Advances in Selective Plastic Scintillators

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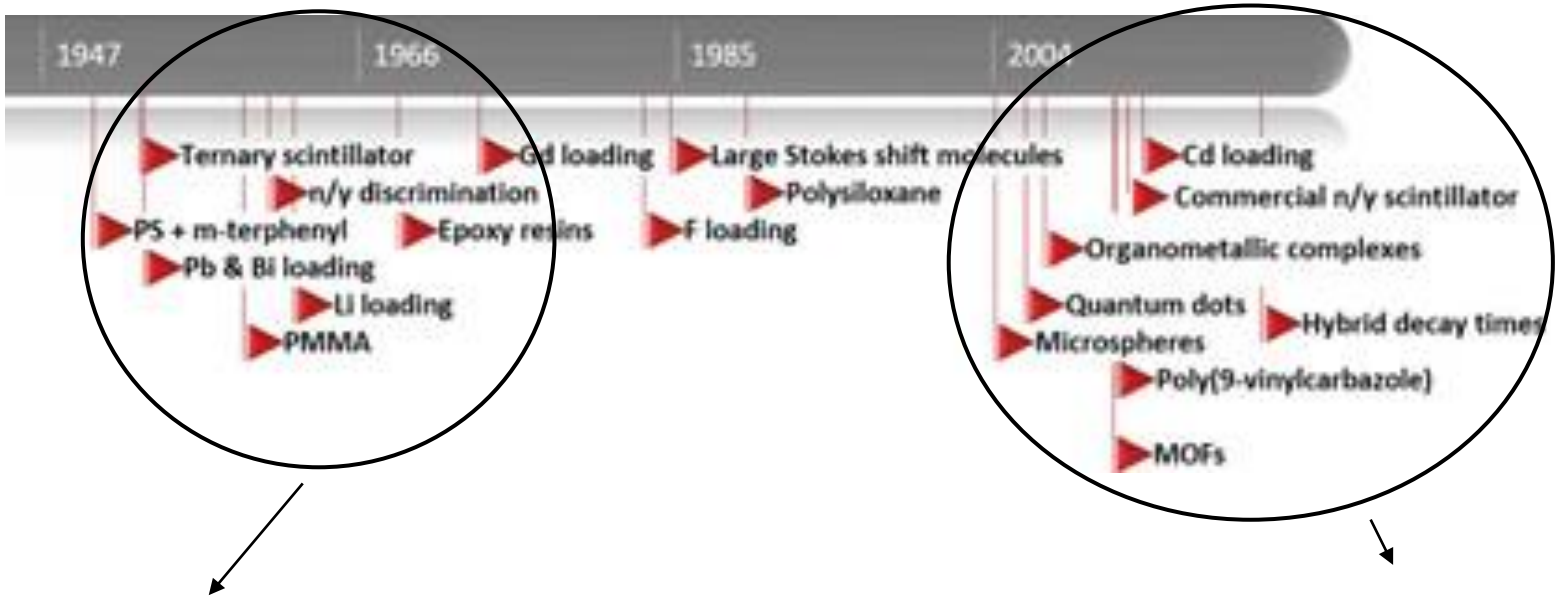
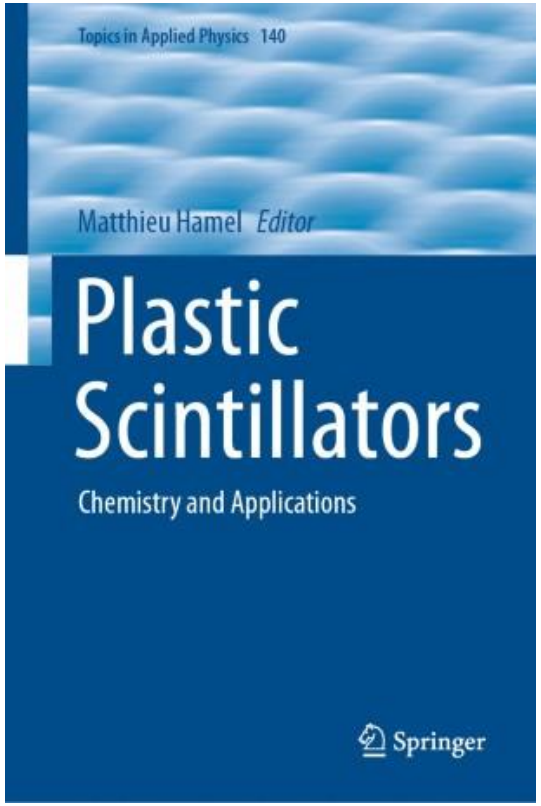
1953: m-terphenyl dissolved in polystyrene



- Discovery and definition of characteristics
- First applications

- New and advanced PS
- New applications

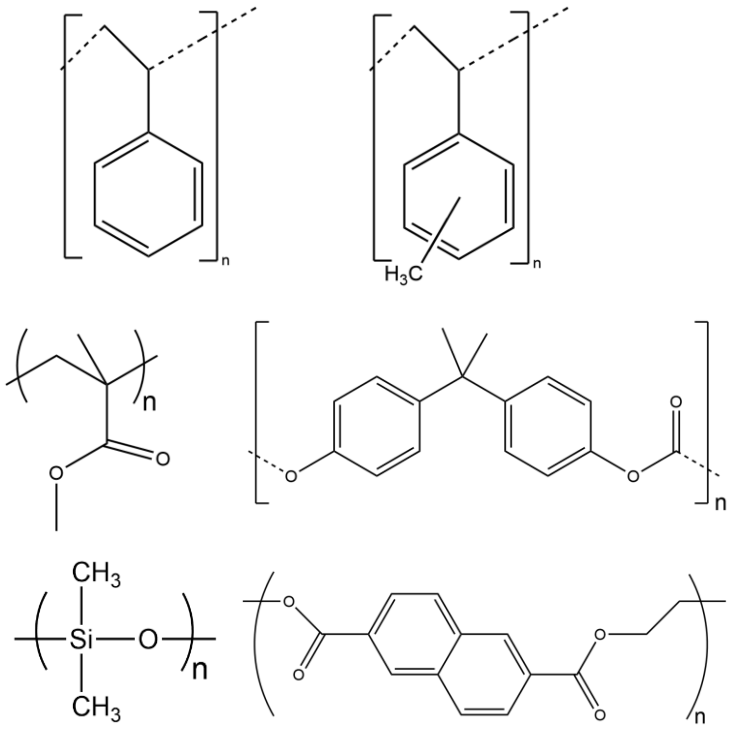


Hamel M.
Topics in Applied Physics 140.
Springer. 2021

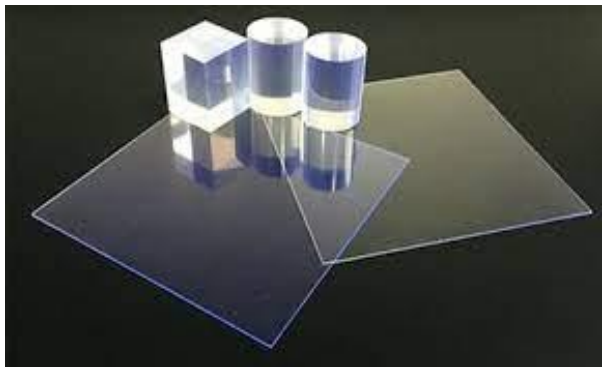
➢ PLASTIC SCINTILLATORS FOR RADIATION DETECTION

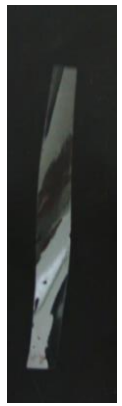
✓ Versatility

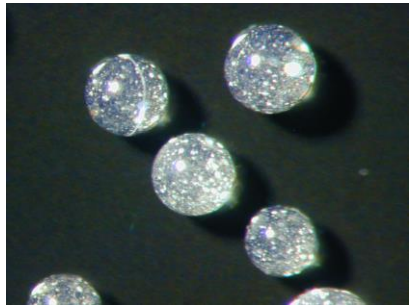
BASE POLYMERS



SHAPES







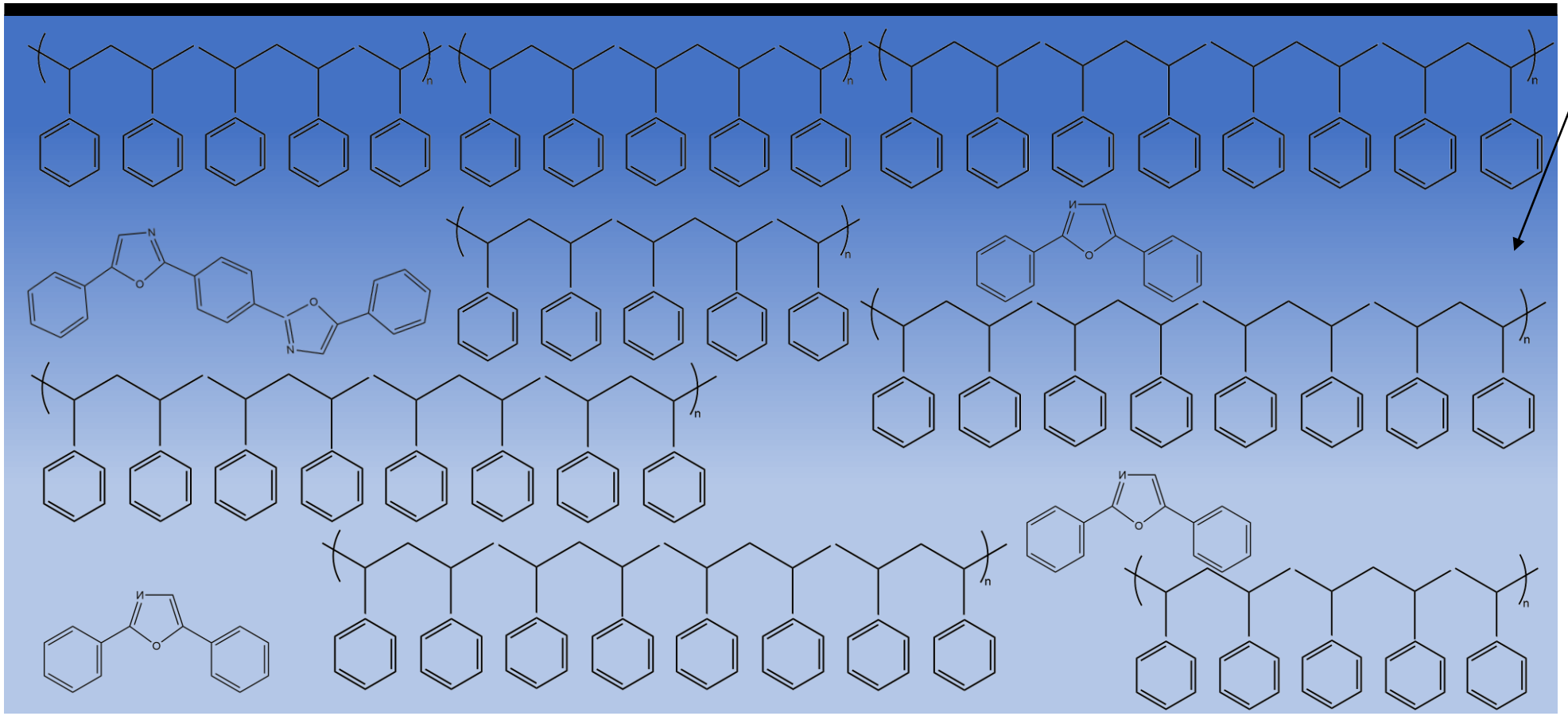
ADDITIVES

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

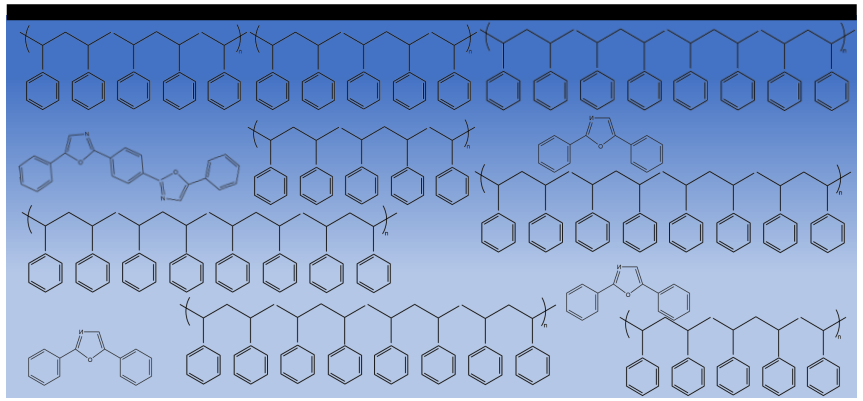
SEVERAL APPLICATIONS derived

➢ SELECTIVITY IN PLASTIC SCINTILLATORS

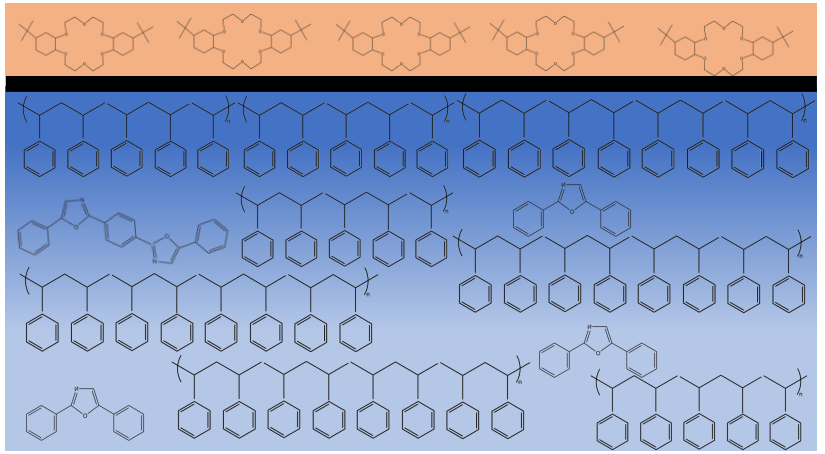
MODIFICATIONS



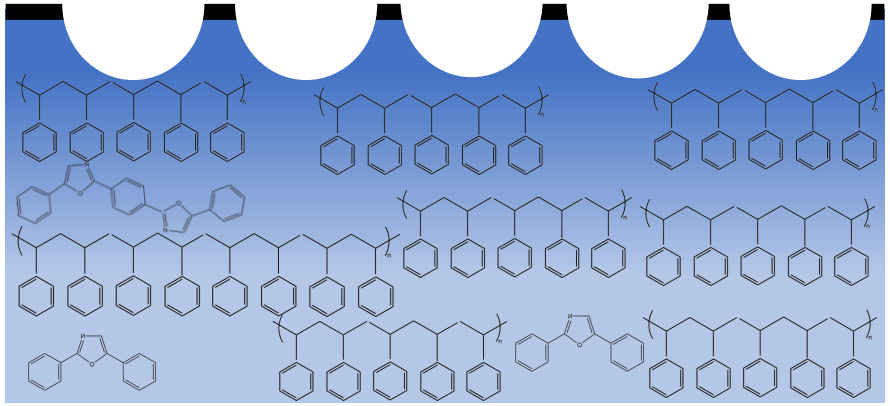
➢ SELECTIVITY IN PLASTIC SCINTILLATORS



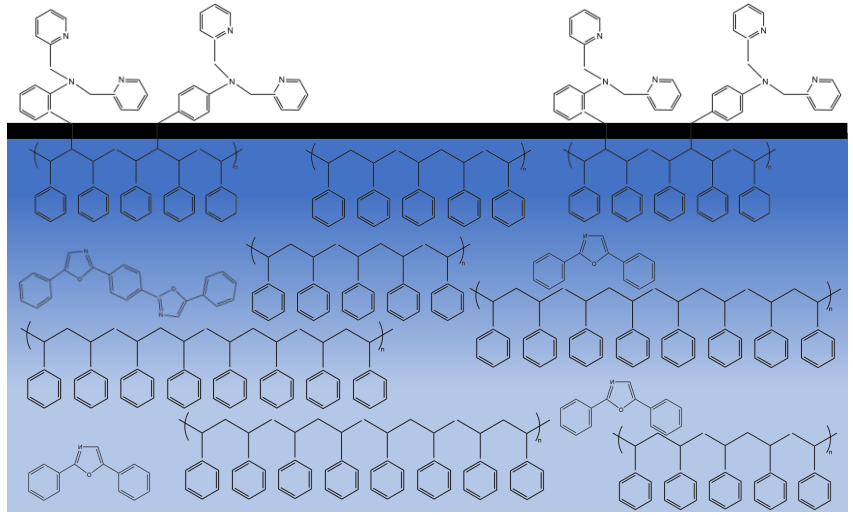
Extractant deposited on the surface

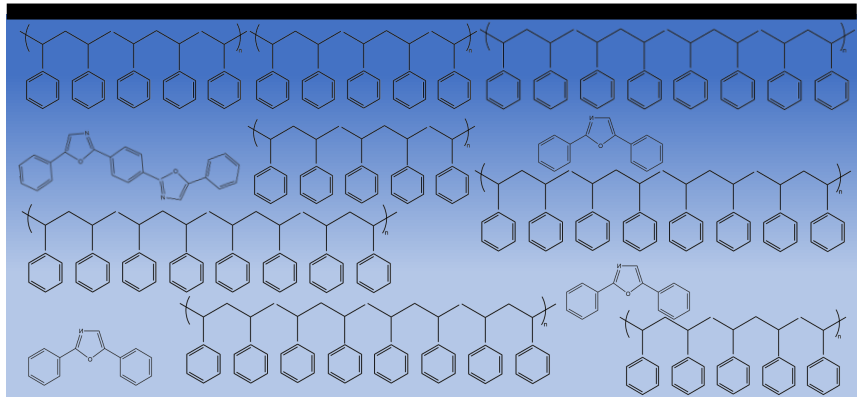


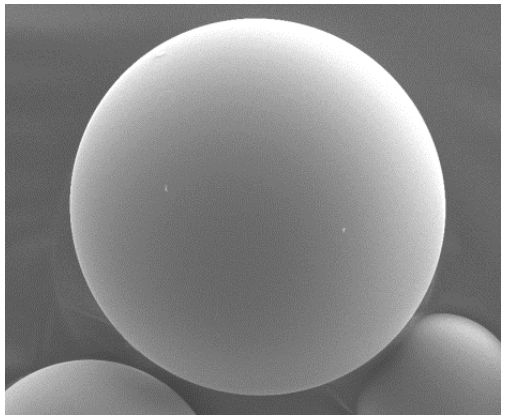
Imprinting the surface



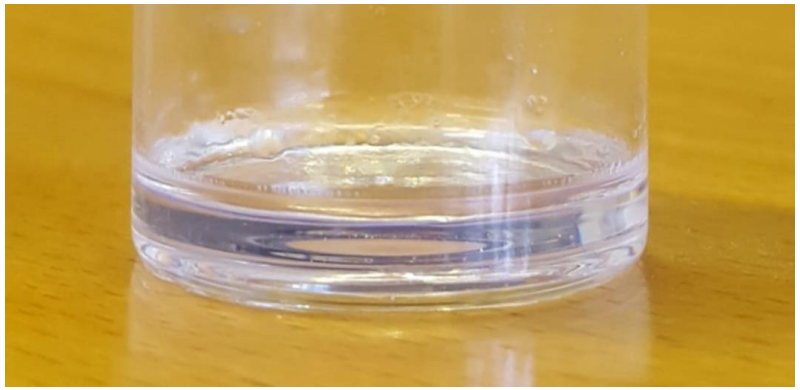
Extractant linked to the the surface



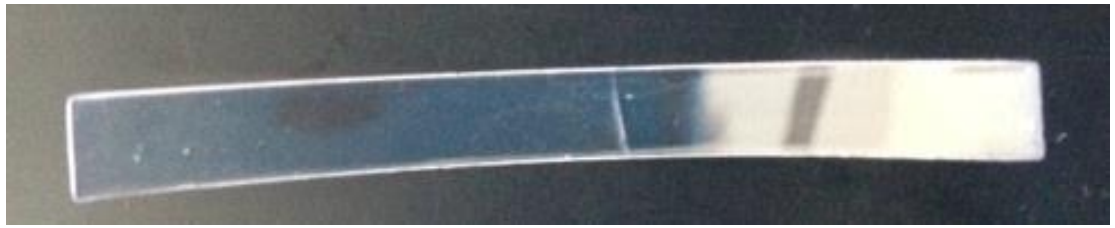




PSresins (microshperes)

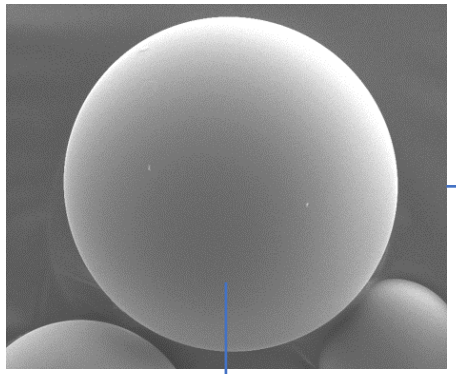


PSkits (sheets)



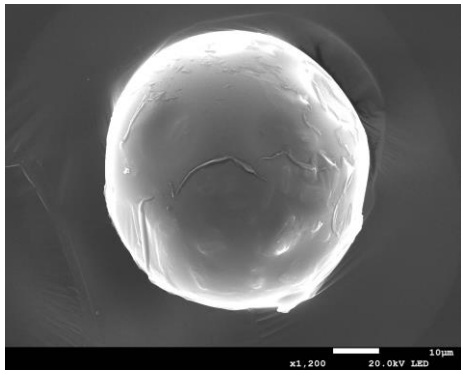
PS-sticks (foils)

PSresin

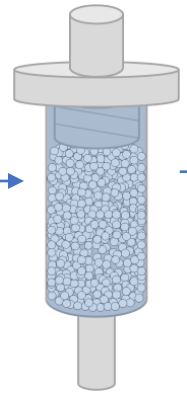


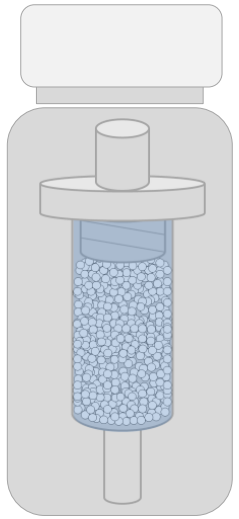
PSm
Aromatic solvent
(polystyrene)
+
Fluorescents

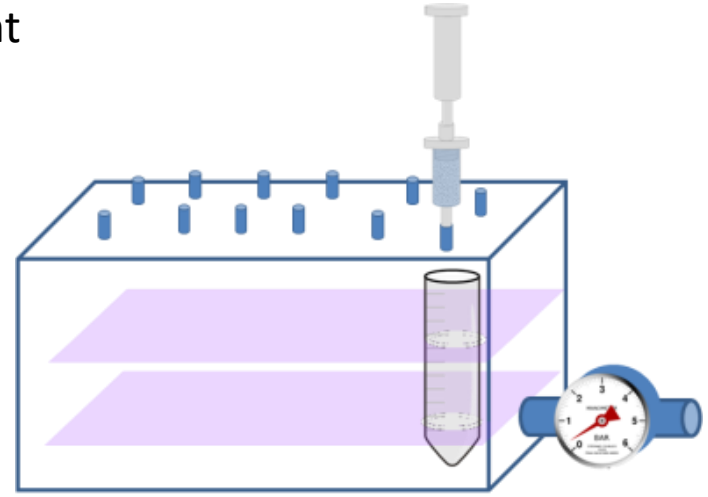
Extractant

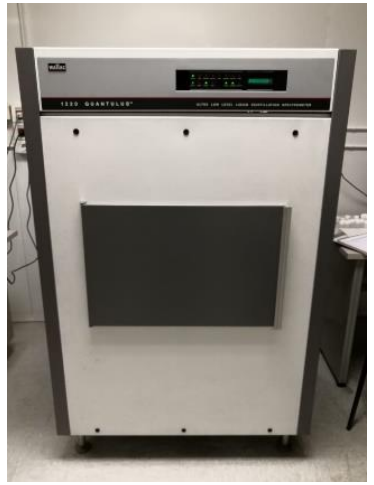


PSresin
PSm + Extractant

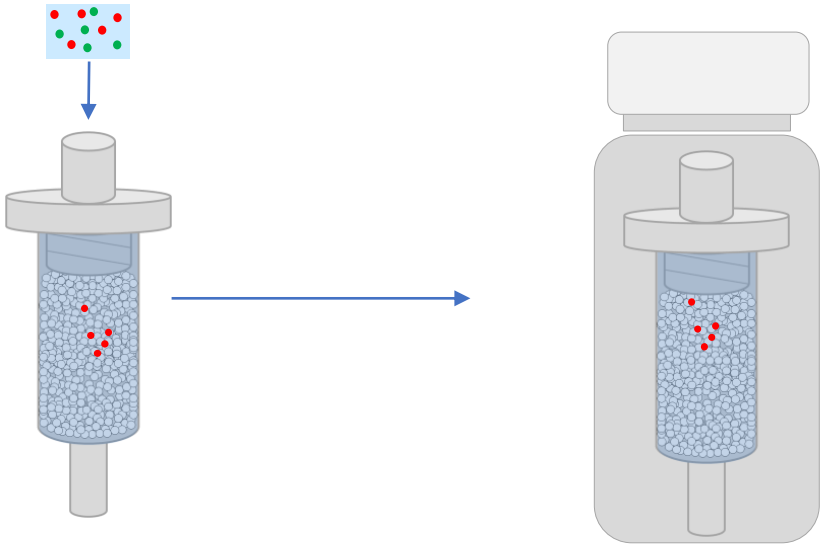






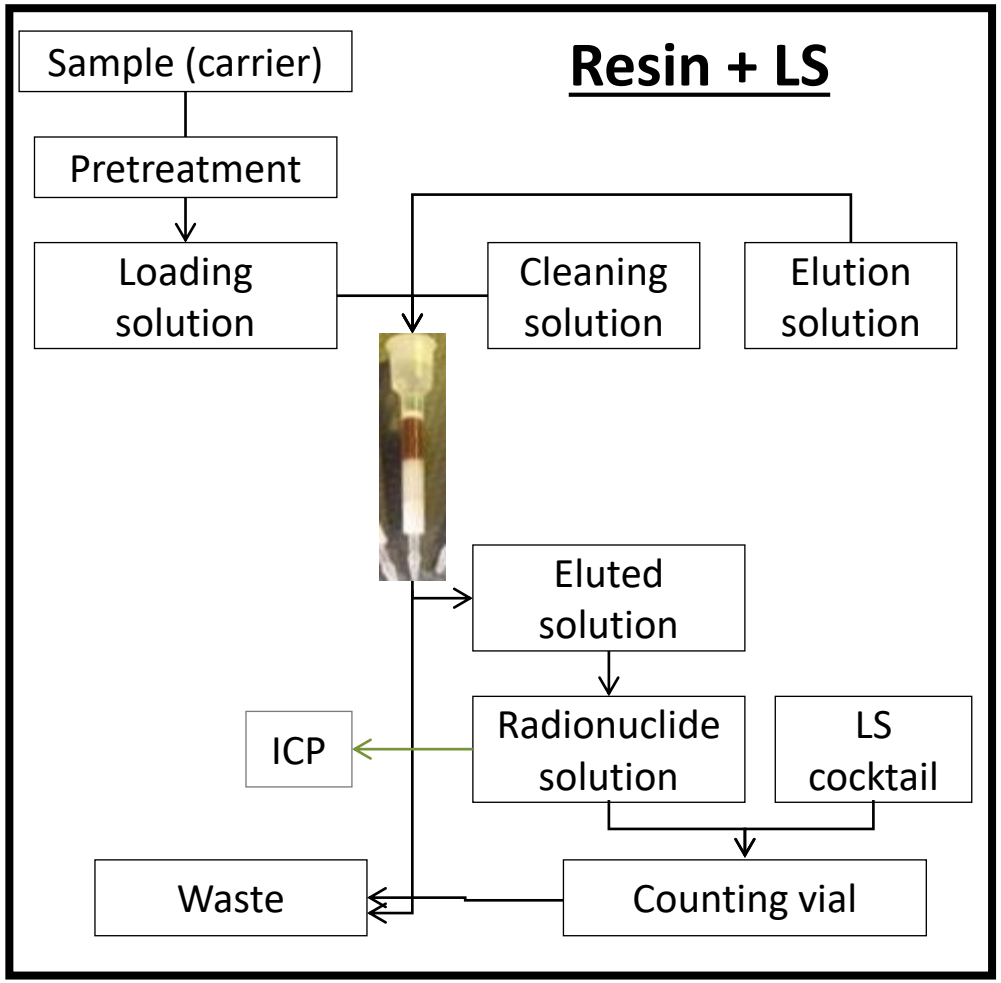


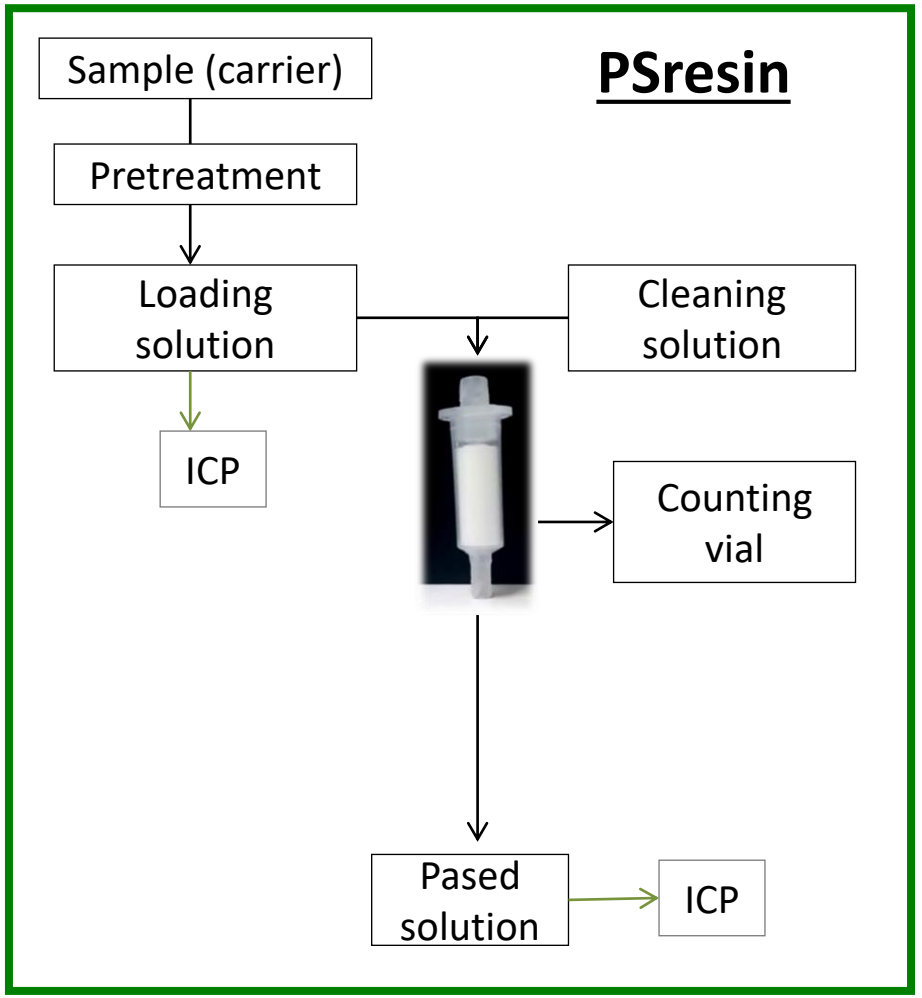
PSresin



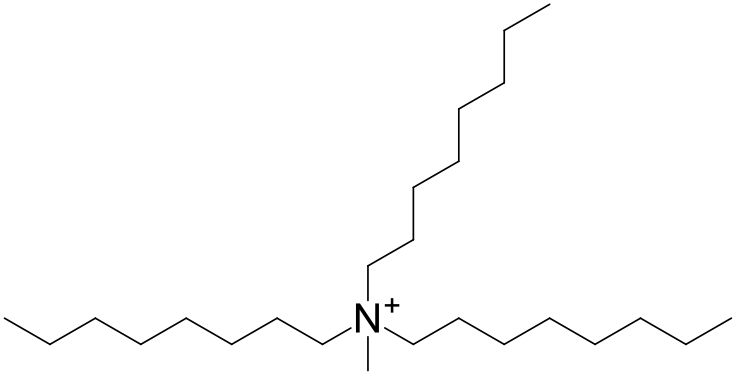
MEASUREMENT AND DETECTION WITH THE SAME MATERIAL

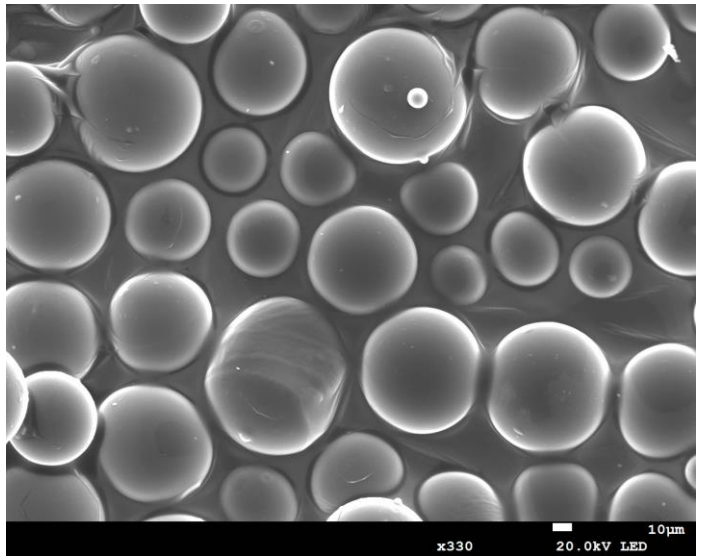
PSresin


Resin + LS
Sample (carrier)
Pretreatment
Loading solution
Cleaning solution
Elution solution
Eluted solution
ICP
Radionuclide solution
LS cocktail
Waste
Counting vial


PSresin
Sample (carrier)
Pretreatment
Loading solution
Cleaning solution
ICP
Counting vial
Pased solution
ICP

➢ 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
- $S^{14}CN^-$
- $^{36}Cl^-$

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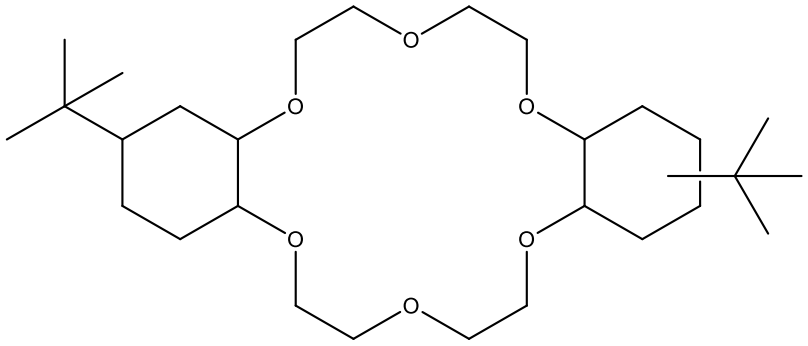
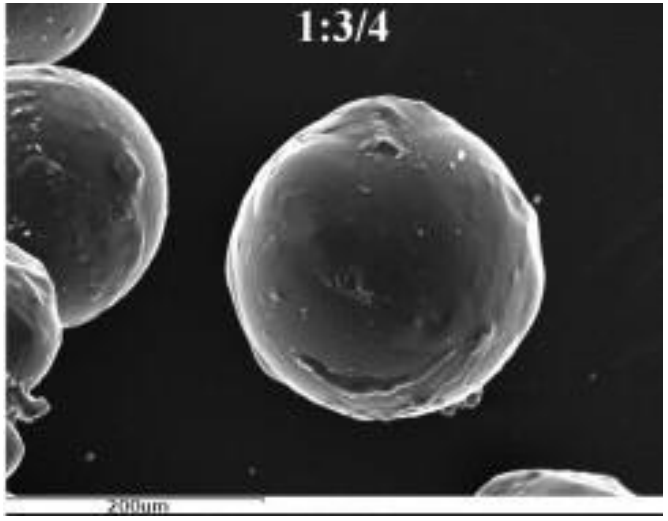
➢ Crown-ether PSresin



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

in 1M Octanol



UNIVERSITAT DE BARCELONA → TRISKEM Expertise in Separation Chemistry

- ✓ **^{90}Sr in water**
- ✓ **^{90}Sr analysis in milk**
- ✓ **^{90}Sr analysis filters and vegetation**
- ✓ **^{90}Sr in concrete decommissioning samples**
- ✓ **^{90}Sr in sediments**

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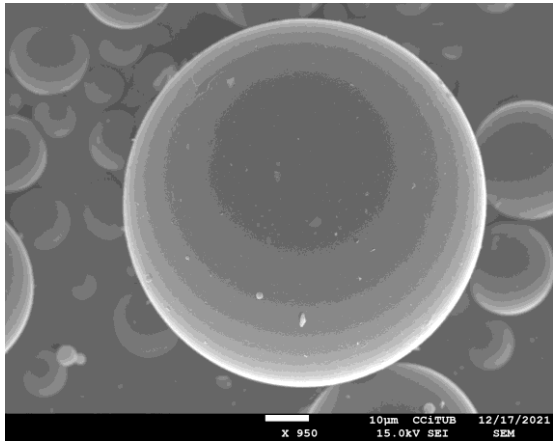
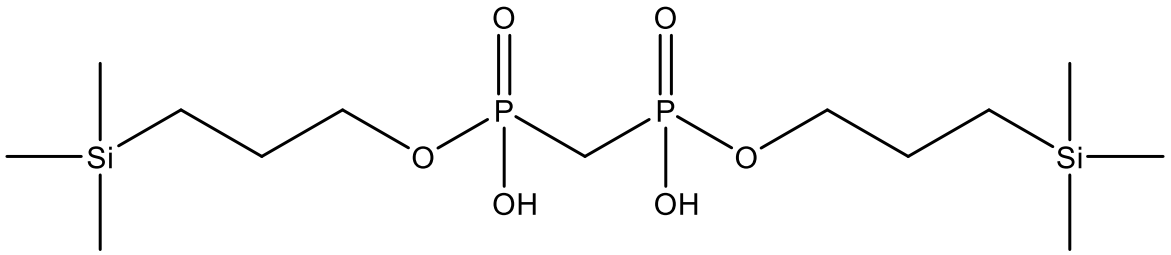
cea

- ✓ New α-Psresin: Application to gross Alpha in water samples

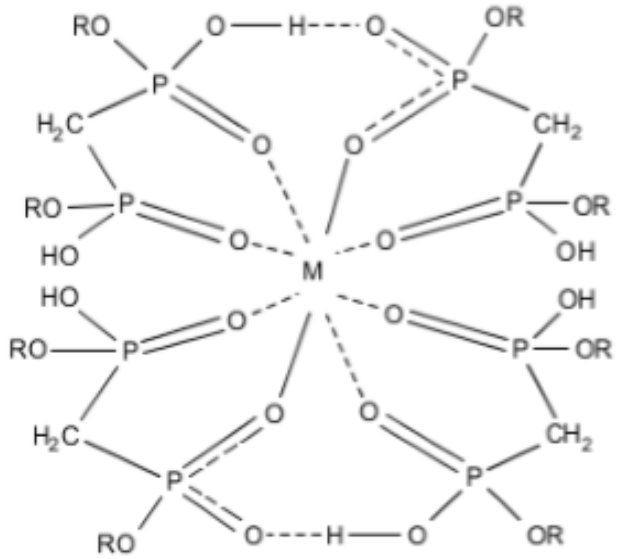
- ✓ Improvement on new PSmicrospheres



α-PSresin:



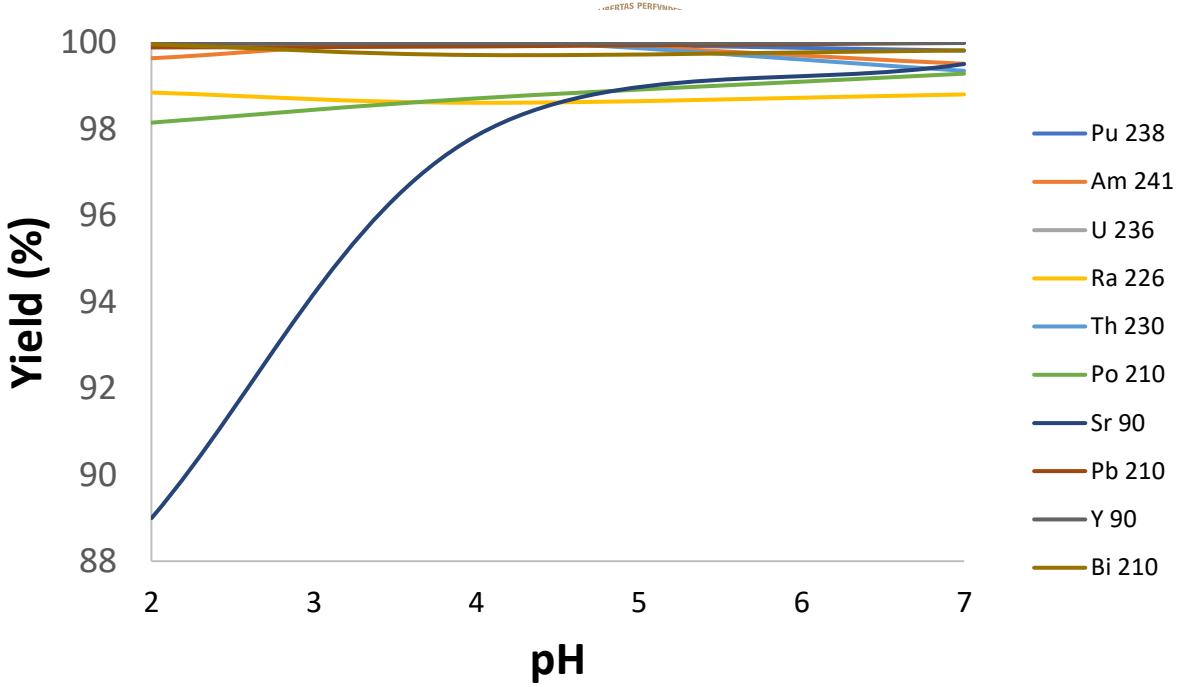
bis(3-trimethylsilyl-1-propyl)methandisphosphonic acid

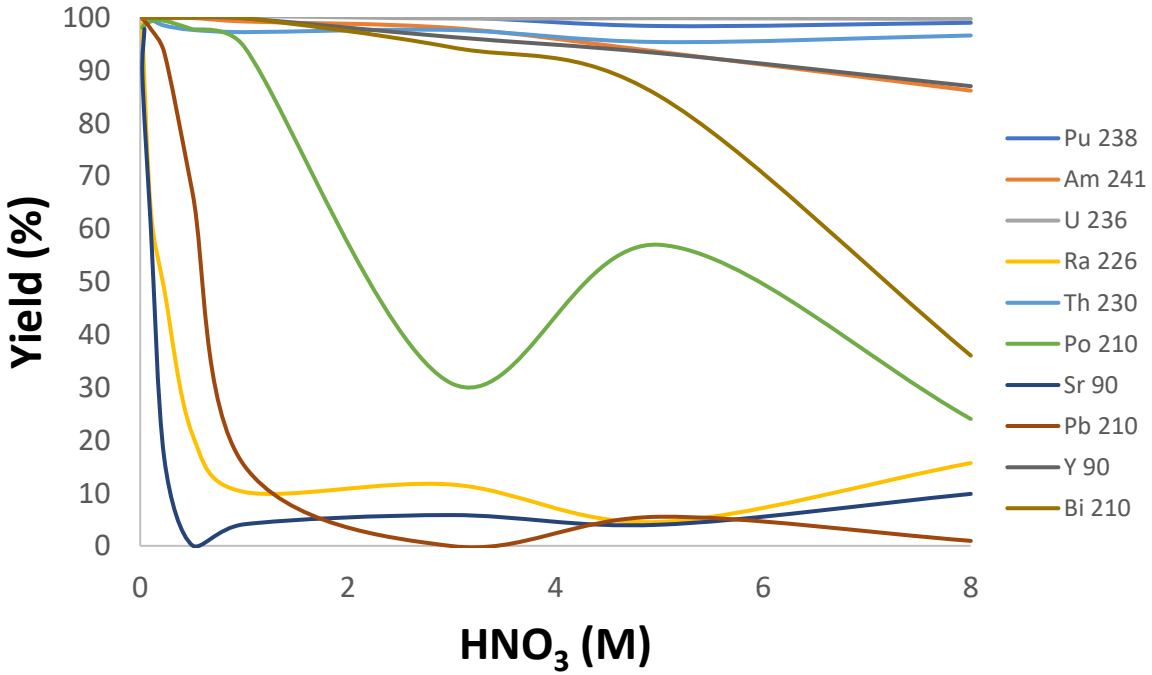


- ✓ Quantitative retention of actinides HCl 0.5M
- ✓ Quantitative Detection Efficiency
- ✓ Breakthrough volume > 400 ml for both PSresin
- ✓ 6 mg capacity for Eu (tracer)

α-PSresin: retention media

- HCl
- HNO_3
- H_3PO_4





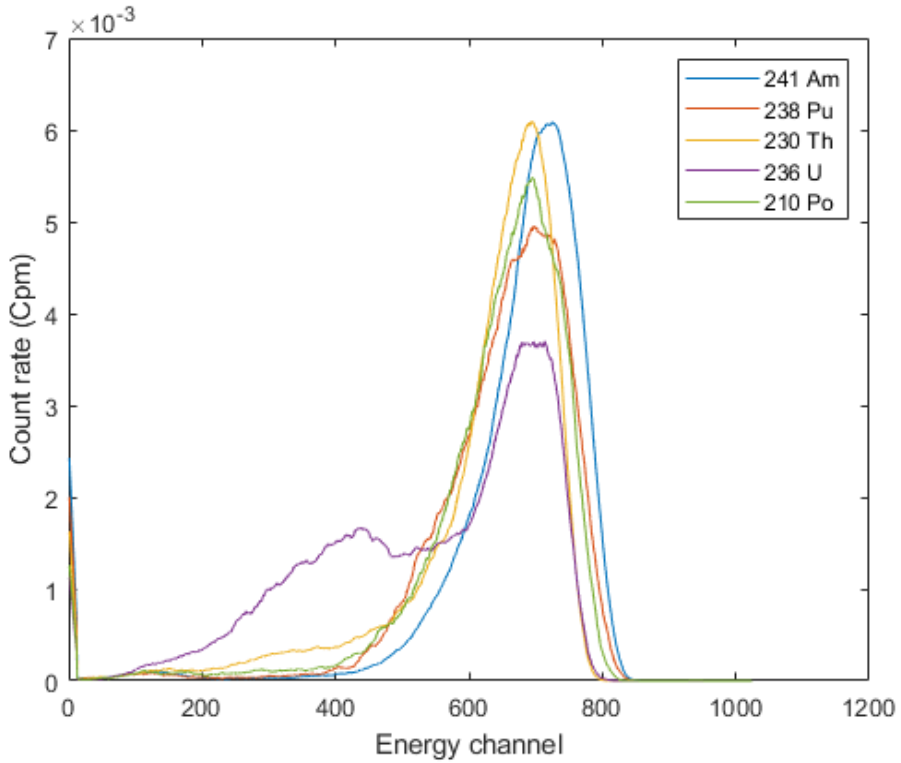
- ✓ GROSS ALPHA
- ✓ ACTINIDES (all)
- ✓ ^{90}Y ($^{89}Sr/^{90}Sr$)

α-PSresin: α emitters retention and efficiency

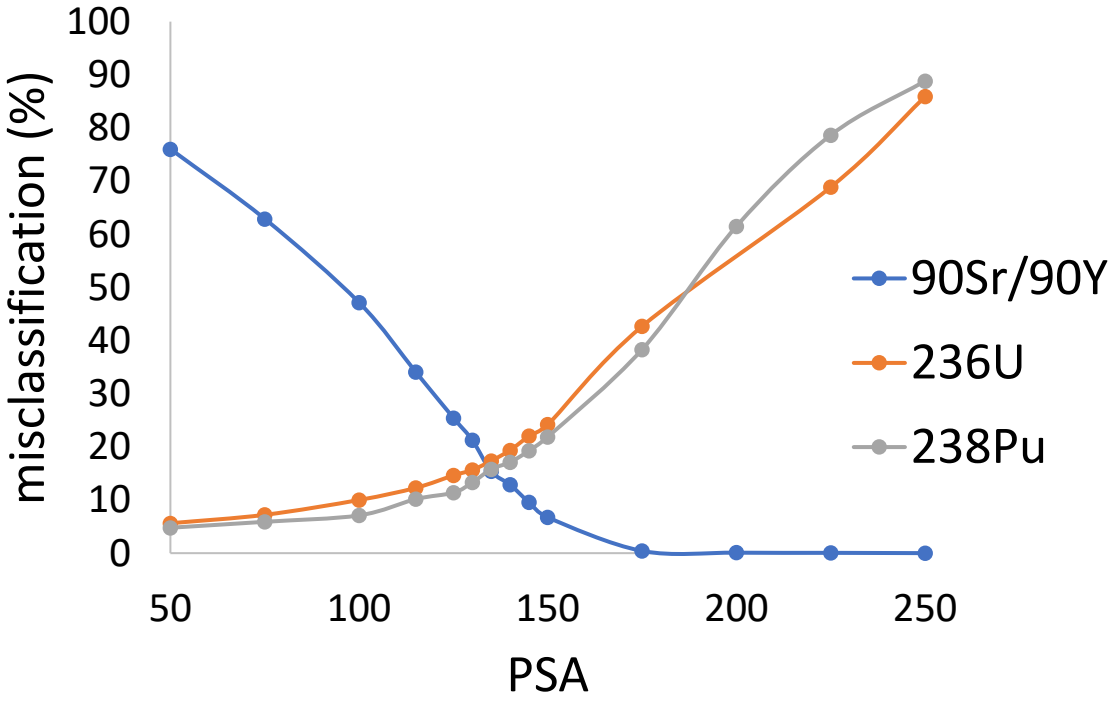
- ✓ pH 2:
  - Actinides and Radium quantitively retained
  - Polonium: **X** no quantitative retention

- ✓ Finals conditions:
  - 1% on hydrogen peroxide
  - 30 minutes at 50ºC to oxidize all polonium to polonium (IV).
  - Actinides, polonium and Radium quantitatively retained

	Retention (%)	Detection efficiency (%)
^{241}Am	>99.5	100(2)
^{238}Pu	>99.5	100.5(0.8)
^{236}U	>99.5	101(1)
^{230}Th	>99.5	97.3(0.2)
^{226}Ra	>99.5	-
^{210}Po	97(1)	88(1)



α-PSresin: alpha-beta dicrimination



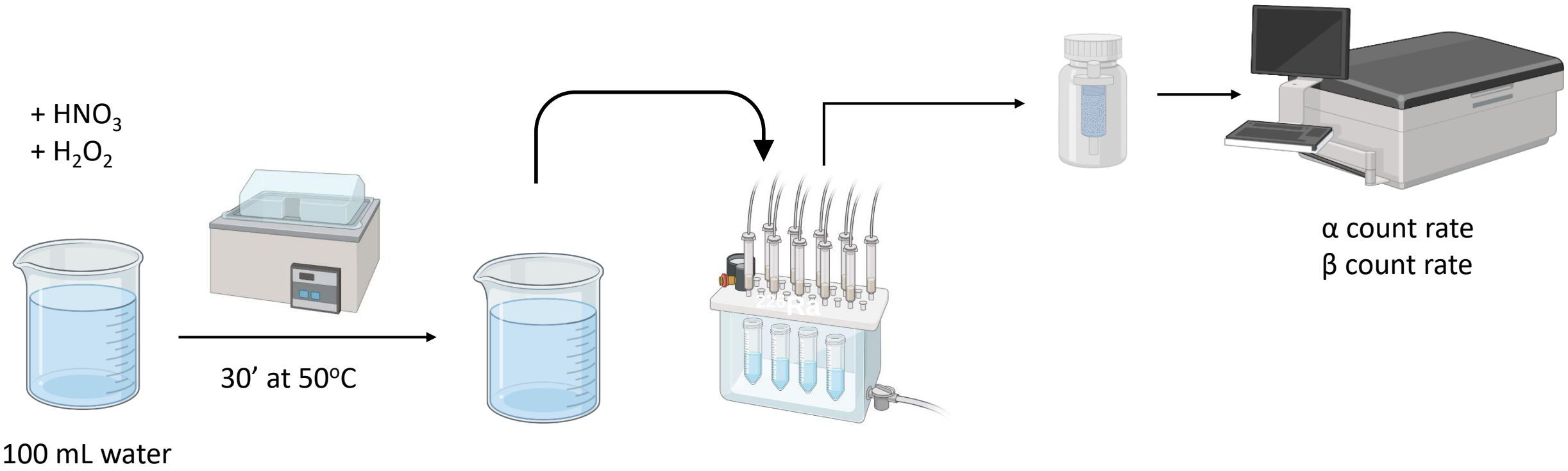
Detection efficiency (%)

	^{238}Pu	^{236}U	^{90}Sr	Pu + U
135	84.2 (3)	82.6 (1)	84.7 (0.1)	85 (4)
150	78.1 (4)	75.8 (2)	91.9 (0.2)	77 (2)
175	61.7 (4)	57.3 (0.2)	95.4 (0.1)	59.5 (3)

Misclassification (%)

	^{238}Pu	^{236}U	^{90}Sr	
PSA 135 →	15.76	17.3	12.4	→ **Crossing point** PSA
PSA 150 →	21.90	24.2	3.9	→ **Lower** influence of beta emitting radionuclides
PSA 175 →	38.30	42.6	0.2	→ **NO** influence of beta emitting radionuclides

α-PSresin: Sample analysis (PSA optimization)



- ✓ IAEA-TEL-202-013
- ✓ Mreal_1

α-PSresin: Sample analysis (PSA optimization)

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
150	1	1.7	-10.9
	2	-7.4	-17.3
	3	-1.4	-11.4
175	1	0.7	-7.2
	2	-10.9	-4.4
	3	3.0	-13.0

PSA 135 → **Crossing point** PSA

PSA 150 → **Low** influence of beta emitting radionuclides

PSA 175 → **NO** influence of beta emitting radionuclides

→ Better results with PSA 135

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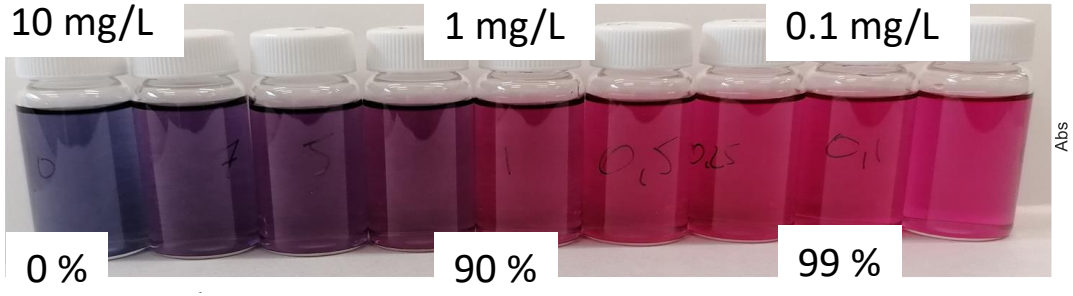
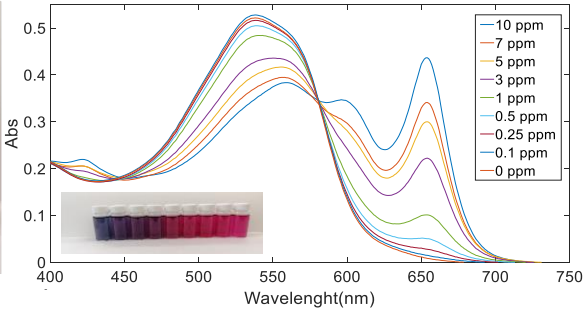
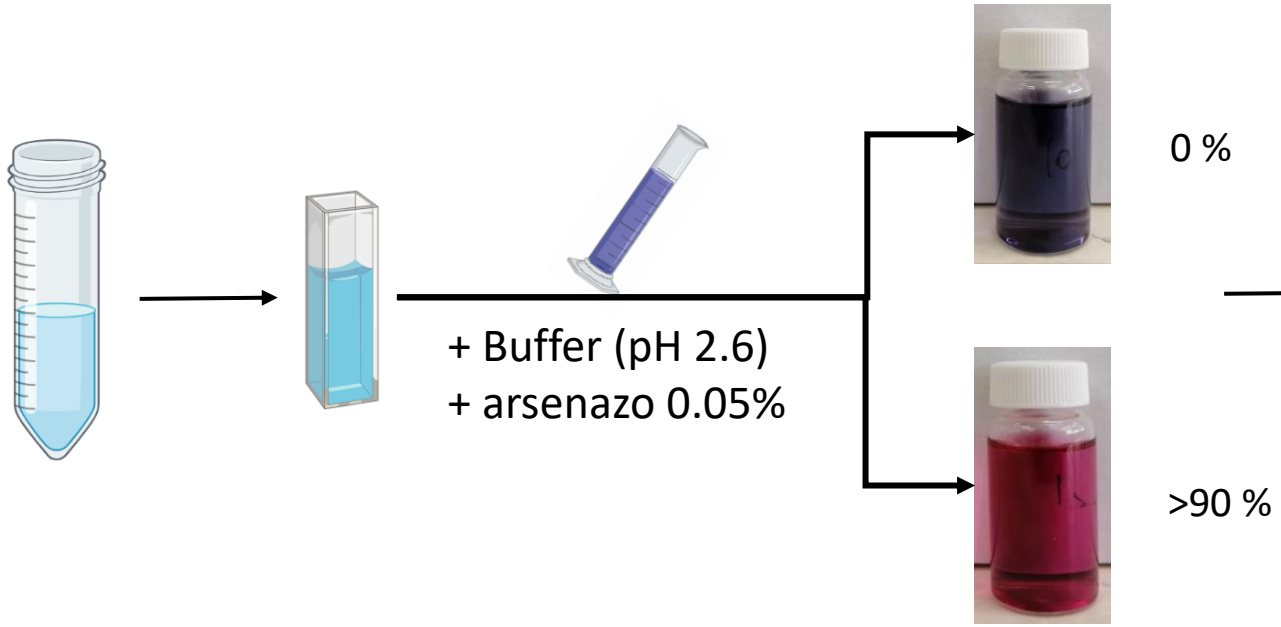
α-PSresin: Yield estimation

Colored complex of Eu(III) and Arsenazo

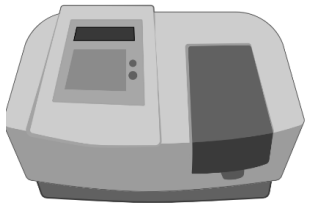


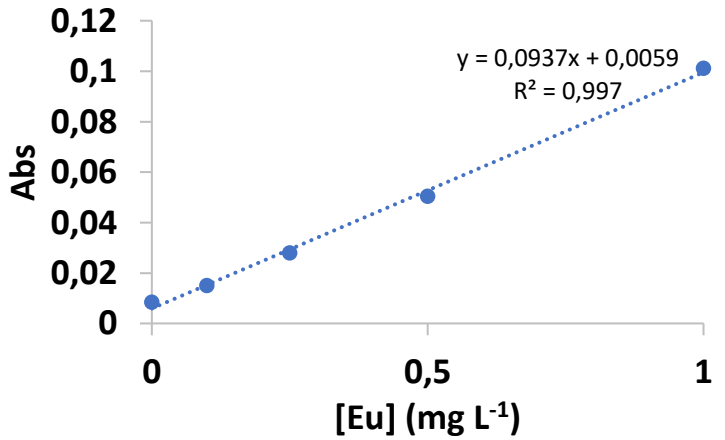


Yield estimation



Yield calculation





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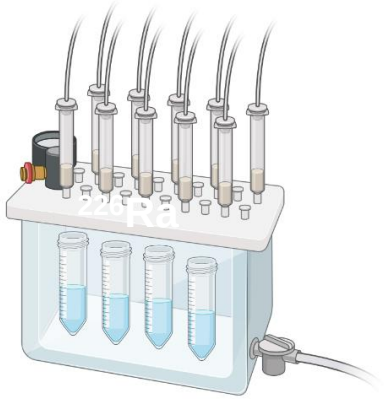
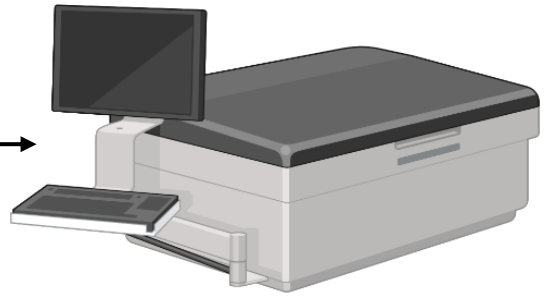
α-PSresin: Sample analysis

+ HNO_3
+ H_2O_2
+ 1 mg Eu(III)

100 mL water

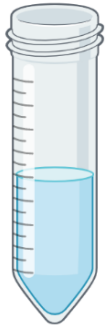
30’ at 50ºC

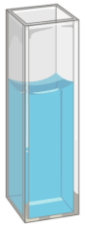




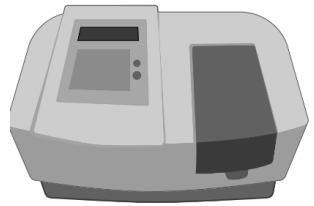
α count rate
β count rate

yield





+ Buffer (pH 2.6)
+ arsenazo 0.05%



α-PSresin: Sample analysis

	Reference value (Bq/L)	PSresin visual check (Bq/L)	PSresin UV-VIS (Bq/L)	visual check colour and retention	UV-VIS spectrometry retention
JRC-GAB-1	0.37(0.01)	0.35(0.03)	0.35(0.04)	**Pink (100 %)**	98.3 %
JRC-GAB-2	0.73(0.02)	0.70(0.06)	0.71(0.06)	**Pink (100 %)**	99.1 %
A21/071	<LoD	<LoD	<LoD	**Pink (100 %)**	98.8 %
A21/044	0.07(0.02)	0.06(0.01)	0.06(0.02)	**Pink (100 %)**	97.5 %
A21/074	0.53(0.09)	0.46(0.04)	0.48(0.05)	**Pink (100 %)**	95.5 %
A21/118	0.9(0.2)	0.65(0.07)	0.66(0.07)	**Pink (100 %)**	99.2 %
A21/031	1.4(0.3)	1.26(0.09)	1.3(0.1)	**Pink (100 %)**	95.1 %

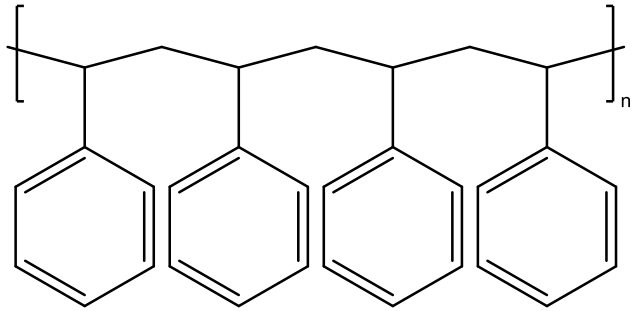
- ✓ **Minimum detectable activity: 0.025 Bq/L**
- ✓ Sample volume: **100 mL;** Background of **0.063 cpm**; **2 H** of measurement.
- ✓ Time of analysis: < 5 hours (possibility of multi-sample processing)

α-PSresin: conclusion

The proposed method allows:

- **Retention of actinides, Ra and Po.**
- **Simplicity** in the pretreatment (pH 2, 1% H_2O_2, 1 mg Eu(III) and 30’ at 50ºC)
- **Lower** counting time (2 h) and **less time of analysis** (4-5 hours)
- **Similar** uncertainty and MDA (0.025 Bq/L)
- **Yield calculation** (UV spectrometry) **or estimation**(visual check)

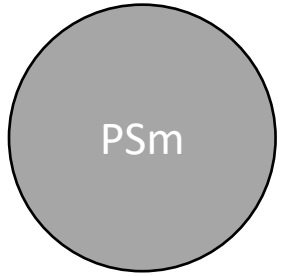
Classical method for PSm obtention



Solved in CH_2Cl_2

Solutes PPO/POPOP

Evaporation/extraction



20-300 µm

Santiago, L.M., et. al. ***Nucl. Instr.*** *Methods Phys. Res. A: Accel. Spectrom. Detect. Assoc. Equip.*, 698 (2013)

LIMITATIONS

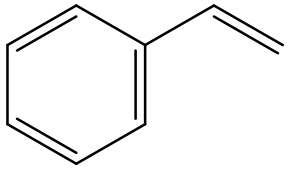
Soluble in organic media

Affected by aggressive media (acid, temperature…)

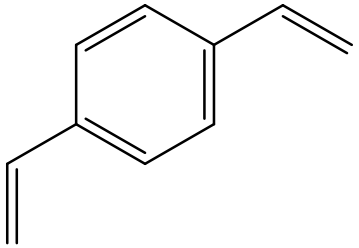
Extractant coated on surface by weak forces: possible lixiviation

Crosslinked Plastic Scintillation microspheres - CPSm

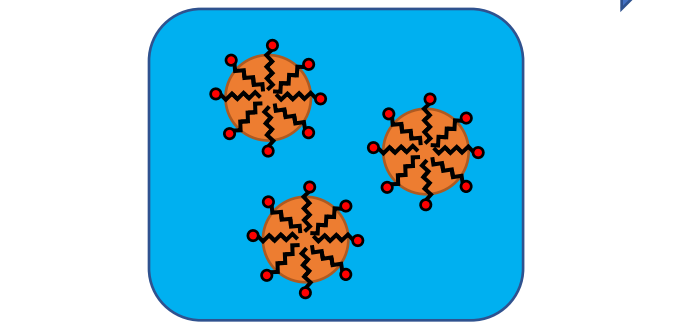
Styrene



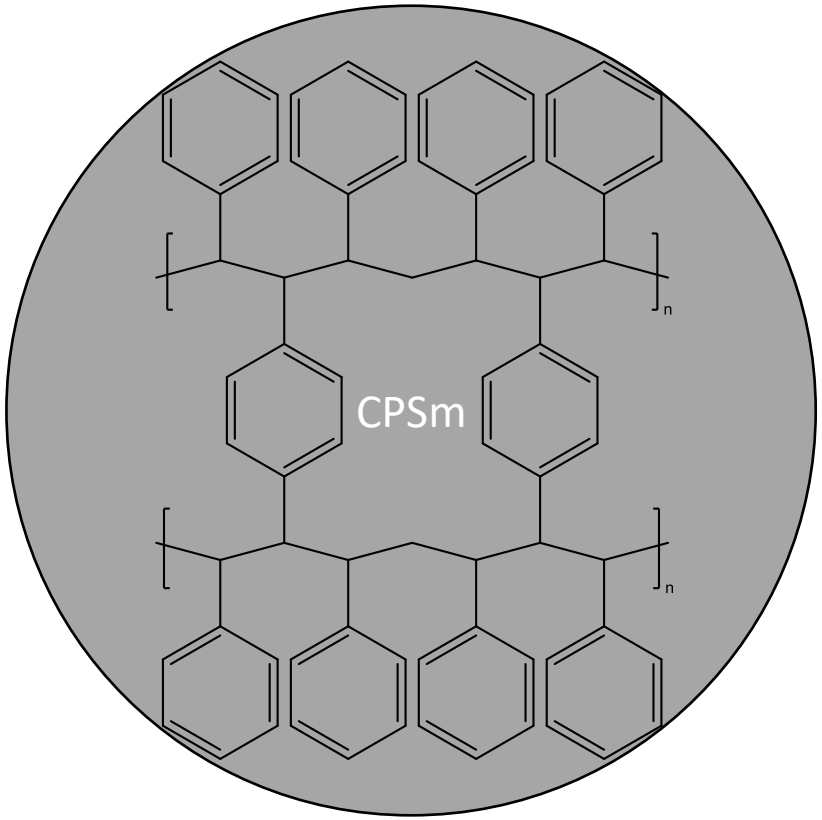
Divinylbenzene



Radical Polymerisation

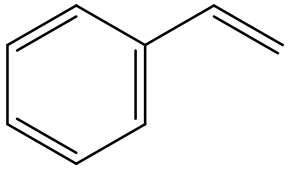


Stabilized by the surfactant and agitation

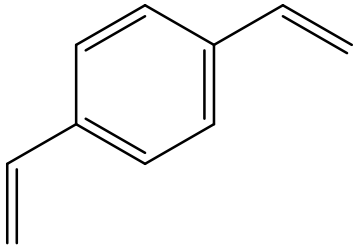


Crosslinked Plastic Scintillation microspheres - CPSm

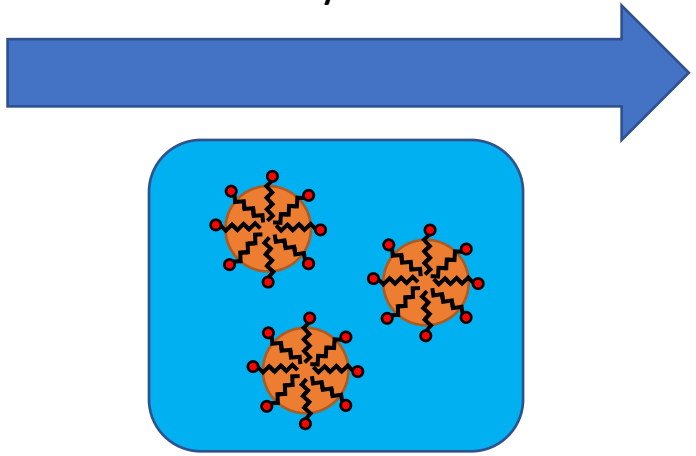
Styrene



Divinylbenzene



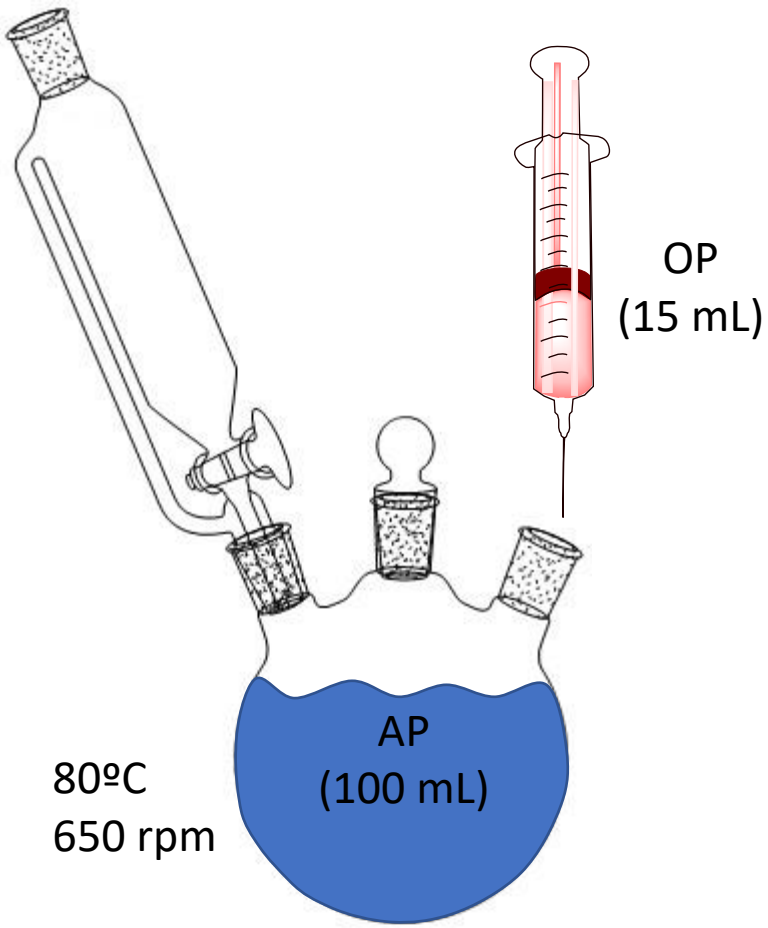
Radical Polymerisation



Stabilized by the surfactant and agitation

- Porous CPSm
- Use of CPSm in organic mediums
- Functionalization of the surface
- Extractants with covalent bonds on the CPSm

CPSm: synthesis procedure



Aqueous phase (AP)

1. Bubble the water with N2 during 10 min
2. Mix and dissolve the aqueous phase components:

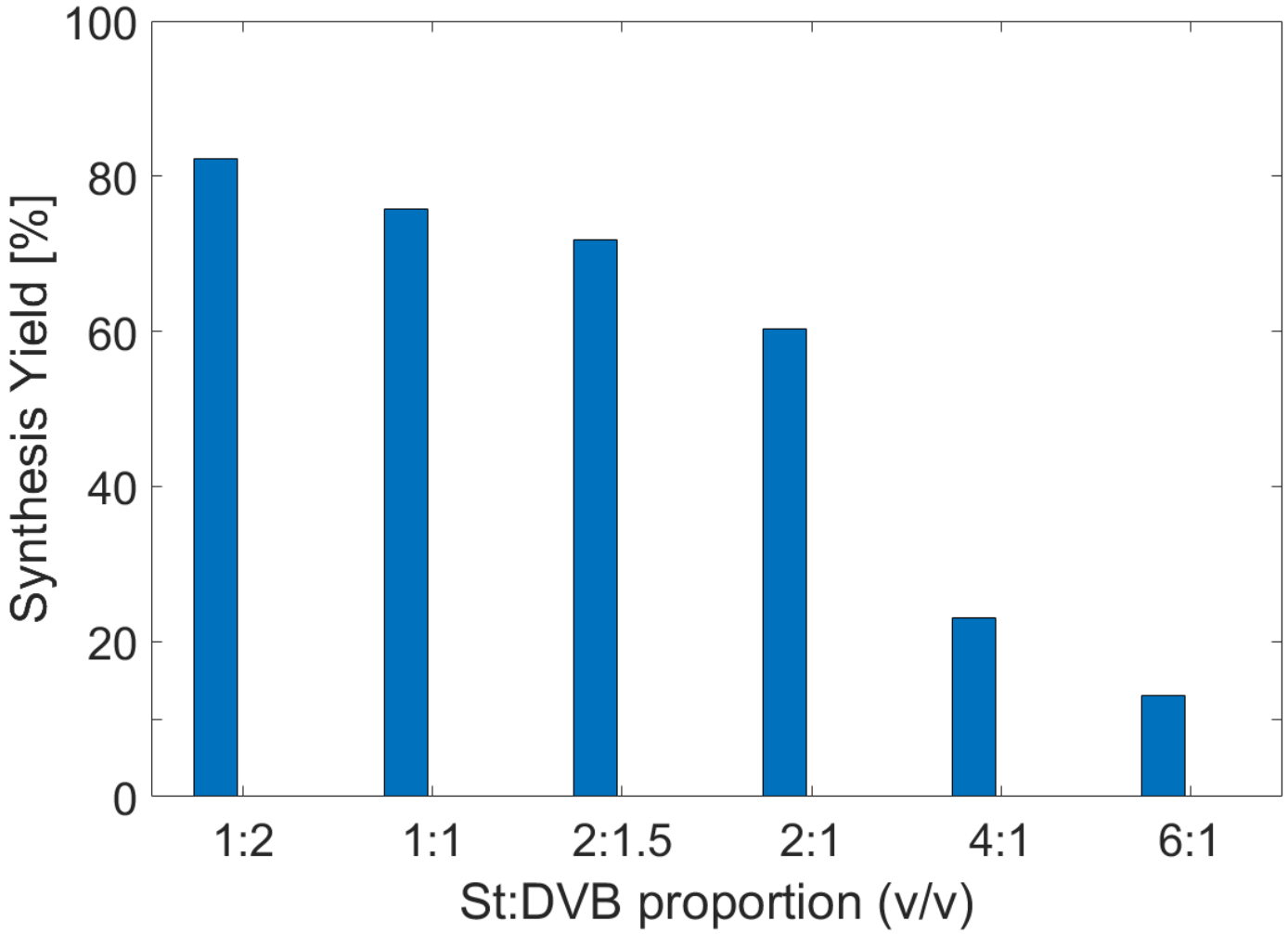
Organic phase (OP)

3. Mix styrene and DVB monomers with fluoresecent solutes and initiator:

- PPO 2.5%
- POPOP 0.07%
- AIBN 0.08%

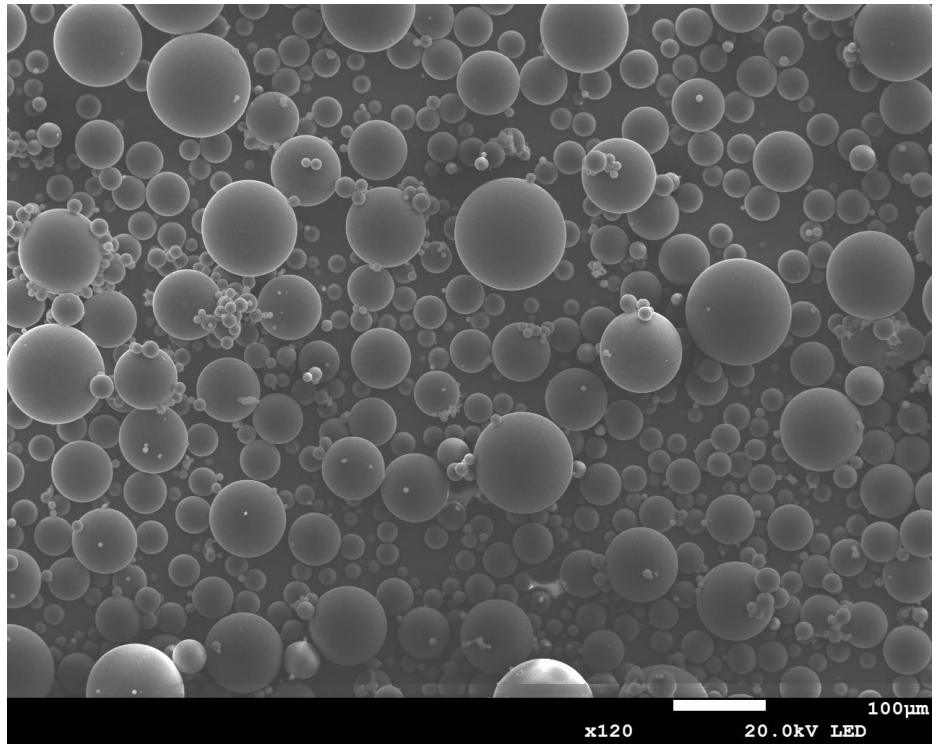
4. Inject OP slowly with a syringe

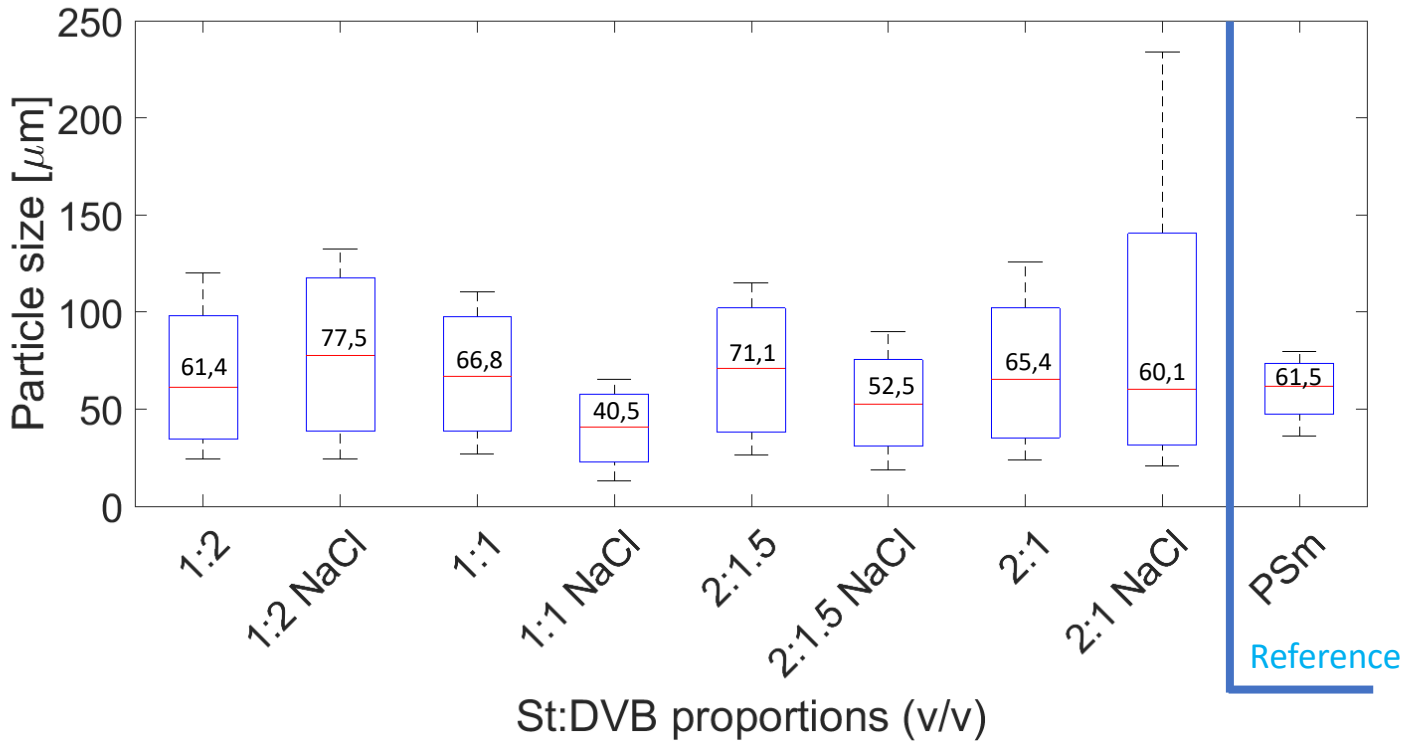
CPSm: synthesis yield



↑DVB --- ↑Synth. Yield

CPSm: shape and size

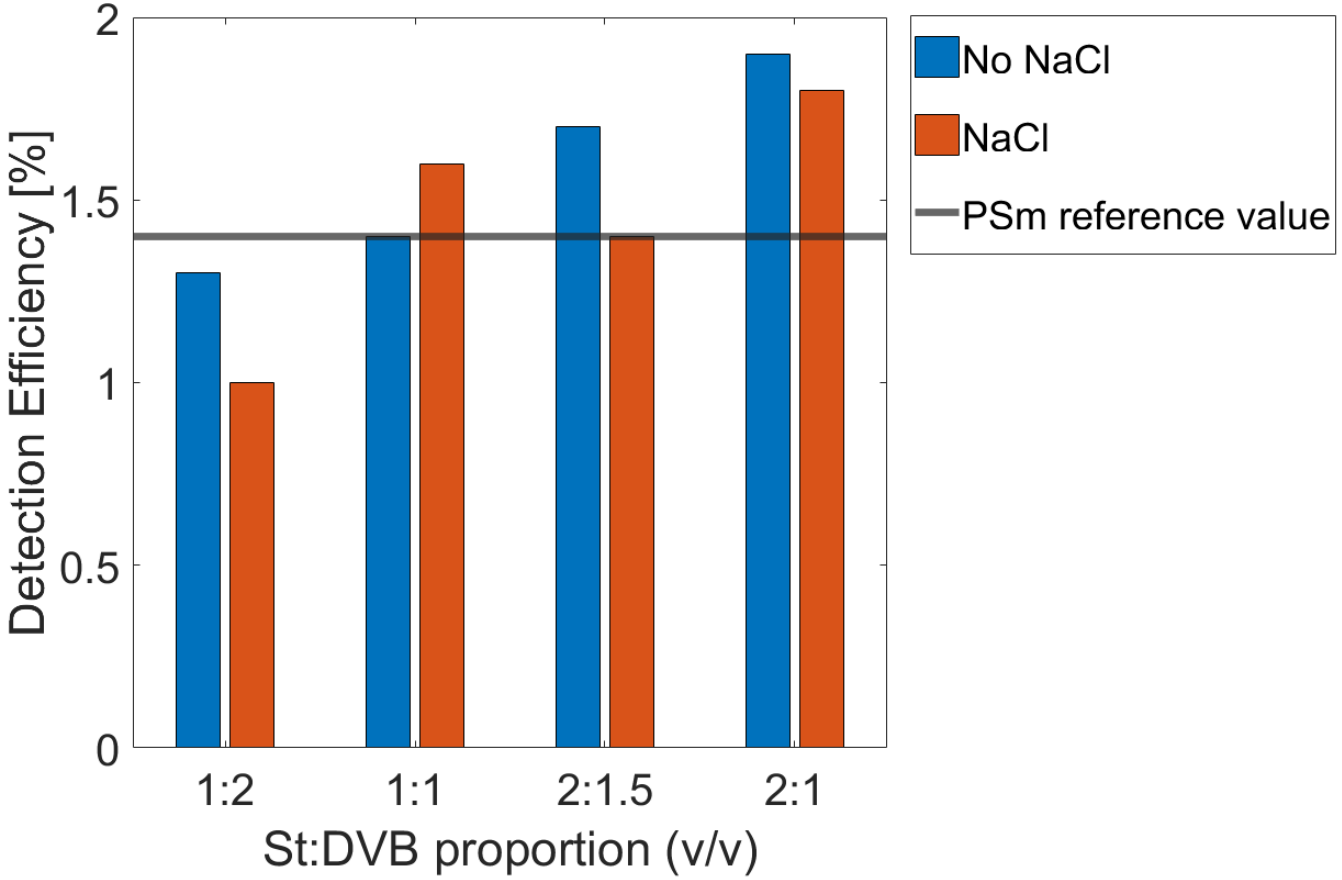




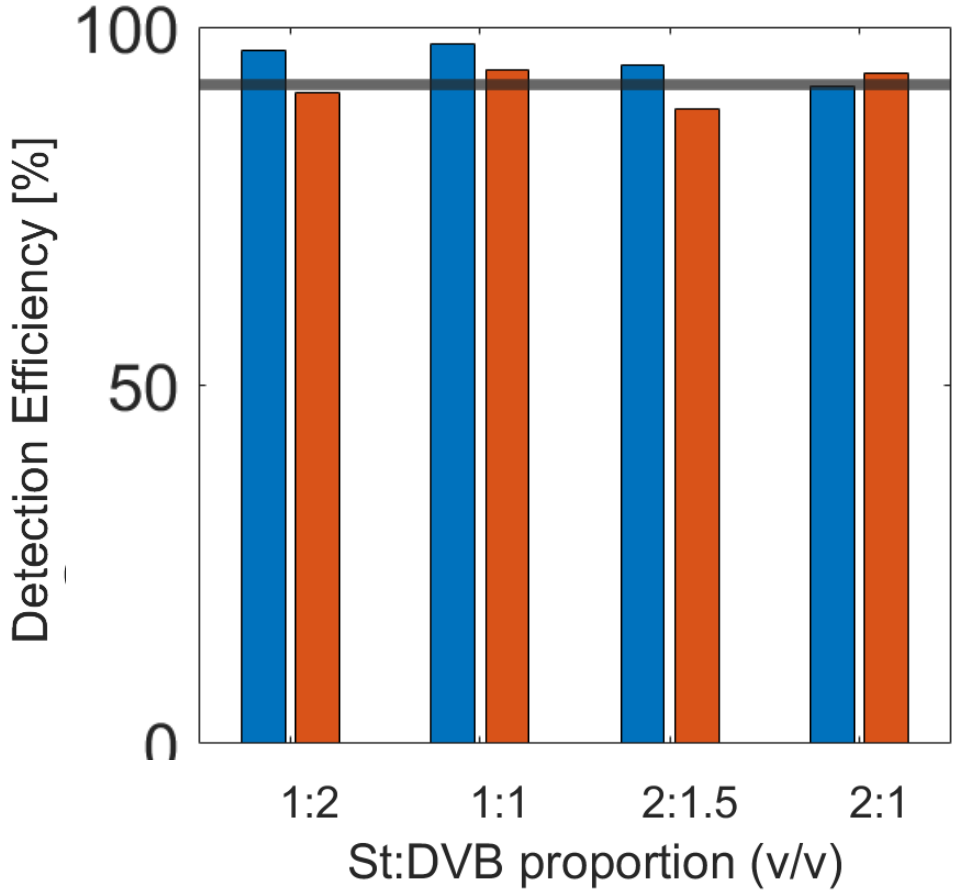
CPSm: Scintillation capacities

0.5 CPSm and 0.2 mL of solution in a 6 mL PE vial

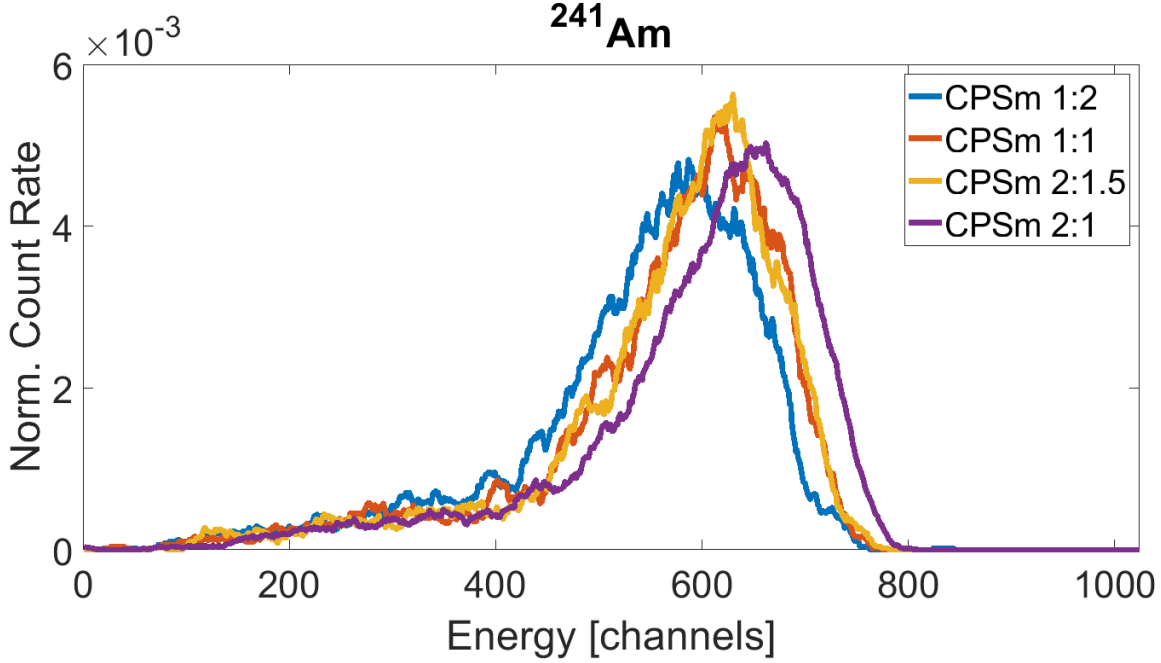
^{3}H



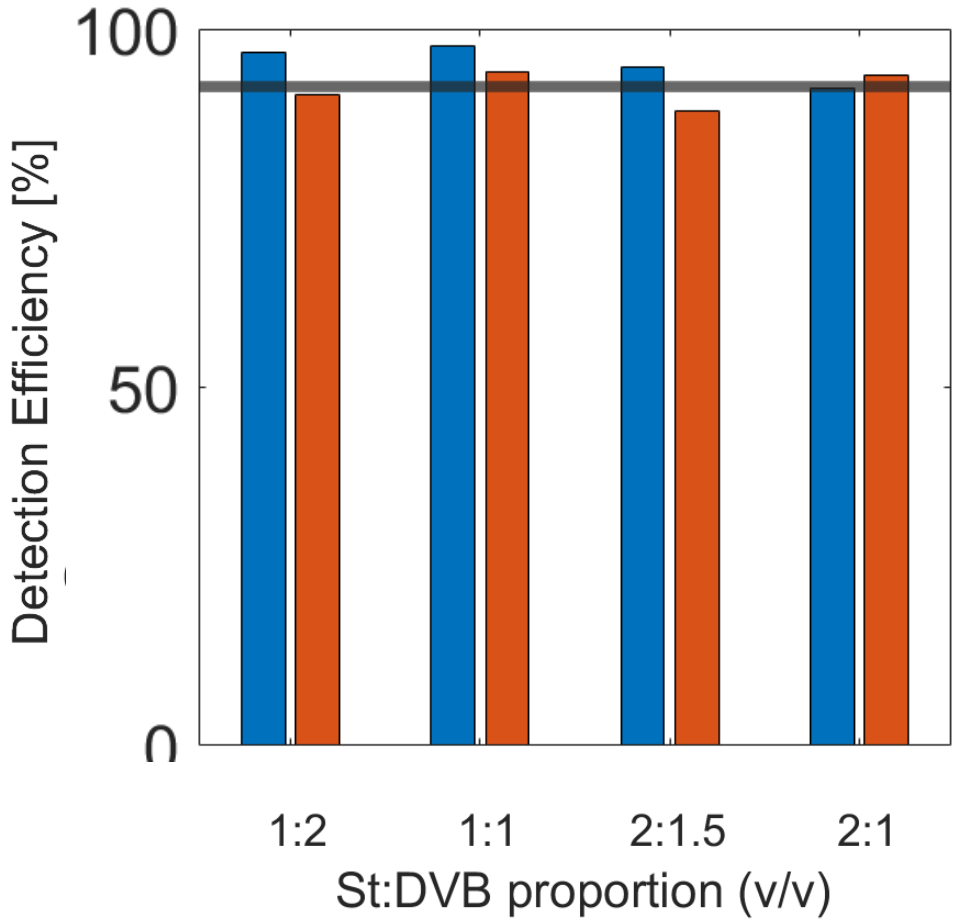
^{241}Am



CPSm: Scintillation capacities

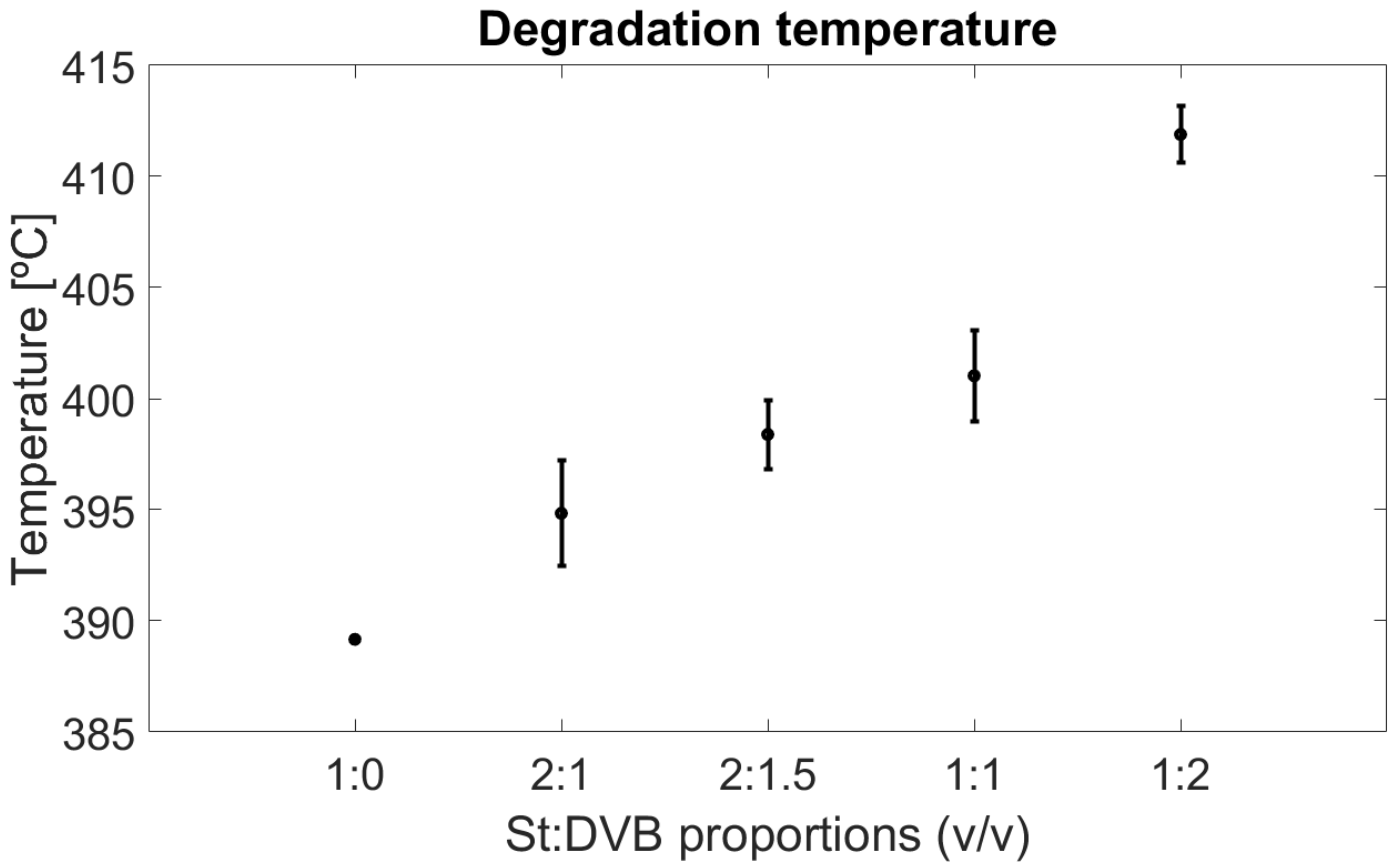


^{241}Am

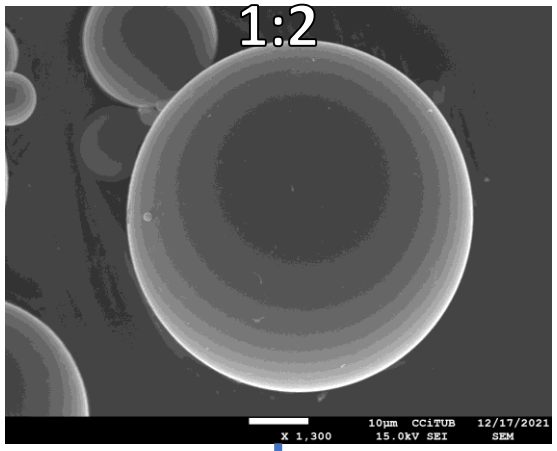


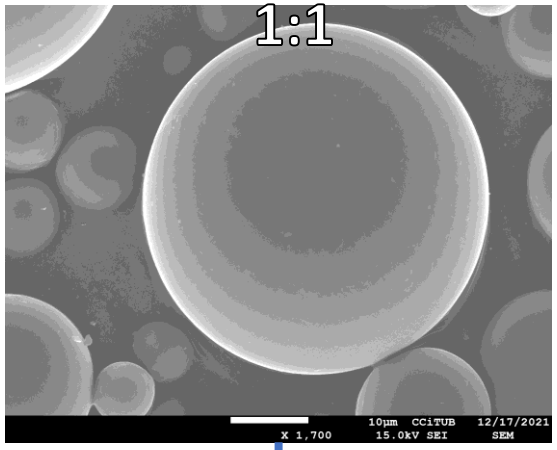
- ✓ Quenching effect of DVB (small)
- ✓ Poor mixibility due to hidrophobicity

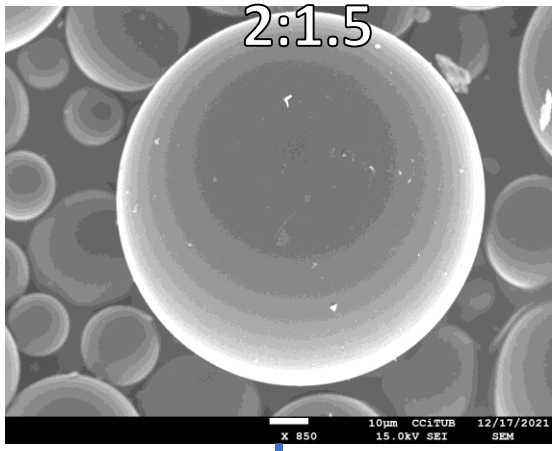
CPSm: Thermal resistance

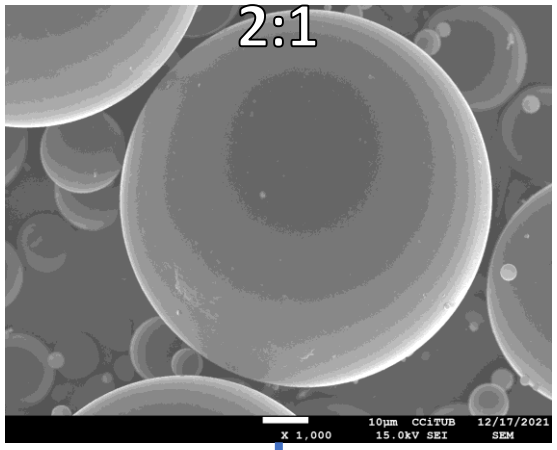


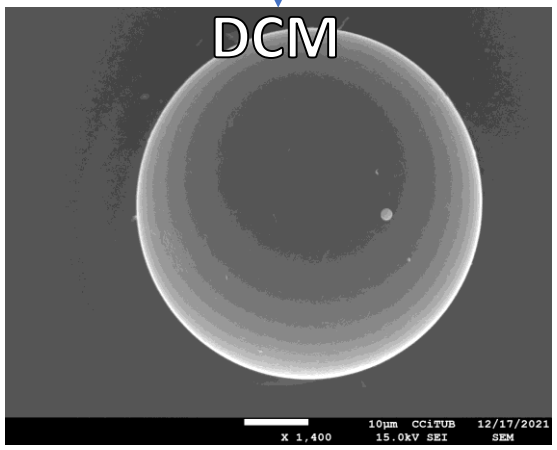
CPSm: Solute extraction with solvents

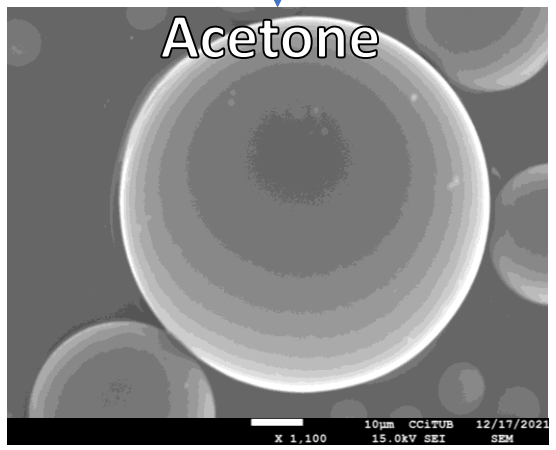


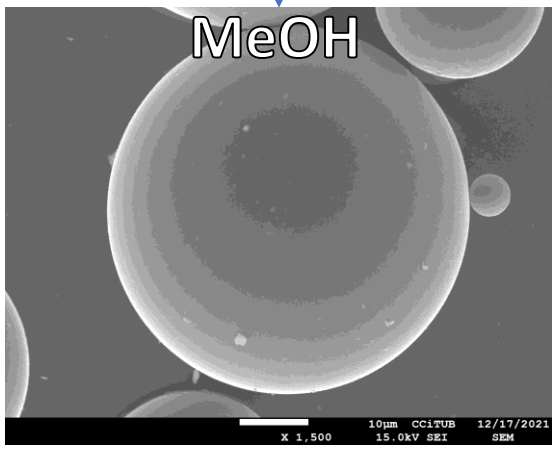


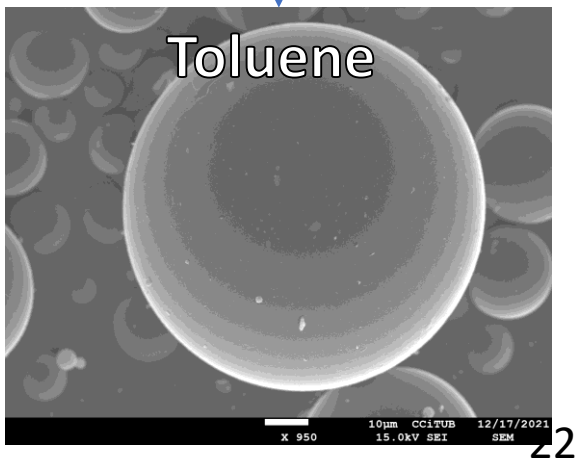




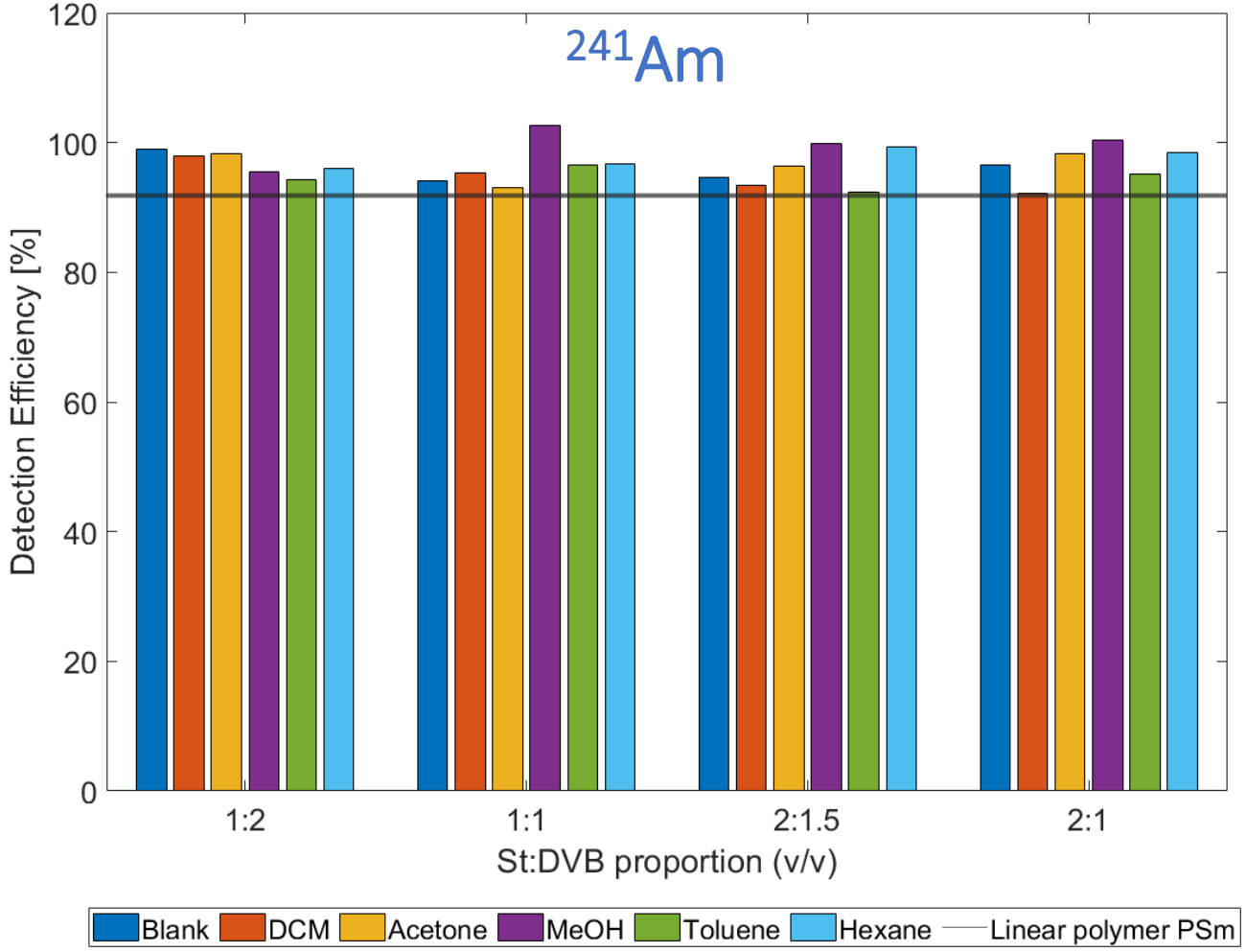


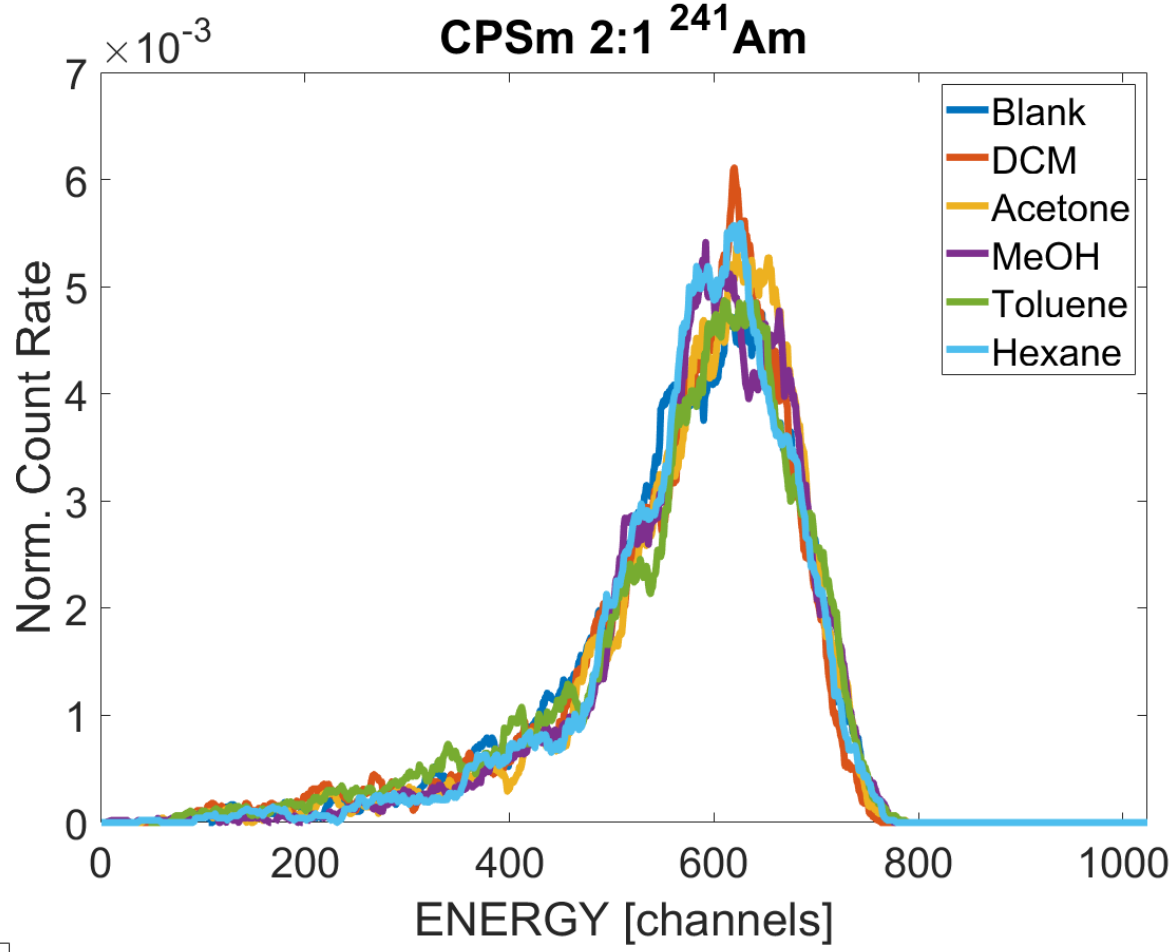




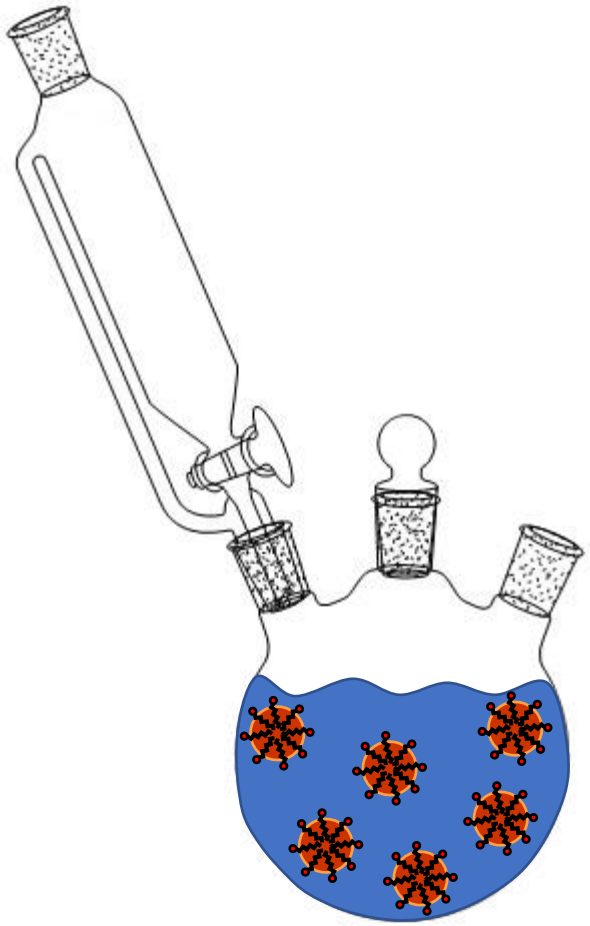


CPSm: Solute extraction with solvents





Porous-CPSm: Synthesis



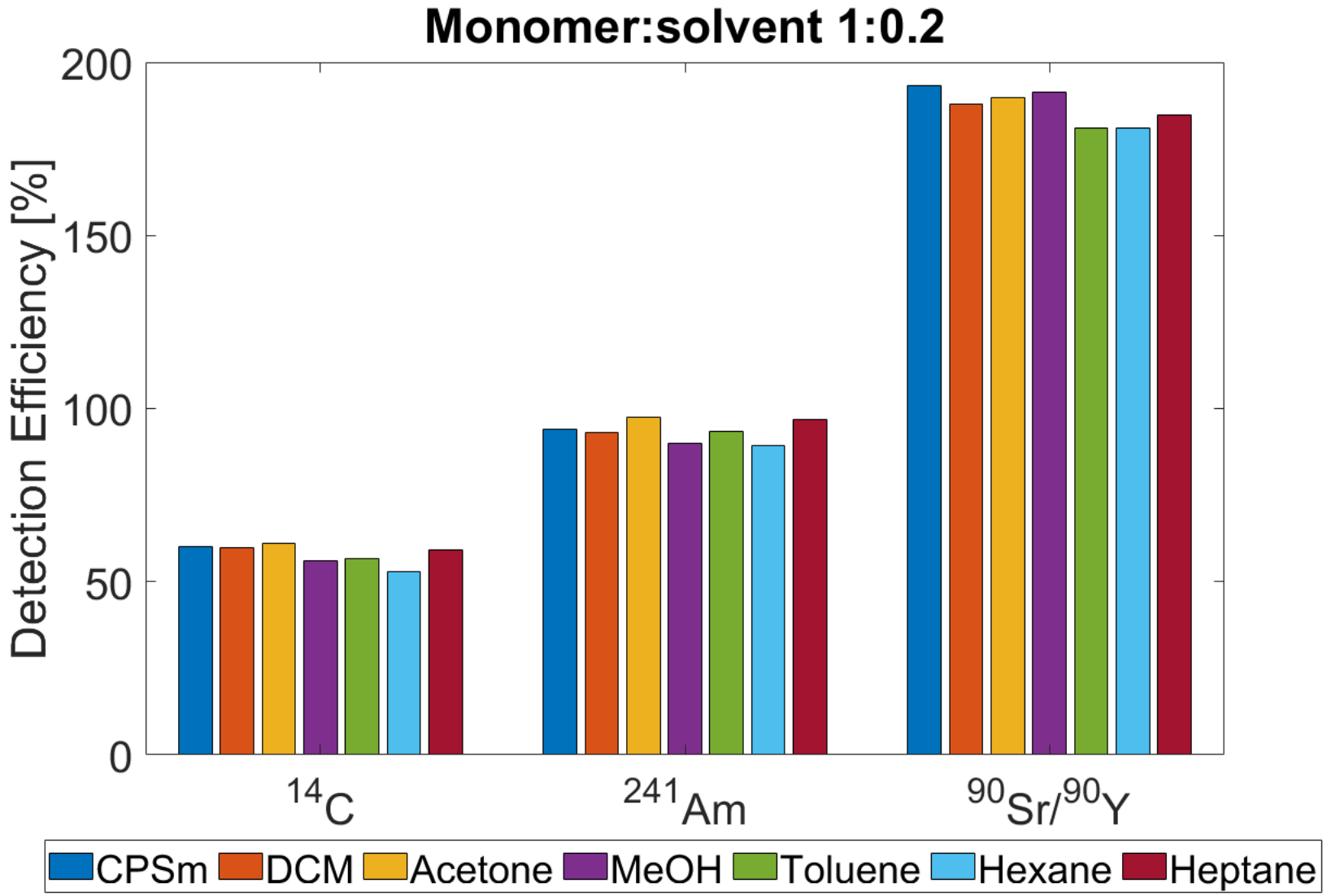
Condicions:

- Fase Aquosa
  - PVA 10%
  - NaCl 1%
- Fase orgànica
  - Estirè 7.5 mL
  - DVB 7.5 mL
  - PPO 2.5%
  - POPOP 0.08%
  - AIBN 0,07%
  - Proporcions solvents

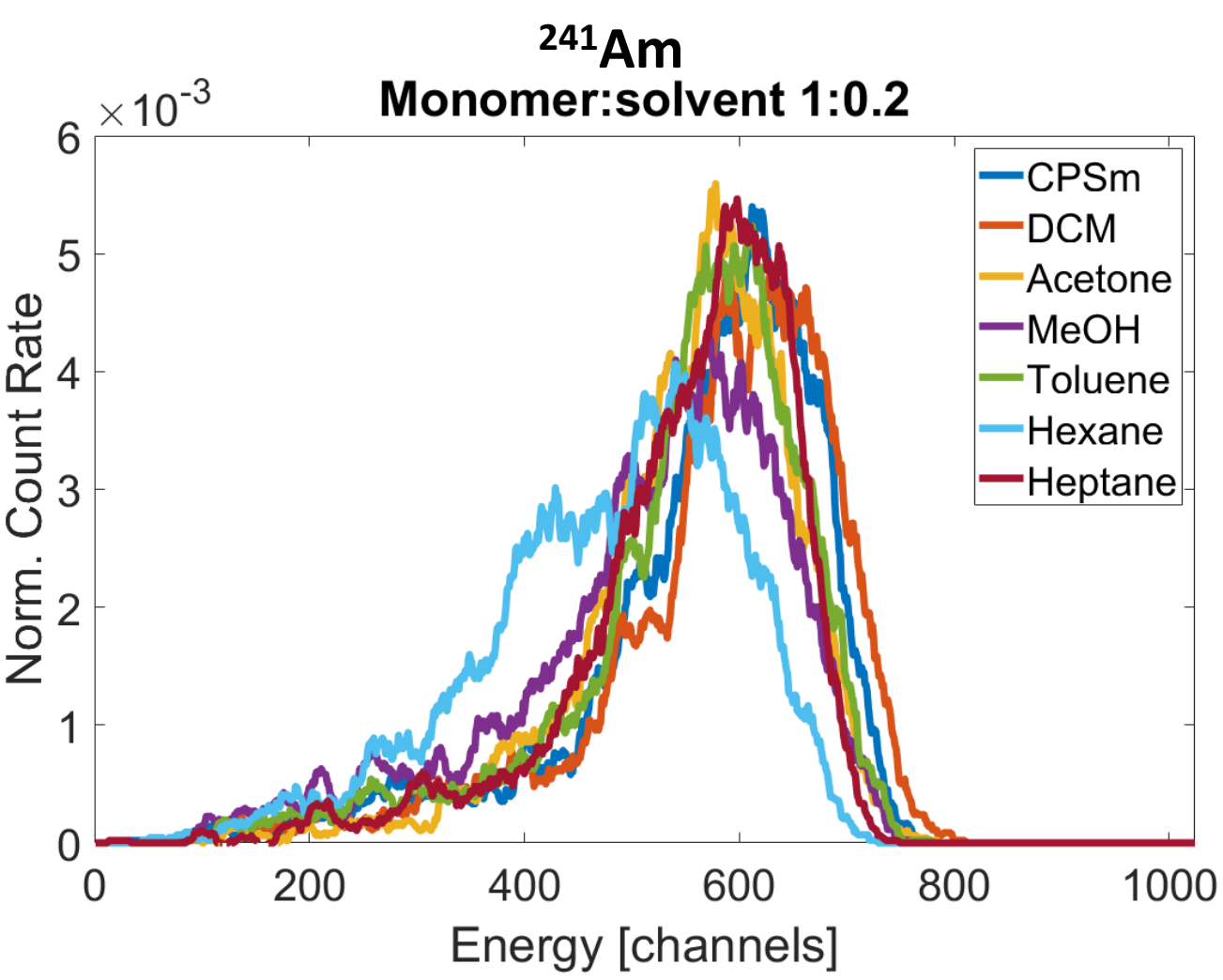
Proporcions monòmers:solvent

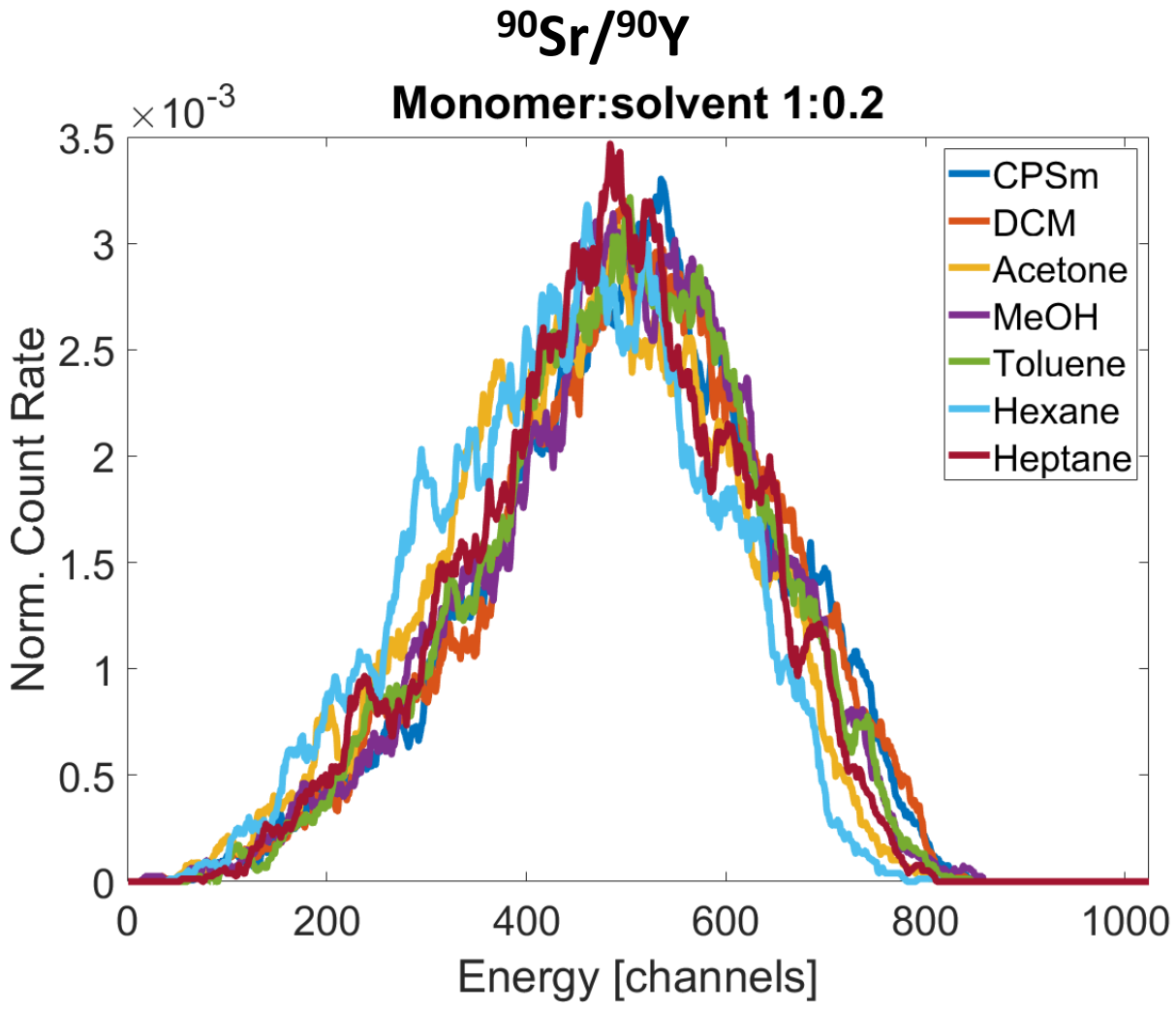
- DCM 1:0.2
- Acetona 1:0.2, 1:0.5, 1:1
- MeOH 1:0.2
- Toluè 1:0.2, 1:0.5, 1:1
- Hexà 1:0.2
- Heptà 1:0.2, 1:0.5, 1:1

Porous-CPSm: Scintillation capacities

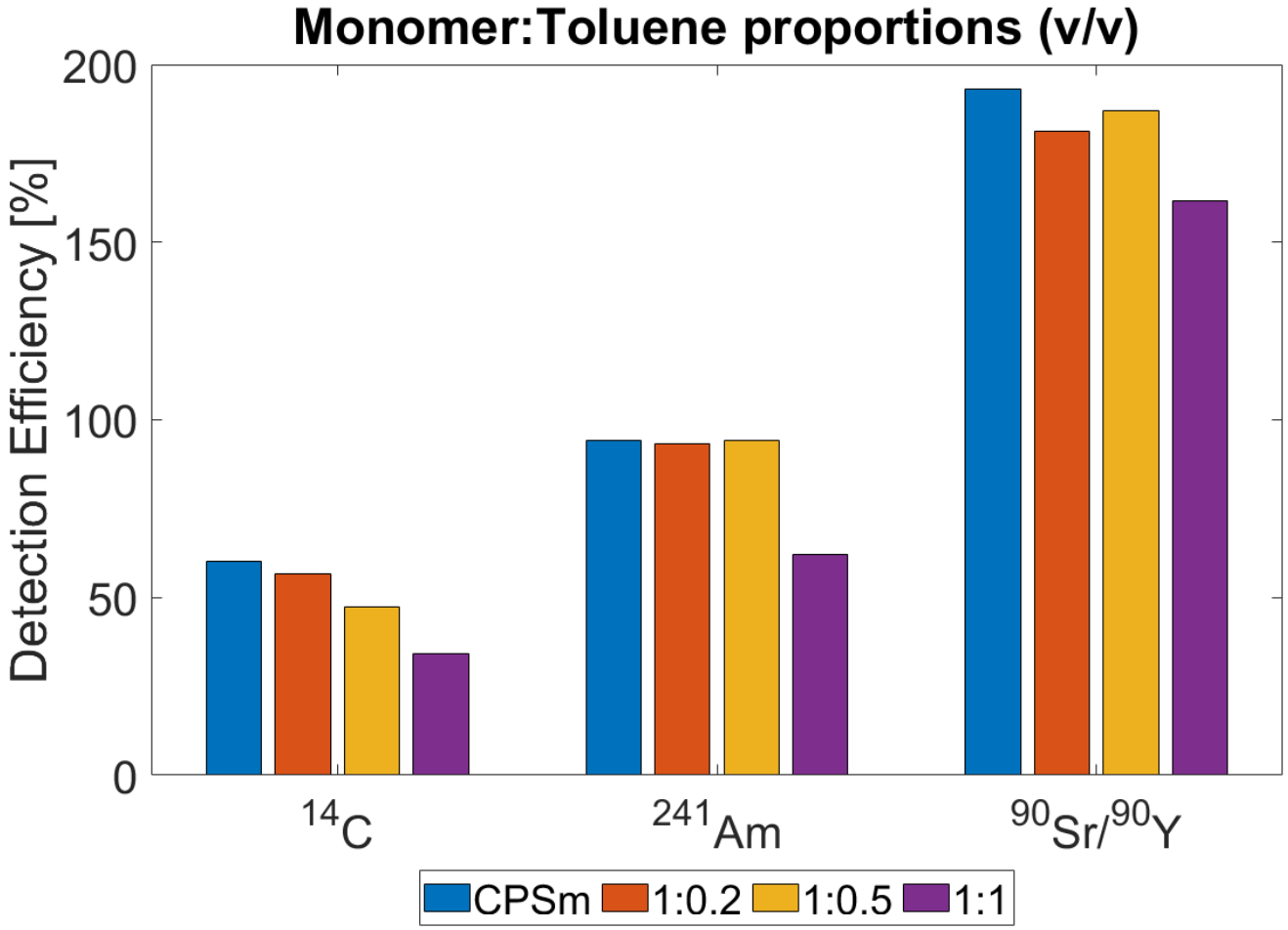


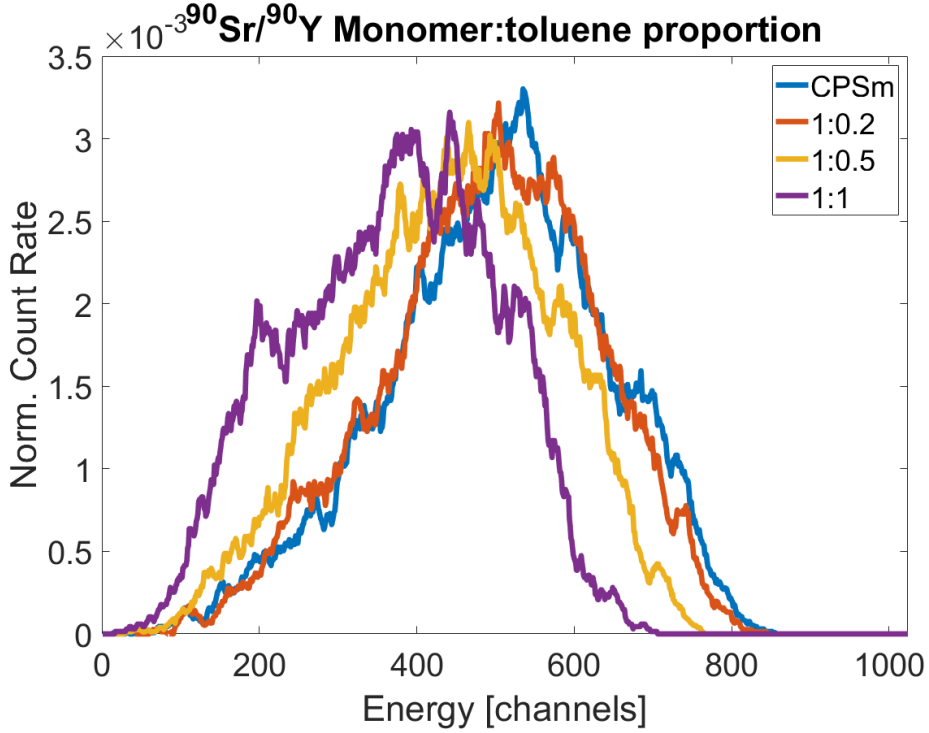
Porous-CPSm: Scintillation capacities





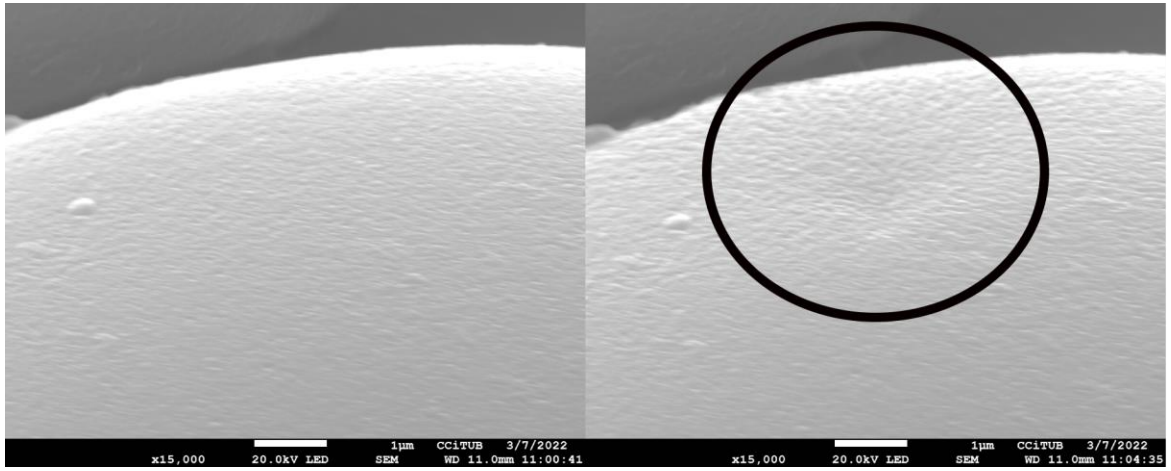
Porous-CPSm: Scintillation capacities



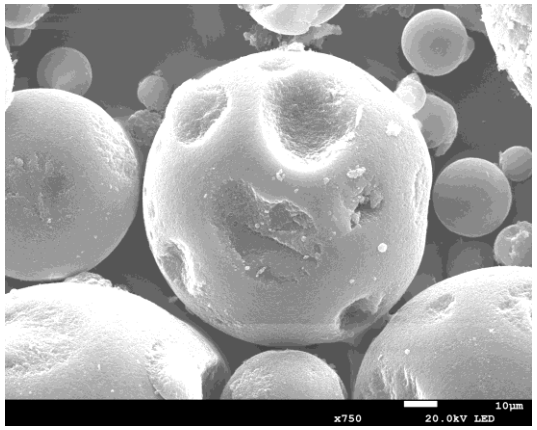


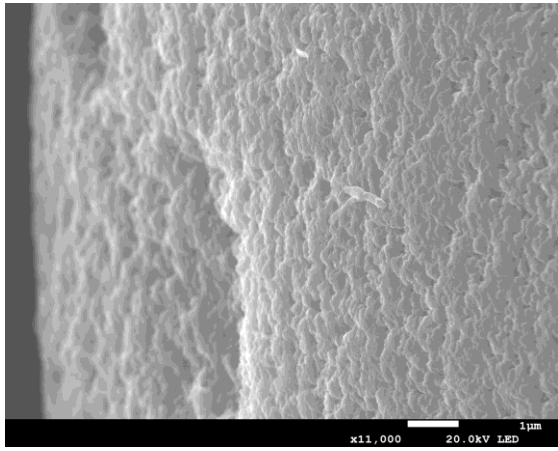
Porous-CPSm: porosity

Toluene (1:0.5)



Heptane (1:0.5)





- ✓ More active surface (to be confirmed)
- ✓ Coating studies on-going

CPSm and Porous-CPSm

- It is possible to obtain Crosslinked Plastic Scintillation Microspheres with sizes in range from 20 µm to 100 µm with the method described.
- The effect of the addition of DVB is not appreciable in the detection efficiencies (except for low energy beta emitters), but it is slightly relevant in the spectra position.
- Scintillation capacities of the CPSm are comparable with ones obtained for PSm, so CPSm can be used as a good scintillators for radionuclide determinations.
- The addition of DVB in the polymeric structure produces an increase in thermal resistance as well as in resistance to organic agents.
- Presence of porogen (toluene and heptane) causes changes in the CPSm Surface and in the scintillation capacities
- More studies are needed to confirm improvement in impregnation capactity and the effect on scintillation

On-going and future work

- Application of PSresin developed to new type of samples (aliquat; crown-ether, Si-dipex)
- New PSresin
  - Pb-210 (fast method for waters)
  - Ni-63 (covalent bonding)
  - Fe-55 (imprinted and non-imprinted polymer)
- PSkits (fast and pseudo-quantitative selective analysis): Technology development and assays
- Porous and functionalized CPSm

➢ ACKNOWLEDGEMENTS

- Ministerio de Economia y Competitividad (MINECO) for financial support under PID2020-114551RB-I00 (MCIN/AEI/10.13039/501100011033)
- University of Barcelona for PREDOCS-UB grants

Thank you for your attention

Advance in Selective Plastic Scintillators

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