RAPID METHOD FOR DETERMINATION OF ACTINIDES AND ^{90}Sr FROM SMALL AMOUNTS OF SAMPLES

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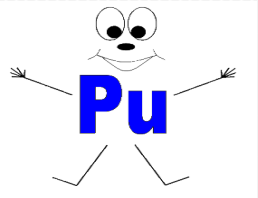
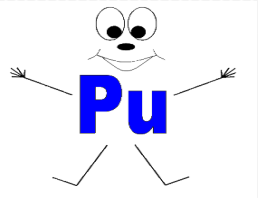


CONTENT

- Long-lived radionuclides from nuclear facilities
- Rapid separation procedure for actinides
  - Examples for actinides measurements
- Extension of rapid method for Sr isotopes determination by β spectrometry
  - Examples for Sr determination



ACTINIDES

LONG-LIVED ACTINIDES RELEVANT IN ENVIRONMENTAL MONITORING AND RADIOACTIVE WASTE ANALYSIS

Isotope	Half life		Decay mode	Specific activity Bq/g
^{89}Sr	50	d	β–	1,09E+15
^{134}Cs	2,06	y	β–, γ	4,78E+13
^{55}Fe	2,73	y	EC	8,36E+13
^{125}Sb	2,76	y	β–, γ	3,82E+13
^{60}Co	5,27	y	β–, γ	5,88E+13
^{228}Ra	5,75	y	β–	1,01E+13
^{3}H	12,30	y	β–	3,57E+14
^{241}Pu	14,35	y	β–	3,82E+12
^{93m}Nb	16,1	y	EC	8,81E+12
^{244}Cm	18,1	y	α	3,00E+12
^{210}Pb	22,3	y	β–, γ	2,83E+12
^{90}Sr	29,1	y	β–	5,06E+12
^{137}Cs	30,2	y	β–, γ	3,20E+12
^{238}Pu	87,7	y	α	6,34E+11
^{63}Ni	100,1	y	β–	2,10E+12
^{241}Am	432,2	y	α	1,27E+11
^{226}Ra	1600	y	α	3,66E+10
^{14}C	5730	y	β–	1,65E+11
^{240}Pu	6563	y	α	8,40E+09
^{94}Nb	20300	y	β–, γ	6,91E+09

Isotope	Half life		Decay mode	Specific activity Bq/g
^{239}Pu	24110	y	α	2,30E+09
^{230}Th	75380	y	α	7,63E+08
^{59}Ni	76400	y	EC, β+	2,94E+09
^{41}Ca	0,103	My	EC	3,14E+09
^{233}U	0,1492	My	α	3,80E+08
^{99}Tc	0,211	My	β–	6,34E+08
^{234}U	0,2455	My	α	2,30E+08
^{36}Cl	0,301	My	β–	1,22E+09
^{242}Pu	0,3733	My	α	1,46E+08
^{79}Se	1,13	My	β–	2,08E+08
^{93}Zr	1,53	My	β–	9,27E+07
^{237}Np	2,144	My	α	2,60E+07
^{135}Cs	2,3	My	β–	4,26E+07
^{107}Pd	6,5	My	β–	1,90E+07
^{129}I	15,7	My	β–	6,49E+06
^{236}U	23,4	My	α	2,40E+06
^{244}Pu	80,8	My	α	6,71E+05
^{235}U	703,8	My	α	8,00E+04
^{238}U	4468	My	α	1,24E+04
^{232}Th	14050	My	α	4,06E+03

Analyses:
by alpha and beta spectrometry

Requiremets: complete separation

RAPID METHOD

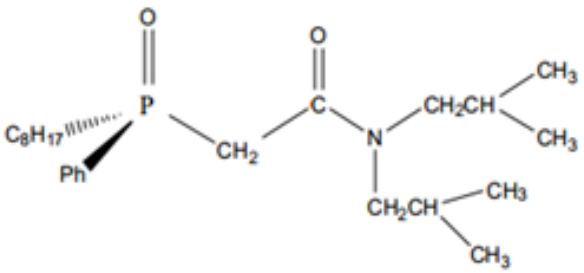
Recommended procedure IAEA/AQ/11 (2009) developed by Nóra Vajda, et al
Simultaneous determination of actinides on a single column filled **with TRU resin** from small amounts of sample

Advantage for emergency and nuclear waste analysis

rapid: within 1 day
small sample: 0.1 – 1 g solid sample
less than 10 ml liquid sample

Provide adequate information on environment in emergency situation
Characterisation of nuclear waste
Control of contamination after work with radioisotopes (Decontamination and Decommissioning of nuclear facilities)
Safeguards

TRU resin

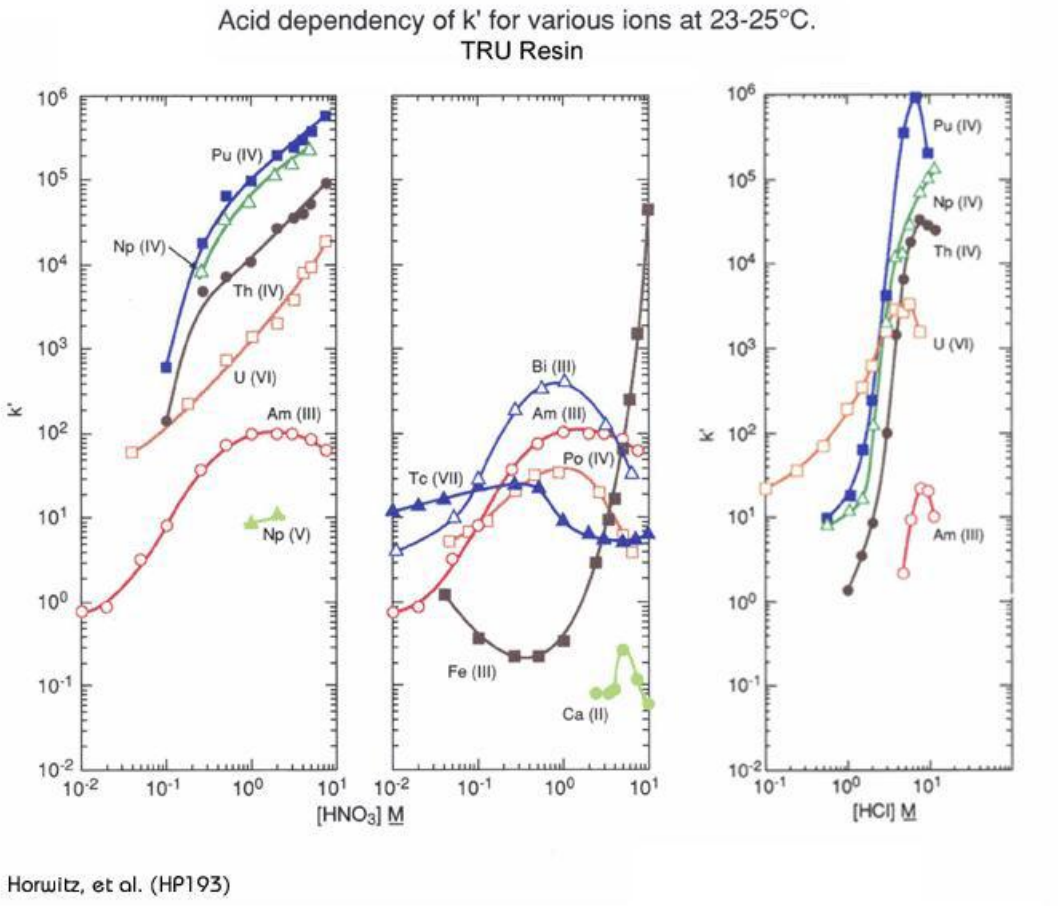


carbamoyl-methyl-phosphine oxide (CMPO)

-Extractant: CMPO / TBP

-Retention of Pu(IV) Th(IV) Np(IV)

-U(VI) and Am(III)



FLOW CHART OF RAPID RADIOCHEMICAL PROCEDURE

ACID DIGESTION or FUSION
dissolution: 1M HCl

→ Fast and complete destruction

ADDITION TRACERS & CARRIER
Tracer: ^{242}Pu, ^{243}Am,^{232}U
Carrier : Sr

→ to determine chemical recovery

reduction
CaF_2 or $Ca(COO)_2$
CO-PRECIPITATION

CHEMICAL SEPARATION
TRU extraction chromatography

SOURCE PREPARATION
micro-coprecipitation

MEASUREMENT
by α spectrometry

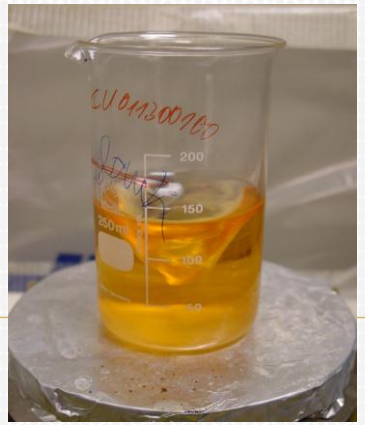
Advantage
less reagents and chemicals are used
less hazardous waste is produced, and
the process is more economic

Complete sample destruction /dissolution

Samples: liquid or solid environmental samples or waste from NPP

Conventional technique
wet digestion: evaporation on a hot plate with mineral acids

to destroy organics, possible complexing agents
<10 ml liquid waste



Rapid technique
Fusion: In Pt crucible with gas burner with alkaline flux

The fusion melt is dissolved in 1M HCl
up to 1 g of soil or sediment

0.5 g dry sample
Reagents
0.2 g $NaNO_3$ (oxidizing agent)
0.2 g Na_2CO_3 (additive)
2.0 g $LiBO_2$
0.1 g KI (non weting agent)

Co-precipitation of actinides

necessary reductive media to avoid losses: Pu(III) U(IV)
+Mohr's Salt + hydrazine

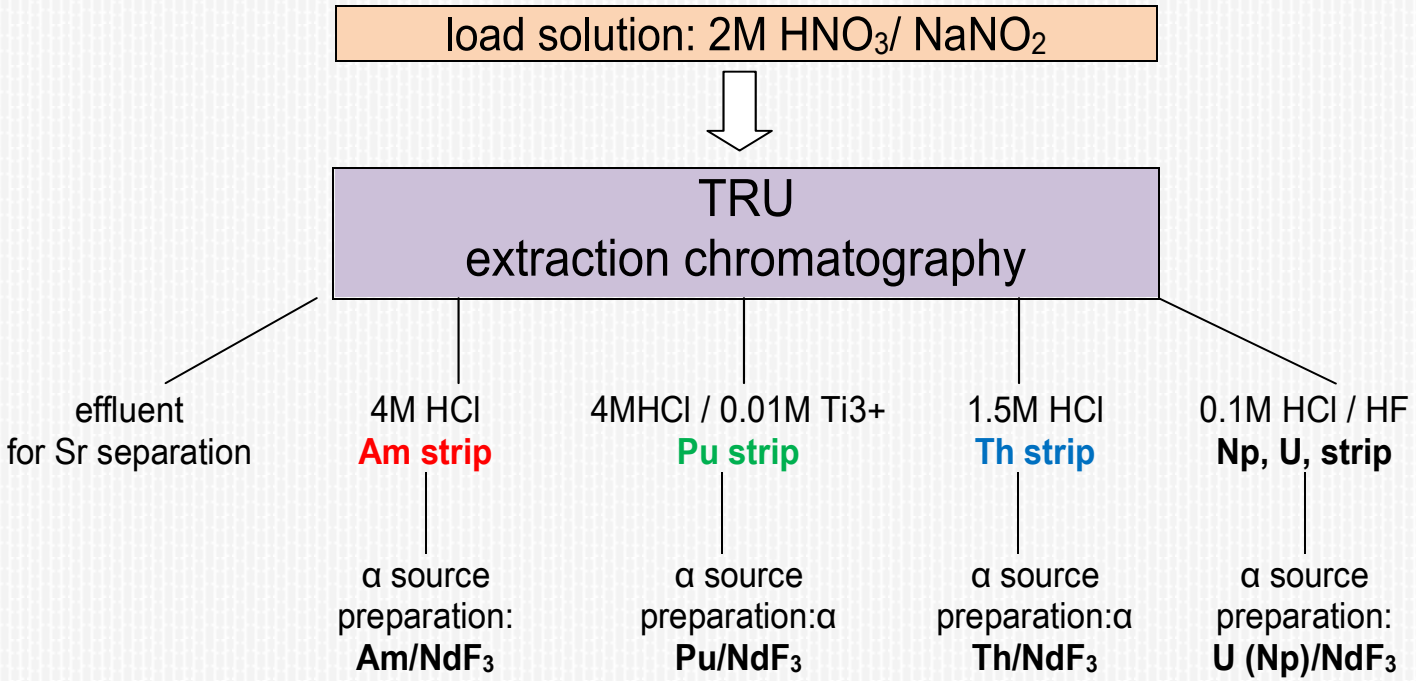
CaF_2

- fusion melt is in 100 ml 1M HCl
  + Ca
  + 20-30 mL 40% HF
- Heated then cooled down
- Filtration through 0.45 µm pore size membrane.
- Solution in 2M HNO_3 / H_3BO_3

$Ca(COO)_2$

- Dry residue is solved in 50 ml 1M HCl
- Ca and oxalic acid to samples
  pH 4-5
  heated , cooled down
- Filtration through 0.45 µm pore size membrane
- destroy oxalate with cc HNO_3
- dry residue is taken up in 2 M HNO_3
- adjust oxidation state with hydrazine and stabilize with $NaNO_2$

Extraction chromatography



Source preparation and nuclear measurement

α Source preparation

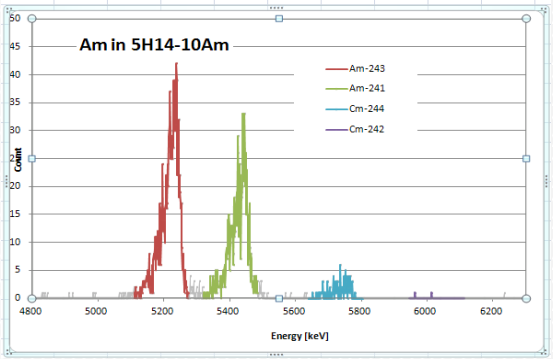
Strip solution
50µg Nd/100µl
5 ml 40 % HF
Pu , U +Mohr's salt
Filtration of micro-precipitate

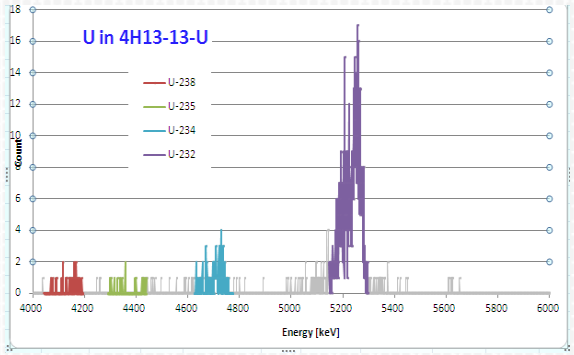
Measurement by α spectrometry
Si semiconductor (PIPS) detector

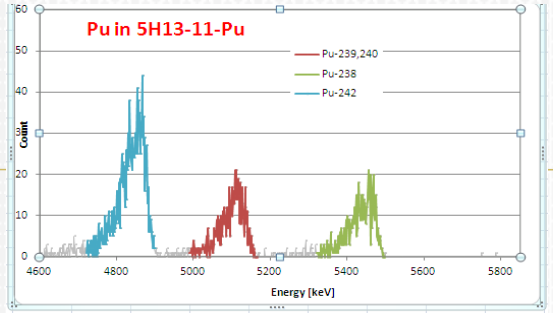
Detection limit 0.1 mBq

Requirements for α source

Purity of source
Infinetly thin layer ⇨ good resolution of α spectra







Chemical yield

radioactive waste routine analysis

Waste samples from NPP 2012

	Sample V mL	U yiel %	Pu yield %	Am-Cm- yield %
H12-9	0.0015	41%	41%	65%
H12-11	1	34%	76%	67%
H12-12	0.01	69%	51%	46%
H12-13	10	69%	67%	75%
H12-14	10	87%	42%	56%
H12-15	1	94%	68%	48%
H12-4	10	70%	84%	119%
H12-5	10	81%	80%	95%
H12-6	10	92%	84%	100%
Average		**71%**	**66%**	**75%**

Environmental reference material analysis

Soil and sediment samples

Sample code	Am yield	Pu yield	Th yield	U yield
IAEA-384	96%	91%	72%	91%
IAEA-367	100%	92%	95%	92%
IAEA-368	93%	94%	73%	81%
NIST-4357	103%	91%	94%	91%
IAEA-385	91%	59%	84%	21%
IAEA-135	89%	75%	83%	43%
Average	**96%**	**85%**	**84%**	**75%**

Results of analysis of waste samples from NPP using TRU resin

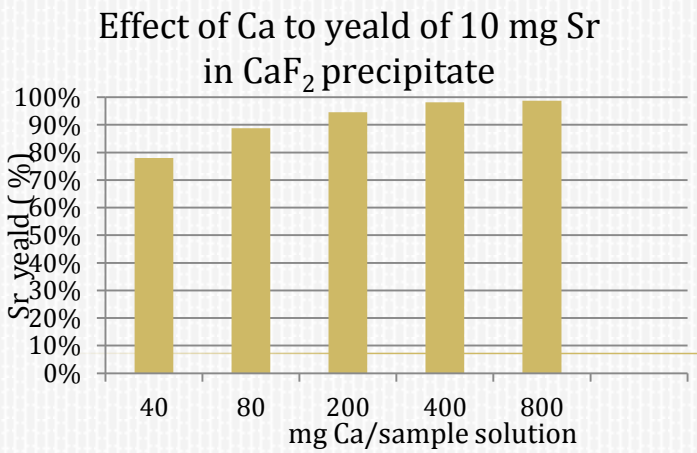
Container code	top layer			middle layer			bottom layer		
	act. (Bq/l)		σ (Bq/l)	act. (Bq/l)		σ (Bq/l)	act. (Bq/l)		σ (Bq/l)
U-234	3,68E+00	±	9,0E-01	4,34E+00	±	9,9E-01	3,39E+01	±	6,9E+00
U-235		≤	1,2E+00		≤	1,5E+00		≤	7,7E+00
U-238	1,61E+00	±	5,6E-01	8,60E-01	±	4,9E-01	8,79E+00	±	3,6E+00
Pu-239,240	1,21E+02	±	5,8E+00	1,53E+02	±	5,4E+00	1,25E+04	±	4,1E+02
Pu-238	1,35E+02	±	6,3E+00	1,88E+02	±	6,6E+00	1,38E+04	±	4,5E+02
Am-241	5,05E+01	±	6,0E+00	1,00E+02	±	4,7E+00	1,33E+04	±	4,6E+02
Cm-244	1,29E+01	±	2,8E+00	1,48E+01	±	1,4E+00	2,77E+03	±	1,2E+02
Cm-242		≤	6,6E+00		≤	1,4E+00	3,81E+01	±	9,5E+00

≤10 mL sample

TRU method

Sr separation fitted to rapid method for actinde

ICP MS measurements	Chemical yields (%) during CaF_2 co precipitation			
	IAEA soil-6	IAEA- SL-3 sediment	NBS-4355	NIST694 phosphate ore
Ca	46	34	17	45
Sr	48	74	83	67



ACID DIGESTION or FUSION
dissolution: 1M HCl

ADDITION TRACERS & CARRIER
Tracer: ^{242}Pu, ^{243}Am,^{232}U
Carrier : Sr

reduction
CaF_2 or $Ca(COO)_2$
CO-RECIPITATION

CHEMICAL SEPARATION
TRU extraction chromatography

Sr separation on Sr resin from efluent of TRU column

SOURCE PREPERATION
micro-coprecipitation

MEASUREMENT
by α spectrometry

Method for Sr determination

a

Sr separation

effluent from TRU column (2M HNO_3)

↓

Adjust load to 3M HNO_3

↓

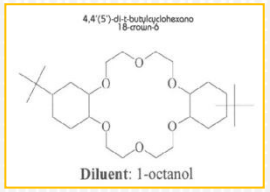
Radiochemical separation of Sr
3 g Sr resin in column

↓

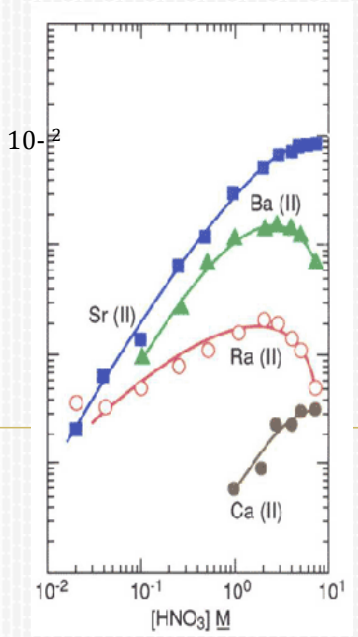
Sr-oxalate precipitation → Chemical yeald determnation by gravimetry

↓

Measurement of Sr isotopes by LSC



acid dependence of k' for alkaline earth element



Results of analysis of Sr isotope in swipe and waste samples

RA cod	DM1		DM2	
	Calcium oxalate precipitate			
isotopes	yeald %	activity± σ Bq/sample	yeald %	activity± σ Bq/sample
Sr-89	64%	LD ≤ 0.01	63%	LD ≤ 0.009
Sr-90		0.477 ± 0.058		0.37 ± 0.058

RA cod	H12-12			H12-11		
	Calcium fluorid precipitate					
	ml	yeald	activity± σ Bq/l	ml	yeald	activity± σ Bq/l
Sr-89	0.1	86%	LD ≤ 6.8E+03	1	79%	LD ≤ 2.6E+02
Sr-90			3.04E+05 ± 2.3E+04			3.5E+03 ± 2.5E+02

actinide recovery from swipe samples

	chemical yield	
	DM1	DM2
	oxalate pr.	
U	89%	95%
Pu	60%	52%
Am	59%	60%

actinide recovery from waste samples

	chemical yield	
	H12-12	H12-11
	fluorid pr.	
U	63%	54%
Pu	66%	76%
Am	72%	67%

Conclusion

- This radiochemical procedure is capable for rapid determination of actinides (Am PU, Th, and U radioisotopes) and Sr isotopes in small amounts of contaminated samples (swipe, waste, sediment) by alpha spectrometry.

- The procedure is based on wet digestion of liquid samples and fusion of solid samples with $LiBO_2$.

- CaF_2 or $Ca(COO)_2$ co-precipitation is used for pre-concentration of actinides and Sr.

- Ca addition to the sample makes Sr precipitation complete and the method becomes suitable for Sr isotopes determination from the same samples.

References

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Thank you for your attention