Selective Plastic Scintillators for Radioactivity Analysis

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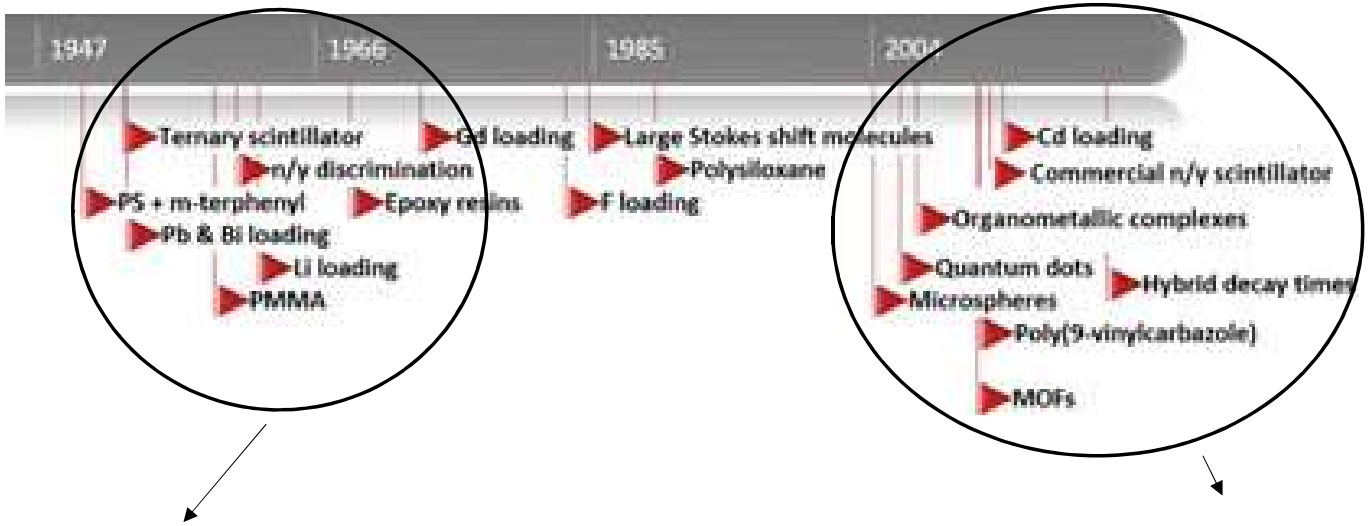
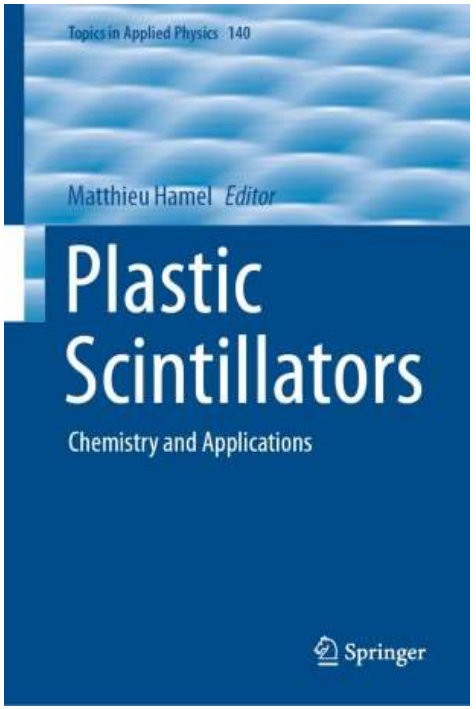
1953: m-terphenyl dissolved in polystyrene



- Discovery and definition of characteristics
- First applications

- New and advanced PS
- New applications



Hamel M.
Topics in Applied Physics 140.
Springer. 2021

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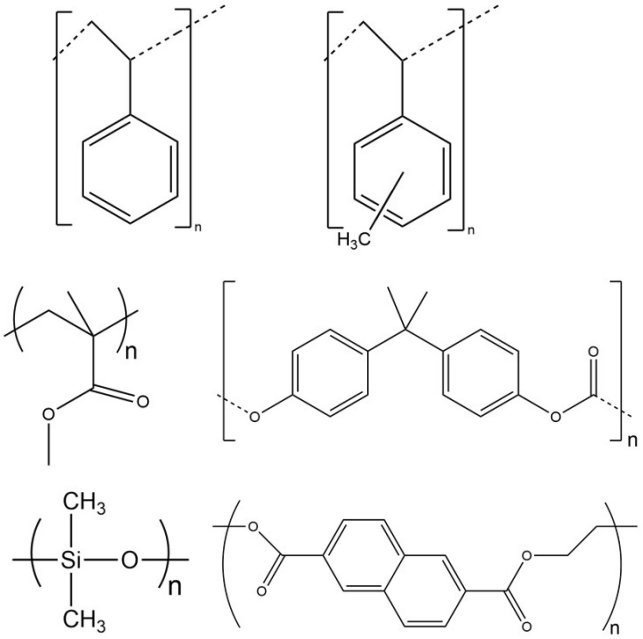
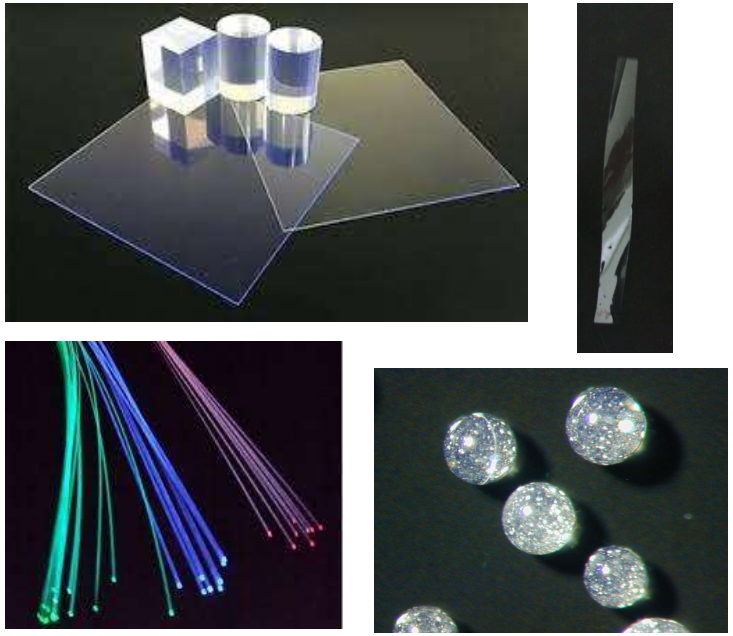
➢ PLASTIC SCINTILLATORS FOR RADIATION DETECTION

✓ Versatility

BASE POLYMERS



SHAPES



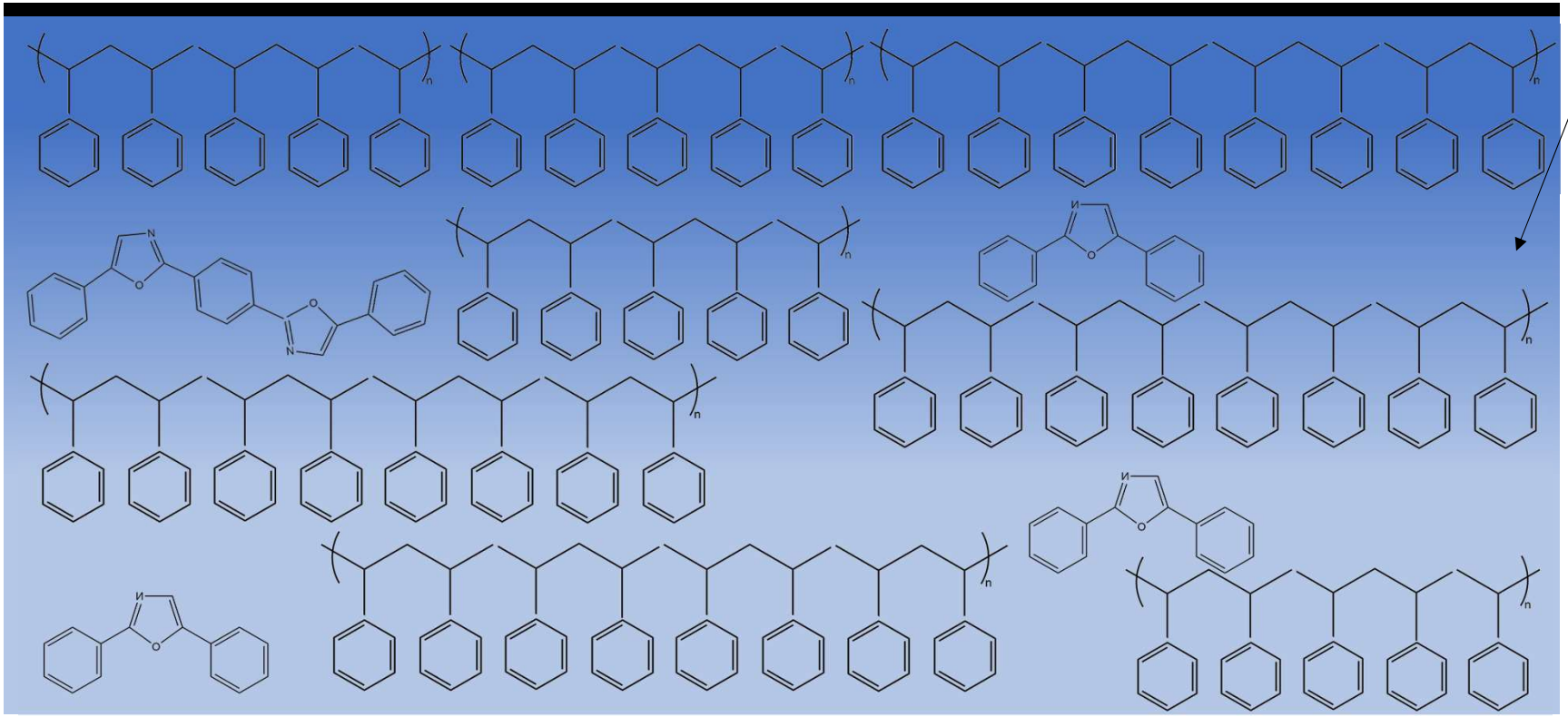
ADDITIVES

- ✓ Pulse Delayers (DIN….)
- ✓ Neutron detection (^{10}B. ^{6}Li...)
- ✓ Organometalic complexes (Ir. Sn. Gd. Cd…)
- ✓ Nanoparticles. QD's
- ✓ Extractants (aliquat·336)

SEVERAL APPLICATIONS derived

➢ SELECTIVITY IN PLASTIC SCINTILLATORS

MODIFICATIONS



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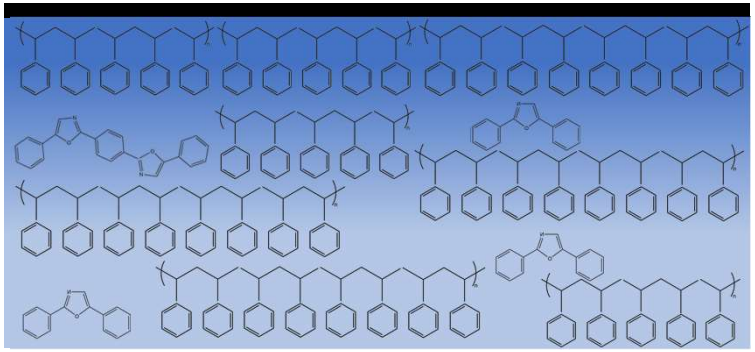
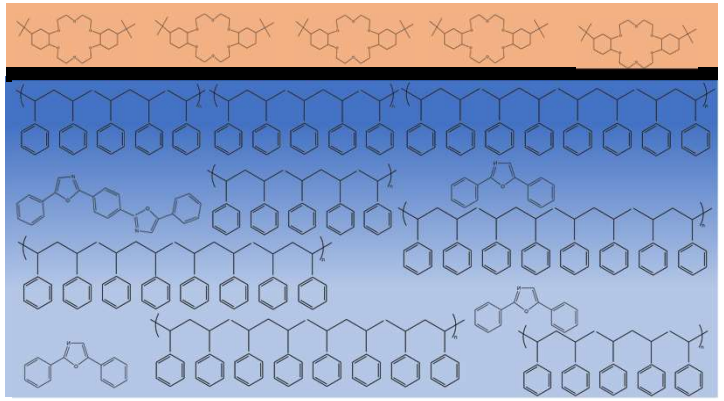
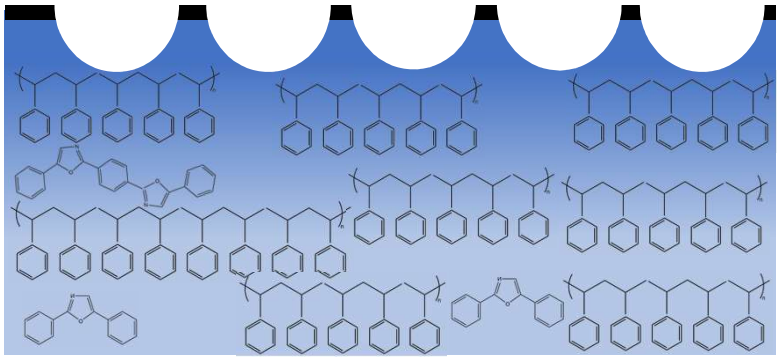
➢ SELECTIVITY IN PLASTIC SCINTILLATORS



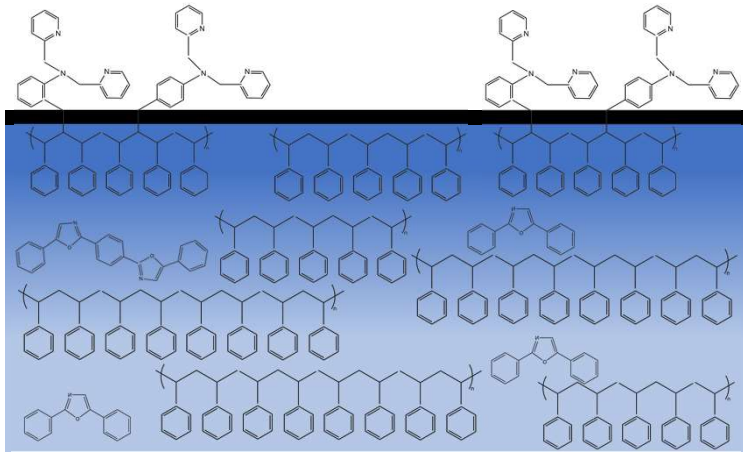
Extractant deposited on the surface

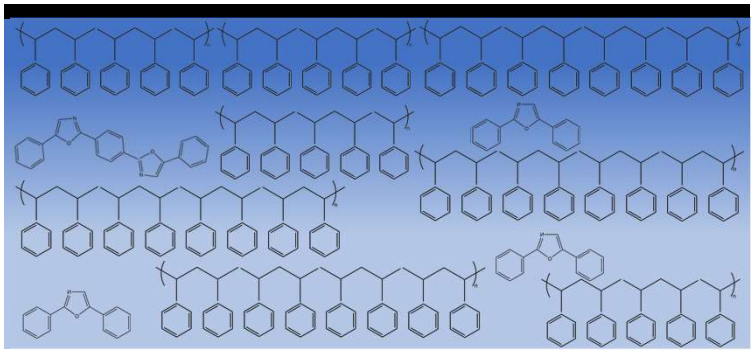


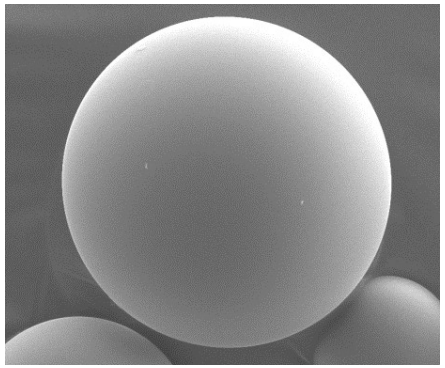
Imprinting the surface



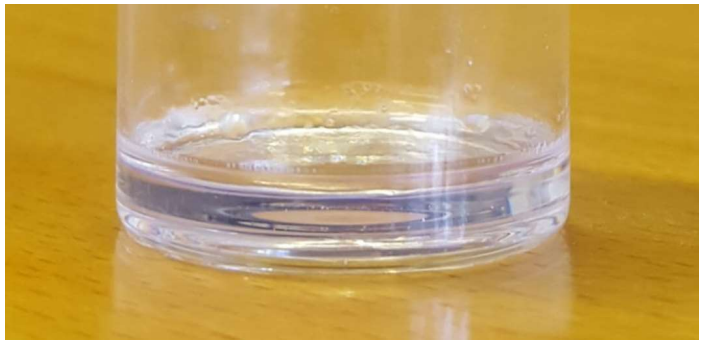
Extractant linked to the the surface







PSresins (microshperes)



PSkits (sheets)

PS-sticks (foils)

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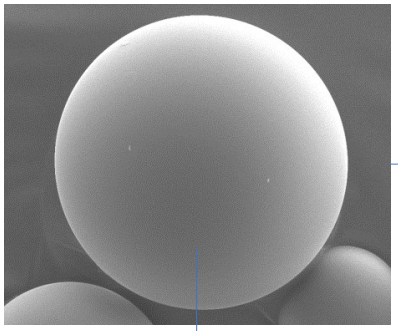
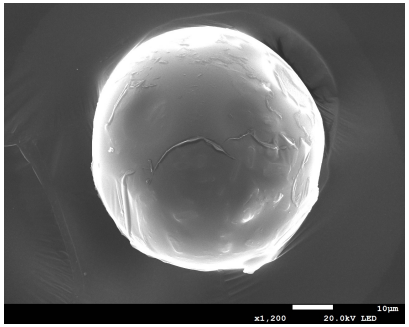
➢ PSresin: Plastic Scintillation Resins

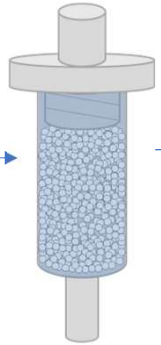


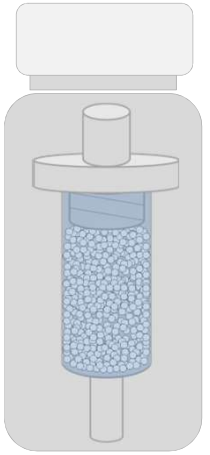
PSm
Aromatic solvent
(polystyrene)
+
Fluorescents

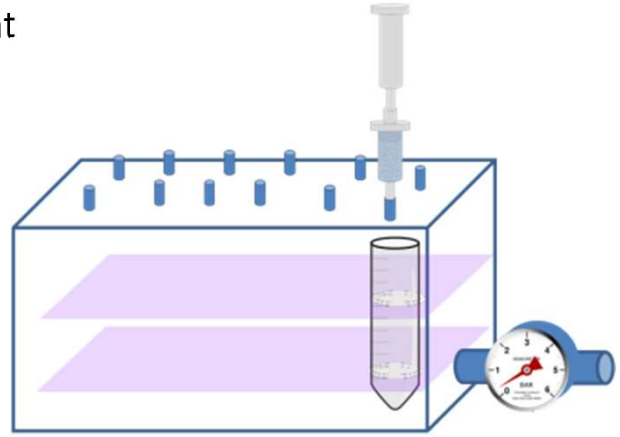
Extractant



PSresin
PSm + Extractant







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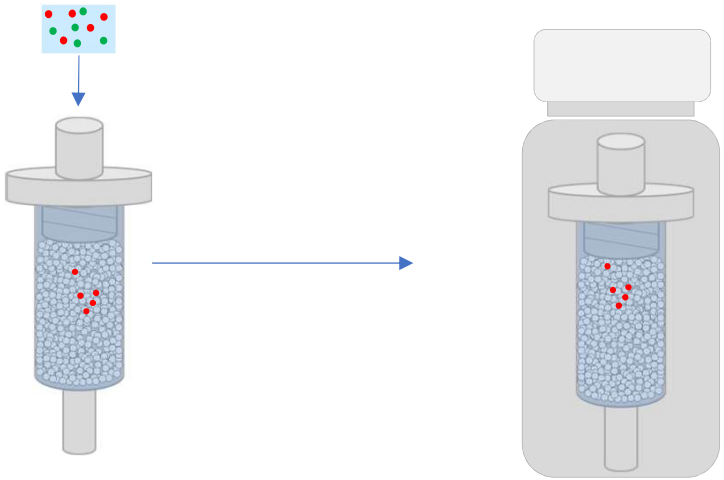
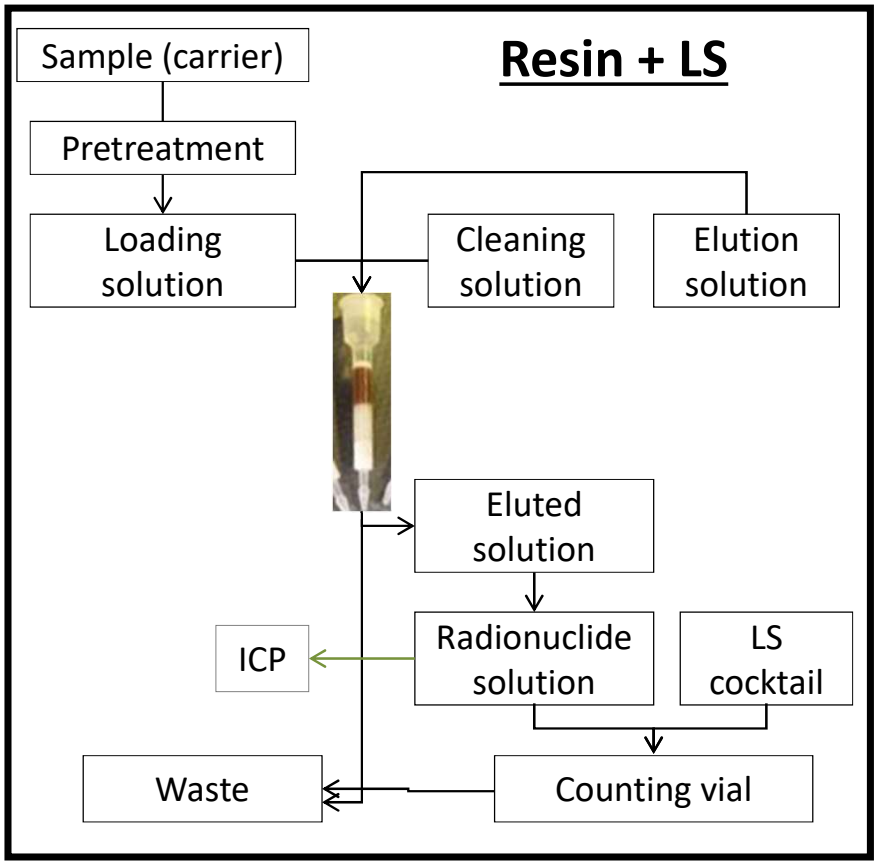
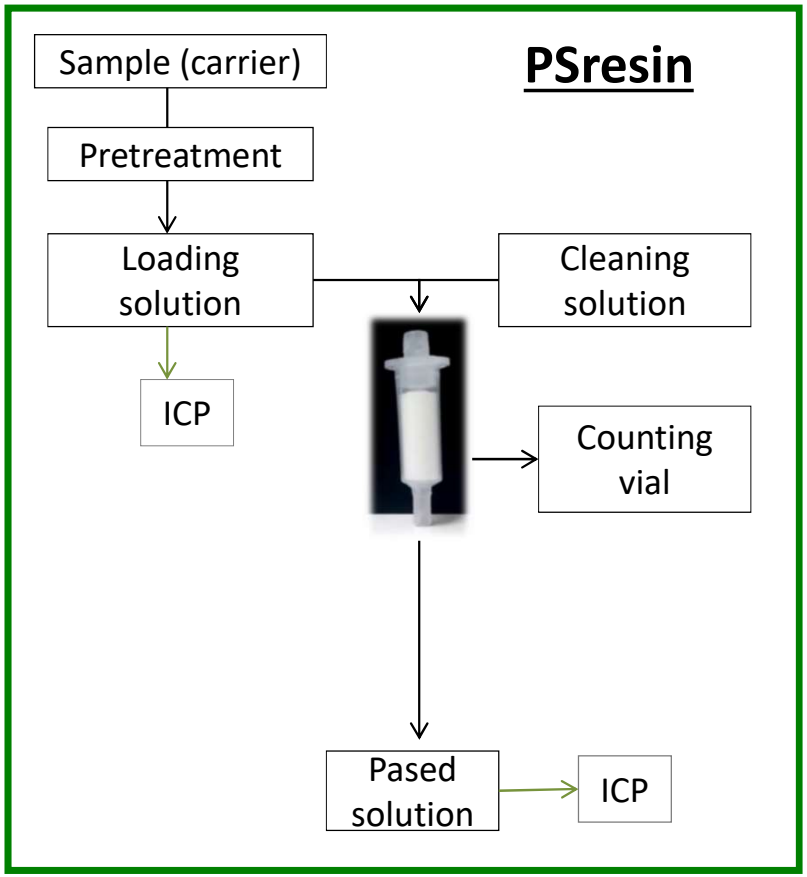
➢ PSresin: Plastic Scintillation Resins



MEASUREMENT AND DETECTION WITH THE SAME MATERIAL

➢ PSresin: Plastic Scintillation Resins





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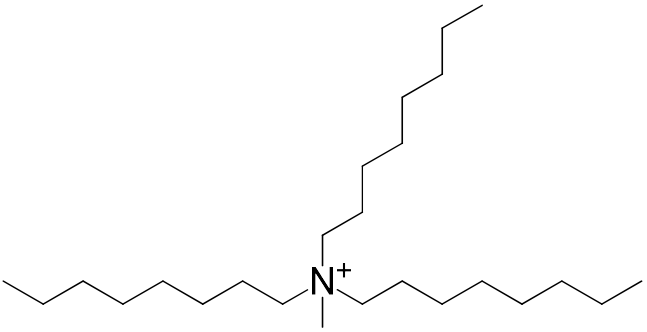
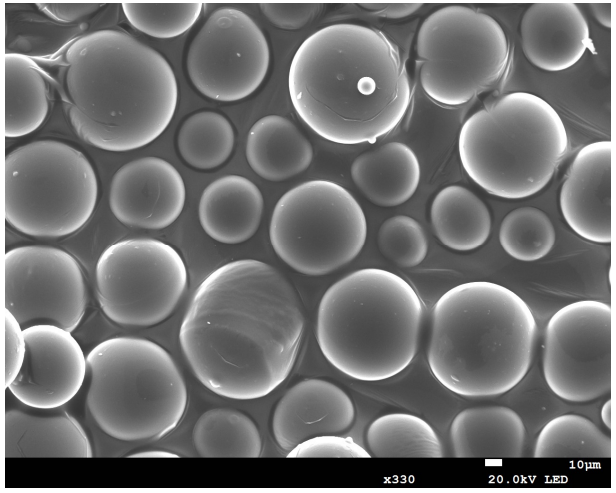
➢ Aliquat·336 PSresin





TRISKEM
Expertise in Separation Chemistry

PRODUCT SHEET

TK-TcScint

Main Applications

- Separation and LSC measurement of technetium

↓

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

^{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

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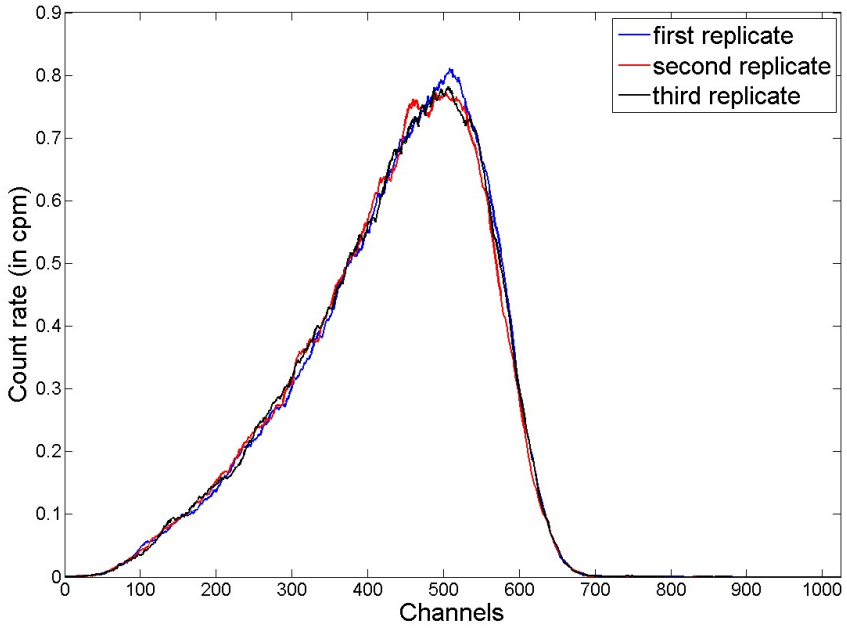
^{99}Tc analysis in TK-TcScint

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**

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^{99}Tc analysis in TK-TcScint

Sample	Activity (dpm mL^{-1})	Activity Calc (dpm mL^{-1})	Error (%)
Sea Water	24.3	23.0	-5.3
Sea Water	24.3	25.1	3.3
Sea Water	24.2	22.8	-6.2

- **Recovery:** 100 %
- **Background (1-1024):** 1.09 cpm
- **Detection efficiency:** 89.5 %
- **MDA (100 mL. 24 hour):** 0.024 Bq L^{-1}

Sample	Activity (dpm mL^{-1})	Activity Calc (dpm mL^{-1})	Error (%)
Urine	0.43	0.44	2.4
Urine	0.46	0.42	-6.5

Sample: 100 mL of urine

Pretreatment:

- Add 10 mL of 65% HNO_3 and evaporate to dryness
- Dissolved in 5 mL of 65% HNO_3
- Evaporated to dryness
- Heat at 550 C in a muffle oven for 30 min.
- Dissolved in 3mL of HNO_3
- Treated with 100 mL of D.D. water
- Add 5 mL of H_2O_2 and heated to 90 C for 1 hour

Cleaning: Water

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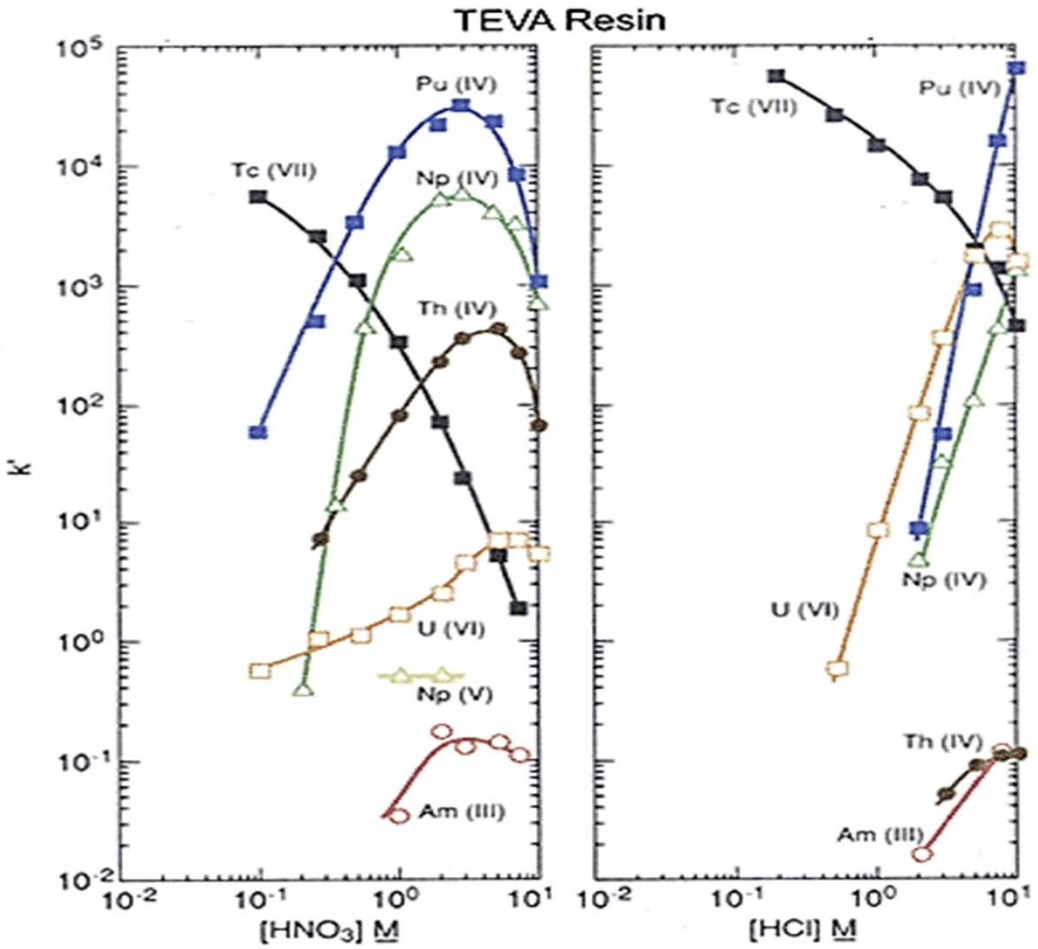
Plutonium isotopes analysis in TK-TcScint



Plutonium isotopes analysis in TK-TcScint

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

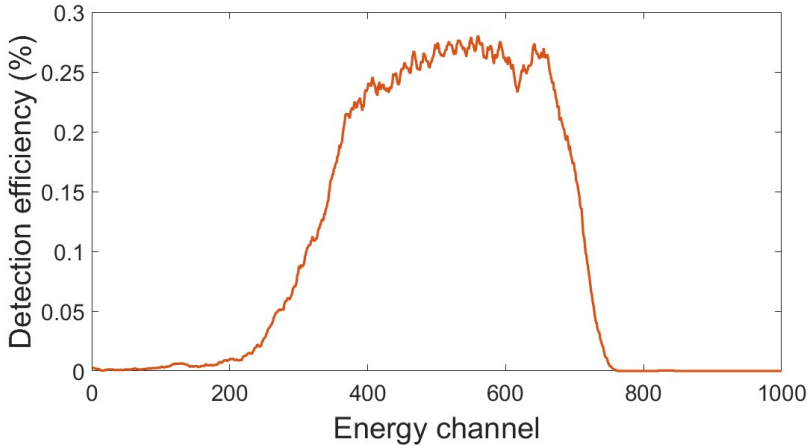
2. Loading medium:

- 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

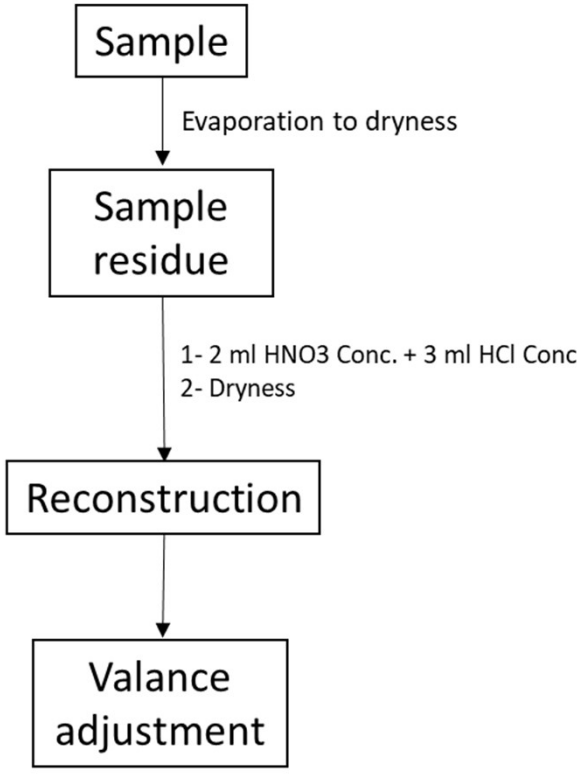
➢ **Stable tracer: 0.25 mg Au**



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

Plutonium isotopes analysis in TK-TCscint

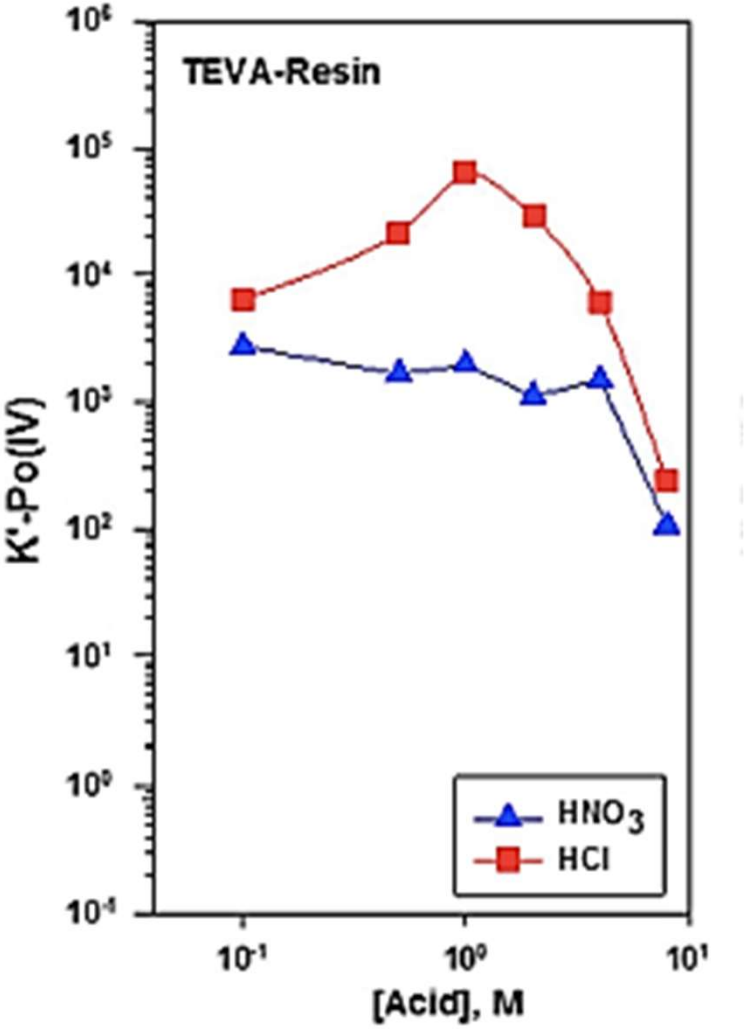
Water sample analysis (sea and river)
100 mL (10 Bq/L)



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)

^{210}Po analysis in TK-TcScint



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

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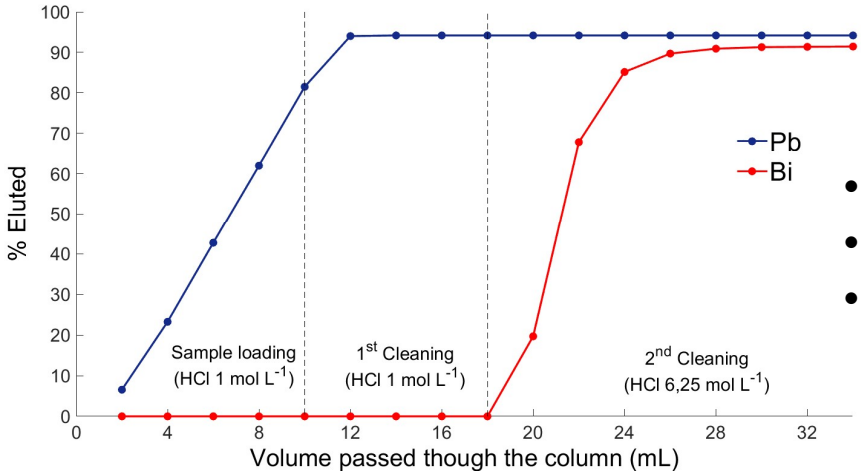
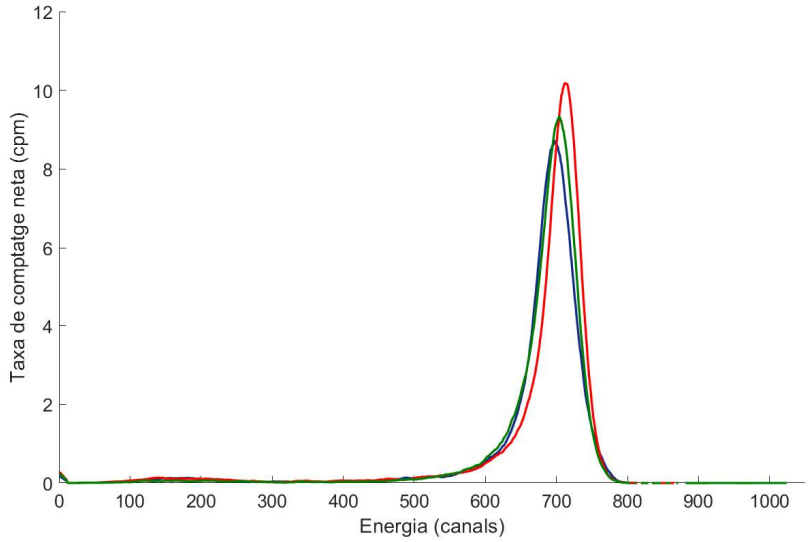
^{210}Po analysis in TK-TcScint



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

Column Retention [%]
99.9 (0.1)



Efficiency [%]
100(6)

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^{210}Po analysis in TK-TcScint

Precipitat MnO_2 (Cd i ^{210}Po)

0.75 mg $Cd2^+$ (tracer))

2 mL HCl conc.

0.5 L water

1 mL $KMnO_4$ 0.2 mol L^{-1}

1 mL $MnCl_2$ 0.3 mol L^{-1}

NH_3 conc. Until pH=8 – 9

Sobrenedate

Precipitate

Filtration

Precipitate

20 mL HCl 2 mol L^{-1}/H_2O_2 1 %

Digestion in water bath at 50 ºC (30 min)

Conditioning: 3 mL HCl 1 mol L^{-1}

Sample loading

8 mL HCl 1 mol L^{-1}

12 mL HCl 6.25 mol L^{-1}

ICP-OES
ICP-MS

LS COUNTER

^{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

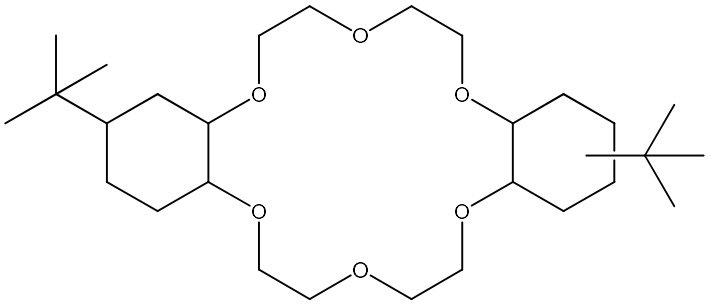
L_D: 69 hour counting

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

	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

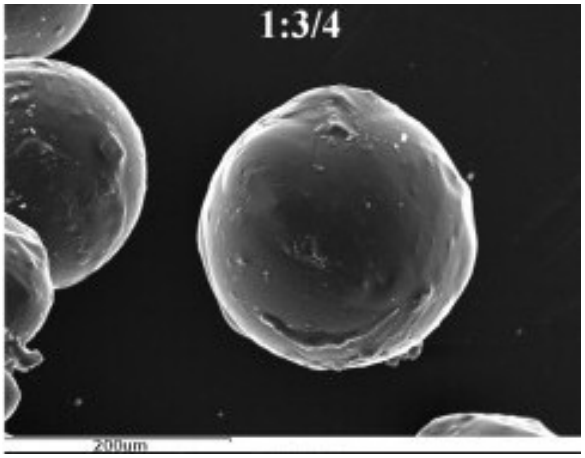
	Activity [Bq kg^{-1}]
Co-60	307(3)
Ba-133	171(2)
Cs-134	210(2)
Cs-137	210(2)
Pb-210	905(17)
Po-210	921(20)
Am-241	117(1)

➢ Crown-ether PSresin



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

in 1M Octanol



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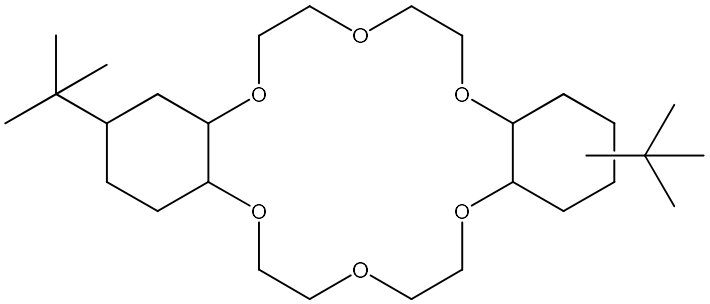
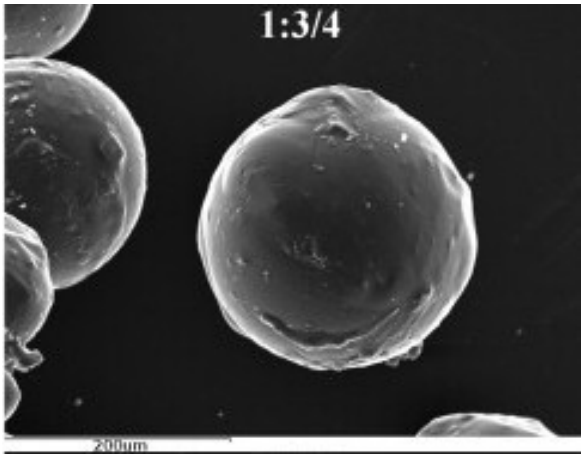
➢ Crown-ether PSresin: ^{90}Sr or ^{89}Sr



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

in 1M Octanol

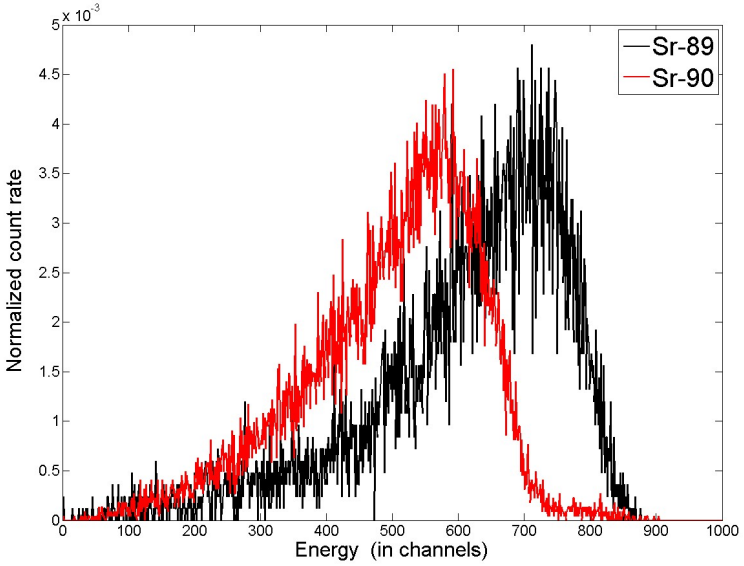


Column conditioning: **HNO_3 6 M or 8 M (2 mL)**

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

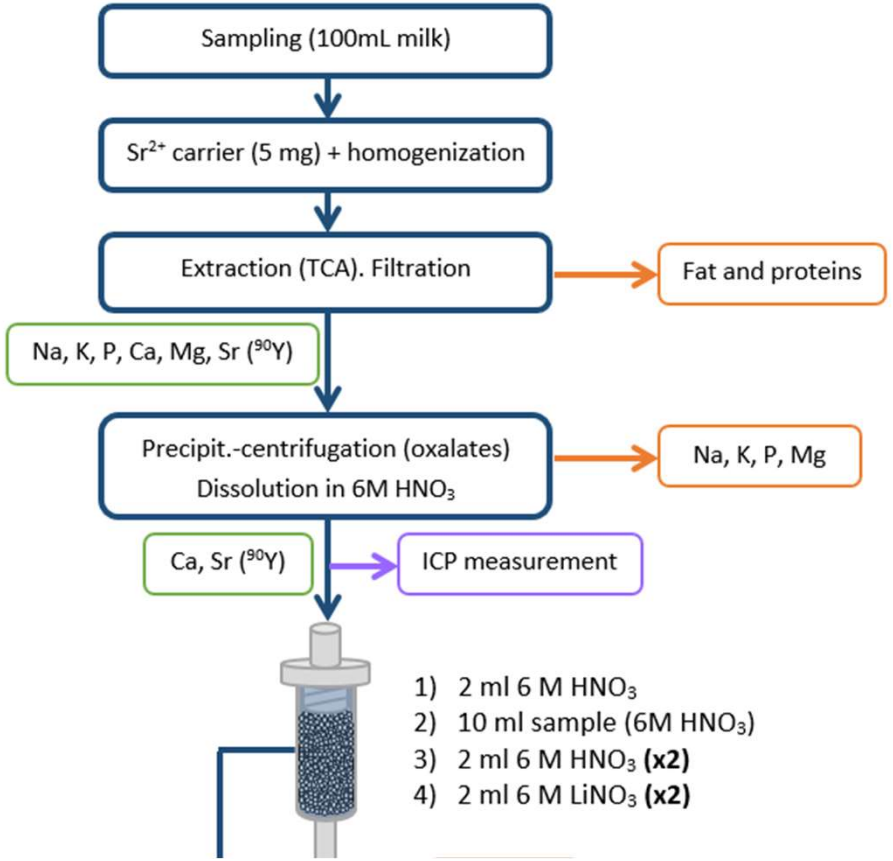
Cleaning: **HNO_3 6M (2*2 mL) and $LiNO_3$ 6 M (2*2 mL)**

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



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

^{90}Sr analysis in Crown-ether PSresin. MILK



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)

^{90}Sr analysis in Crown-ether PSresin. FILTERS AND VEGETATION

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

	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

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^{90}Sr analysis in Crown-ether PSresin.

- ^{90}Sr in Environmental samples → $Pb(IO_3)_2$ (prec) in hot HNO_3 8M solution

^{90}Sr → 4.2(0.2) Bq/L

Interferences → ^{210}Pb, ^{226}Ra, ^{137}Cs, ^{222}Rn, ^{230}Th

yield (%)		Bkg	^{90}Sr [Bq/kg] activity	
Sr	Pb	[cpm]	t = 0	t > 21 days
87.6(0.4)	6(2)	0.18(0.03)	4.6(0.6)	4.1(0.1)

- ^{210}Pb + ^{90}Sr + ^{210}Po in sediements →
  - Loading medium: HNO_3 3M + HCl 1M
  - Elution ^{210}Po : HNO_3 8M
  - Elution ^{90}Sr: HNO_3 0.5M

URAIS

Universitat Rovira i Virgili (URV)
Tarragona. Spain

- ^{90}Sr in concrete decommissioning samples

cea

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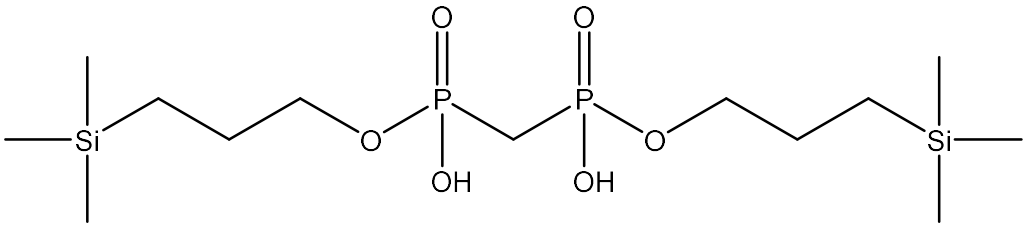
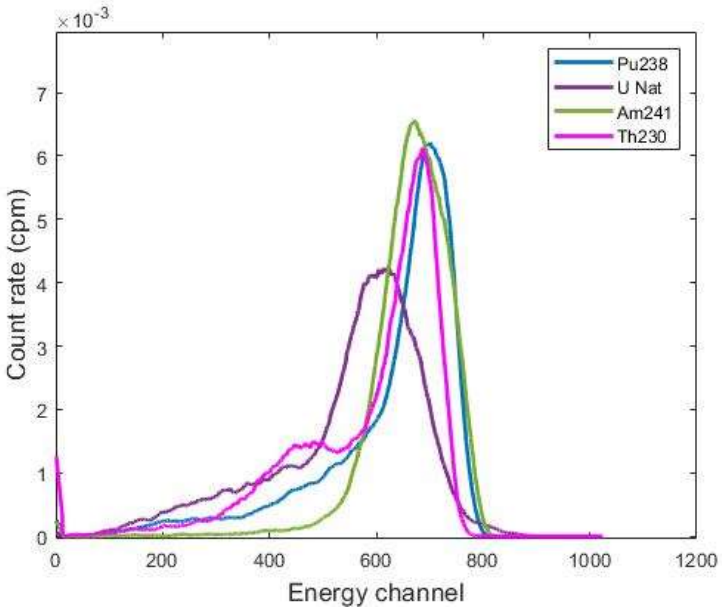
➢ DIPEX-based PSresin



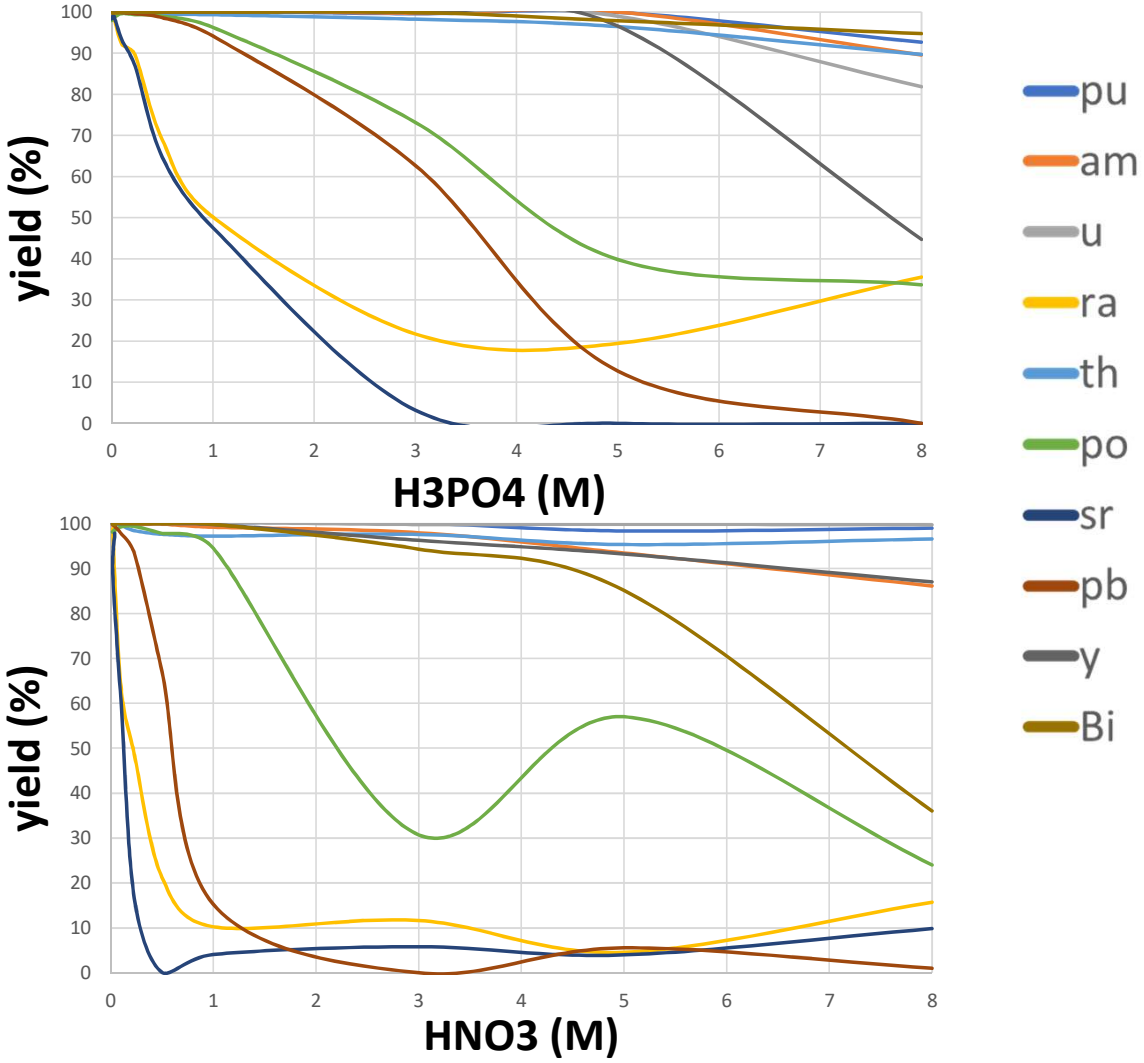
(3-trimethylsilyl-1-propyl)methandisphosphonic acid

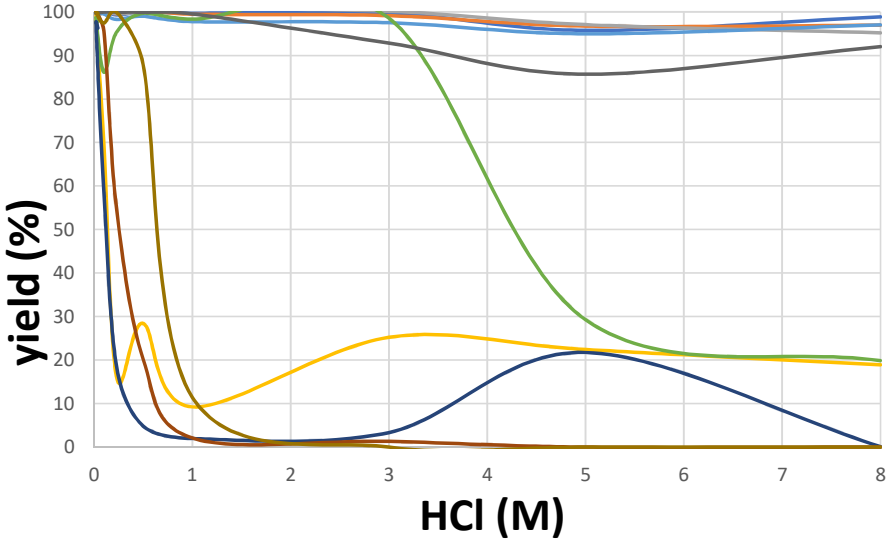
	Energy (MeV)	Det. Eff. (%)
^{241}Am	5.48	100 (1)
^{238}Pu	5.59	97 (3)
natural U	4.27/4.86	95.9 (0.8)
^{230}Th	4.77	98 (4)

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



➢ DIPEX-based PSresin

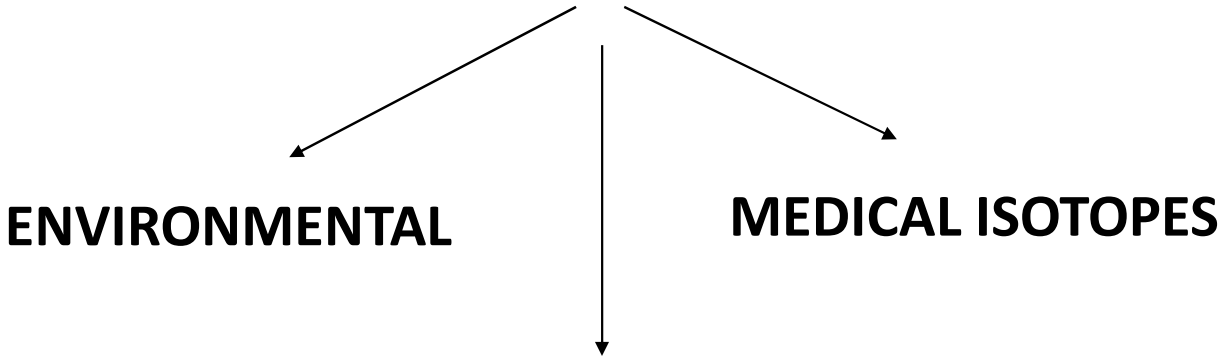




- ✓ **TOTAL ACTINIDES**
- ✓ **GROSS-ALPHA (including Po and Ra)**
- ✓ **INDIVIDUAL ELEMENTS? (U, ^{90}Y, …)**

➢ PSKITS

ULTRAFAST PSEUDO-QUANTITATIVE SELECTIVE MEASUREMENT



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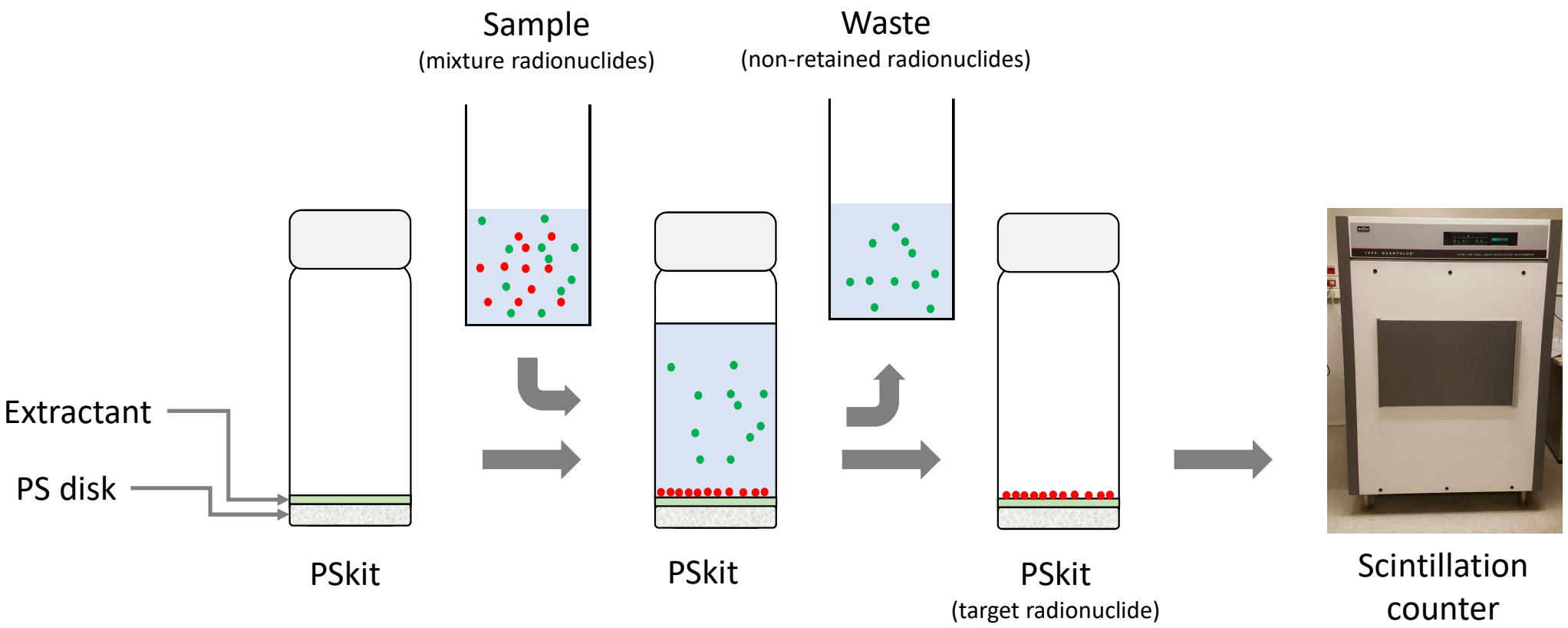
➢ PSKITS

ULTRAFAST PSEUDO-QUANTITATIVE SELECTIVE MEASUREMENT



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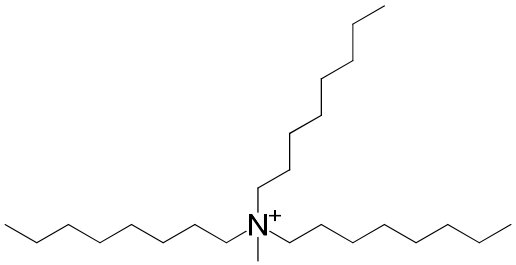
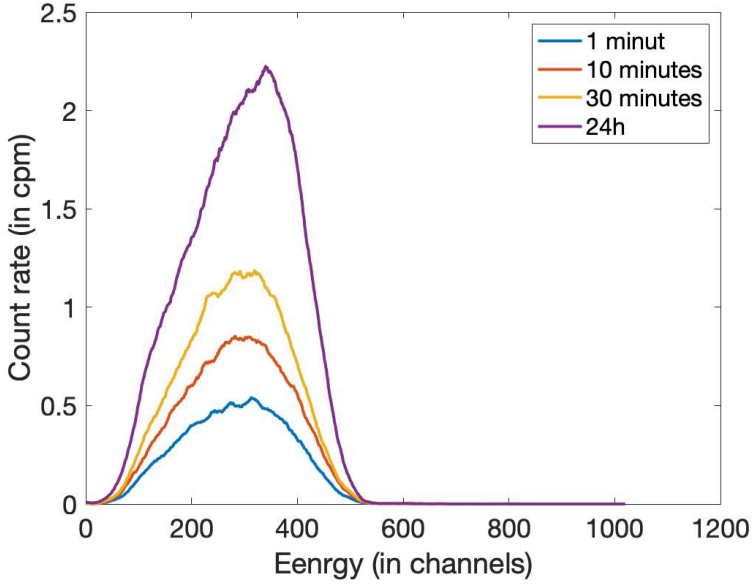
➢ PSKITS (for ^{99}Tc)



Contact time	^{99}Tc Efficiency detection	Retention
1 minute	32 ± 9	52 ± 8
10 minutes	44 ± 8	62 ± 12
30 minutes	54 ± 2	57 ± 1
24 hours	60 ± 1	96.9 ± 0.3

^{99}Tc



➢ FUTURE WORK

- ✓ **NEW PLASTIC SCINTILLATORS (crosslinked, porous, …)**
- ✓ **NEW APPLICATIONS**
  - **Tk-TcScint:**
    - **^{210}Po: NORM soil lixiviates**
    - **Pu: vegetation and filters**
  - **Dipex-based:**
    - **Gross-alpha**
- ✓ **PSKits "proof of concept": + extractants + samples (real)**
- ✓ **PSresin-TANDEM**
- ✓ **NEW PSRESINS**
  - **^{210}Pb based on crown-ether/ionic liquid extractant**
  - **Imprinted scintillating polymers (^{55}Fe, ^{210}Po, ….)**
  - **Covalent bonding PSresin (^{63}Ni)**

➢ ACKNOWLEDGEMENTS

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Thank you for your attention

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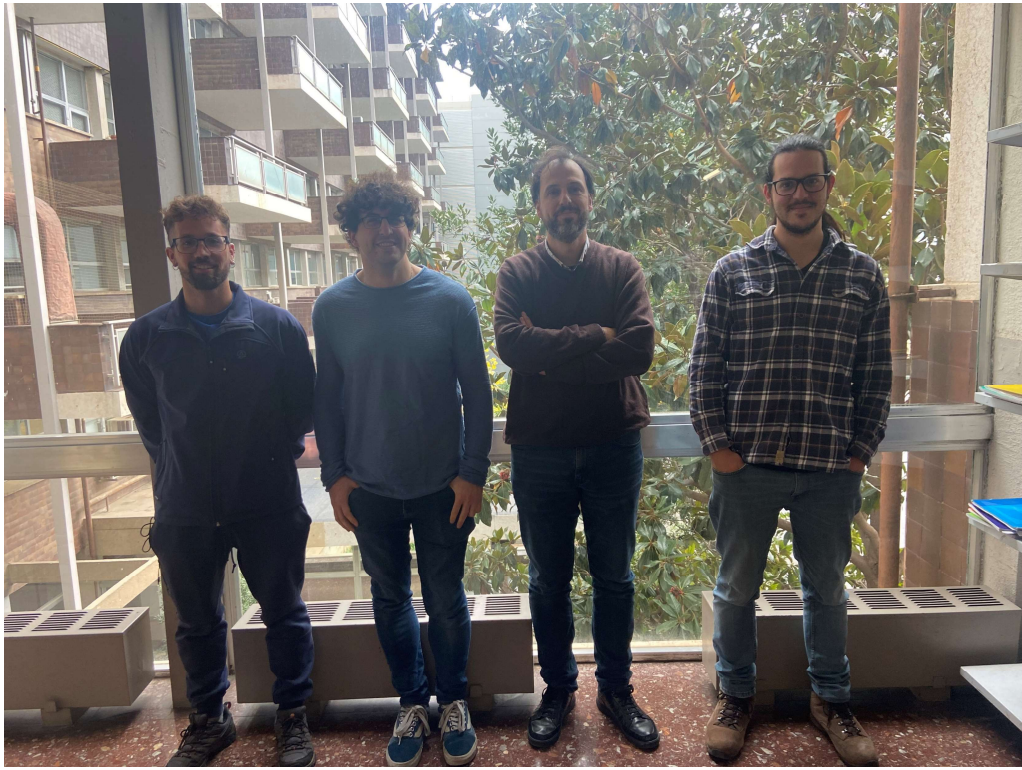

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