co-precipitation,

TEVA/TK221 separation,

µ-co-precipitation

α spectrometry

	Actinides determination			
	without Np		with Np separation	
	yield %	yield unc %	**yield** %	yield unc %
TAP water				
^{230}Th	**90**	8	**86**	7
^{239}Pu	**108**	7	**95**	7
^{237}Np	-		**91**	9
^{241}Am	**103**	7	**97**	6
^{233}U	**103**	7	**70**	7
SEA water				
^{230}Th	**71**	7	**61**	6
^{239}Pu	**91**	7	**87**	6
^{237}Np	-		**93**	8
^{241}Am	**89**	7	**92**	6
^{233}U	**88**	7	**59**	6

Results

Recoveries of all An's are acceptable high:
> 60%

Recoveries in TAP are higher than in SEA.

Detectable contamination in α sources:
< 1% ^{239}Pu in ^{237}Np source

To get high Pu recovery in α source the Pu strip solution (9M HCl) has to be evaporated, diluted.

Summary

A new procedure *for the separation of U, Pu, Am-Cm and Np in water samples has been developed where Actinides are*

- *pre-concentrated with Ca phosphate precipitate*
- *chromatographically separated on TEVA/TK221 cartridges,*
- *determined by alpha spectrometry.*

For all actinides

- *chemical recoveries are acceptable high (≥ 60%),*
- *decontamination factors are acceptable high (>100),*
- *resolution of the alpha sources are acceptable good (< 40 keV),*
- *sensitivities are acceptable high (<0.1 Bq/kg)*

The whole analysis can be done in ***1 day****.*