DETERMINATION OF URANIUM, PLUTONIUM AND AMERICIUM IN SOIL AND SEDIMENT BY A SEQUENTIAL SEPARATION PROCEDURE USING A SINGLE DGA COLUMN

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  - Determination of U, Pu, Am in SRMs, method & results
  - Separation of Am from lanthanides

Goal

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

The procedure should be

- adequate for various sample types
- adequate for measurement by α spectrometry and/or ICP-MS
- accurate, sensitive
- simple, cheap, fast

to analyse high activity wastes,

low activity environmental samples.

Resin of high distribution ratios and selectivities for actinides is needed.

DGA

Properties of DGA resin

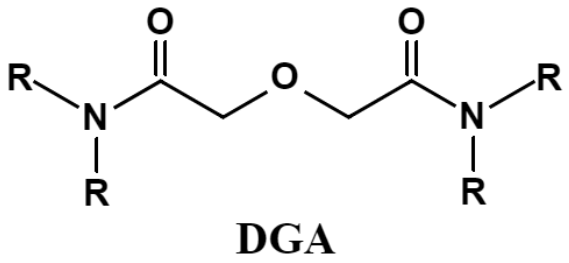
® Triskem International homepage: https://www.triskem-international.com/ resins-and-accessories.php

Horwitz E P, McAlister D R, Bond A H, Barrans R E Jr (2005) Solvent Extr. Ion Exchange 23: 319-344

Pourmand A., Dauphas N.(2010) Talanta, 81(3), 741-753

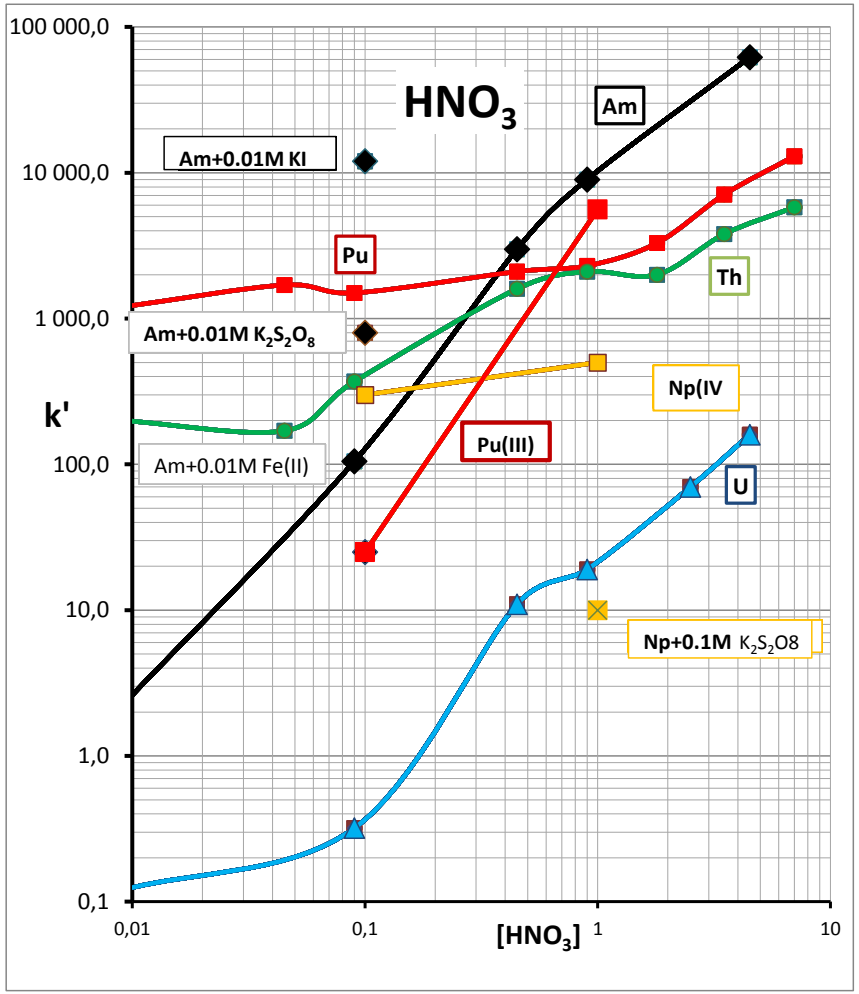
Capacity factors of DGA resin ®

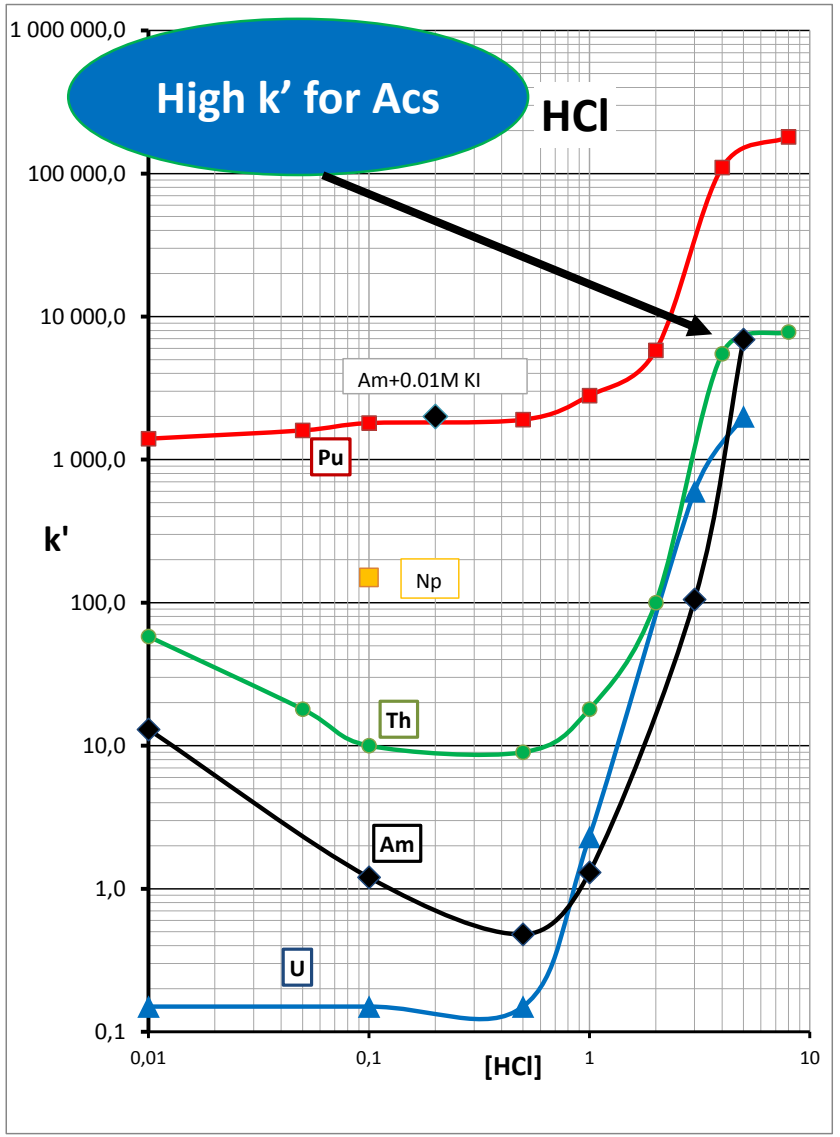
Pu
Am
U
Th
Np



DGA

R = n-octyl





Separation of actinides on DGA column

Groska J, Vajda N, Molnar Zs, Bokori E, Szeredy P, Zagyvai M (2016)
Determination of actinides in radioactive waste after separation on a single DGA resin column.
J. RADIOANAL. NUCLEAR CHEM., 309 (3) 1145-1158. DOI 10.1007/s10967-016-4729-1

Basic concept

- **Load**: retention of all actinides in reduced forms from 4M HCl/ Na_2SO_3
  U(IV), Th(IV), Np(IV), Pu(III), Am(III)

- **Elution of U** with dilute HNO_3 after oxidation to U(VI), while
  Pu and Np are oxidized to Pu(IV), Np(IV)/Np(VI) - retained,
- Reduction of Pu and Np to Pu(III) and Np(IV),

- **Elution of Th, Np** with complexing agent oxalic acid, while
  trivalent actinides (Pu(III), Am) are retained,

- **Elution of Pu** with oxalic acid after oxidation to Pu(IV)

- **Elution of Am** with dilute HCl.

Ac(III) and Ac(IV) are completely retained!

On-column redox reactions are feasible!

Only Ac(IV) form oxalate complexes

Optimization of the chromatographic procedure

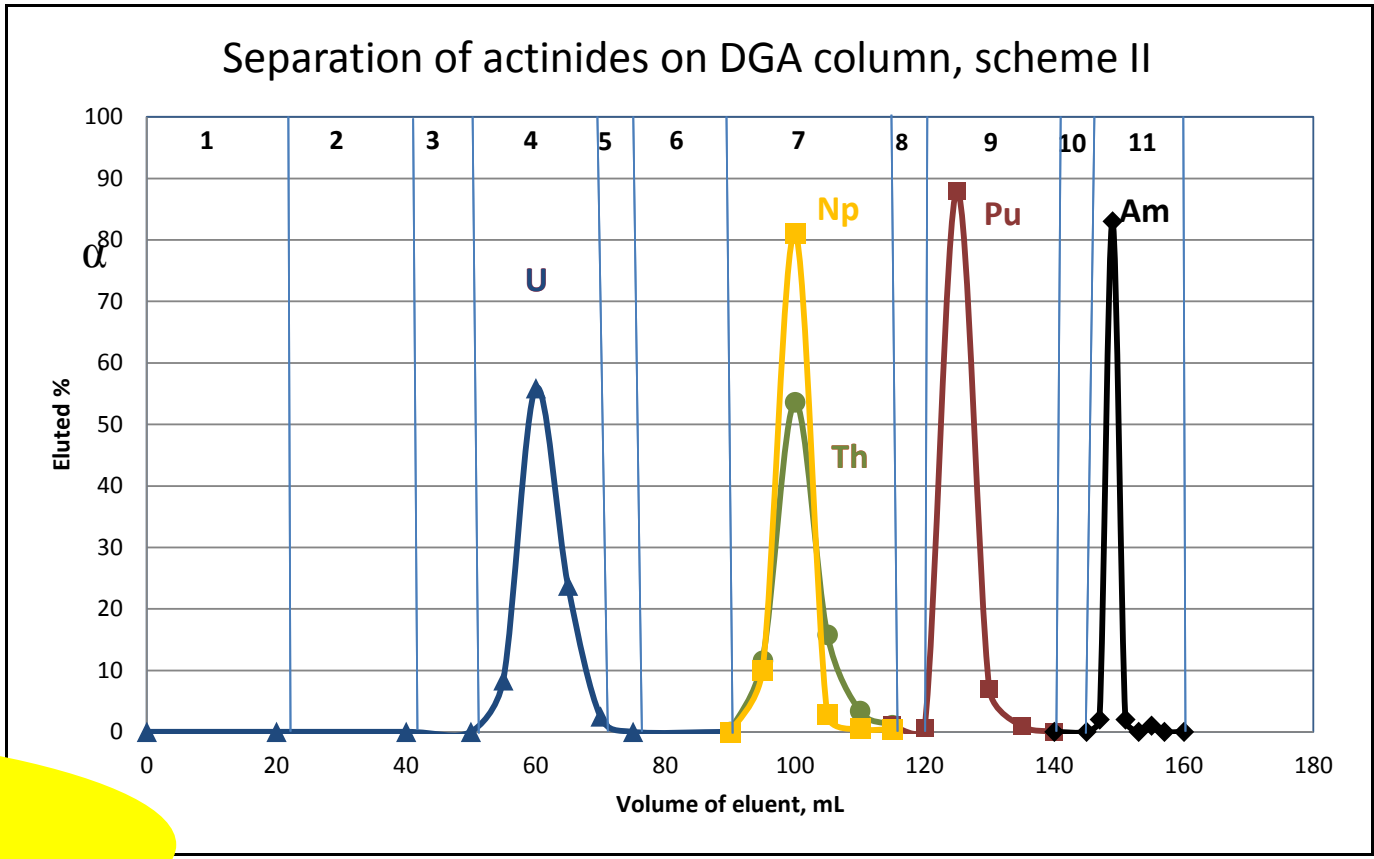
Studied by **model experiments**

with single tracers

Recoveries

U	Th	Np	Pu	Am
90%	86%	95%	96%	88%

1.	load: 4 M HCl/0.15 M Na_2SO_3	25°C
2.	25 mL 4 M HCl	25°C
3.	10 mL 4 M HNO_3	30°C
4.	***15 mL 0.5 M HNO_3***	30°C
5.	5 mL 0.5 M HNO_3	30°C
6.	15 mL 4 M HCl/0.05 M Fe(II)	30°C→40°C
7.	***25 mL 0.5 M HNO_3/0.05 M oxalic acid/0.01 M Fe(II)***	40°C
8.	5 mL 0.5 M HNO_3/0.05 M oxalic acid	40°C
9.	***20 mL 0.5 M HNO_3/0.05 M oxalic acid/0.1 M $K_2S_2O_8$***	40°C
10.	5 mL 0.5 M HNO_3	40°C
11.	***15 mL 0.5 M HCl***	40°C

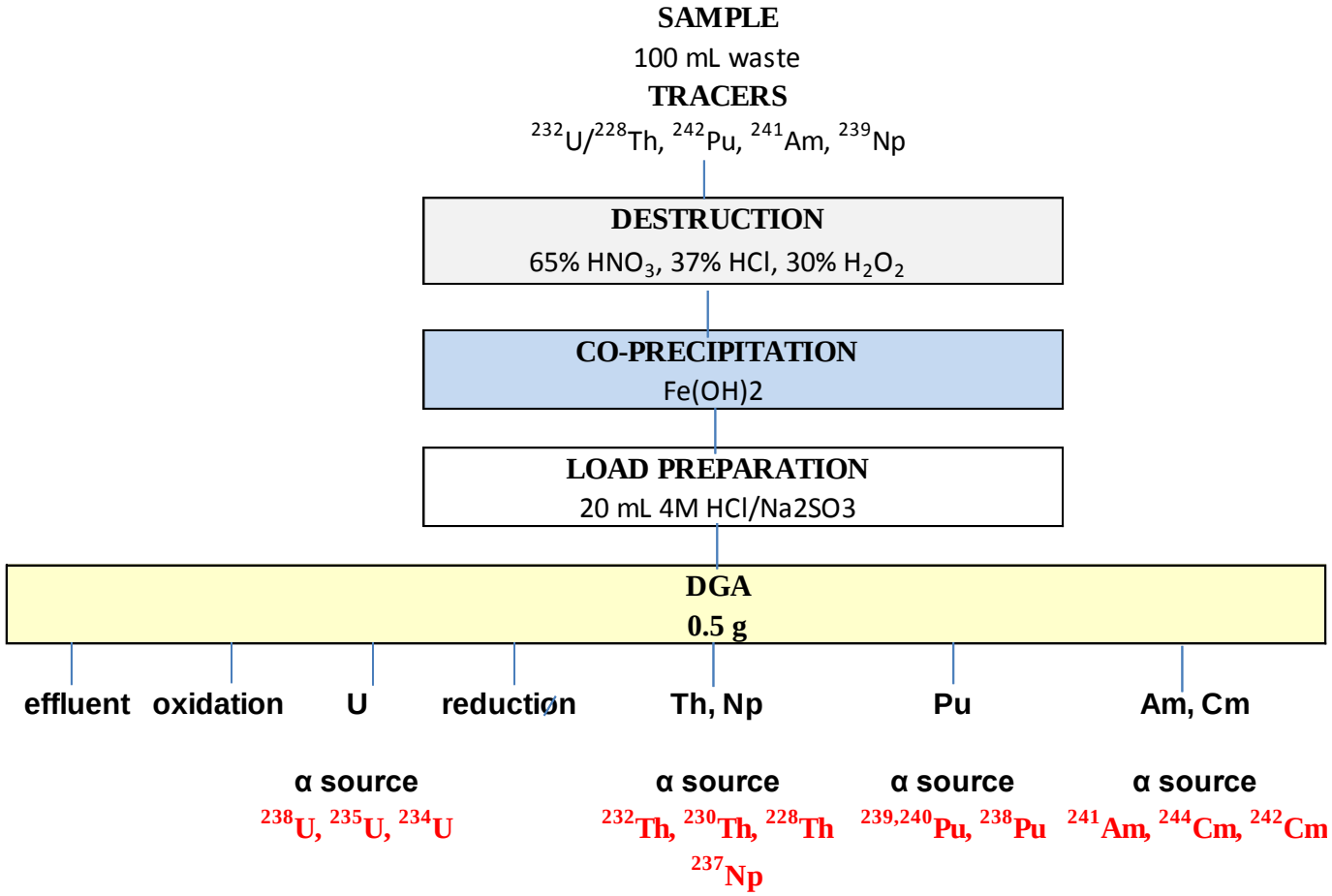


Use of small (0.5 g), temperature controlled DGA column!

Determination of actinides in radioactive wastes

Groska J, Vajda N, Molnar Zs, Bokori E, Szeredy P, Zagyvai M (2016)
Determination of actinides in radioactive waste after separation on a single DGA resin column.
J. RADIOANAL. NUCLEAR CHEM., 309 (3) 1145-1158. DOI 10.1007/s10967-016-4729-1

Flowchart & results



Chemical recoveries in waste samples, %
with co-precipitation, α source preparation

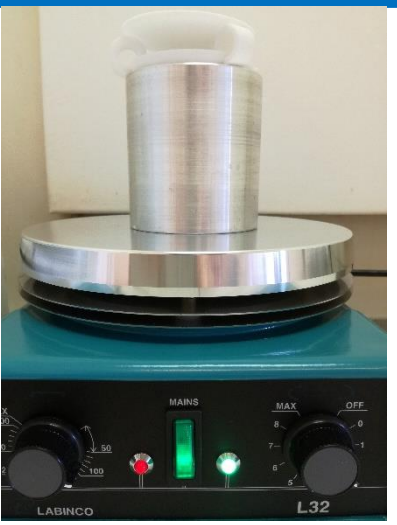
U	Th	Np	Pu	Am
94	62	74	77	67

Recoveries and DFs were acceptable high.
Co-precipitation is not necessary.

Actinides in soil and sediment

N Vajda, M Zagyvai, J Groska, E Bokori, Zs Molnár, M Braun (2020) Determination of uranium, plutonium and americium in soil and sediment by a sequential separation procedure using a single DGA column. *J. RADIOANAL. NUCLEAR CHEM.* 326, 695–710., DOI 10.1007/s10967-020-07337-9

Sample destruction and preliminary tests



ACID DESTRUCTION
3 days

SAMPLE
5 g soil
TRACERS
$^{232}U/^{228}Th$, ^{242}Pu, ^{241}Am

DESTRUCTION: MW+evaporation
65% HNO_3, 37% HCl, 40% HF

LOAD PREPARATION
100 mL 4M HCl/Na2SO3

DGA
0.5 g

effluent | U α source | Th α source | Pu α source | Am, Cm α source

FUSION + Silica removal
2 days

SAMPLE
5 g soil
TRACERS
$^{232}U/^{228}Th$, ^{242}Pu, ^{241}Am

DESTRUCTION: Fusion
30 g NaOH

LOAD PREPARATION: Silicagel removal
300 mL 4M HCl/Na2SO3

DGA
0.5 g

effluent | U / α source | Th α source | Pu α source | Am, Cm α source

No preconcentration
High load volume

Sample destruction and preliminary tests

Results of analysis of IAEA SRM soils and sediments

ACID DESTRUCTION

FUSION + Silica removal

Sample code	Sample weight g	Load volume mL	Chemical recovery % U	Th	Pu	Am
Acid destruction						
375	4	80	66	85	**75**	**91**
326	4	80	57	71	**81**	**88**
300	4	90	**5**	100	**73**	**85**
367	4	80	87	**11**	8	34
Fusion						
375	5	300	45	72	35	90
326	5	300	81	78	**48**	**71**
300	5	300	74	**34**	**61**	**84**
367						

PEG
Filtration blocked

- DFs were high.
- Chemical recoveries varied significantly

What can be responsible for poor recovery in certain cases ?

Possible interferences from literature:

Fe(III) – major component ↔ synergistic for Am

Y, Hf, Mo, Pd, Cd, Pt, Au, Ga, In, Tl, Sn, Pb, Sb, Bi – minor components

Zr – minor component except if it dissolves from Zr beaker

Major soil components (beside Si):

Al, Ca, Fe

IAEA SRM	Concentration in soil, mg/kg			ug/kg
	Al	**Ca**	**Fe**	**Zr**
375-Brjansk soil	44290	14270	11000	334
326-Kursk soil		10900	28200	390
300-Baltic sea sediment		10000	**50000***	
367-Pacific ocean sediment		**400000***	10000*	

*estimated by AAS

Batch uptake experiments to study Fe interference

4M HCl/Na_2SO_3

- Am and Pu(III) are better retained in presence of Na_2SO_3
- Th and U are not much affected.

4M HCl/Fe(III)

- Am and Pu(III) are better retained in presence of $FeCl_3$.

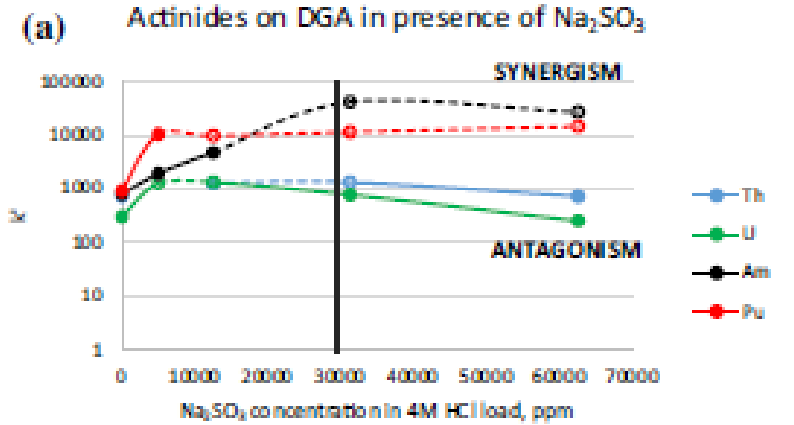
  $Am(FeCl_4^-)_3.(DGA)_3$?

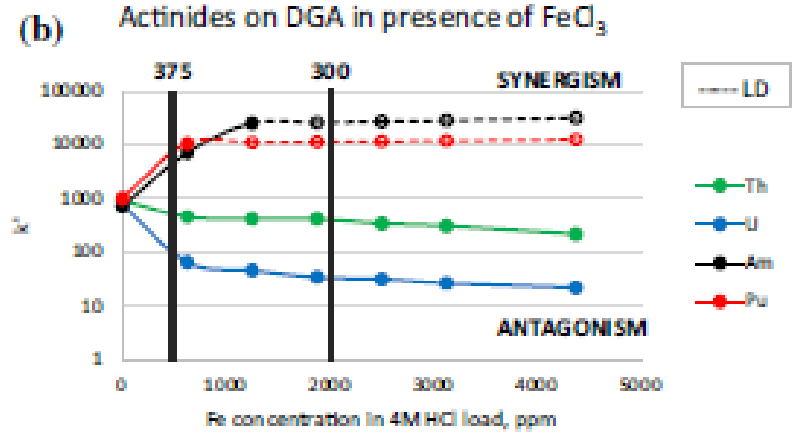
- Th and U are less retained.
  U losses may occur.

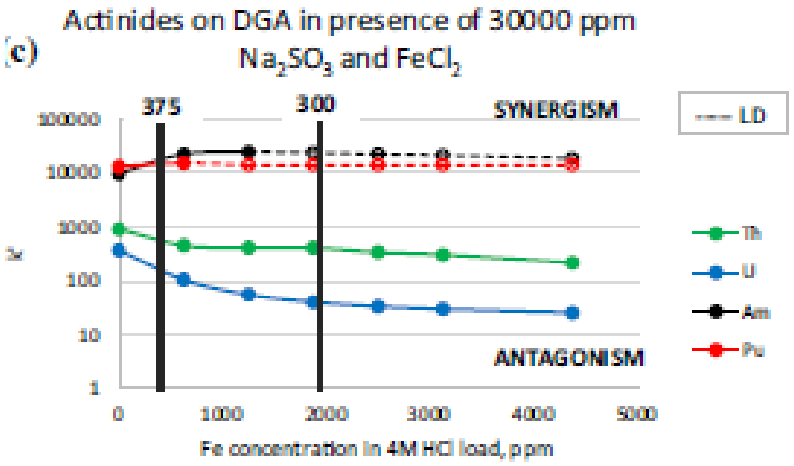
  $FeCl_3.(DGA)_3$?

4M HCl/Na_2SO_3/Fe(II)

- Am and Pu(III) are better retained in presence of $FeCl_2$.
- Th and U(IV) are less retained.
  U losses may occur..







Batch uptake experiments to study Ca interference

4M $HCl/CaCl_2$

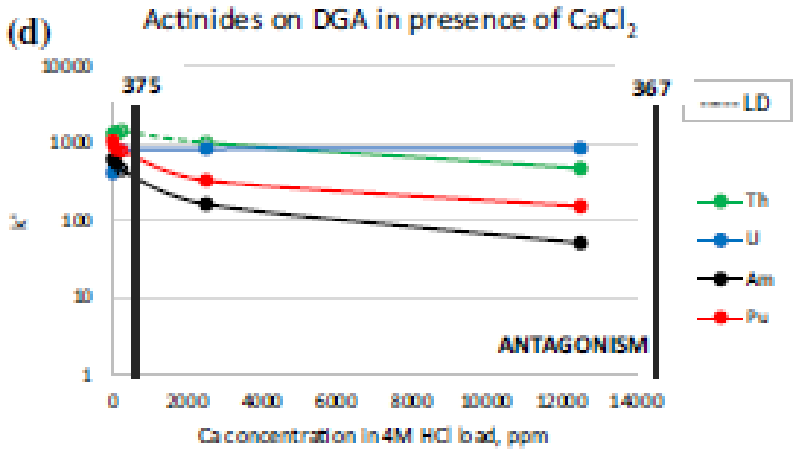
- Am and Pu(?) are less retained in presence of $CaCl_2$
  Am, Pu losses may occur.
- Th and U are not much affected.

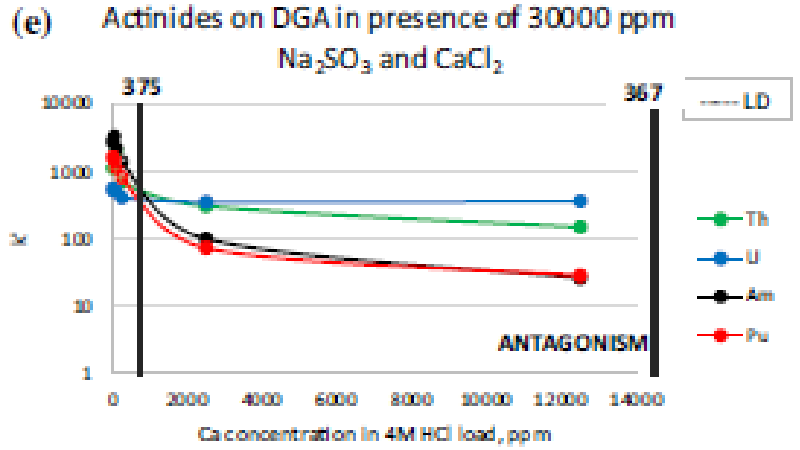
4M $HCl//Na_2SO_3/Ca$

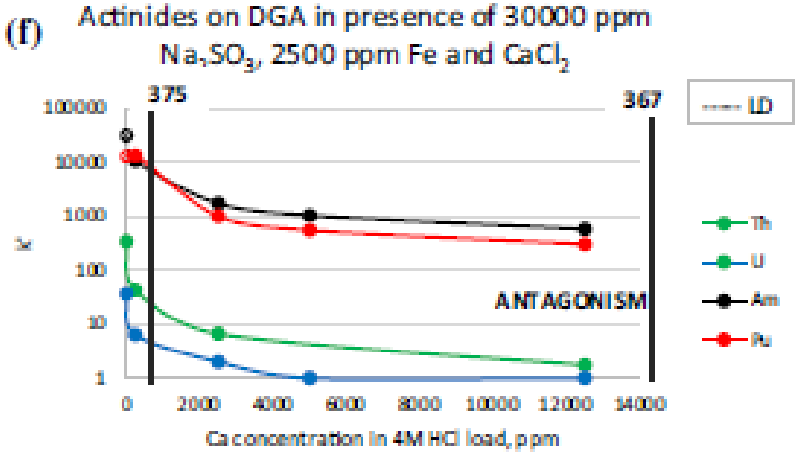
- Am and Pu(III) are less retained in presence of $CaCl_2$.
  Am, Pu losses may occur.
- Th and U are less retained.

4M $HCl/Na_2SO_3/Fe(II)/Ca$

- Am and Pu(III) are less retained in presence of $FeCl_2$ & $CaCl_2$.
- Th and U(IV) are much less retained.
  U and Th losses occur.







Actinides pre-concentration

Goal:

- remove the silica content

- adjust the Fe concentration in the optimized region (reduce Fe concentration)

- minimize the Ca concentration

Solution:

- in NaOH Na_2SiO_3 is soluble while actinides are adsorbed on hydroxide precipitates,
- in HF $[SiF_6]^{2-}$ is soluble while actinides are adsorbed on fluoride prcipitates

in HF $[FeF_4]^-$ is soluble while actinides are adsorbed on fluoride prcipitates

sub-stoichiometric precipitation of Ca in presence of a less soluble alkaline earth metal precipitate:

	solubility product
$Ca(OH)_2$	K_{sp}=5.5E-6
$Mg(OH)_2$	K_{sp}=5.61E-12

Ca2+ remains in solution while actinides are adsorbed on $Mg(OH)_2$ precipitate
supposing that Mg does not interfere with actinides on DGA

Actinides pre-concentration

Sub-stoichiometric precipitation of Ca in presence of Mg

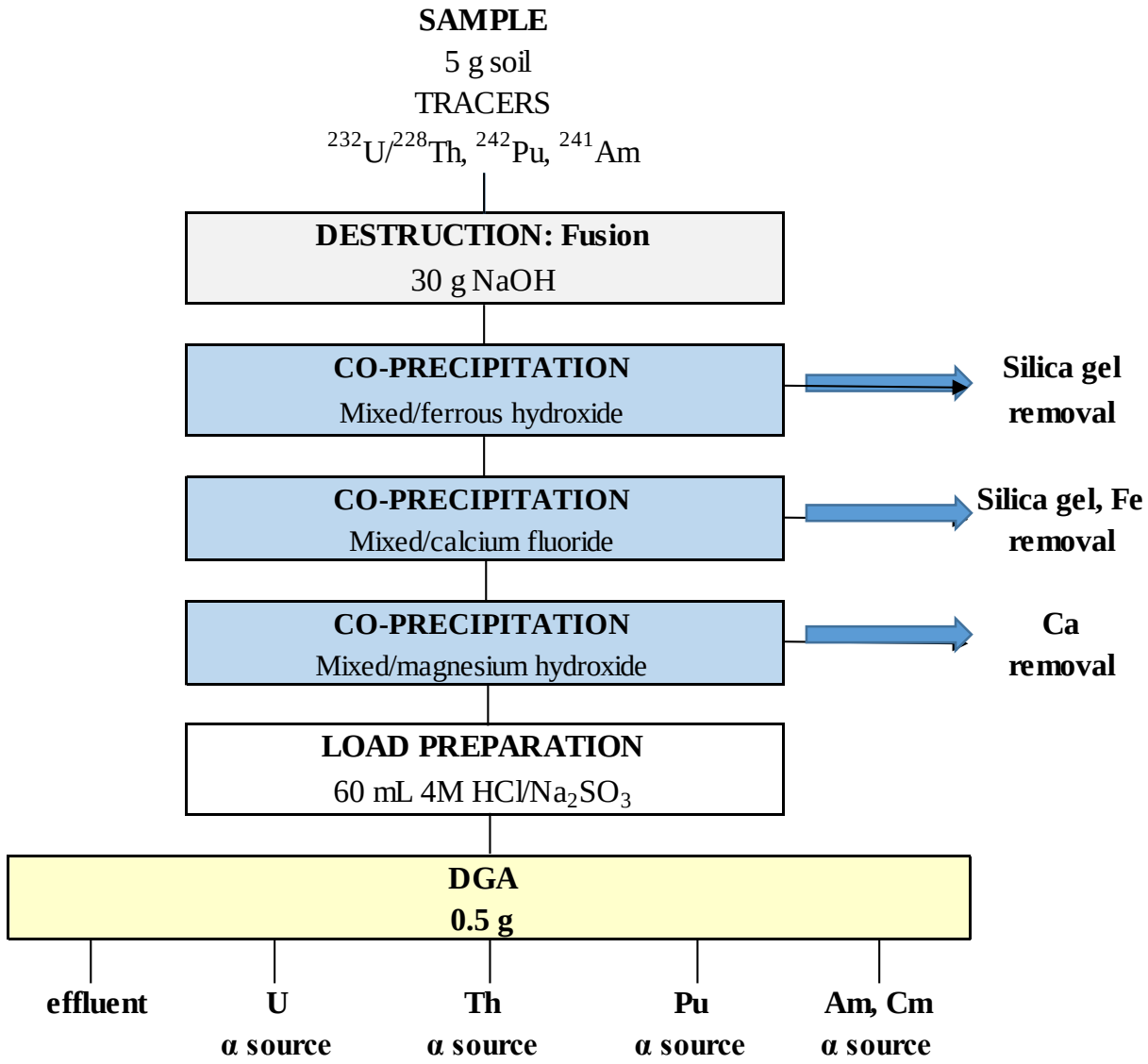
	$Ca(OH)_2$ test only Ca present	mixed $Mg(OH)_2/Ca(OH)_2$ test Ca and Mg present	
Ca in original solution, mg	150	150	
Mg in original solution, mg	0	84	
5M NaOH volume , µL	% of Ca precipitated	% of Ca precipitated	% of Mg precipitated
500	0	14	0,4
750	17	9	7,7
1000	30	14	36
1500	65	14	67

Remark: Theoretically 1500 µL 5M NaOH is equivalent with Ca or Mg in sample

Actinides retained on Mg(OH)2

5M NaOH volume , µL	**pH**	**Am** %	**U** %	**Pu** %	**Th** %
100	**2**	**23**	**6**	n.m.	n.m.
500	**3-3.5**	**87**	**96**	**86**	**80**
750	**7**	n.m.	n.m.	**95**	**79**
1000	**8-8.5**	**85**	**97**	**99**	**83**
1500	**9**	**86**	**104**	**103**	**93**

Flowchart
Destruction with fusion + preconcentration + DGA separation



Actinides in soil and sediment
Results

SRM code	Sample weight g	Load volume mL	Chemical recovery, % U	Th	Pu	Am
IAEA-375	5	60	83	16	85	95
IAEA-326	5	60	64	33	62	100
IAEA-300	5	60	75	2	95	92
IAEA-367	5	60	82	5	54	97
Average			**76**	14	**74**	**96**

- Chemical recoveries for U, Pu, Am (+Np) are acceptable high.
- The method is not adequate for Th determination.
- Decontamination factors for other actinides are high.
- The procedure can be performed in 2 days.
- The procedure is robust.

Separation of Am from lanthanides

Goal:

Separation of Am-Cm from Lns on the same DGA column used for Acs separation in order to obtain a thin α source for Am-Cm determination

Solution:

Elution sequence on the standard DGA column was optimized with model solutions of mixed Lns and Am.

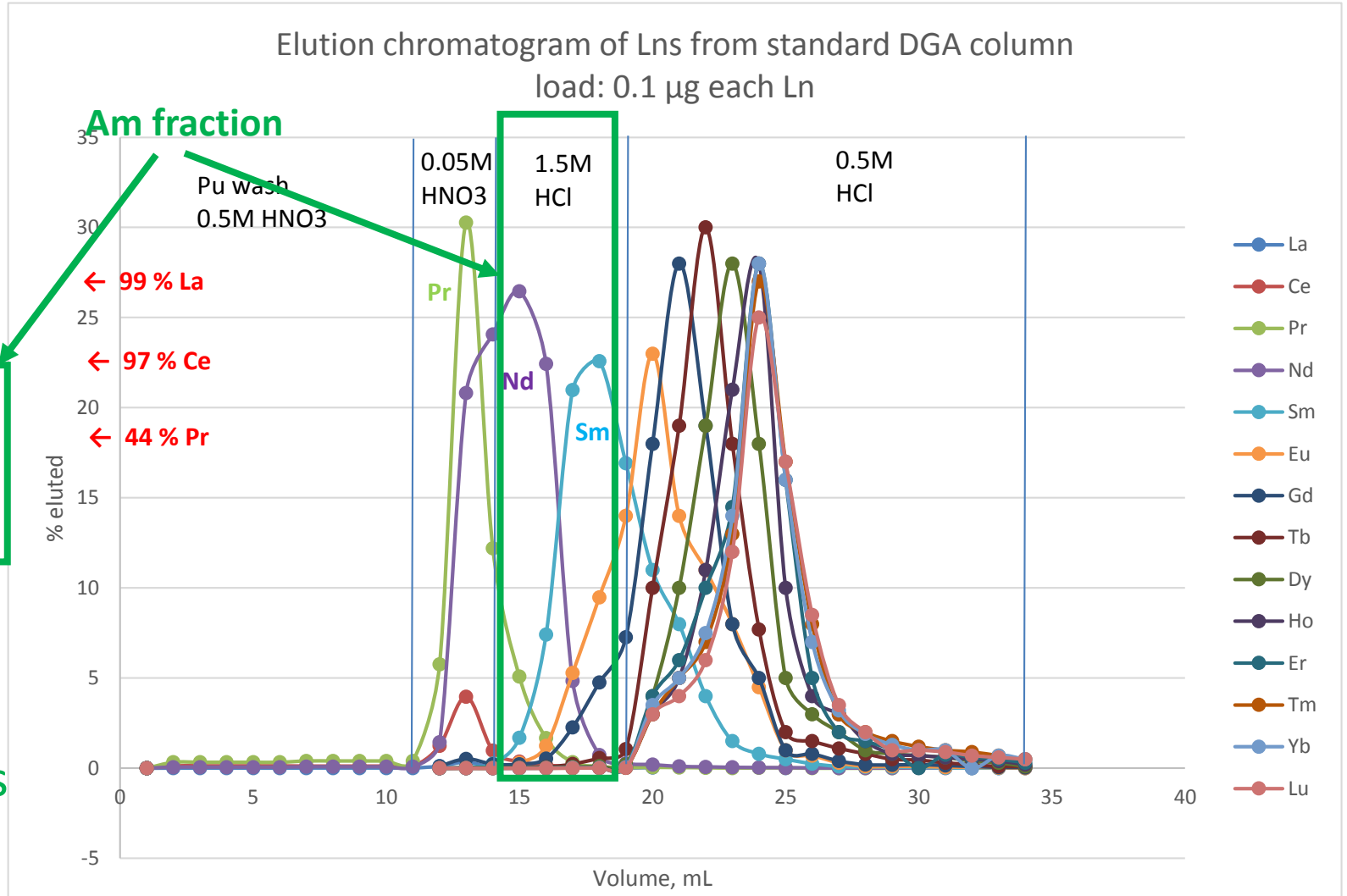
Separation of Am from lanthanides

Ln s in Am strip:
5 mL 1.5M HCl

	Model	5g IAEA-300
La	0.1%	0.002 µg
Ce	0.7%	0.11 µg
Pr	7%	1.5 µg
Nd	55%	86 µg
Sm	70%	25 µg
Eu	29%	1.8 µg
Gd	15%	4.6 µg
Tb-Lu	<3%	<0.3 µg

Σ 119 µg out of 340 µg Lns

Good quality Am α source



Measurements by M. Braun, Isotoptech Zrt.

Summary

A new procedure *for the separation of U, Pu, Am-Cm (and Np) in soil and sediment samples has been developed using a single DGA resin column.*

For all actinides *(with the exception of Th)*

- *chemical recoveries are acceptable high (>50%),*
- *decontamination factors are acceptable high (>100),*
- *resolution of the alpha sources is acceptable good (< 40 keV),*
- *sensitivities are acceptable high (<0.1 Bq/kg)*

The whole analysis can be done in ***2 days****.*

adequate

for routine analysis

of environmental samples

Thank you for your attention!