Recent applications of Plastic Scintillation Resins

A. Tarancón, H. Bagán, I. Giménez, A. Coma, X. Mendo, Y. Zhou

Raddec-Triskem International Workshop

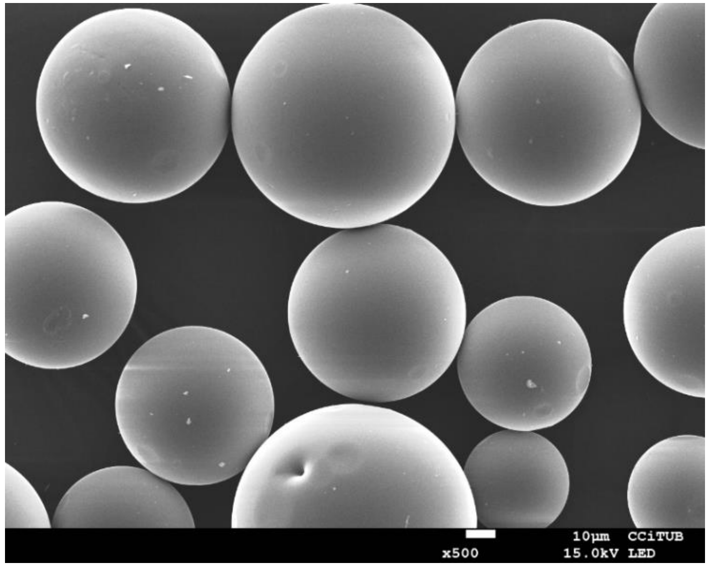
April of 2024

UNIVERSITAT DE BARCELONA

OUTLINE

- **Plastic Scintillators and Plastic Scintillation Resins**
- **TK-TcScint**
- **TK-SrScint**
- **α-PSresin**
- **PSkits**
- **On going developments**

Plastic Scintillators as an alternative to LSC



As the diameter is low (10 to 100 micrometers) beta and alpha particles emitted in the solution are capable to reach the scintillator.

- ✓ No mixed-waste
- ✓ Caducity time
- ✓ New applications
- ✓ On-line detection
- ✓ Modified surface

→ **Radioactivity measurements**

→ **Radioactivity Sensors**

→ **Extractive plastic scintillators**

✓Solid solution of fluorescent solutes into polystyrene.

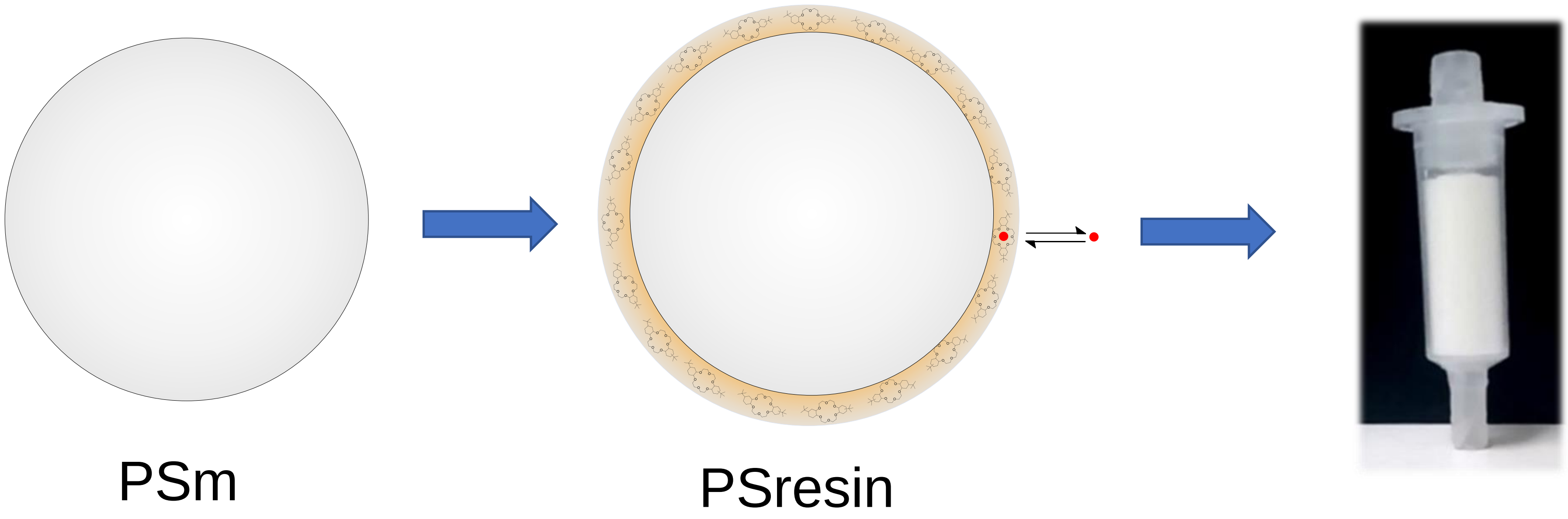
✓Size between 10-100 micrometers

PSresin: Extractive Plastic Scintillators

- ✓ The measurement of alpha and beta emitters though liquid scintillation IS NOT SELECTIVE
- ✓ Several previous steps are needed (precipitation, SPE,…)

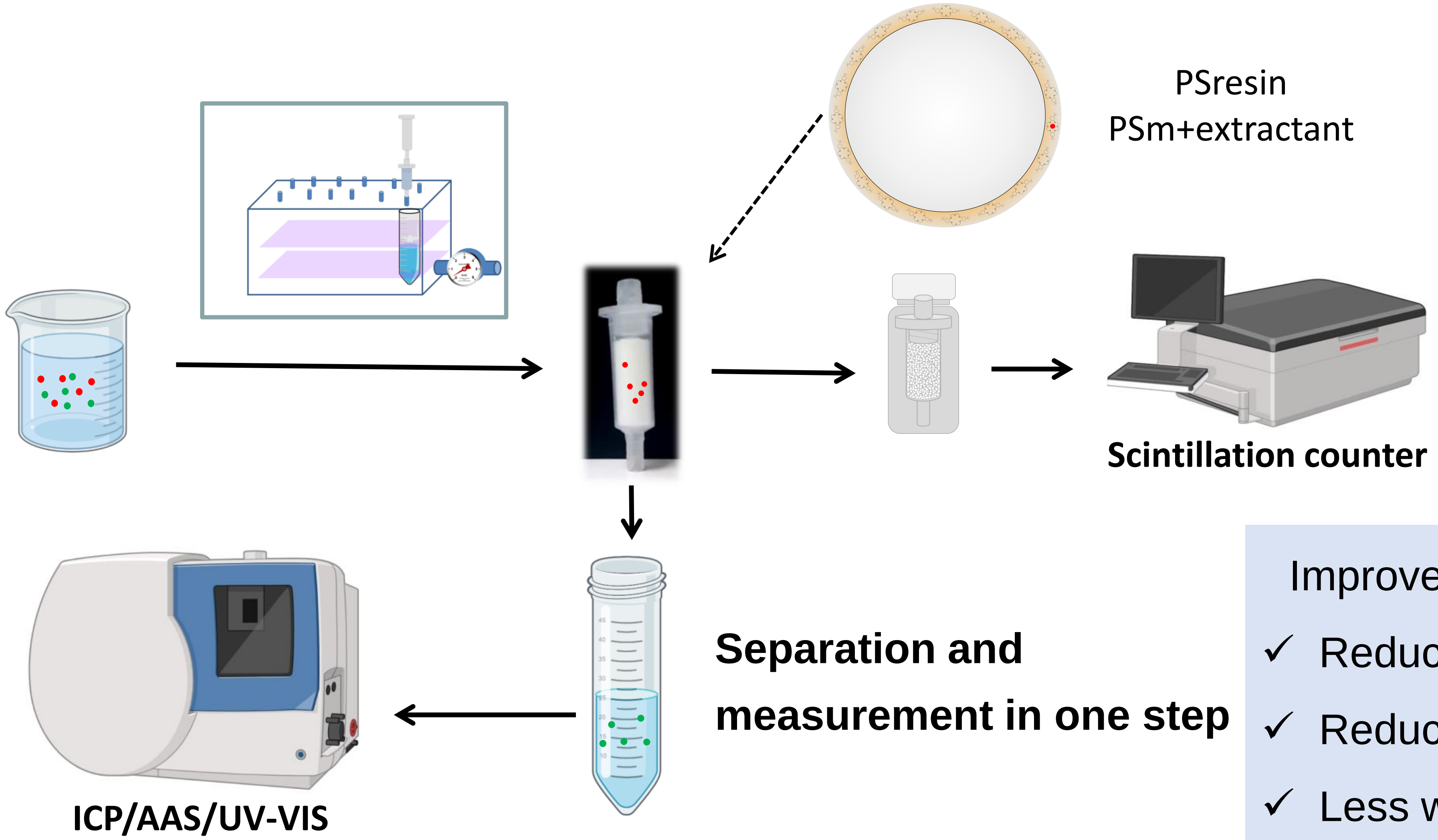
Extractive plastic scintillators (PSresin)

Plastic Scintillation microsphere coated with a selective extractant



UNIVERSITAT DE BARCELONA

PSresin: Plastic Scintillation Resins



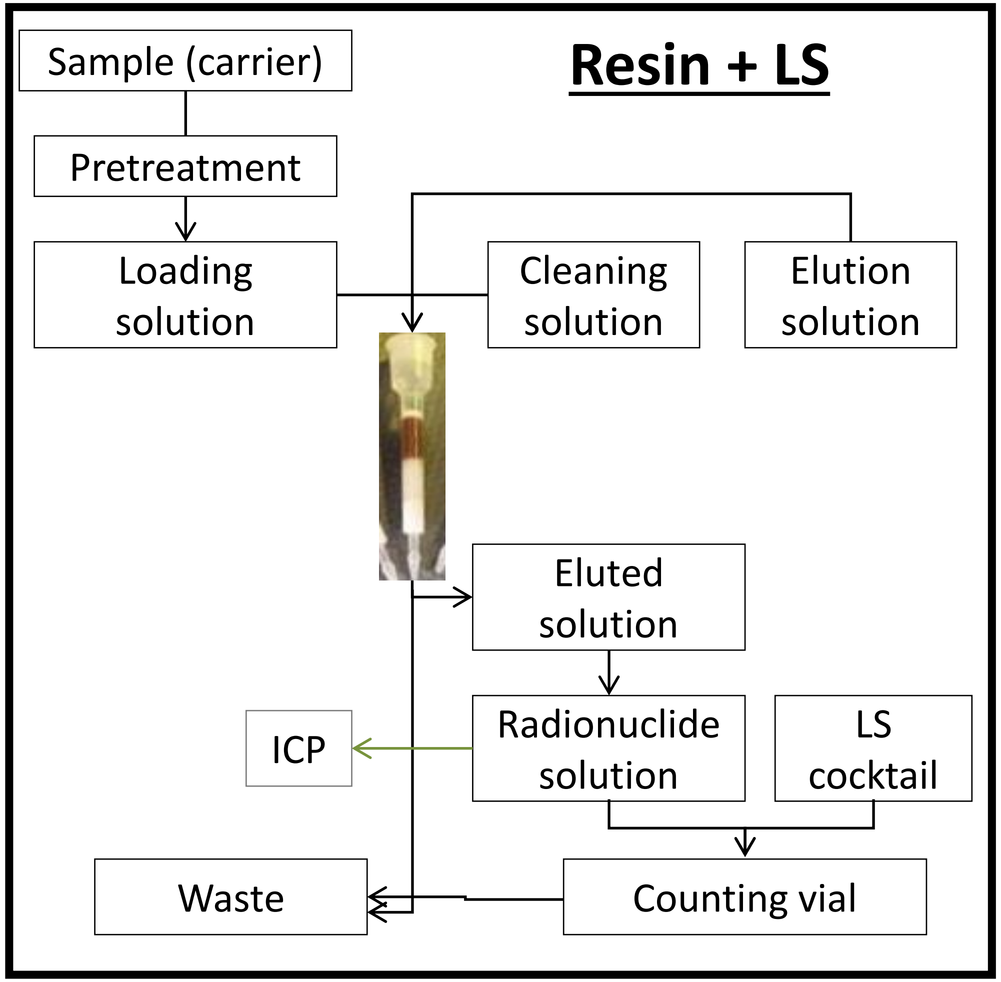
Separation and measurement in one step

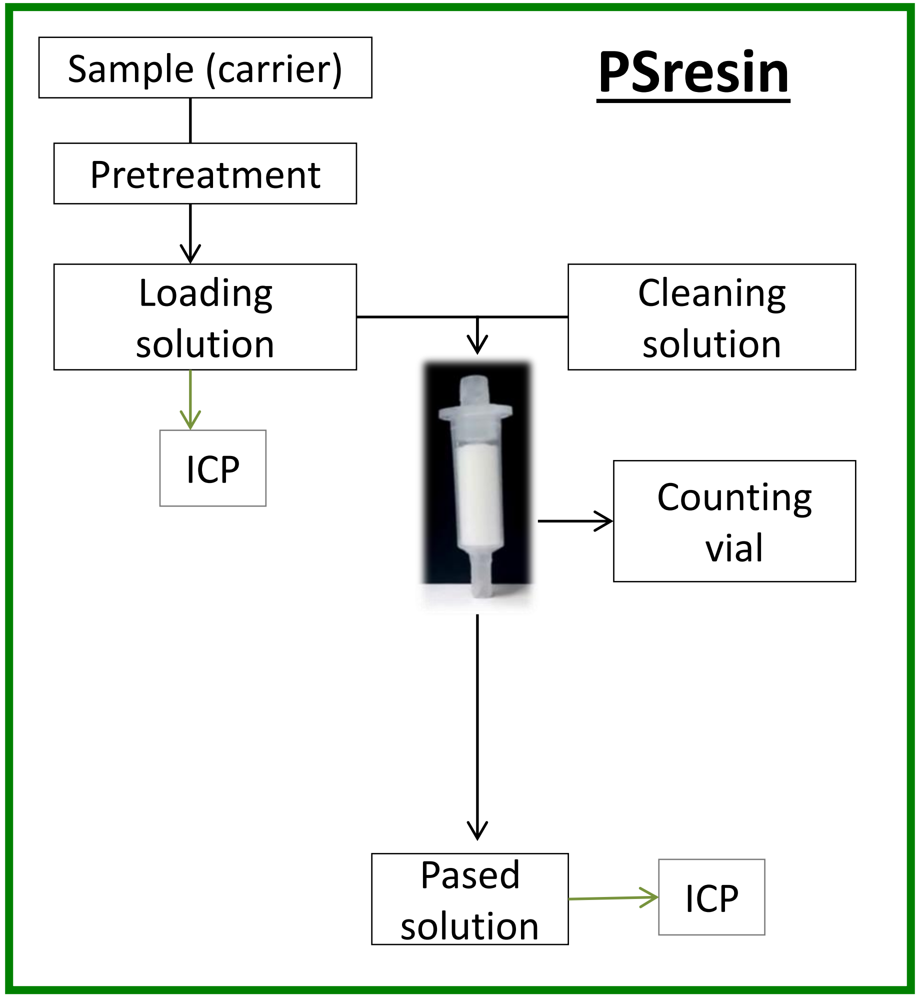
Improvement on productivity:

- ✓ Reduce time of analysis
- ✓ Reduce reagents
- ✓ Less waste

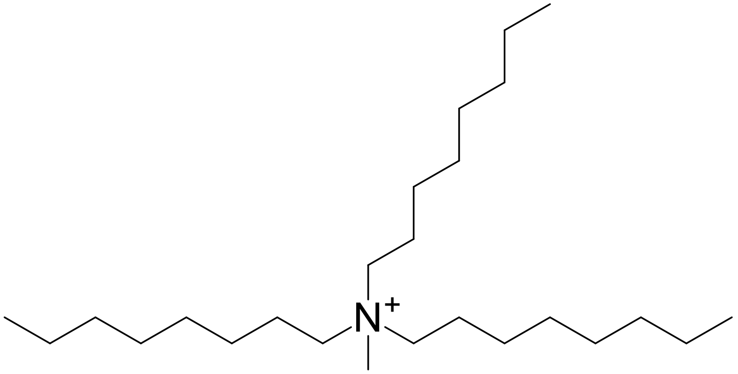
UNIVERSITAT DE BARCELONA

PSresin: Plastic Scintillation Resins

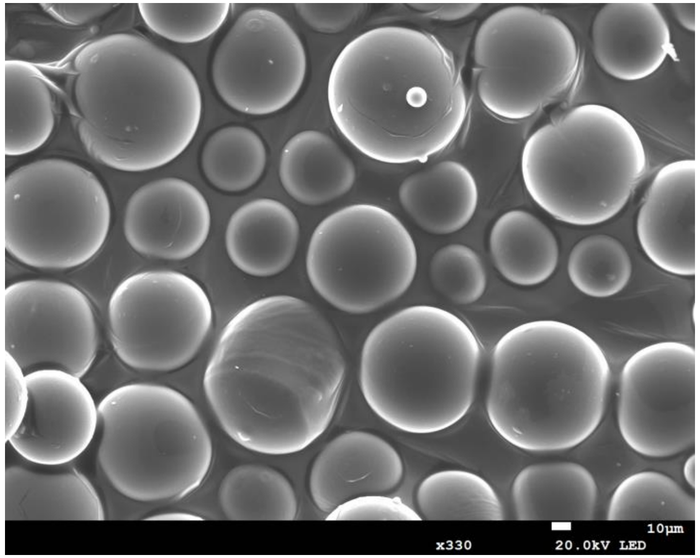




1. TK-TcScint PSresin



Aliquat·336



TRISKEM
Expertise in Separation Chemistry

PRODUCT SHEET

TK-TcScint

Main Applications

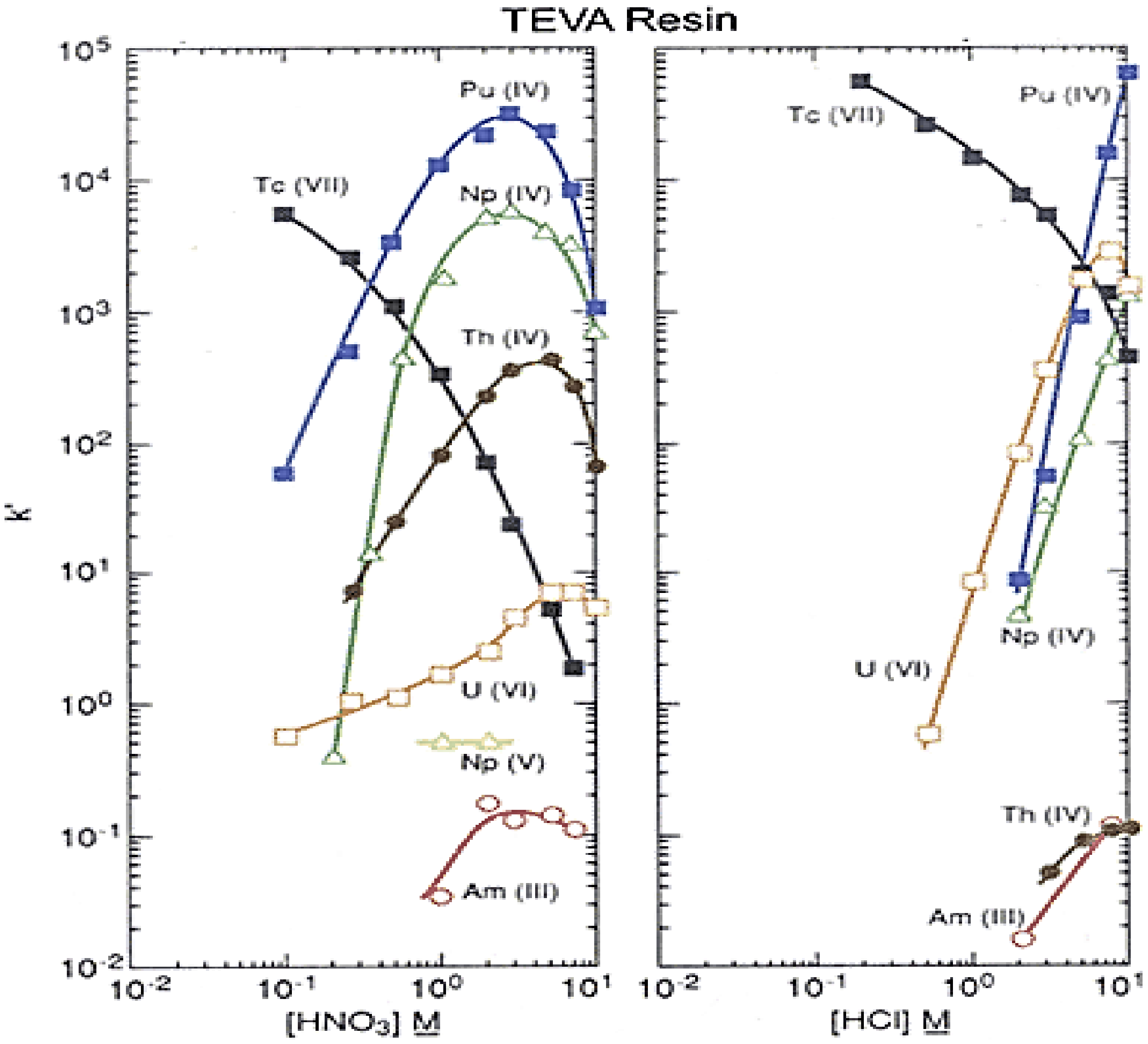
- Separation and LSC measurement of technetium

↓

- **^{99}Tc**
- ^{210}Po
- ^{36}Cl
- Pu Isotopes
- $S^{14}CN^-$

UNIVERSITAT DE BARCELONA

1. TK-TcScint PSresin



1A. ^{99}Tc analysis in TK-TcScint

Conditioning: 2 mL HCl 0.1M

Sample: 10 mL in HCl 0.1M

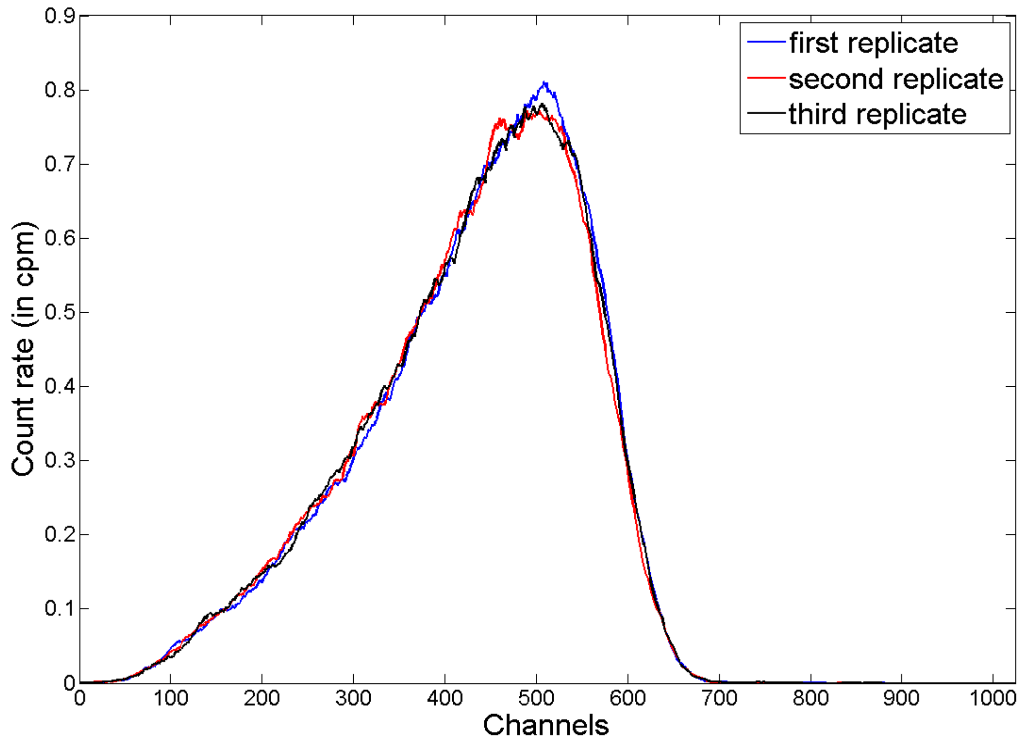
Cleaning: 2 mL water 4 times

Cleaning (if U present): 2 mL 0.1 HNO3/ 0.1M HF three times

Tracer: 1 mg of Re

Recovery of Rhenium (by ICP-OES)	> 98.8 %	(n=4)
Recovery of ^{99}Tc (by LS):	> 98.8 %	(n=3)
^{99}Tc Detection Efficiency (%):	89.5(0.6)	(n=3)
Background (cpm):	1.09	(n=1)
Quenching Parameter (SQP(E)):	787(7)	(n=4)

- **Breakthough volumen >200 mL**



- ✓ Surface water
- ✓ Seawater
- ✓ Urine

UNIVERSITAT DE BARCELONA

1B. Pu isotopes analysis with TK-TcScint

UNIVERSITAT POLITÈCNICA DE VALÈNCIA

1. Valence adjustment to Pu (IV):

Pu → Pu (III) → Pu (IV)

- 20 µL of a 0.6 M solution of iron sulphamate (II)
- 1 mL of 1.5 M ascorbic acid
- 1 mL of 3.5 M sodium nitrite solution

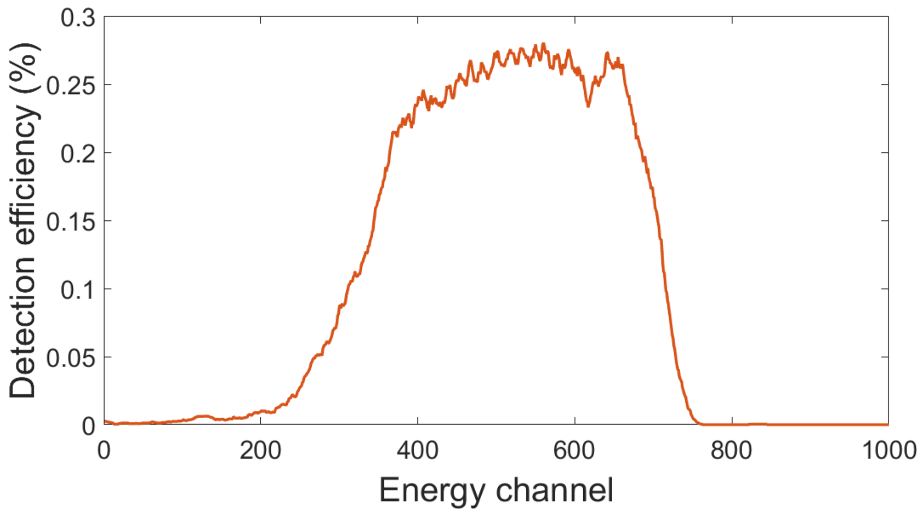
2. Loading medium:

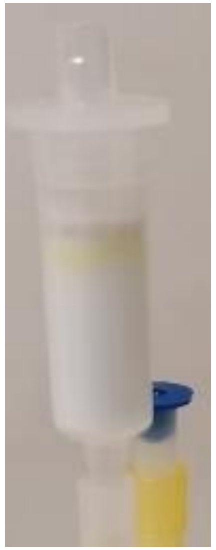
- HNO_3 3 M/ $Al(NO_3)_3$ 0.5 M/ HCl 1M

3. Rinse media:

- 2 mL (2 times) HNO_3 3 M
- 2 mL (2 times) HCl 9 M
- 2 mL (2 times) HNO_3 0.5 M

➢ **Stable tracer: 0.25 mg Au**



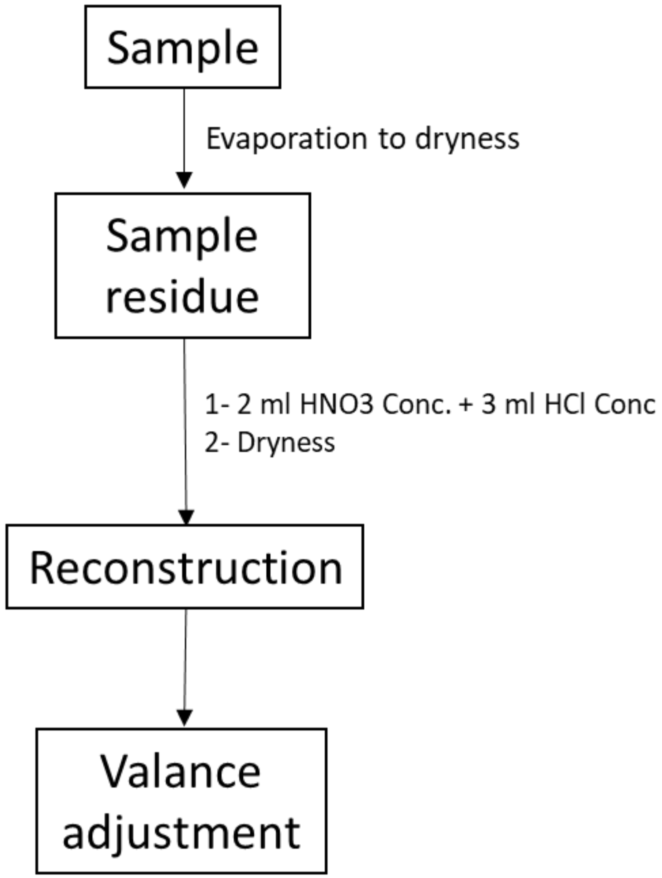


Yield (%)	99.5(0.2)
Efficiency (%)	95
SQP(E)	720

UNIVERSITAT DE BARCELONA

1B. Pu isotopes analysis with TK-TcScint

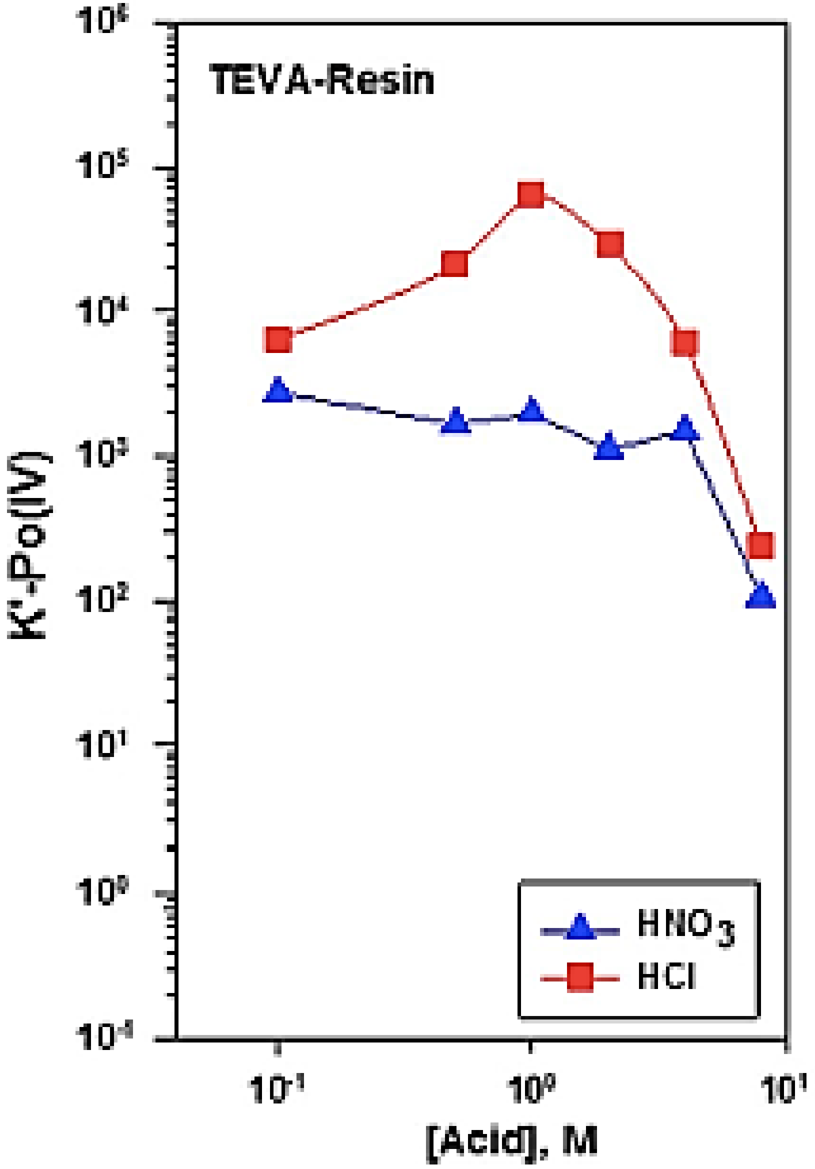
Water sample analysis (sea and river)
100 mL (10 Bq/L)



Sample	Recovery (%)	Quantification error (%)
River water R1	92.2	9
River water R2	99.4	6
River water R3	99.9	8
Sea water R1	76.6	-4
Sea water R2	99.9	-4
Sea water R3	99.9	10

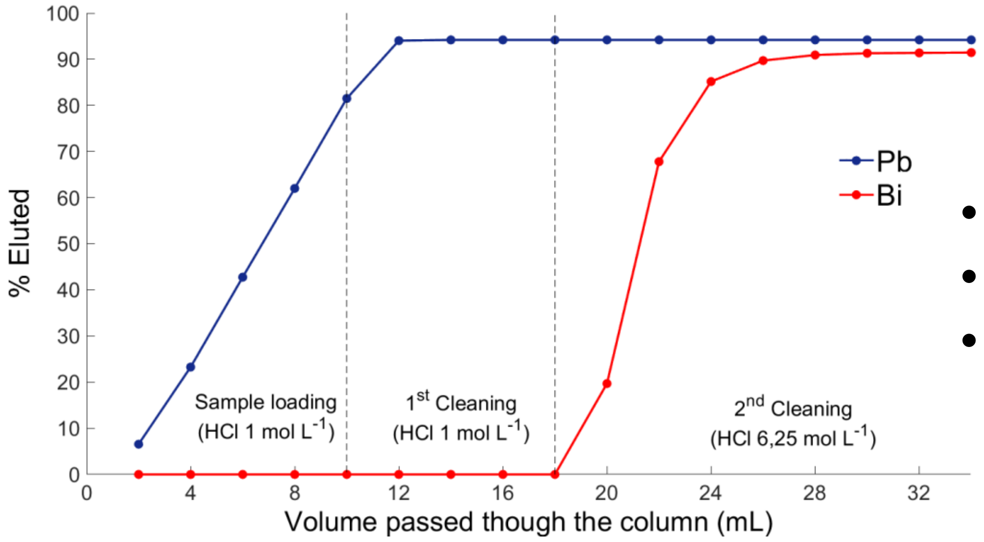
- ✓ Errors lower than 10%
- ✓ LD: 0.073 Bq/L (100 mL, 3 hours)

1C. ^{210}Po analysis with TK-TcScint



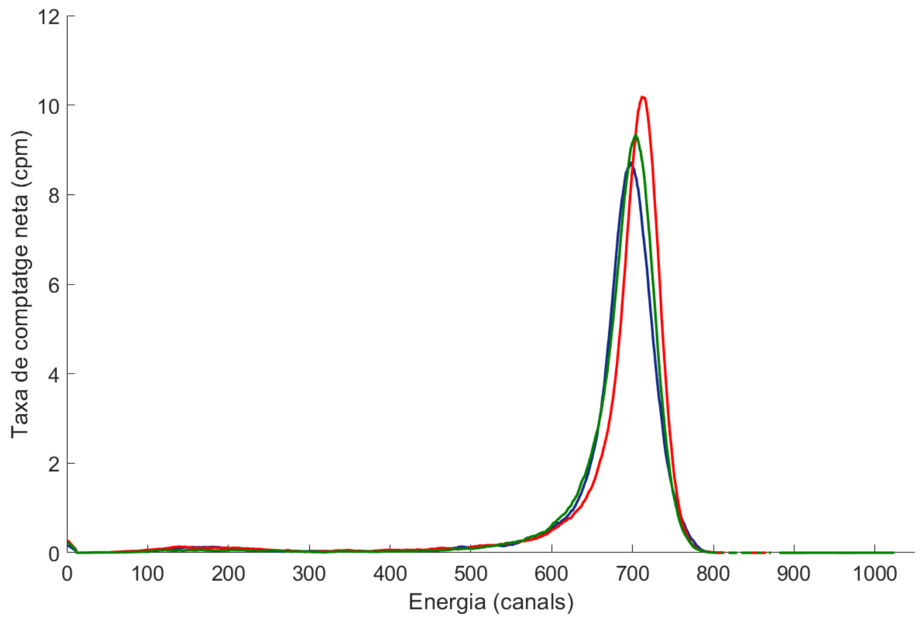
(Thakur et al. (2020). JRNC).

1C. ^{210}Po analysis with TK-TcScint



- Tracer: Cd
- Loading: HCl 1M
- Rinsing: 8 mL HCl 1M
  12 mL HCL 6,25M

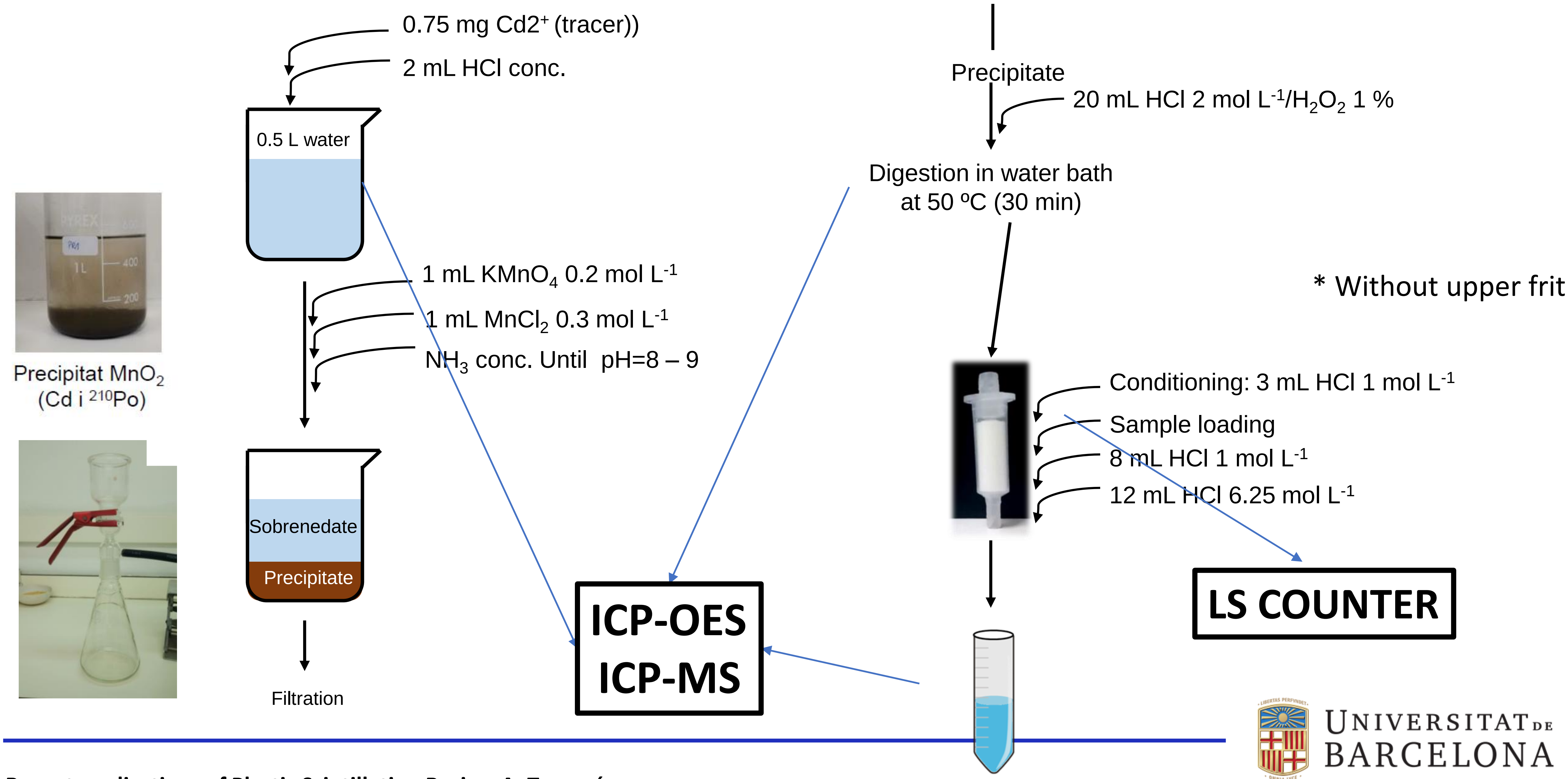
Column Retention [%]
99.9 (0.1)



Efficiency [%]
100(6)

UNIVERSITAT DE BARCELONA

1C. ^{210}Po analysis in TK-TcScint



1C. ^{210}Po analysis in TK-TcScint

UNE-EN ISO 13161 (autodeposition, α-spec.)

IAEA/AQ/12 (MnO_4^- precipitation, autodeposition, α-spec.)

	Det. Eff. [%]	Global recovery [%]		BKg [cpm]	L_D [Bq L^{-1}]
		Rep.1	Rep. 2		
TK-Tcscint PSresin	100(6)	97.5	96.3	1.5	0.003
UNE-EN ISO 13161	17.1	81.5	74.4	0.002	0.0007
IAEA/AQ/12	17.1	82.6	53.9	0.01	0.001

L_D: 69 hour counting

- 0.5L tap water sample spiked whit IAEA-TEL-2020-03 reference material sample (0.15 Bq/L)

	Activity [Bq kg^{-1}]
Co-60	307(3)
Ba-133	171(2)
Cs-134	210(2)
Cs-137	210(2)
Pb-210	905(17)
Po-210	921(20)
Am-241	117(1)

	Yield [%]	Relative error [%]	RSD [%]	Time required (days)
TK-Tcscint PSresin(n=3)	89.5(0.4)	1.9	3.8	2
UNE-EN ISO 13161 (n=3)	89(1)	5.4	7.5	2.5
IAEA/AQ/12 (n=2)	79(22)	-5.7	2.5	3.5

1D. ^{36}Cl analysis in concrete with TK-TcScint

sck cen
Belgian Nuclear Research Centre

VUB VRIJE UNIVERSITEIT BRUSSEL

DTU

Applied Radiation and Isotopes 193 (2023) 110646

ELSEVIER

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Investigation of a new approach for ^{36}Cl determination in solid samples using plastic scintillators

I. Llopart-Babot [a,c,*], M. Vasile [a], A. Tarancón [b], H. Bagán [b], A. Dobney [a], S. Boden [a], M. Bruggeman [a], M. Leermakers [c], J. Qiao [d], P. Warwick [e]

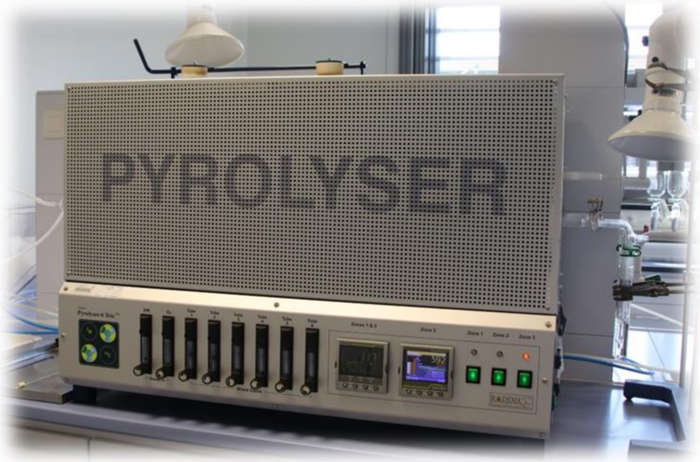
UNIVERSITAT DE BARCELONA

1D. ^{36}Cl analysis in concrete with TK-TcScint

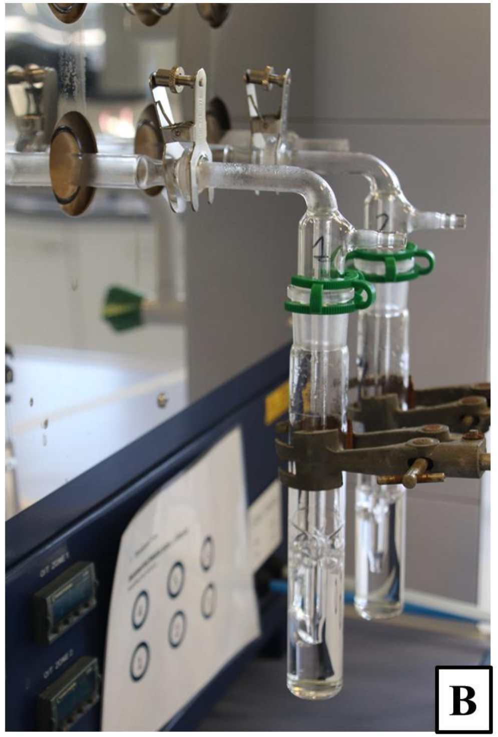
sck cen
Belgian Nuclear Research Centre

VUB VRIJE UNIVERSITEIT BRUSSEL

DTU



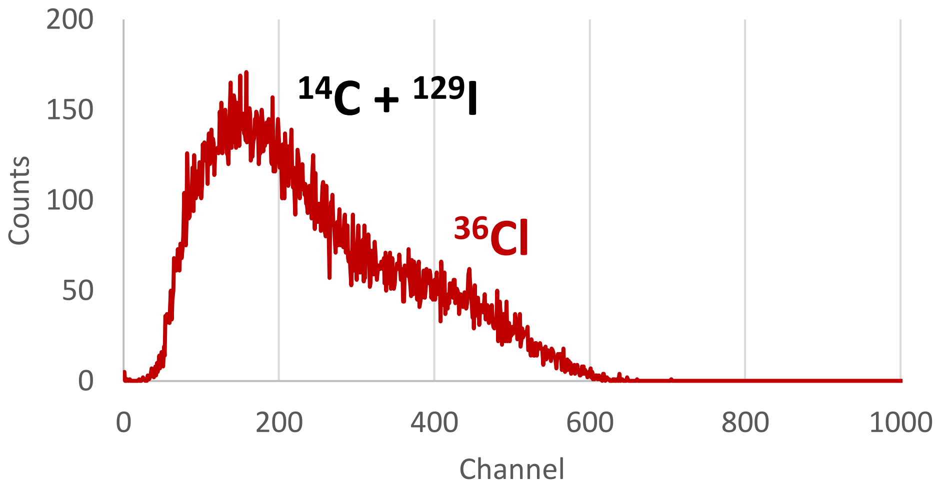
- Temperature up to **900°C**
- **5 h 25 min** protocol
- Glass connections and quartz tubes
- **200 mL min^{-1}** flow rate



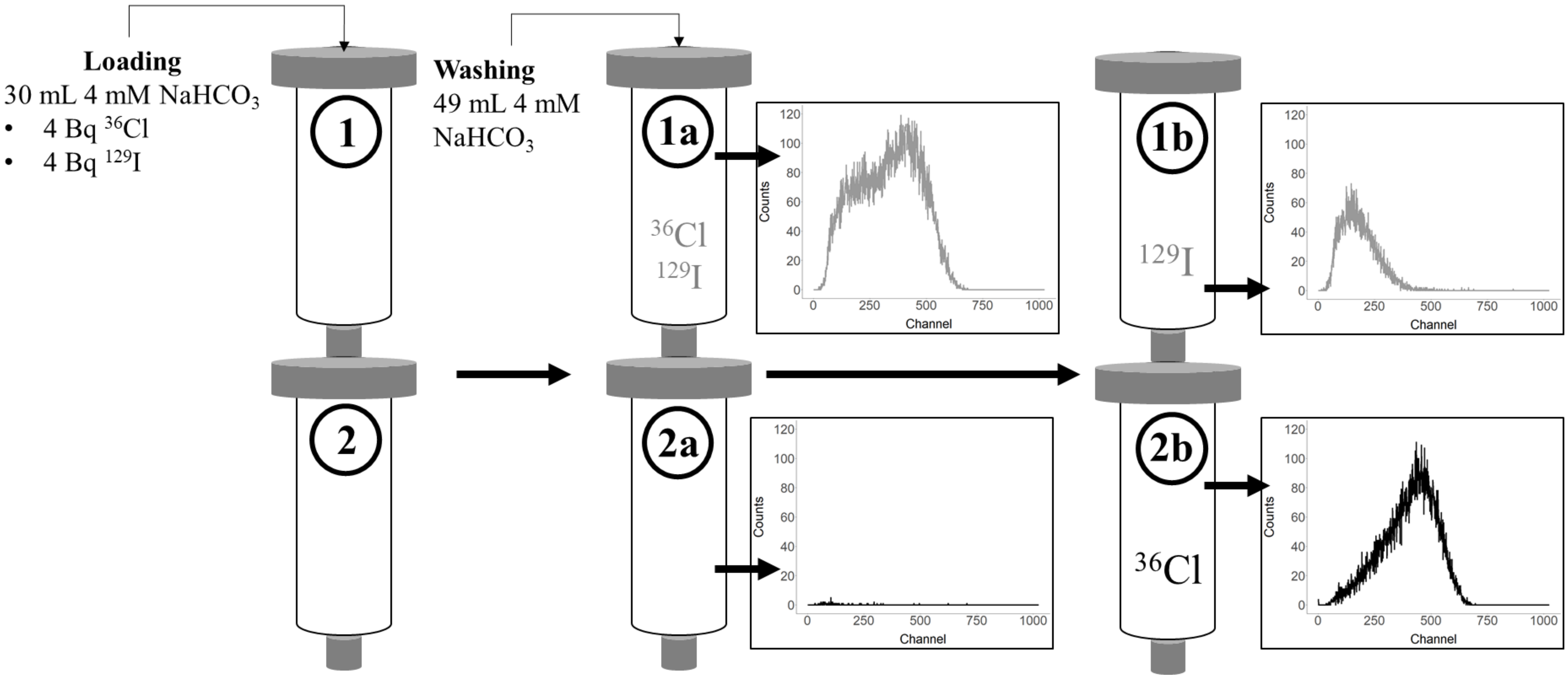
Trapping solution

30 mL 4 mM $NaHCO_3$

Loading sample

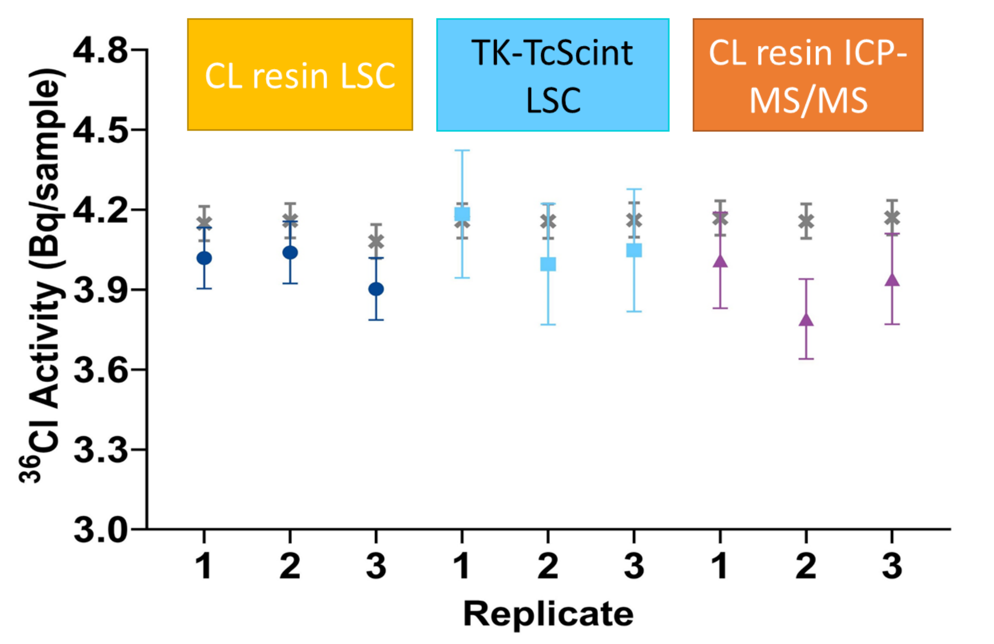


1D. ^{36}Cl analysis in concrete with TK-TcScint

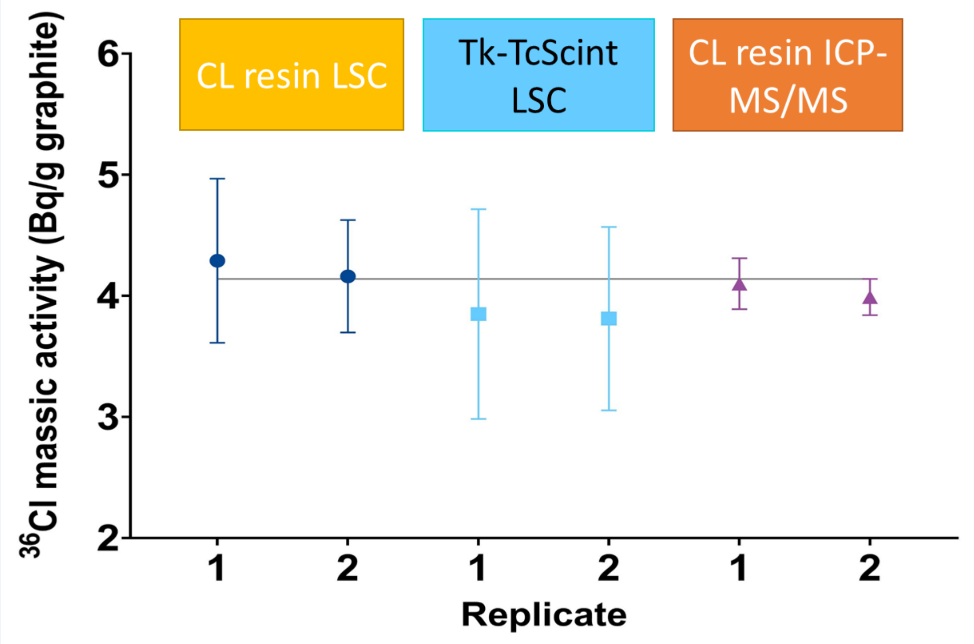


1D. ^{36}Cl analysis in concrete with TK-TcScint

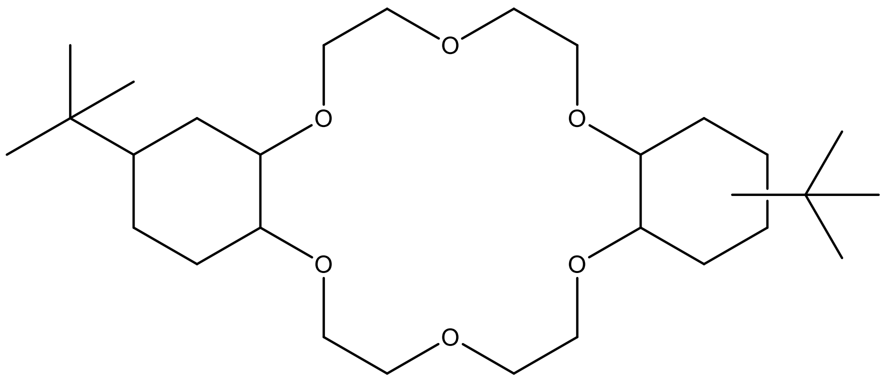
^{36}Cl quantification in spiked blank graphite samples



^{36}Cl quantification in real activated graphite samples



2. ^{90}Sr analysis with crown-ether PSresin



4.4'(5')-di-t butylcyclohexane 18-crown-6

in 1-octanol

↓

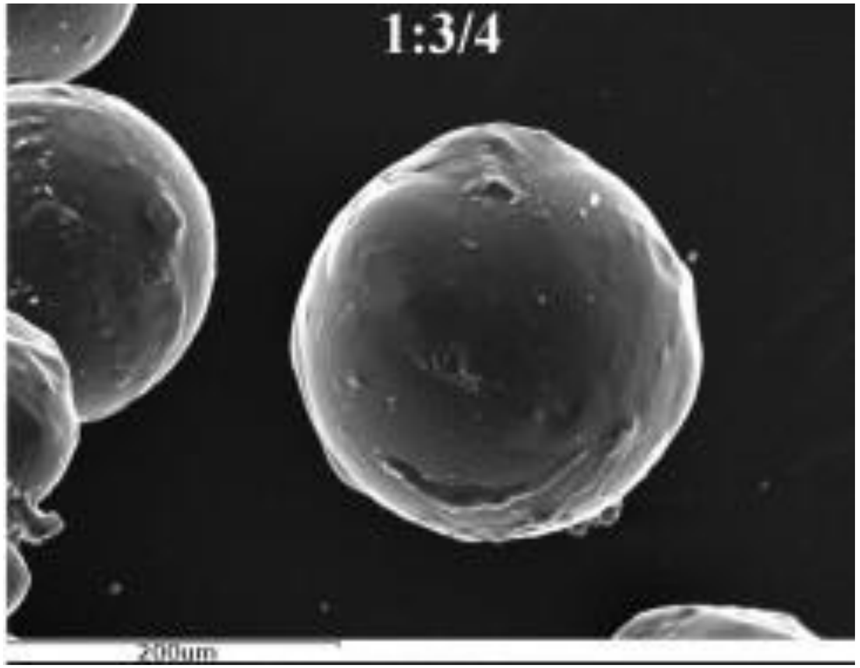
4.4'(5')-di-t butylcyclohexane 18-crown-6

in fluorinated alcohol

(TK102 PSresin version)

TK-SrScint

TRISKEM
Expertise in Separation Chemistry

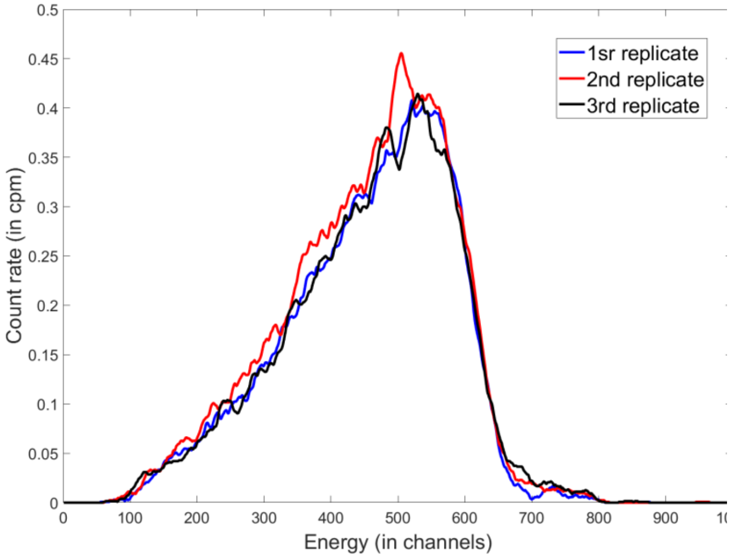


- ✓ River and sea water
- ✓ Milk
- ✓ Vegetation
- ✓ Air filter
- ✓ Sediments

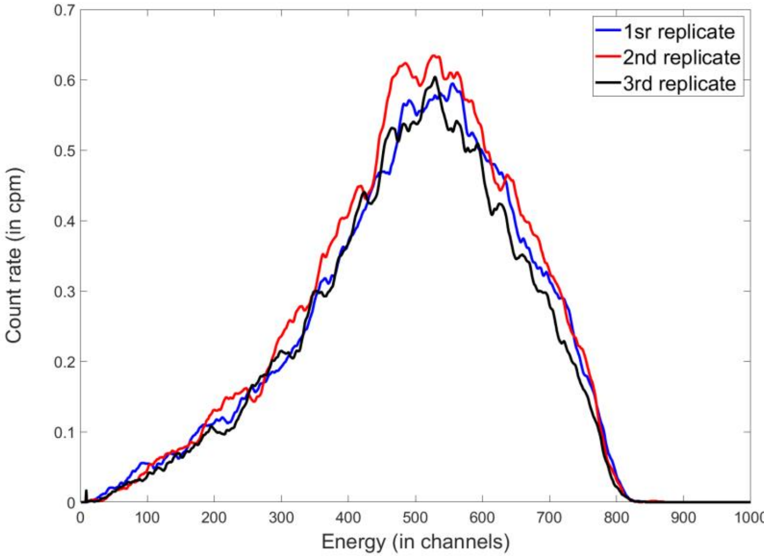
UNIVERSITAT DE BARCELONA

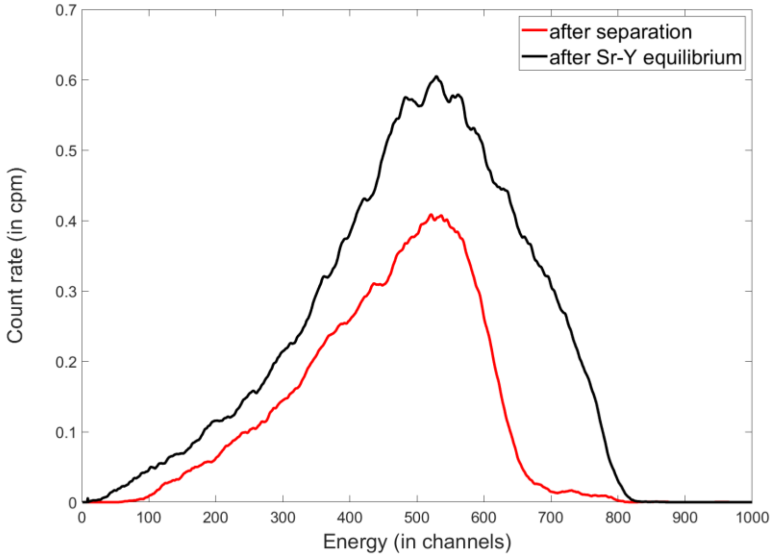
2. ^{90}Sr analysis with Tk-SrScint

^{90}Sr t = 0



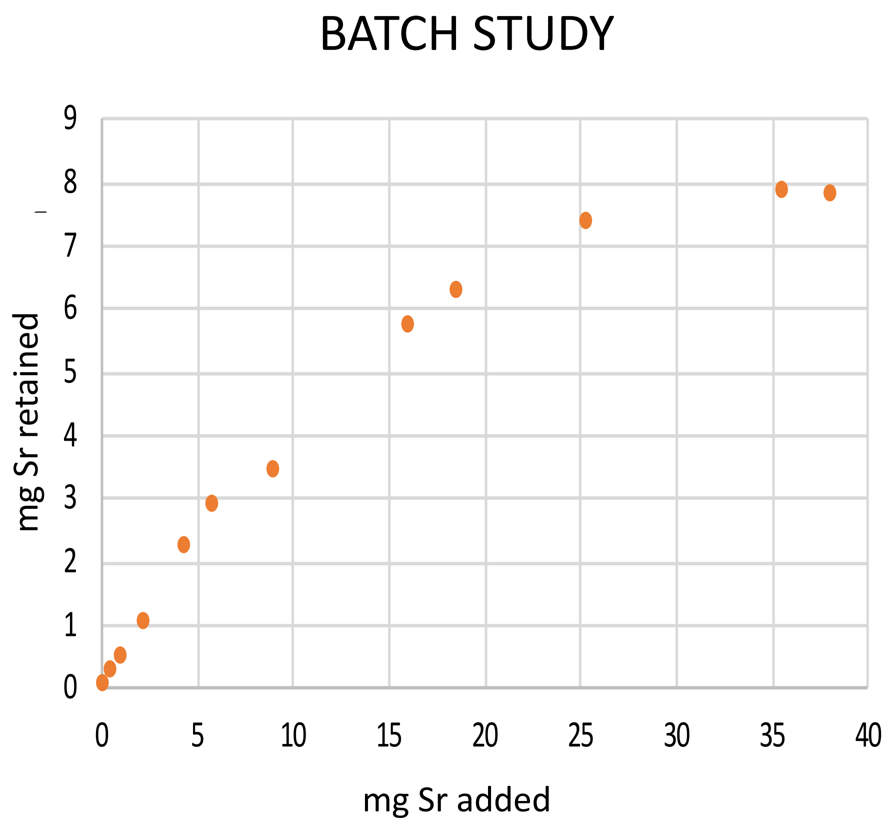
$^{90}Sr/^{90}Y$ t = 28 days

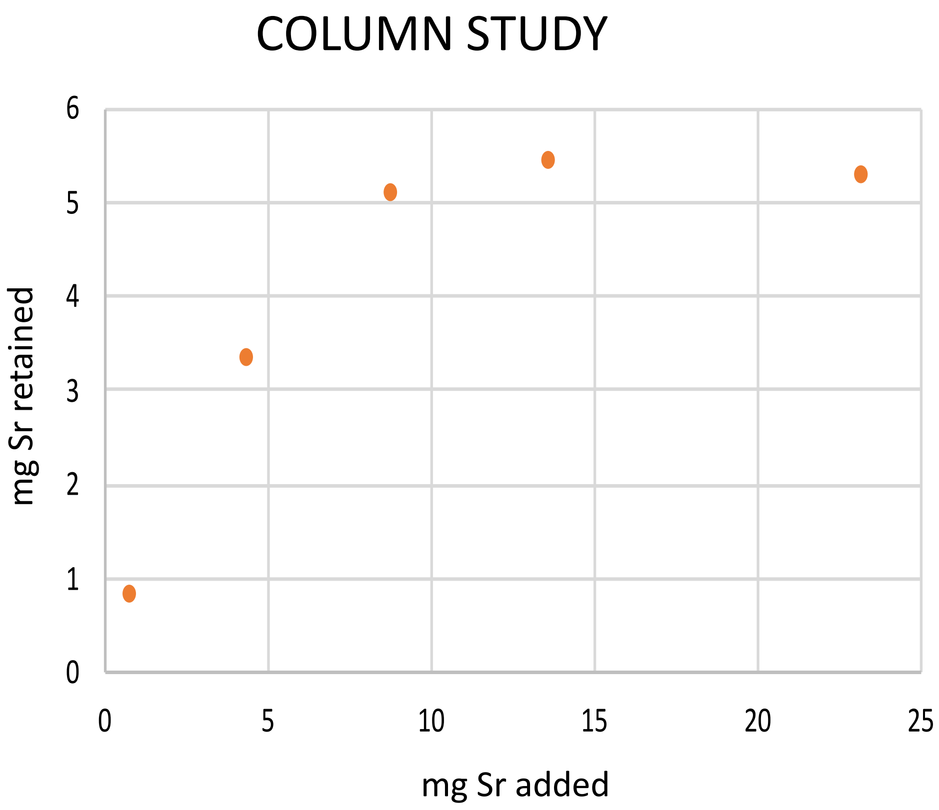




2. ^{90}Sr analysis with Tk-SrScint

Capacity study

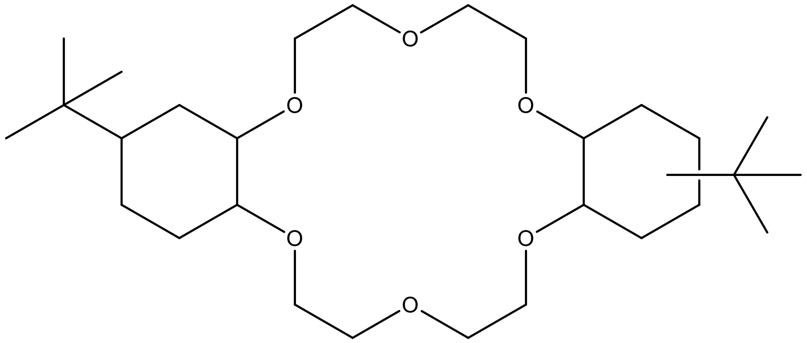




8 mg/g in batch conditions

5.5 mg/g in column conditions

2A. ^{90}Sr analysis with Tk-SrScint



4.4'(5')-di-t butylcyclohexane 18-crown-6

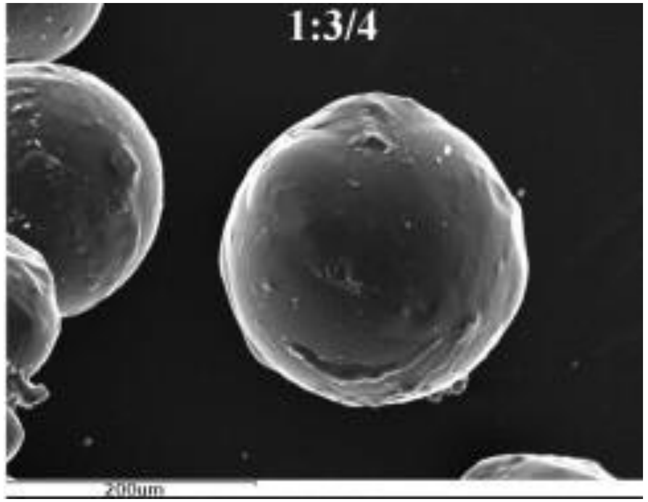
in fluorinated alcohol

Column conditioning: **HNO_3 6 M or 8 M (2 mL)**

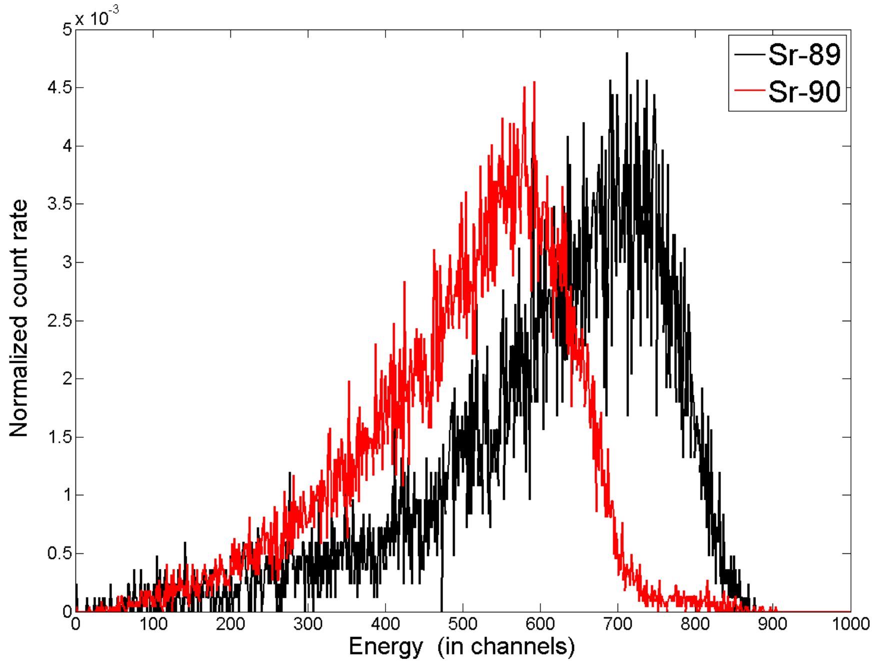
Sample volume: 10 mL in **HNO_3 6 M or 8 M**

Cleaning: **HNO_3 6M (2*2 mL) and $LiNO_3$ 6 M (2*2 mL)**

Tracer: **1 to 5 mg Sr^{2+} (1 or 1.4 g of PSresin)**



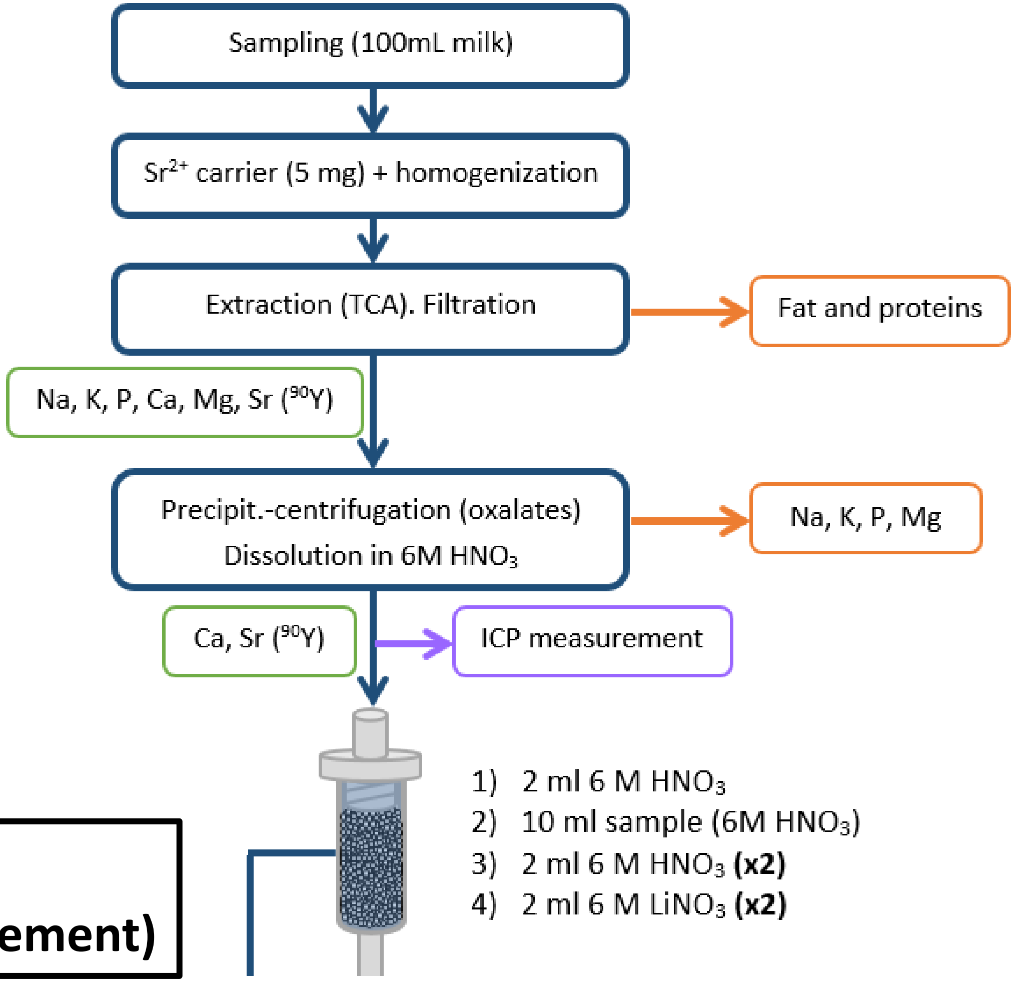
	Efficiency [%]
^{90}Sr	86(6)
^{89}Sr	91(6)



UNIVERSITAT DE BARCELONA

2B. ^{90}Sr analysis with Tk-SrScint. Milk

UNIVERSITAT POLITÈCNICA DE VALÈNCIA



Pre-treatment (%)	Column (%)	Total (%)
93 (4) (4%)	70(4) (6%)	65 (5) (7%)

Type of milk	Relative bias $^{90}Sr+^{89}Sr$ (%)
IAEA-473 milk powder	-3.5 (0.4*)
IAEA-473 milk powder	-4.7 (-0.8*)
IAEA-473 milk powder	-5.2 (-1.4*)

5 Hours
(including 1h measurement)

UNIVERSITAT DE BARCELONA

2C. ^{90}Sr analysis with Tk-SrScint. FILTERS AND VEGETATION

UNIVERSITAT POLITÈCNICA DE VALÈNCIA

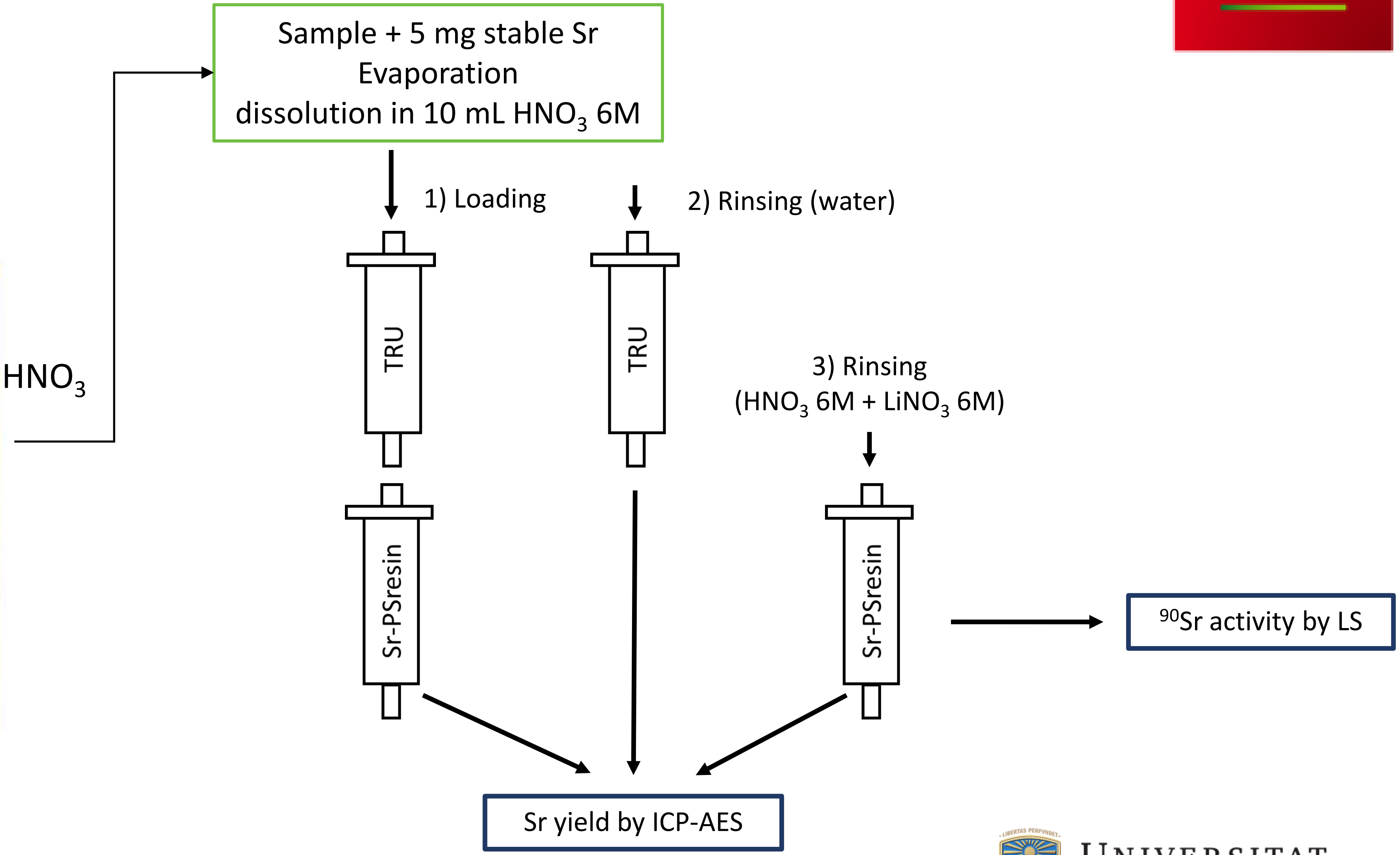
	Prop. ^{89}Sr: ^{90}Sr	Bias ^{89}Sr + ^{90}Sr (%)
Glass-fiber filter	1:1	-2.1
	2:1	-8.5
	8:1	1.1
Cellulose filter	1:2	4.1
	1:1	-12.8
	4:1	1.9
Grass	1:1	11.6
	2:1	17.0
Rosemary	1:1	3.8
	2:1	5.6
	8:1	9.0
Pine needles	1:1	9.9
	2:1	13.3
	8:1	10.8
Spruce needles (IAEA-2016) 17 Bq/kg	0:1	25.9

	Total recovery (%)
Glass-fiber filter (x3)	92.0 ± 1.7 (2%)
Cellulose filter (x3)	94.0 ± 1.5 (2%)
Grass (x3)	87.8 ± 7.8 (9%)
Rosemary (x3)	92.0 ± 2.7 (3%)
Pine needles (x3)	92.9 ± 4.1 (4%)
Spruce needles (IAEA-2016)	84.2

Aerosol filter	Vegetation (10 g)
Ash + microwave + calcium oxalate precipitation 5.5 h	Ash + microwave + calcium oxalate precipitation 9.5 h

UNIVERSITAT DE BARCELONA

2D. ^{90}Sr analysis with Tk-SrScin. Nuclear waste



UNIVERSITAT DE BARCELONA

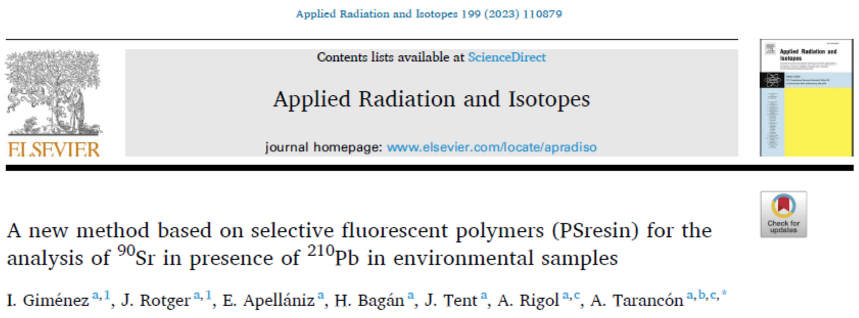
2D. ^{90}Sr analysis with Tk-SrScin. Nuclear waste

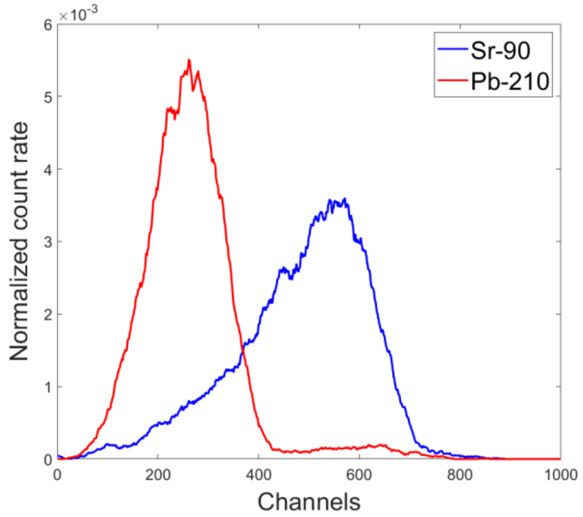
Low concentrated effluent		
Method	Yield	^{90}Sr activity [Bq/g]
Reference	-	32.6 ± 11 %
PS-resin	82 ± 10 %	32.4 ± 12 %

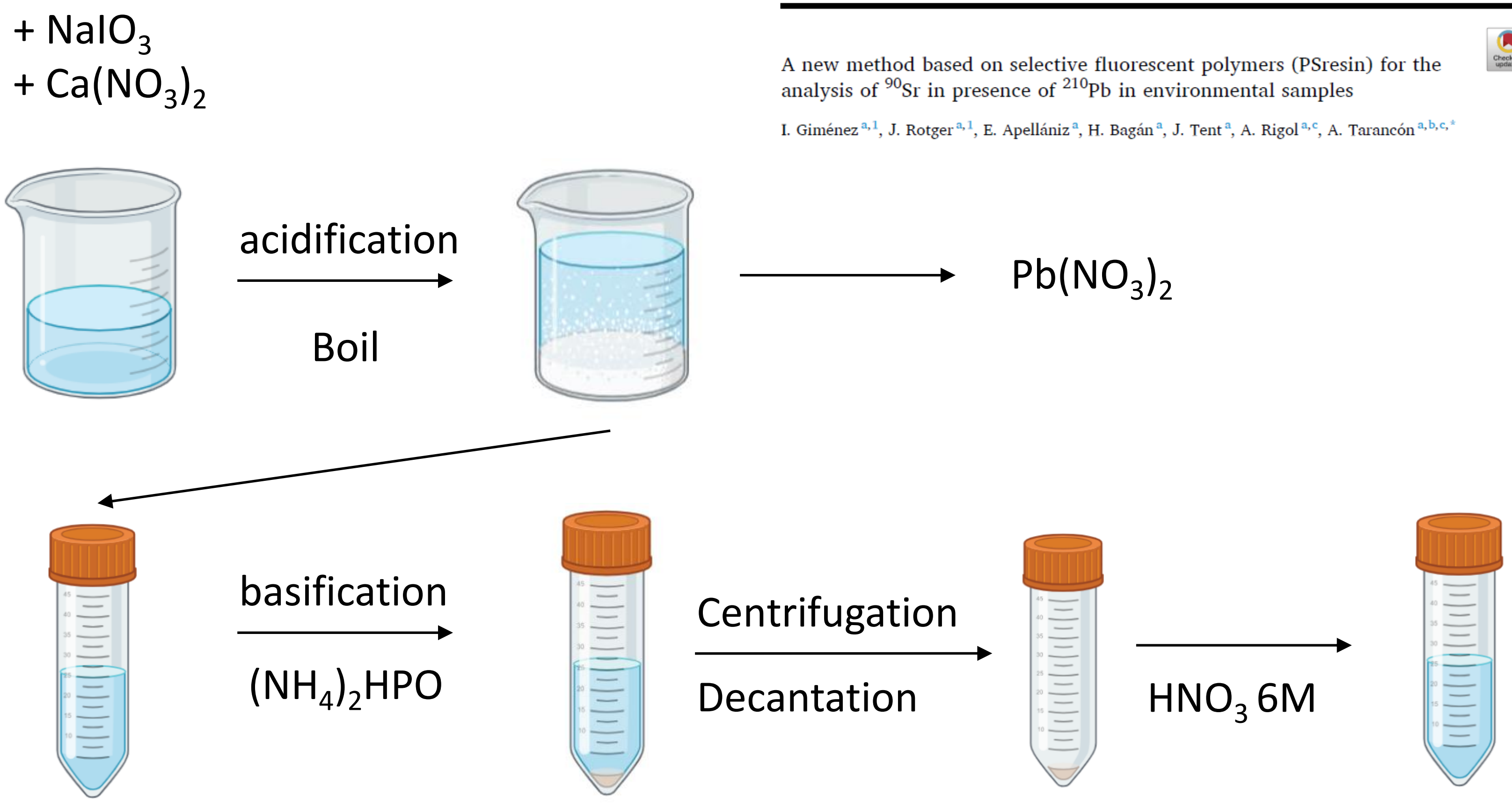
Concrete		
Method	Yield	^{90}Sr activity [Bq/g]
Reference	-	2111 ± 11 %
PS-resin	81 ± 10 %	1943 ± 12 %

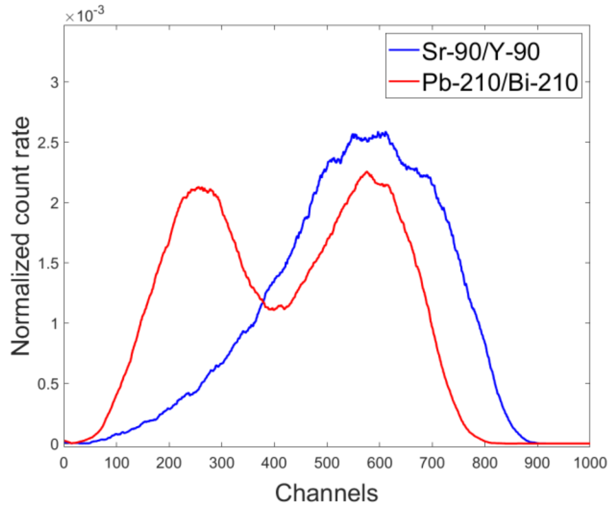
Sludge		
Method	Yield	^{90}Sr activity [Bq/g]
Reference	-	2290 ± 11 %
PS-resin	75 ± 10 %	2122 ± 12 %

2E. ^{90}Sr TK-SrScint. Environmental samples with ^{210}Pb

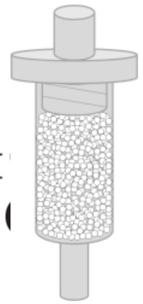








Recovery (%)	
Sr	Pb
87.6 (0.4)	6 (2)



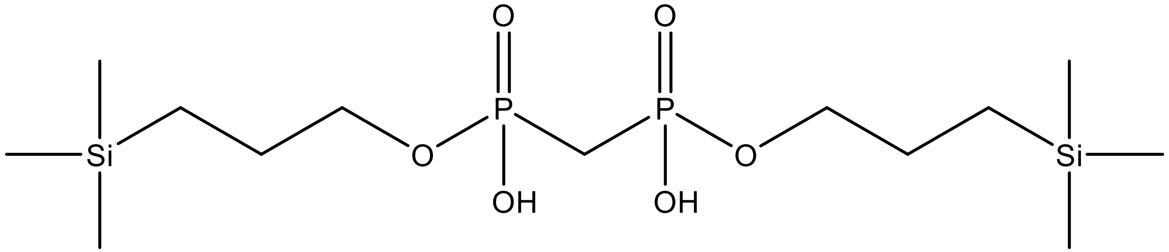
UNIVERSI BARCEL

2E. ^{90}Sr TK-SrScint. Environmental samples with ^{210}Pb

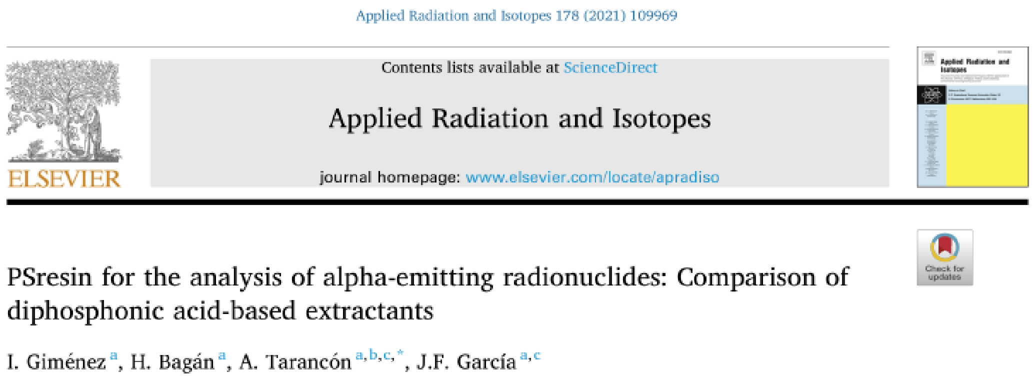
	Efficiency (o.w.)		Background cpm)	LoD (Bq/L)	Time of analysis (hours)
	t = 0	t > 21 days			
EC-LSC	96.5 (0.4)	193 (1)	4.1	0.8*	6-7
SUC-LSC				0.068**	20
PSresin	51 (3)	126 (6)	0.3	0.027**	5-6

* (100 mL and 1 h counting time)
** (1 L and 1 h counting time)

3. α-PSresin



(3-trimethylsilyl-1-propyl)methandisphosphonic acid


Applied Radiation and Isotopes 178 (2021) 109969

Contents lists available at ScienceDirect

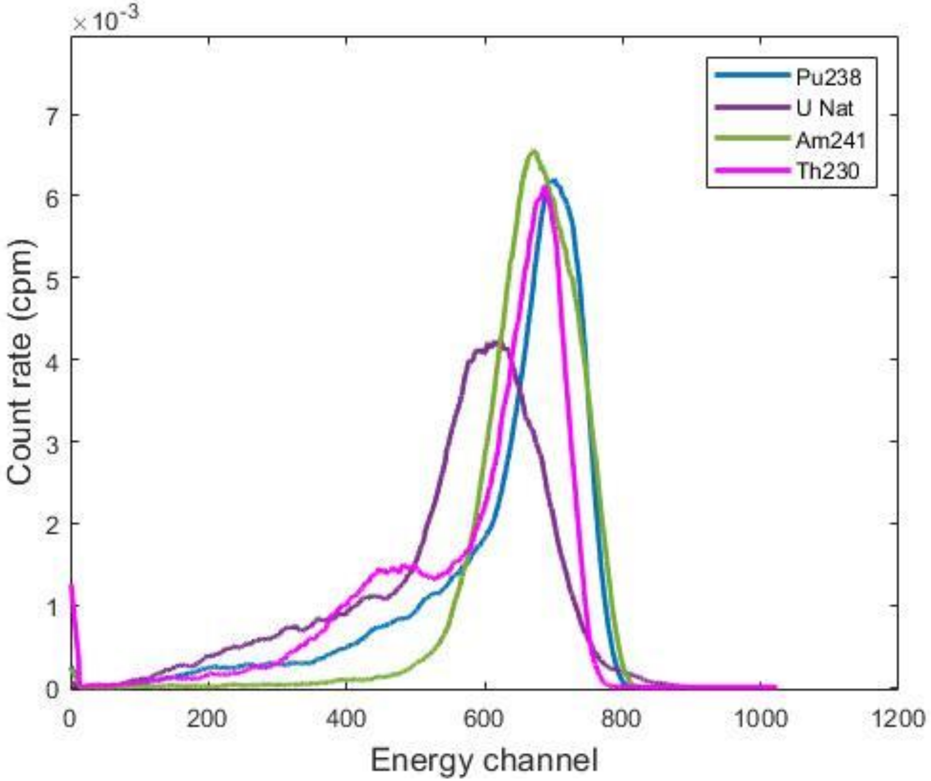
Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

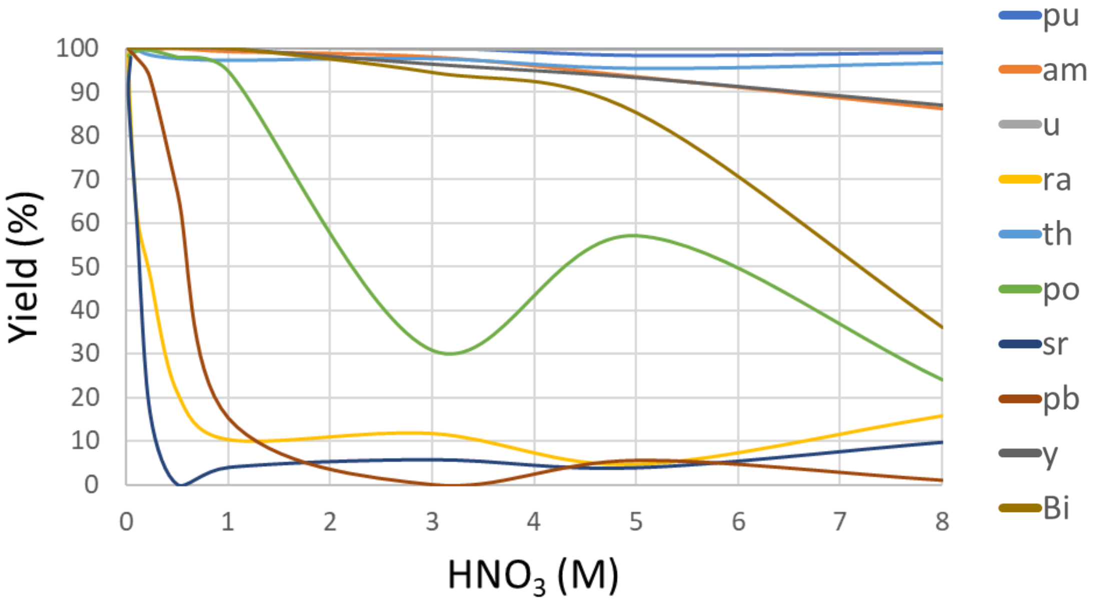
PSresin for the analysis of alpha-emitting radionuclides: Comparison of diphosphonic acid-based extractants

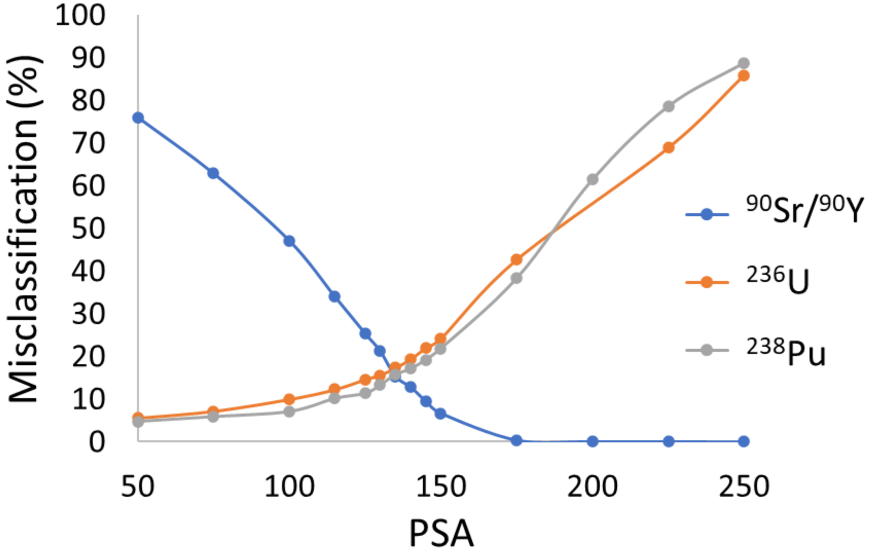
I. Giménez [a], H. Bagán [a], A. Tarancón [a,b,c,*], J.F. García [a,c]

- ✓ Quantitative retention of actinides HCl 0.5M
- ✓ Breakthrough volume > 400 ml
- ✓ 2-3 mg capacity for Eu (tracer)



3. α-PSresin





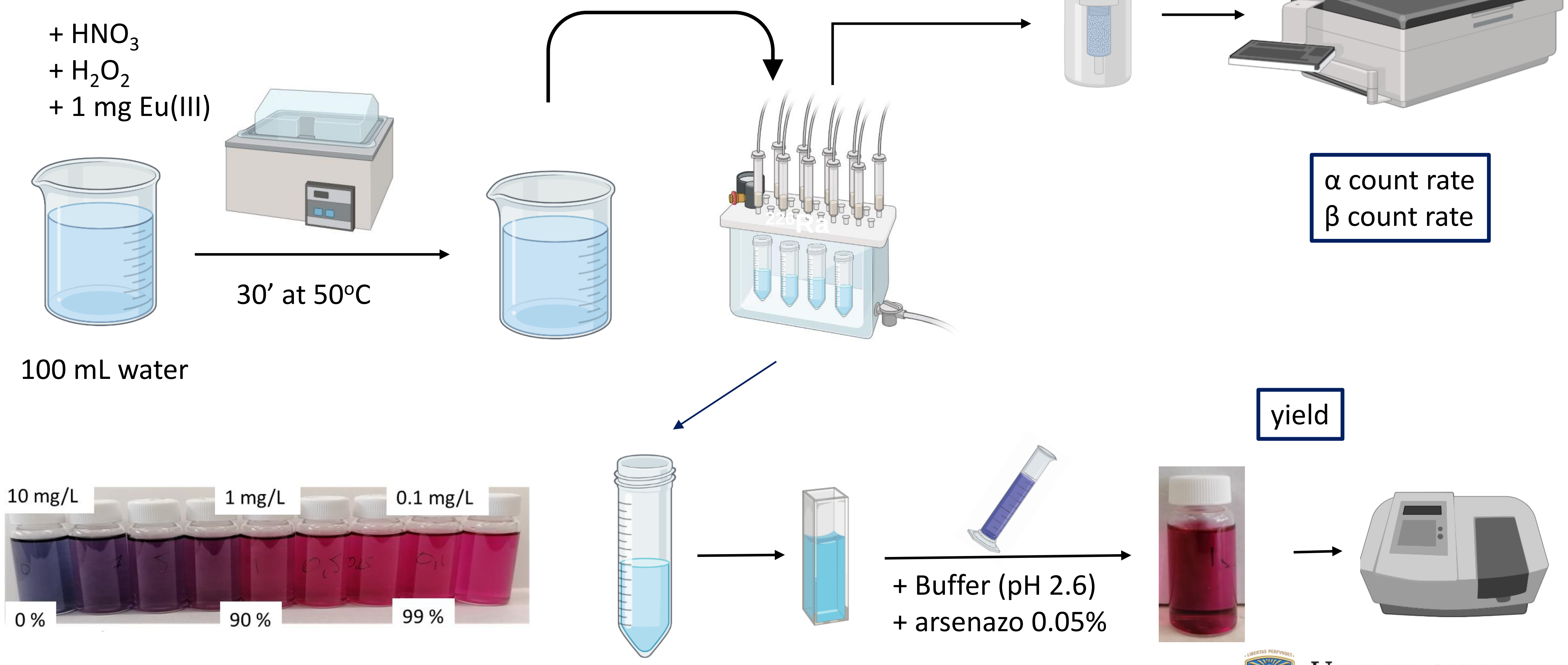
- ✓ pH 2 (actinides and Ra)
- ✓ 1% on H_2O_2
- ✓ 30 minutes at 50ºC to oxidize (Po to Po(IV))

Misclassification (%) PSA 135		
^{238}Pu	^{236}U	^{90}Sr
15.76	17.3	12.4

- ✓ **TOTAL ACTINIDES**
- ✓ **GROSS-ALPHA (including Po and Ra)**
- ✓ **INDIVIDUAL ELEMENTS? (U, ^{90}Y, …)**

UNIVERSITAT DE BARCELONA

3A. α-Psresin. Gross alpha



Universitat de Barcelona

3A. α-Psresin. Gross alpha

- Mreal_1
- IAEA-TEL-202-013

PSA	Replicate	Quantification deviation (%)	
		Mreal_1	IAEA-TEL-202-013
135	1	2.0	-14.8
	2	-1.6	6.3
	3	1.6	-10.7


Analytica Chimica Acta 1248 (2023) 340905

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

ELSEVIER

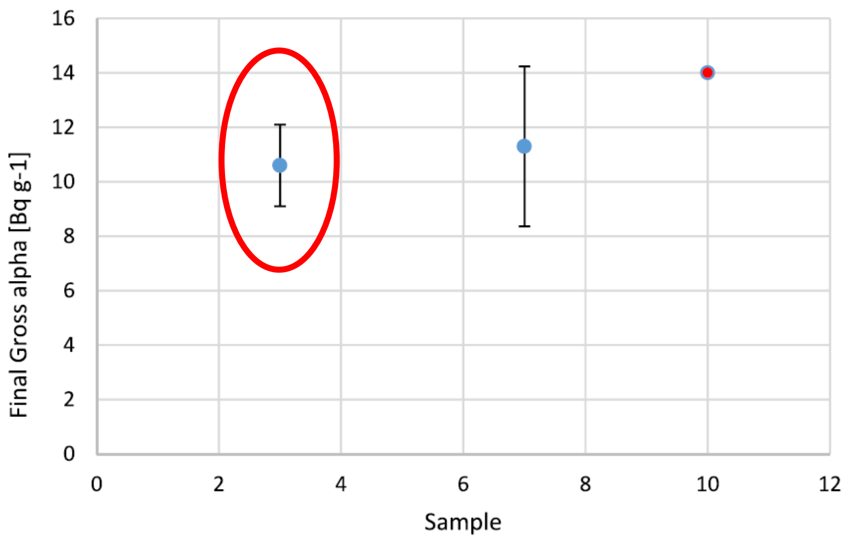
Check for updates

Fast analysis of gross alpha with a new plastic scintillation resin

I. Giménez [a], H. Bagán [a,*], A. Tarancón [a,b,c]

[a] Department d'Enginyeria Química i Química Analítica, Universitat de Barcelona, Martí i Franquès, 1-11, ES-08028, Barcelona, Spain
[b] Serra-Húnter Programme, Generalitat de Catalunya, Barcelona, Spain
[c] Institut de Recerca de l'Aigua, Universitat de Barcelona, Montalegre, 6, ES-08001, Barcelona, Spain

- Spent ion exchange resin



Result after ^{90}Y decay

Leskinen, A., Jerome, S., Lavonen, T. *et al.* Intercomparison exercise on difficult to measure alpha radionuclides in spent ion exchange resin. *J Radioanal Nucl Chem* **333**, 563–584 (2024). https://doi.org/10.1007/s10967-023-09233-4

UNIVERSITAT DE BARCELONA

4. PSkits: Fast, Selective And Pseudo-quantitative Analysis Of Liquid Samples

Waste

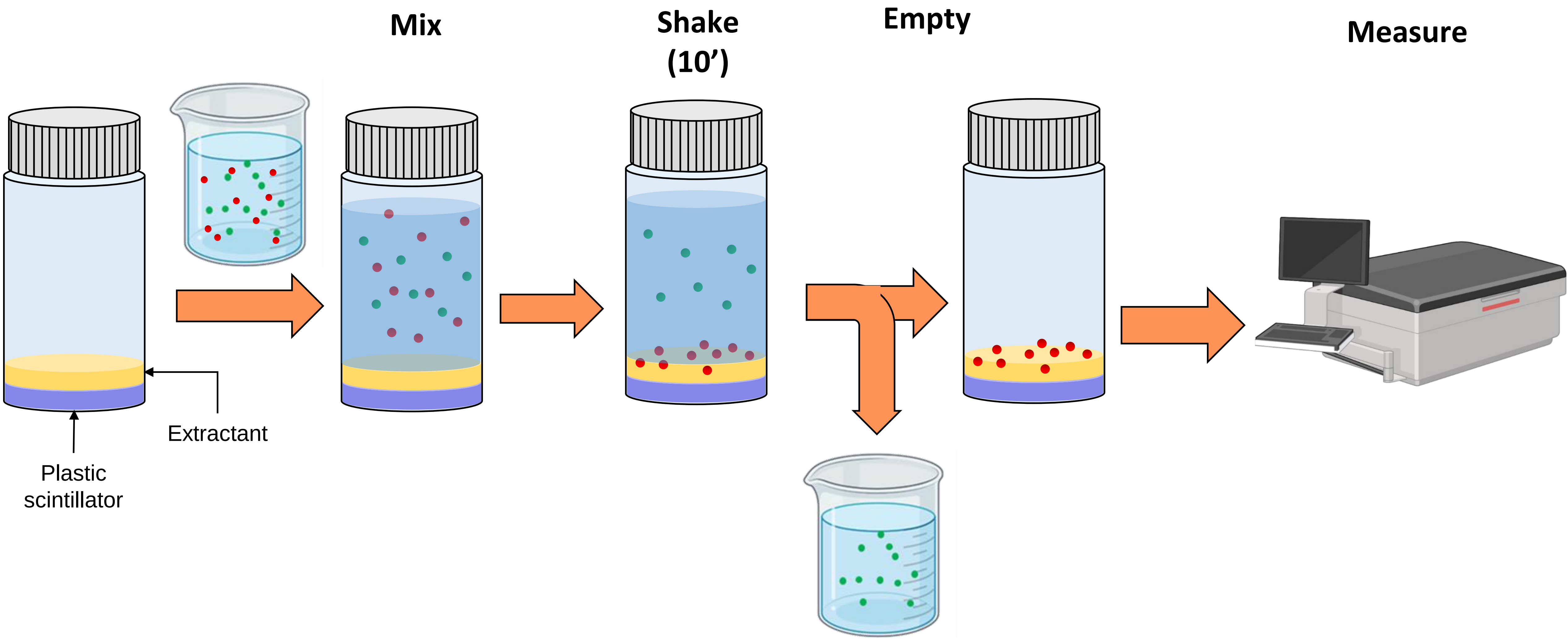
Biological samples

Radiological Characterization

- High amount of samples
- Easy, Fast and Selective **(Screening)**
- α and β emmiters

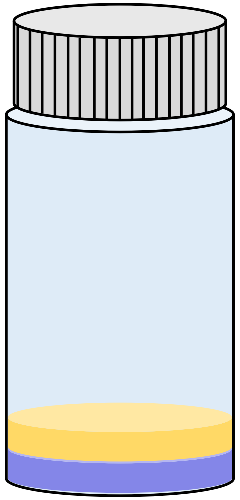
Need of analytical methods for characterization

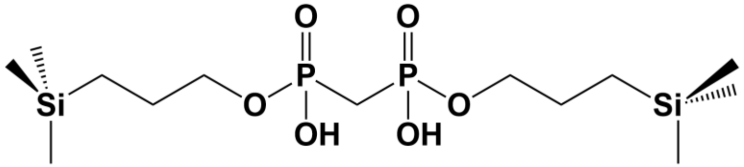
4. PSkits: Fast, Selective And Pseudo-quantitative Analysis Of Liquid Samples



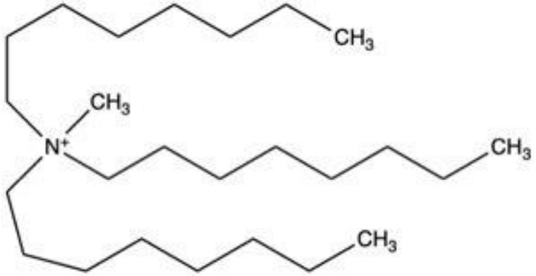
UNIVERSITAT DE BARCELONA

4. PSkits: Fast, Selective And Pseudo-quantitative Analysis Of Liquid Samples



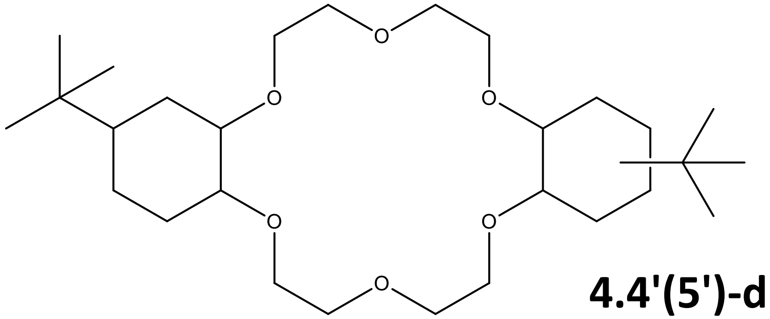


(Bis(3-trimethylsilyl-1-propyl)dimethylendiphosphonic acid) → Gross α



N-methyl-*N*,*N*-dioctyloctan-1-aminium

Aliquat · 336 → Tc, Pu



4.4'(5')-di-t butylcyclohexane 18-crown-6 → Sr

4. PSkits: Fast, Selective And Pseudo-quantitative Analysis Of Liquid Samples

Gross α

2M HCl

Total Efficiency (%)
30(4)

Tc

0.1M HCl

Total Efficiency (%)
22(2)

Pu

3M HNO_3
9M HCl
0.5M HNO_3

Iron sulfamate
Ascorbic acid
Sodium nitrite

Total Efficiency (%)
25(3)

4. PSkits: Fast, Selective And Pseudo-quantitative Analysis Of Liquid Samples

- ^{99}Tc

Hanford Site Simulated Samples

Relative Errors (%)			
	Matrix	Mixture A	Mixture B
P1 Procedure	AN106	-25	3
	AP101	11	3
P2 Procedure	AN106	-36	3
	AP101	**-1**	**18**

Urine

	Activity spiked (Bq)	Count rate (cpm)	Relative error (%)
S1_L	0.069	2.1*	< MDA
S2_L	0.077	2.4	58
S3_L	0.082	2.2*	< MDA
S1_H	0.37	8.2	-3
		7.3	12
		7.2	14
S2_H	0.35	7.9	6
S3_H	0.34	6.9	19

*** Limit of detection was set on 2.3 cpm**

Real Samples from PSI

PAUL SCHERRER INSTITUT

	PSkits (Bq/g)	Reference value	Relative Error (%)
Coating Wood	48.2 (10.2)	54.4 (14.4)	13
Coating Wood	28.8 (6.6)	77.3	168
Linoleum	6.1 (0.8)	7.3 (0.5)	20
PVC	4.5 (0.6)	4.1	-9
Waste water	2.0 (0.4)	0.7	-65

UNIVERSITAT DE BARCELONA

4. PSkits: Fast, Selective And Pseudo-quantitative Analysis Of Liquid Samples

- Gross α
- Pu isotopes

Sample	PSkits		PSI – Alpha Spectrometry		Relative Error (%)	
	Total Alpha (Bq/g)	Pu (Bq/g)	Total Alpha (Bq/g)	Pu (Bq/g)	TA	Pu
P1 Slurry	4.5 (0.7)	0.9 (0.2)	22	6.5	**388**	**622**
P1 Fused	16.8 (2.3)	6.7 (2.2)			**31**	**-3**
P3 Slurry	4.5 (1.0)	1.0 (0.1)			**346**	**313**
P3 Fused	12.4 (1.8)	3.5 (0.3)	16.5	3.3	**33**	**-6**

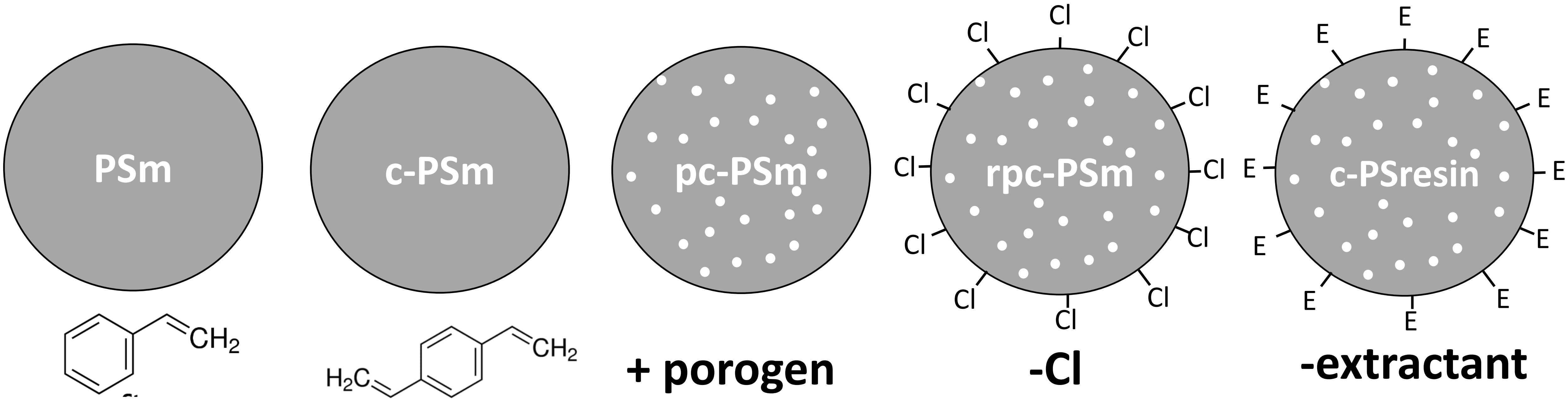
Sample	PSkits		PSI		Relative Error(%)	
	Total Alpha (Bq/g)	Pu (Bq/g)	Total Alpha (Bq/g)	Pu (Bq/g)	TA	Pu
HL4	128.2 (10.3)	79.7 (7.5)	61.6	47.2	**-52**	**-40**
HL6	134.2 (14.4)	86.1 (14.7)	90.9	69.7	**-32**	**-19**
HL7	95.4 (7.7)	65.7 (6.5)	120.4	97.1	**26**	**48**
HL8	42.8 (2.4)	27.8 (4.7)	38.0	26.7	**-11**	**-4**
HL9	66.9 (4.8)	39.4 (0.2)	63.6	41.5	**-5**	**6**

5. On going developments

5A. Covalent bounded PSresin (c-PSresin)

5. On going developments

5A. Covalent bounded PSresin (c-PSresin)



✓ Good efficiency
^{14}C: 57(3)%

✓ Resistance
(^{14}C: 50-60%)

✓ Surface
from 20 to >35 mg
(^{14}C: 58(2)%)

✓ Modified
1.7-2.4 % Cl
(^{14}C: 54(1)%)

✓ Breakthrough
Volume
(70% substitution)

- Leaching?
- Capacity?
- Breakthrough volumen?

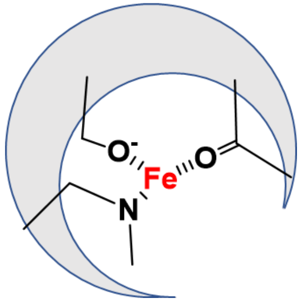
UNIVERSITAT DE BARCELONA

5. On going developments

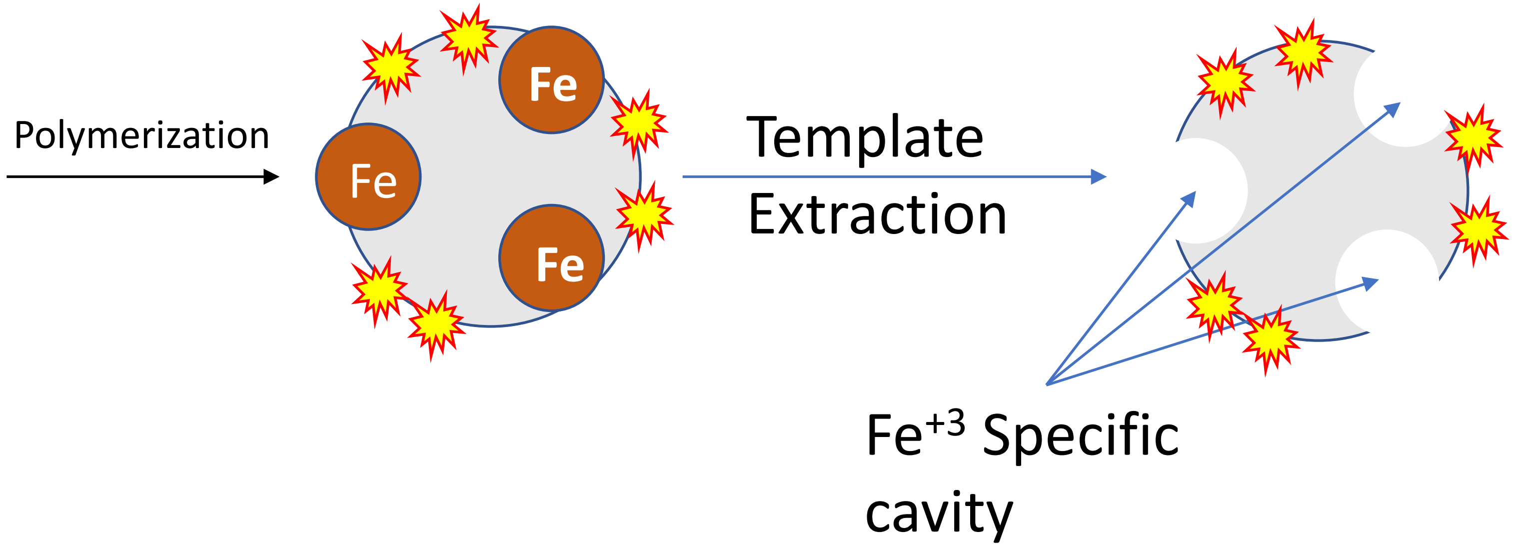
5B. Imprinted scintillation polymers

5. On going developments

5B. Imprinted scintillation polymers



- Monomers
- Crosslinker
- Complexing monomer
- Fluorescent solutes
- Additives

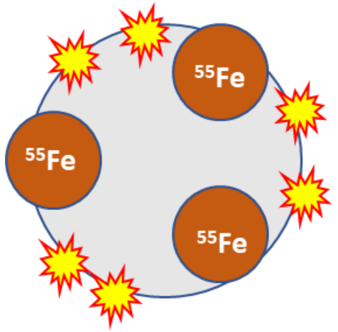


- ✓ **Interaction**
- ✓ **Rigid**
- ✓ **Aromatic System**
- ✓ **Fluorescent solutes**
- ✓ **Colorless**

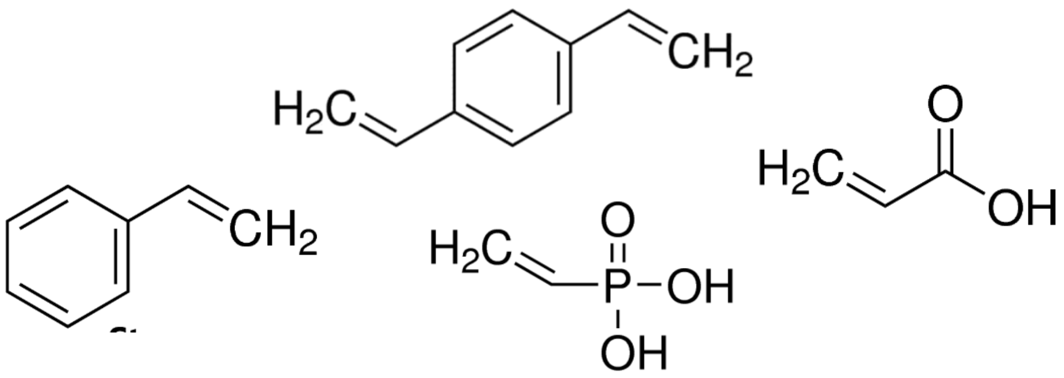
UNIVERSITAT DE BARCELONA

5. On going developments

5B. Imprinted scintillation polymers



- Monomers
- Crosslinker
- Complexing monomer
- Fluorescent solutes
- Additives



Capacity (mg metal/ g Sc-Fe-IIP)			
Fe	**Cu**	**Ni**	**Co**
17.8	0.9	Nd	0.5

Selectivity (%)			
Fe	**Cu**	**Ni**	**Co**
98.1	7.8	4.0	nd

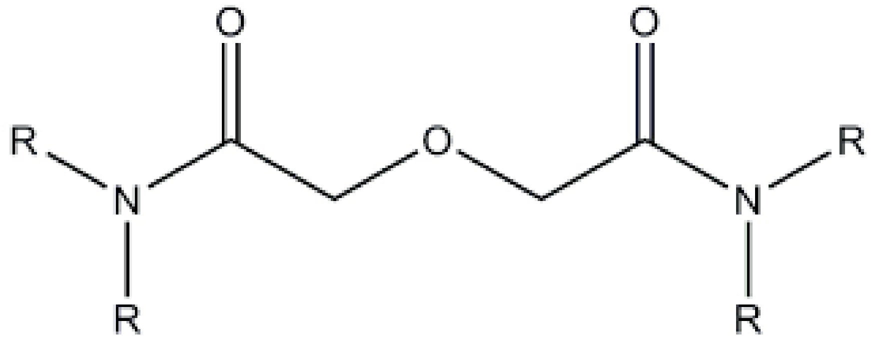
Yield	Detection efficiency
30%	4.90%

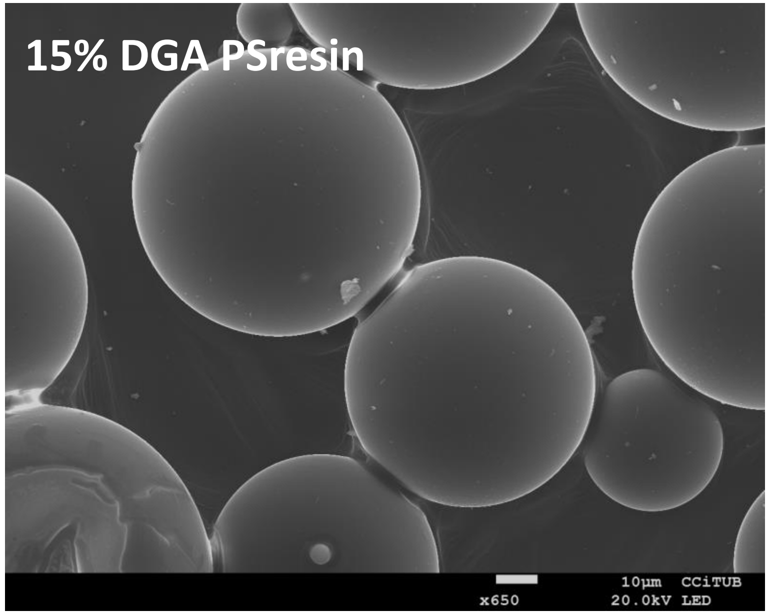
UNIVERSITAT DE BARCELONA

5. On going developments

5C. DGA PSresin

Am/Cm separation and measurement in nuclear reprocessing samples

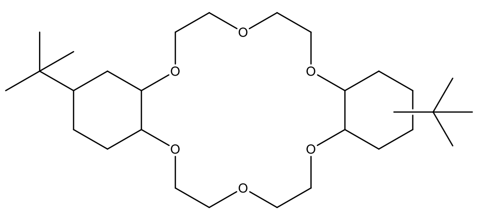




DGA proportion	Detection Efficiency (%)	Am Retention (%)	Eu Retention (%)	Q (mg/g)
5%	99 (1)	> 99.4	> 99.1	3.43
10%	99 (1)	> 99.4	> 99.1	8.79
15%	98 (1)	> 99.3	> 99.1	11.02
20%	96 (2)	> 99.4	> 99.1	13.61

15% DGA PSresin	Am Retention (%)	Detection Efficiency (%)
10mL sample	99.3	98.5
25mL sample	99.6	99.1
50mL sample	99.6	103.1

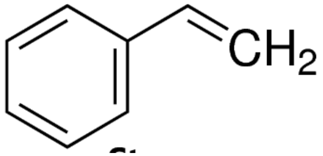
5. On going developments
5D. Pb PSresin

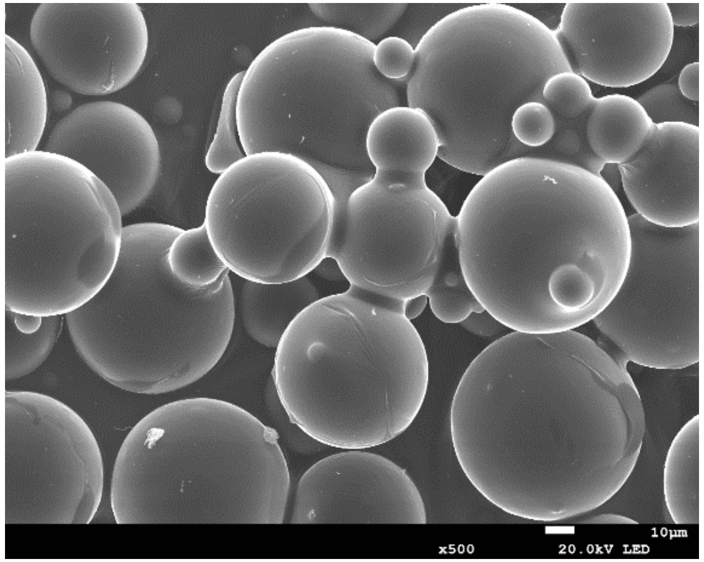


+ ionic liquid

TK101

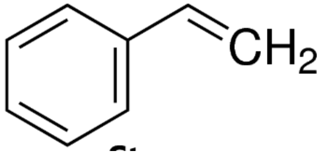
PSm



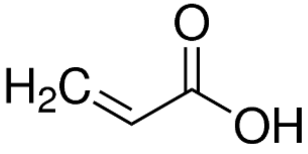


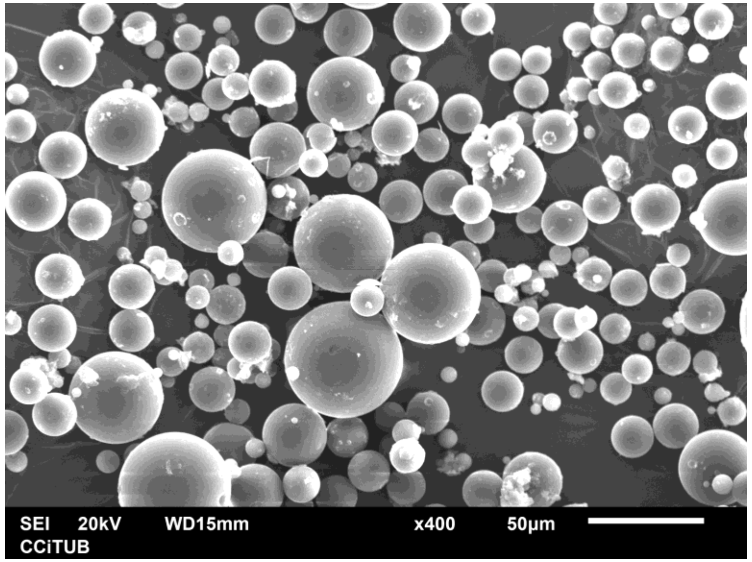
Retention (%)	Efficiency (%)
75,5 (3)	84,9 (1)

Elution of extractant at 25 mL



cPSm





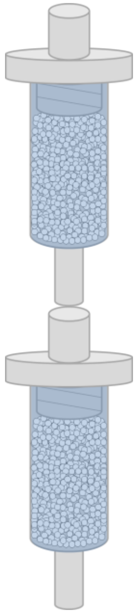
Retention (%)	Efficiency (%)
67 (3)	65 (5)

Constant from 10 to 50 mL

5. On going developments

5G. Tandem PSresin

Two in two



<u>$^{89}Sr/^{90}Sr$</u>

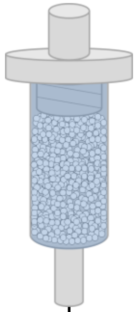
1. Sr-Tkscint (^{89}Sr+ ^{90}Sr)
2. gross α Psresin (^{90}Y)

<u>Plutonium/^{90}Sr</u>

1. Tc-Tkscint (Plutonium)
2. Sr-TkScint (^{89}Sr+ ^{90}Sr)

Two in one

<u>Plutonium/^{90}Sr</u>



mod-Tc-Tkscint (Plutonium). ALFA

mod Sr-TkScint (^{90}Sr). BETA

α/β DISCRIMINATION

Thank you for your attention

Recent applications of Plastic Scintillation Resins

A. Tarancón, H. Bagán, A. Coma, I. Giménez, X. Mendo, Y. Zhou

UNIVERSITAT DE BARCELONA