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PLASTIC SCINTILLATORS and RELATED ANALYTICAL PROPOSALS for RADIONUCLIDE ANALYSIS

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Begining of Plastic Scintillators

The Theory and Practice of Scintillation Counting

J.B. Birks

Pergamon Press 1964

Liquid Scintillation and Plastic Scintillation starts 70's

<u>Liquid Scintillation</u>

Focus: radionuclide analysis

→LS Counter – LS Spectrometers

→Scintillation Cocktails

→ LSC success: . Sample preparation for measurements (easy and homogeneous)

. Many applications

<u>Plastic Scintillation</u>

Focus: large area detectors, dosimetry

Radionuclide analysis

Plastic Scintillators and related analytical proposals

- Plastic Scintillators composition and sample preparation

- Scintillation mechanism

- Direct radionuclide determinations

- Selective radionuclide determinations

- Future challenges

Plastic Scintillators: composition and sample preparation

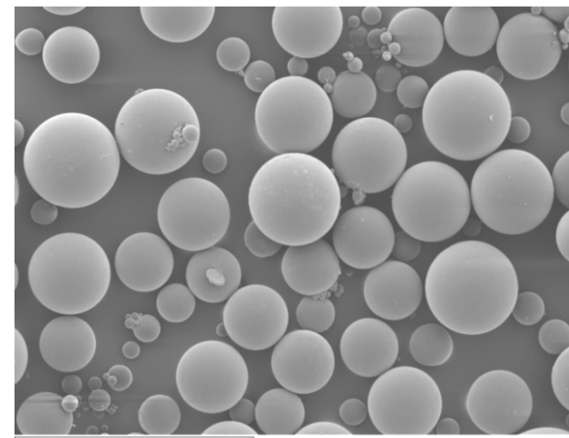
Composition

. Solvent: . Polystyrene, Polyvinyiltoluene → linear (water insoluble)

. Divinylbenzene → crosslinked (aggressive and organic insoluble)

. Secondary solvent: Naphtalene, Disopropilnaphtalene

. Scintillators: PPO, POPOP, p-T, bis-MSB ....



Format

. Plastic scintillator microspheres (PSm) (10 – 300 µm)

. Plastic scintillator foils (PSf) (50 – 100 µm)

. Plastic scintillator pellets (3 mm)

Plastic Scintillators: composition and sample preparation

Sample preparation for measurement.

Steps: . Plastic scintillator

. Sample solution

. Homogenization

LS vs PS: . PS time ↑

. PS difficulty to homogenize

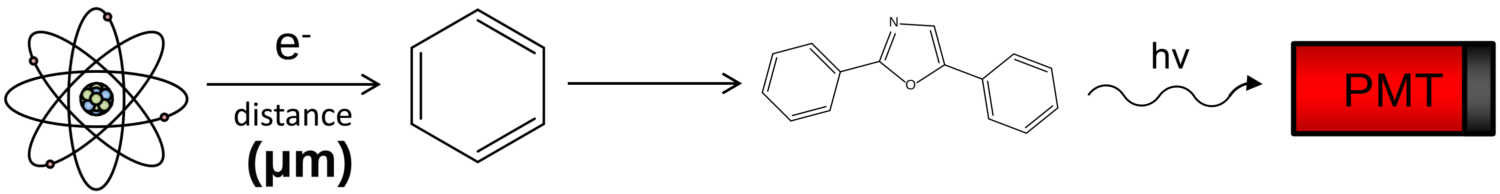
. PS expensive than LS cocktails

. PS sample solution and PSm can be segregated (no mixed waste)

. PS sample stability (no phase separation)

Scintillation mechanism

Scintillation mechanism



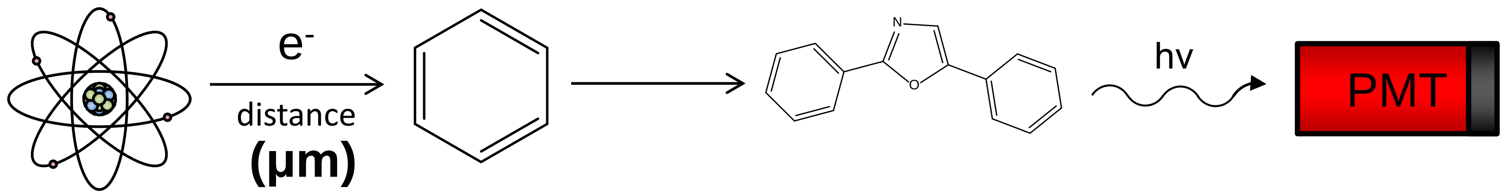
Radionuclide | Solvent | Scintillator | Photomultiplier tube.

Quenching

LS

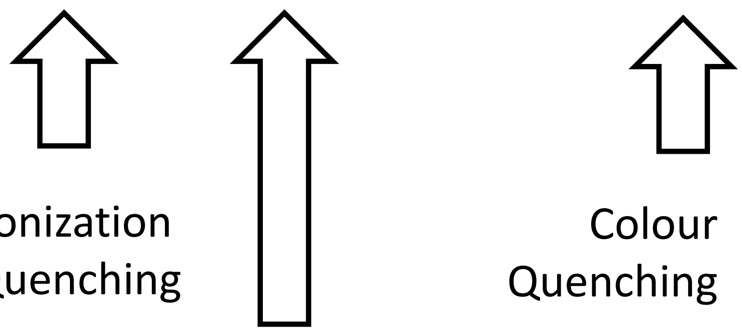
Ionization Quenching | Chemical Quenching | Colour Quenching

Scintillation mechanism



Radionuclide | Solvent | Scintillator | Photomultiplier tube.

Quenching



LS Ionization Quenching — Colour Quenching

PS Chemical Quenching

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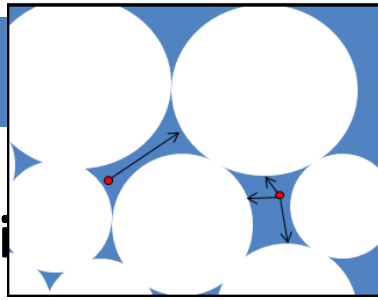
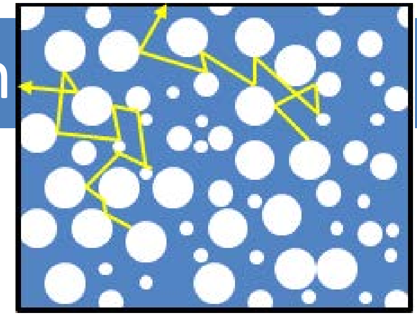
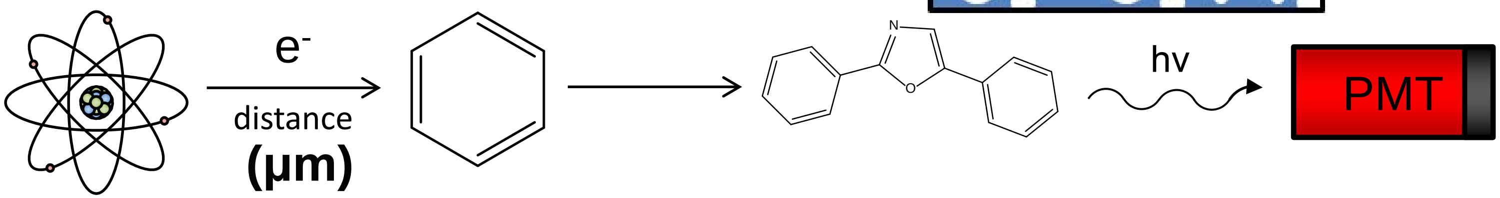




Scintillati n



Radionuclide | Solvent | Scintillator | Photomultiplier tube.

Quenching

LS — Ionization Quenching; Colour Quenching

PS — Particle Quenching; Chemical Quenching; Optical Quenching

PS

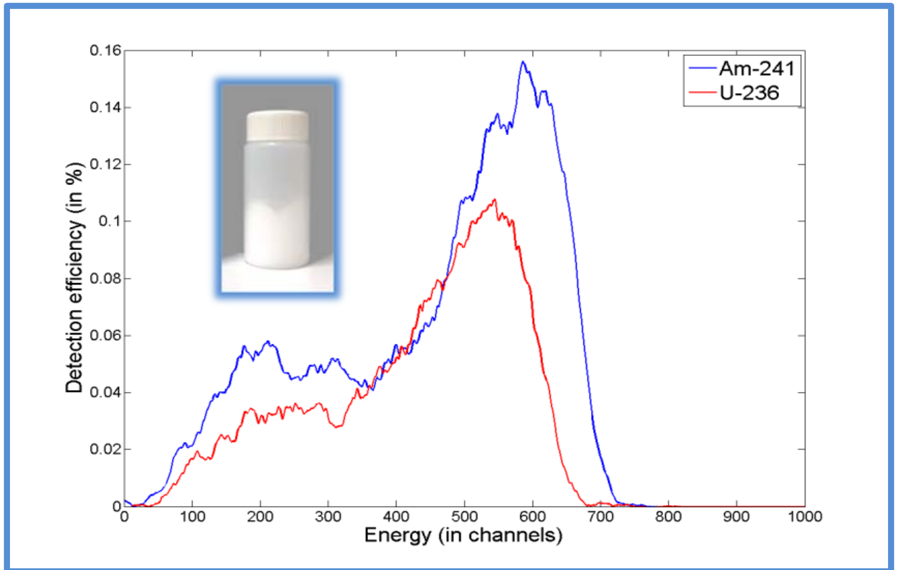
Particle Quenching → ø↑ EFF ↓
Optical Quenching → ø↑ EFF ↑

PSm ø 10 – 300 µm

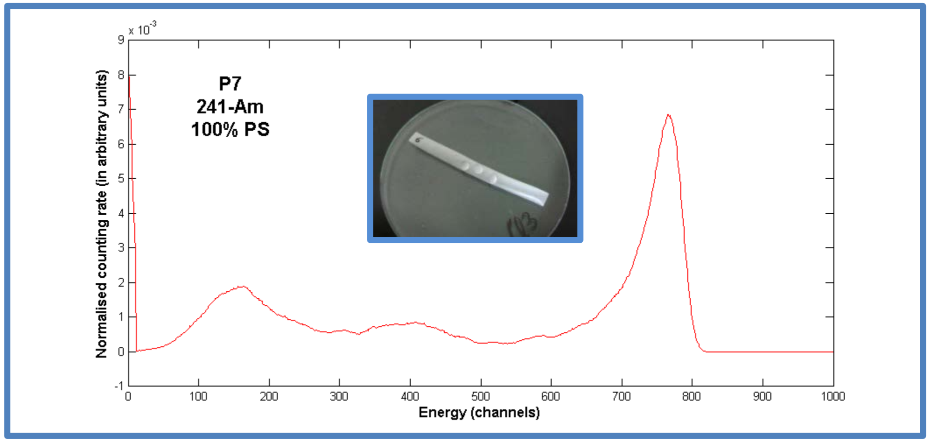
Direct radionuclide determinations - PSm

Alpha emitter radionuclides.

	EFF	
PSm	**^{241}Am (%)** (5552 keV)	**^{236}U (%)** (4573 keV)
D (70 µm)	96	75
D300 (300 µm)	45	29



	EFF
PSf	**^{241}Am (%)**
D (65 µm)	80

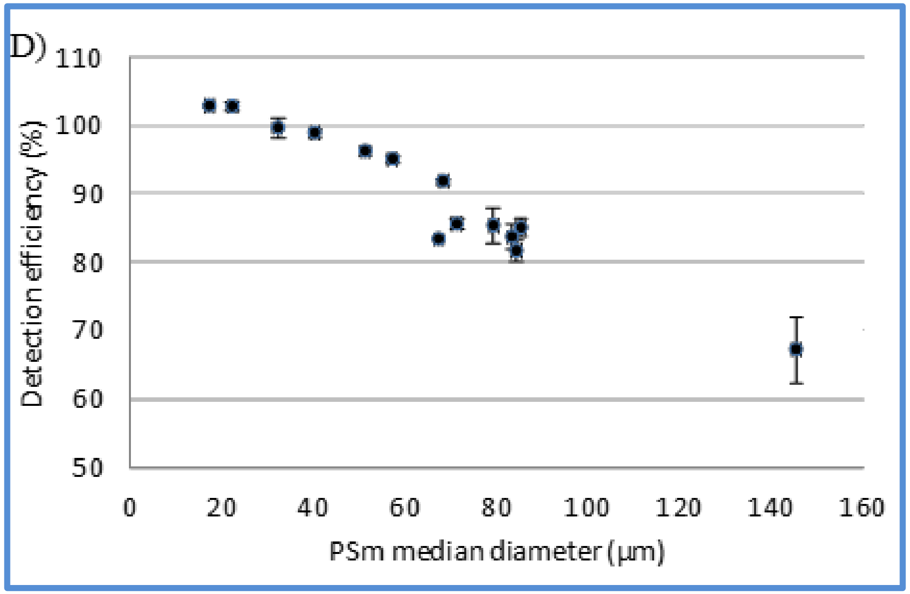


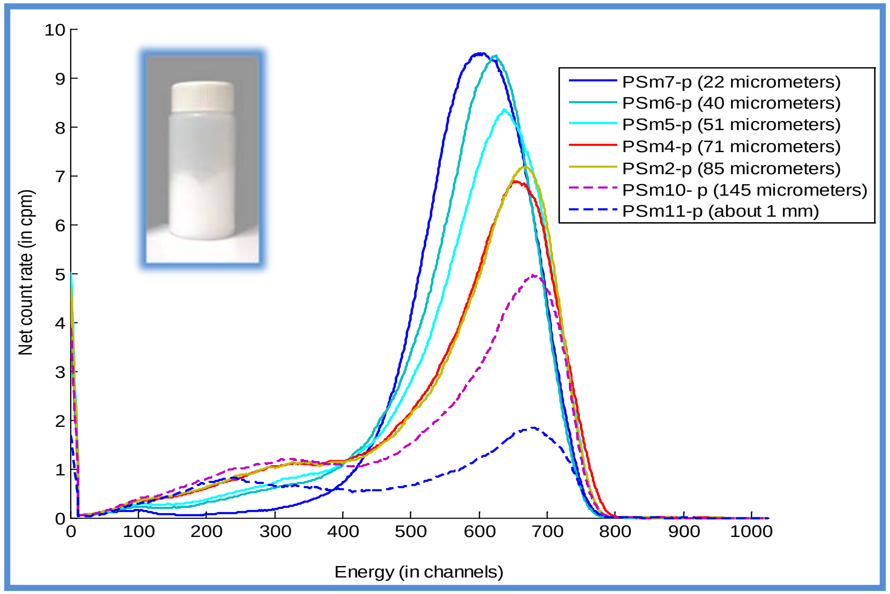
High EFF alpha emitters → ø 50 - 100 µm

Direct radionuclide determinations - PSm

Alpha emitter radionuclides.

^{241}Am





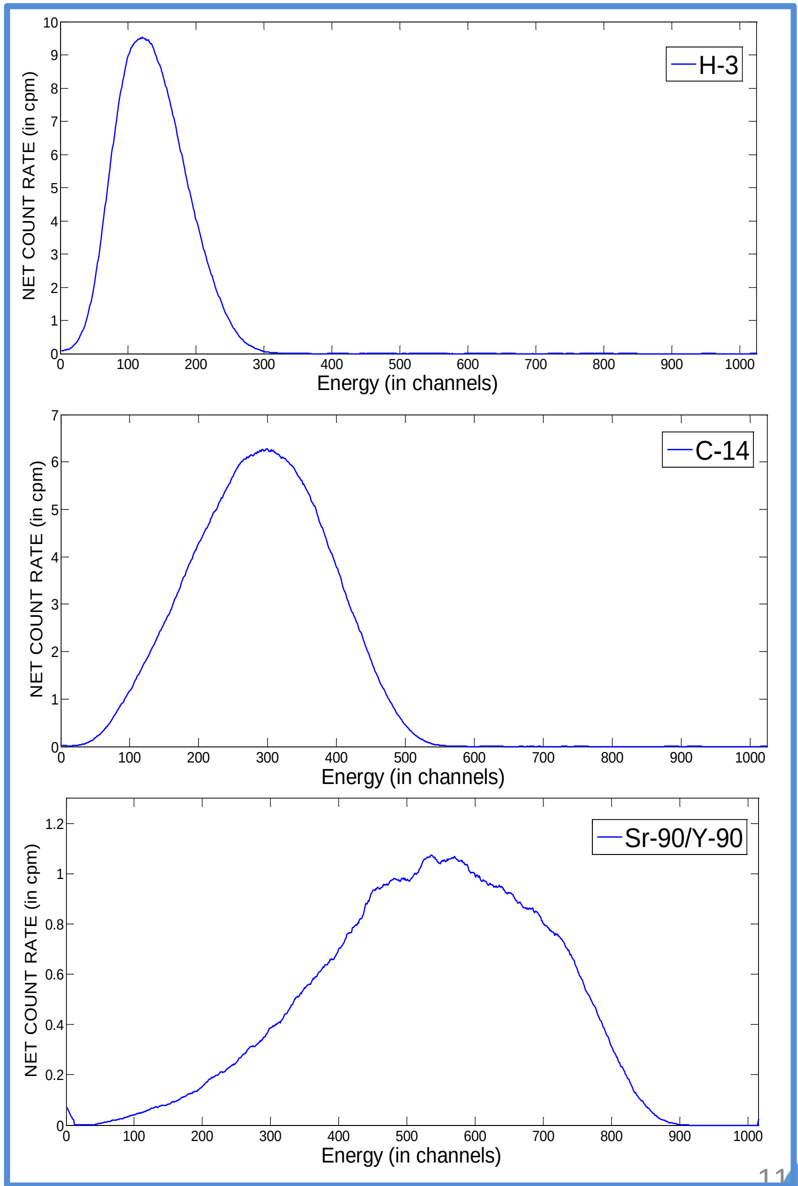
Direct radionuclide determinations - PSm

Beta emitter radionuclides.

Particle size (µm)	^{3}H (%)	^{14}C (%)	$^{90}Sr/^{90}Y$ (%)
17	4,51	74,3	192,9
32	2,69	68,7	189,8
57	1,73	62,7	190,3
79	1,16	54,5	186,7
145	0,81	45,1	184,8

High EFF beta emitters → ø 50- 100 µm

Low EFF low beta emitters ^{3}H

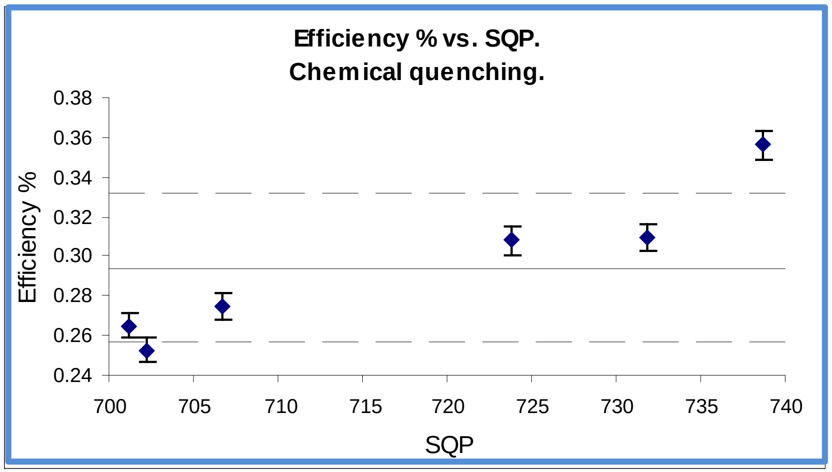


Direct radionuclide determinations - Calibration

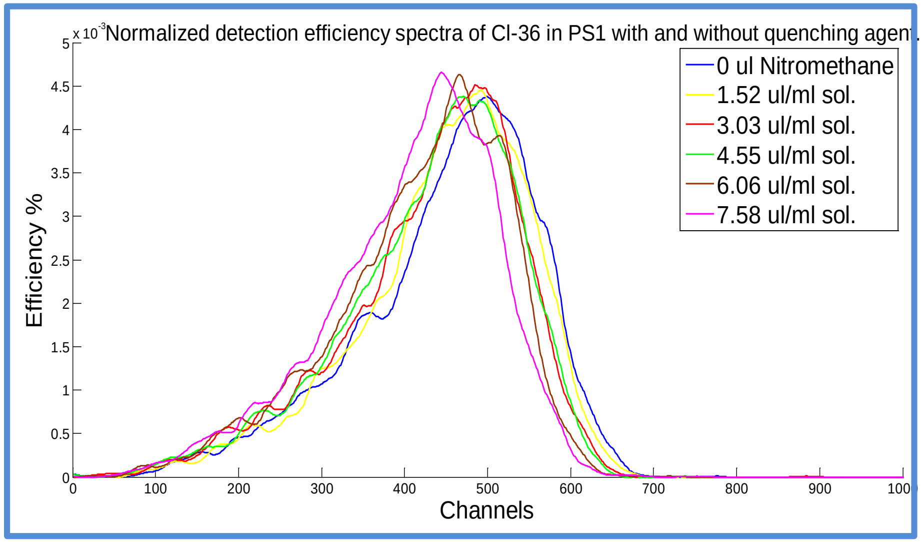
Chemical Quenching.

Nitromethane : 0 - 7.57 µl/mL

^{3}H PSm 400 – 500 µm



^{36}Cl PSm 120 – 180 µm



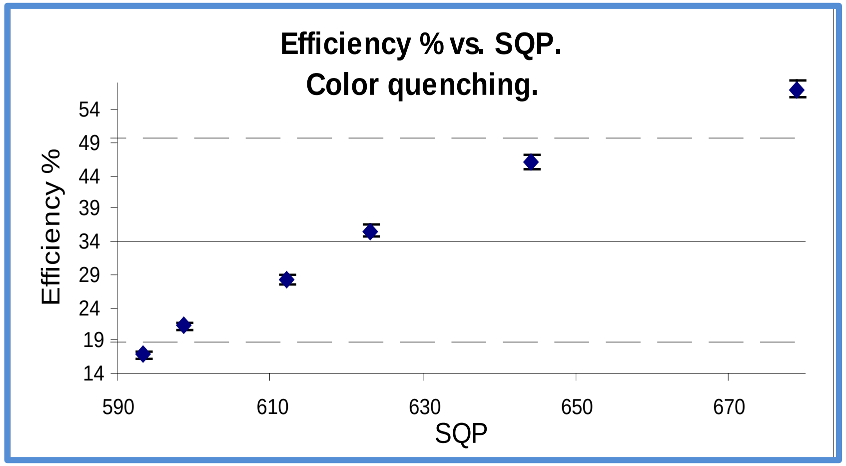
EFF↓→ Quenching parameter (SQP)↓

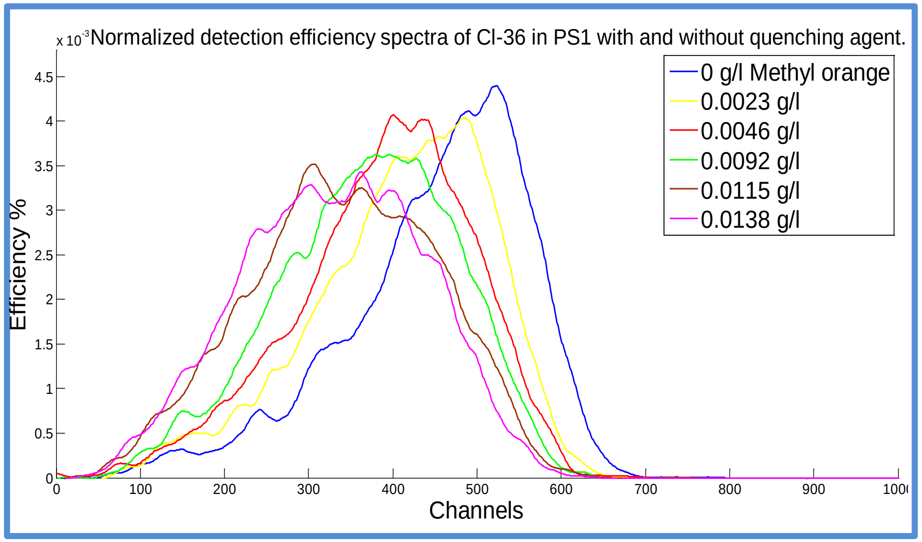
Direct radionuclide determinations - Calibration

Colour Quenching.

Methyl Orange : 0 – 0.014 g/L

^{36}**Cl** PSm 120 – 180 µm





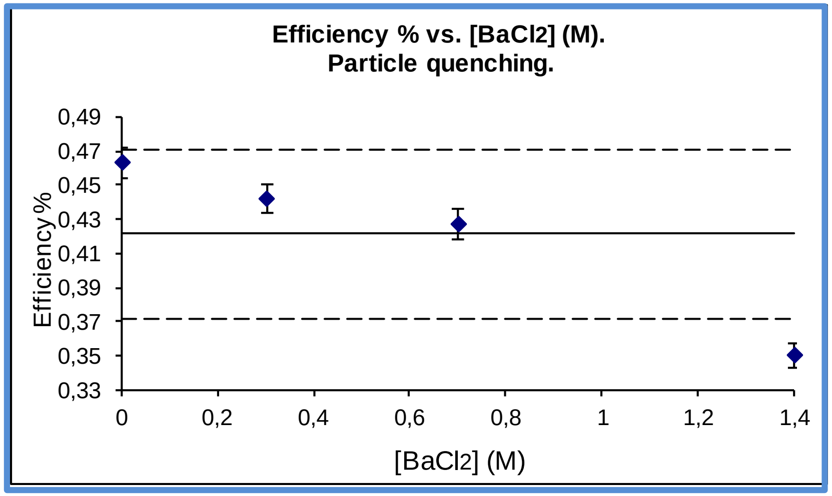
EFF↓→ Quenching parameter (SQP)↓

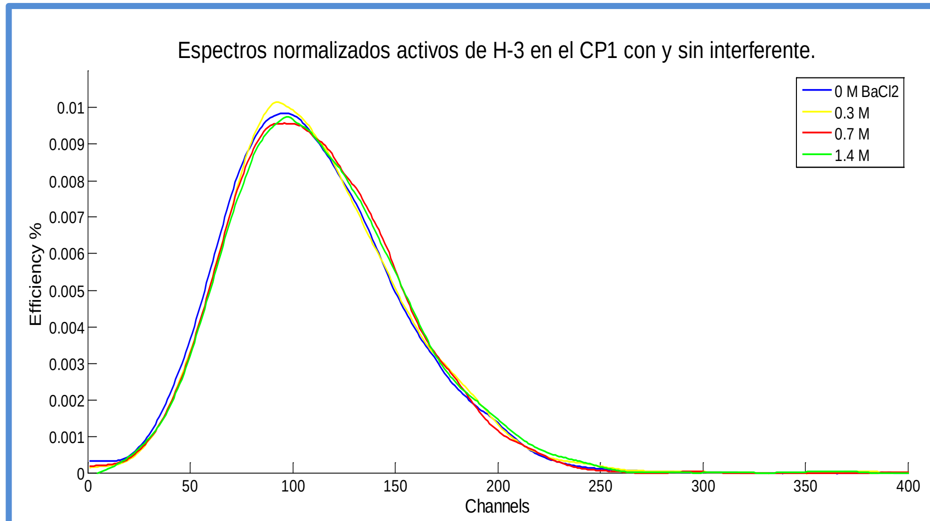
Direct radionuclide determinations - Calibration

Particle Quenching.

$BaCl_2$: 0 – 1.4 M

^{3}**H** PSm 120 – 180 µm





SQP 671 ± 3

Particle Quenching ↑ EFF ↓

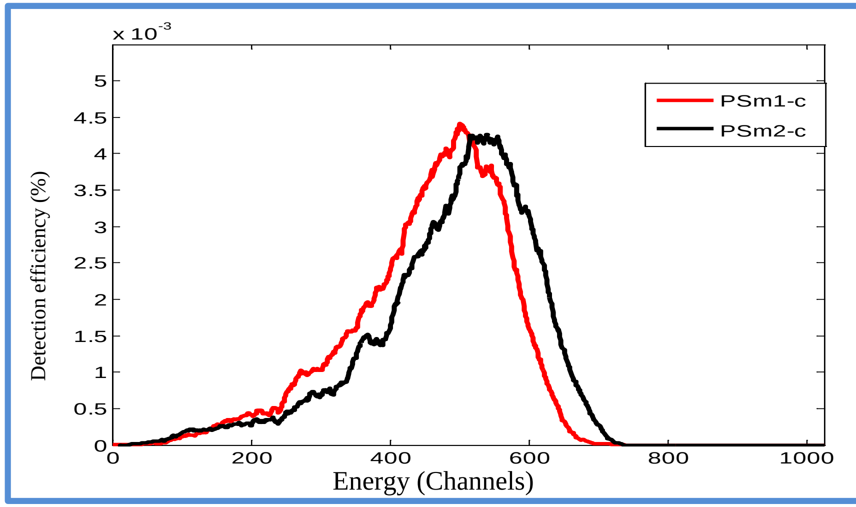
Spectra position ~ slightly change

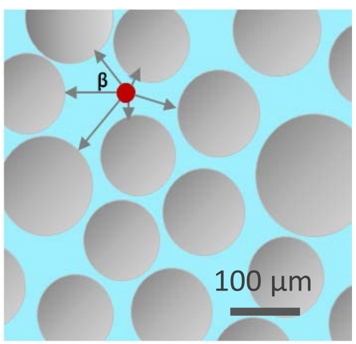
EFF ↓ → Quenching Parameter (density) ↑

Direct radionuclide determinations - Calibration

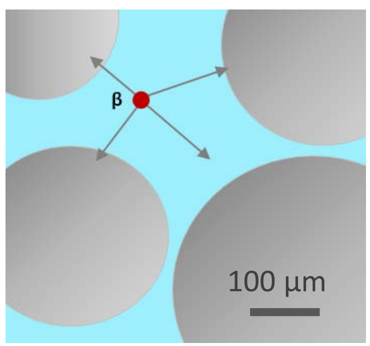
Optical Quenching.

Diameter (μm)	^{36}Cl(%)	SQP(E)
120-180	88.2(10)	680(9)
400-500	83.3(5)	737(4)

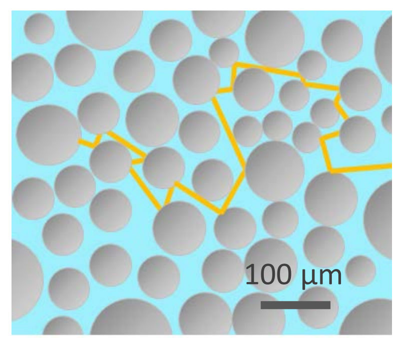




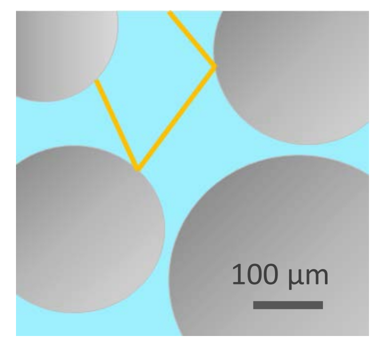
Low particle quenching



High particle quenching



High optical quenching



Low optical quenching

EFF↓→ Quenching parameter (SQP)↑

Direct radionuclide determinations - Calibration

PS Quenching.

Chemical Quenching → Quenching parameter (SQP)

Colour Quenching → Quenching parameter (SQP)

Particle Quenching → Quenching parameter (density)

Optical Quenching → Constant for a defined measurement conditions

Direct radionuclide determinations - Calibration

Ciemat- Nist procedure.

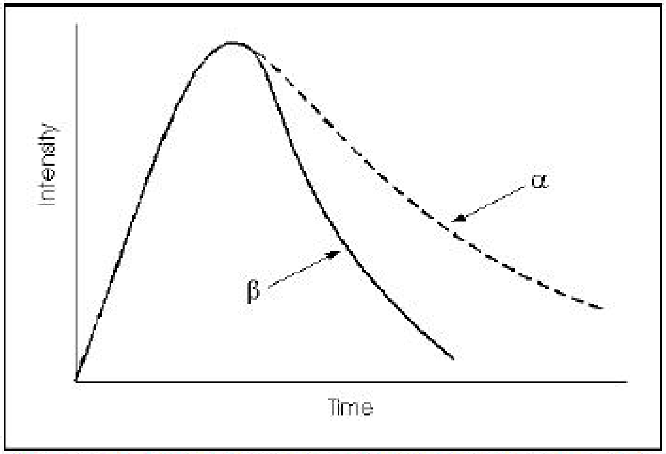
Energy distribution spectrum S(E`) that reach PSm**:** Simulation of particle Quenching by Montecarlo.

Direct Radionuclide determ - Alpha Beta discrimination

Pulse Shape distribution.

Time pulse shape distribution of alpha emitters is longer than beta emitters.

LS alpha >> beta -- PS alpha > beta.



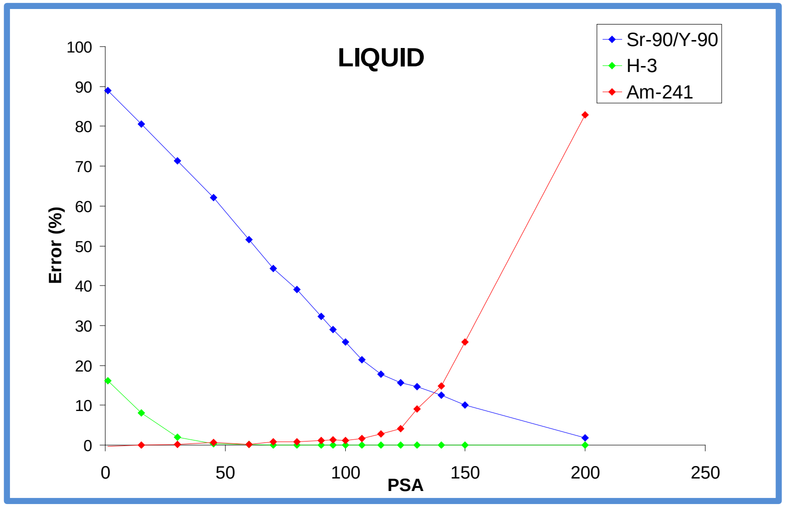
Characteristic Light Pulse Shapes of Alpha and Beta Pulses in LSC

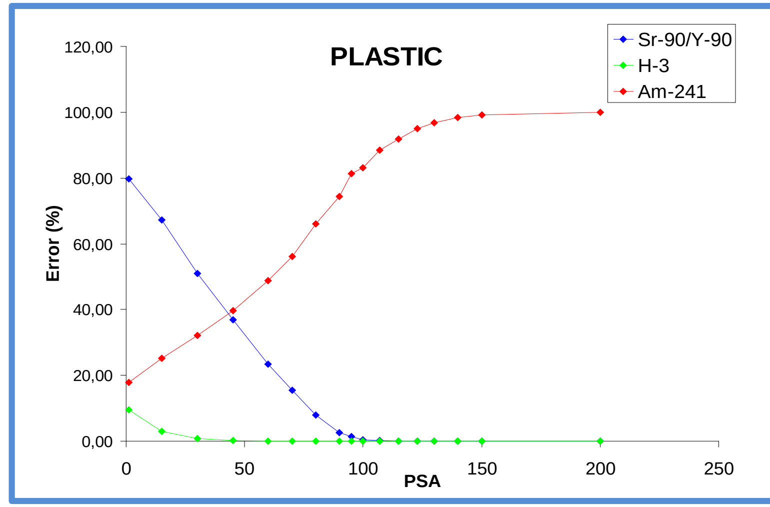
- Delay depends on ^{3}T concentration.
- PS energy spreads faster by polymeric chains.
- Secondary solvent (Nafthalene, Disopropylnaphtalene) delays signal

Direct Radionuclide determ - Alpha Beta discrimination

Pulse Shape distribution.

Quantulus detector

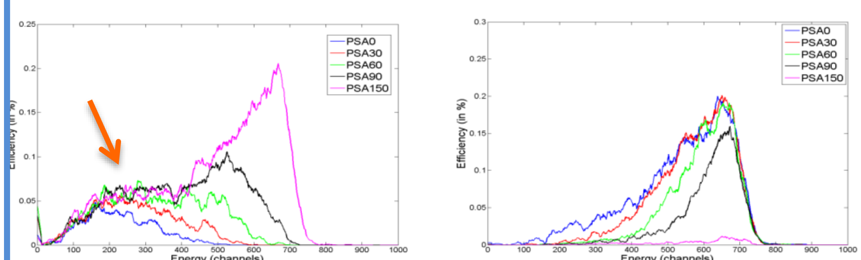




Beta Classification LS = PS

Alpha Classification PS ↓ LS

Alpha misclassified even PSA=0 (fast)



^{241}Am: β-spectrum ^{241}Am: α-spectrum

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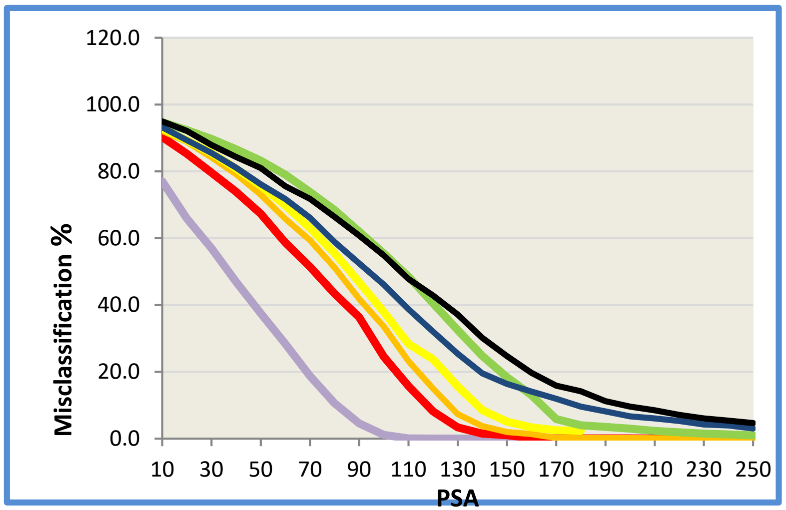
Direct Radionuclide determ - Alpha Beta discrimination

Pulse Shape distribution.

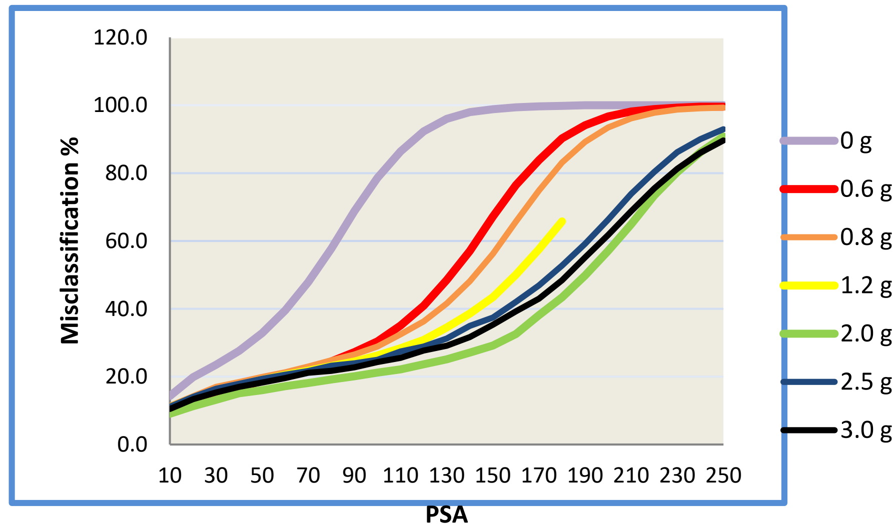
Quantulus detector

PSm: PPO+POPOP+ Naphtalene (120-150 µm)

$^{90}Sr/^{90}Y$



^{241}Am



Alpha Pulses delayed

Alpha Classification PS improve

Direct Radionuclide determ - Alpha Beta discrimination

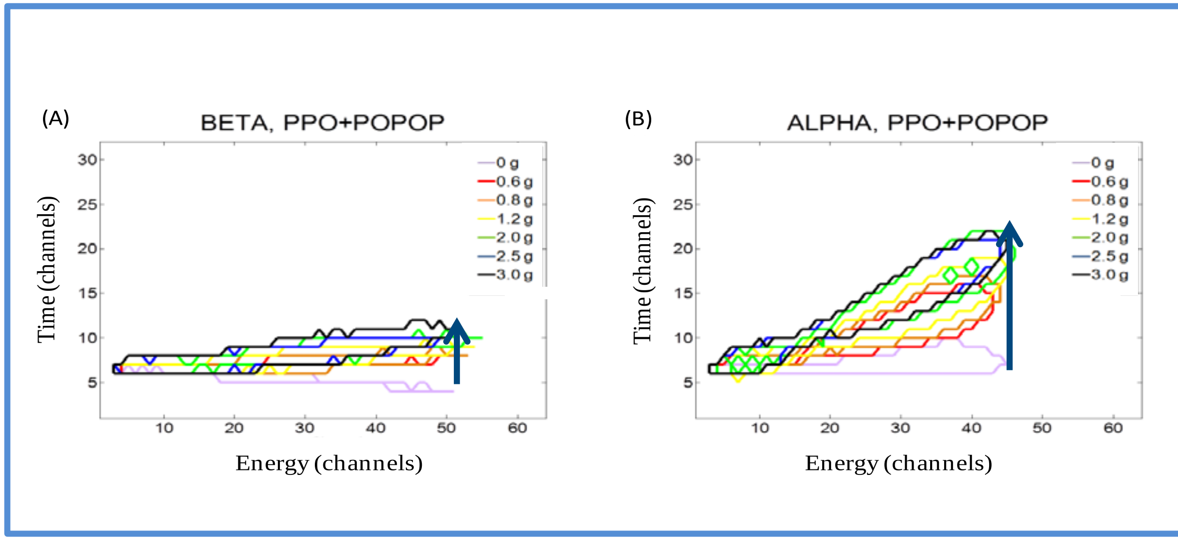
Pulse Shape distribution.

Triathler detector

PSm(120-150 µm)

$^{90}Sr/^{90}Y$ ^{241}Am

PPO+POPOP+ Naphtalene



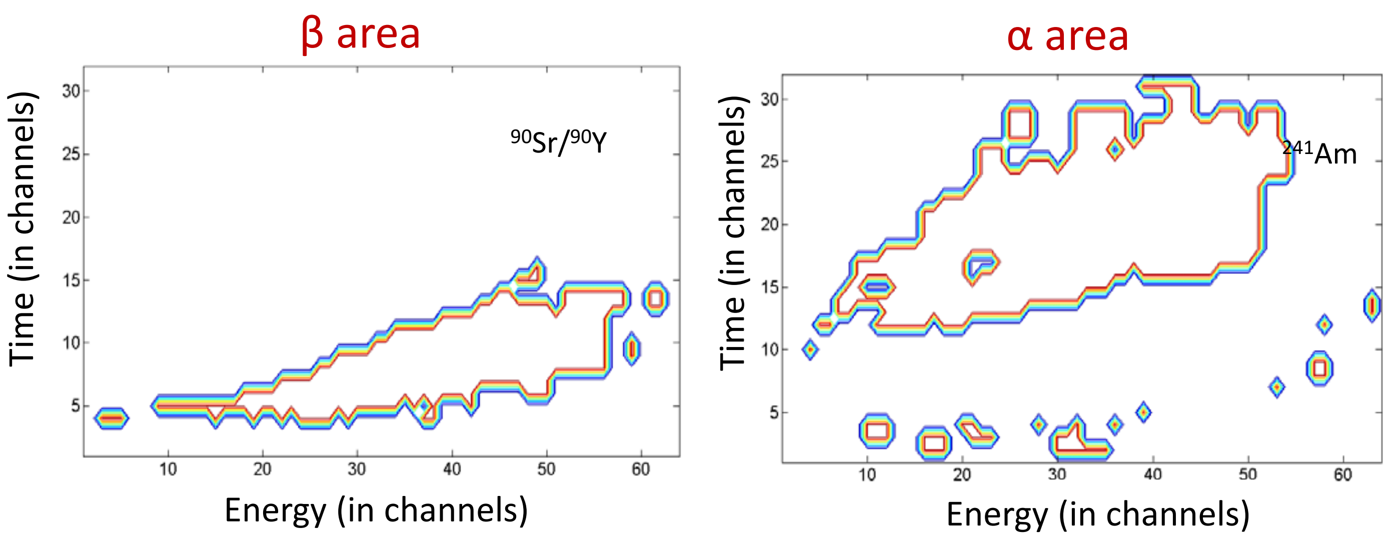
Alpha / Beta discrimination

Direct Radionuclide determ - Alpha Beta discrimination

Pulse Shape distribution.

Triathler detector

PSm(120-150 µm) PPO+POPOP+ 2g Naphtalene



Integrating areas: Beta emitter: misclassification < 2% - EFF 90%
Alpha emitter: misclassification 1 % - EFF 25%

Direct Radionuclide determinations - Applications

Applications

-Limited use for routine radionuclide determinations.

-Useful for specific determinations.

Direct Radionuclide determinations - Applications

Applications

High Salty matrices.

LS – phase separation

PS - stable

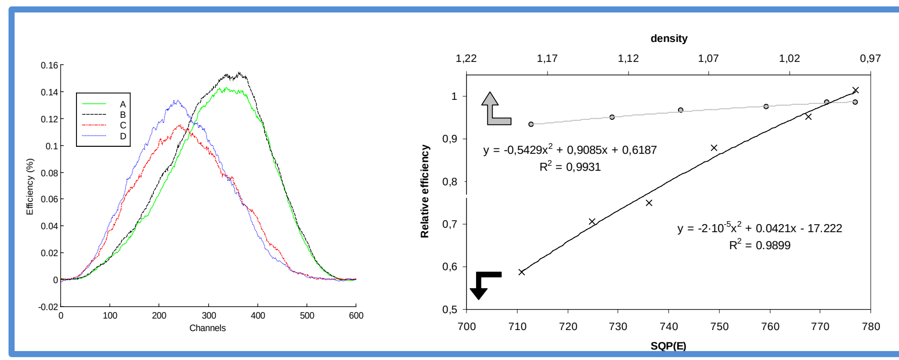
<u>Determination of Radiotracers in oil reservoirs</u>

Institute for Energy Technology (Norway)

Radiotracer: $S^{14}CN^{-}$

Matrix: $NaClO_4$ conc.

Calibration: colour and particle quenching



	AA (dpm/g)	**MA** (dpm/g)
LS – IFE	4.23	0.55
PS - UB	4.32 ± .016	0.59 ± 0.04

Direct Radionuclide determinations - Applications

Applications

Continuous detection.

LS – measurement cell: sample + cocktail mixture

- unstable and reagents consumption, waste generation.

PS – measurement cell : sample + solid scintillator

- stable – EFF detection

. Chromatographic determinations

. Environmental determination (^3H)

Multiple sample analysis.

. Microplates (labelled samples)

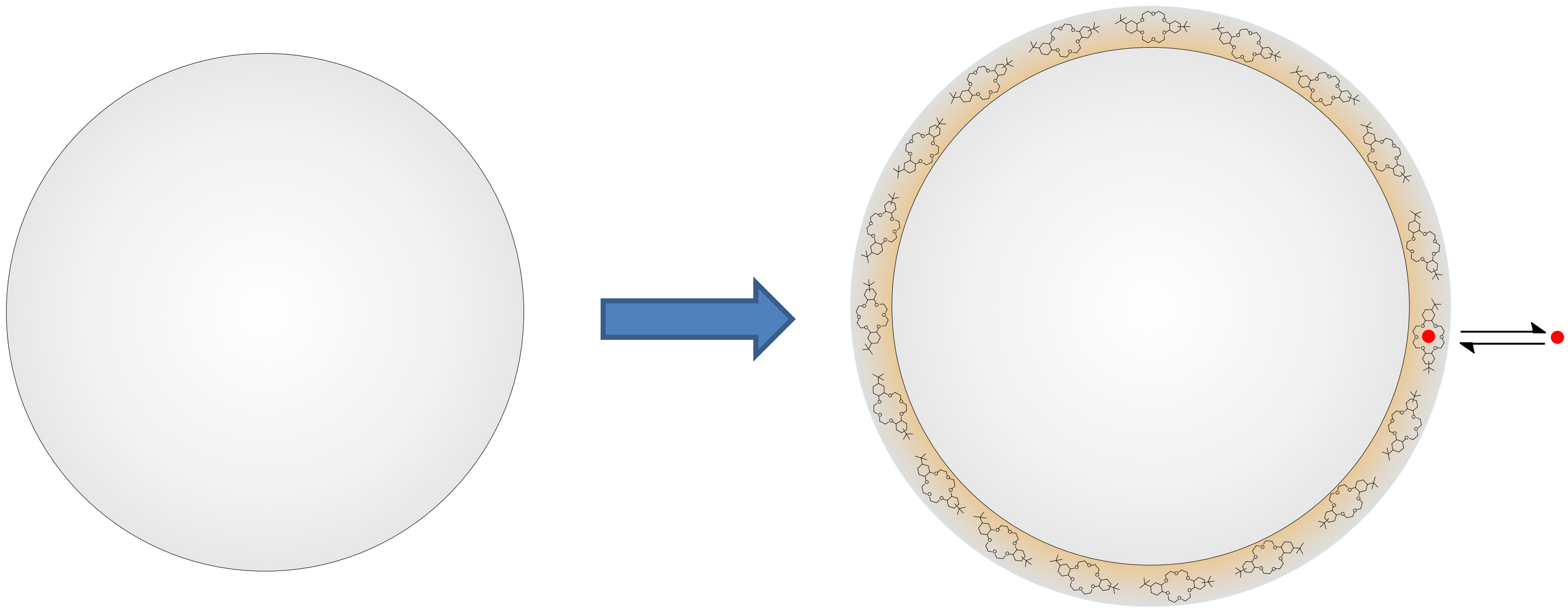
Selective Radionuclide determinations - PSresin

Plastic Scintillating resins – Extractive Scintillating resins

. Alpha and Beta spectra distribution + Scintillation →

no selective technique / spectra overlapping.

. PS → solid platform to implement separation procedures



PSm

Plastic Scintillating resin (PSresin)

Selective Radionuclide determinations - PSresin

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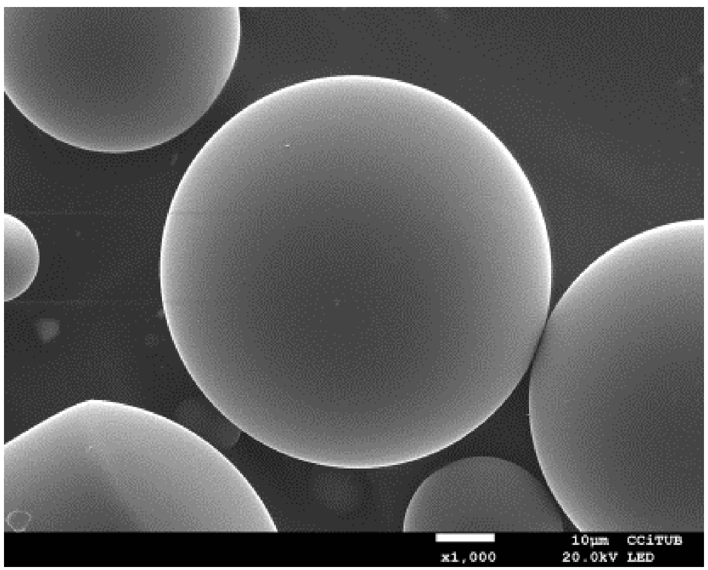
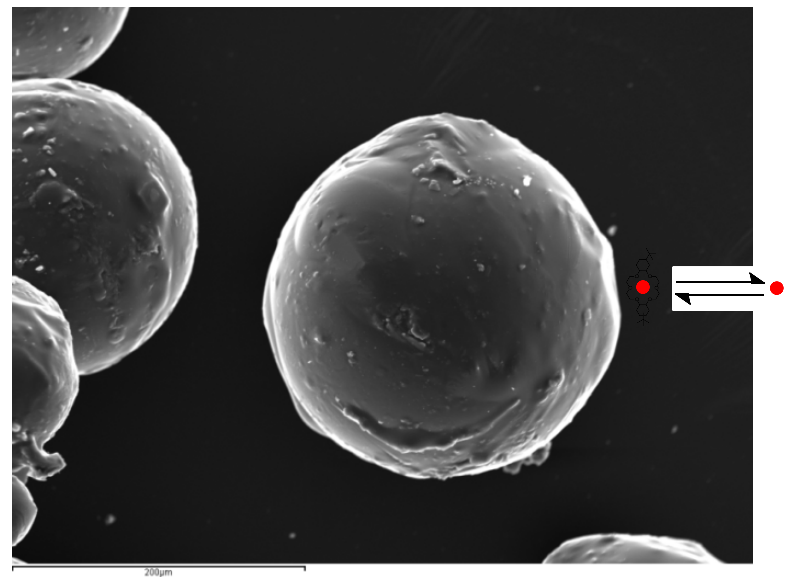


PSm

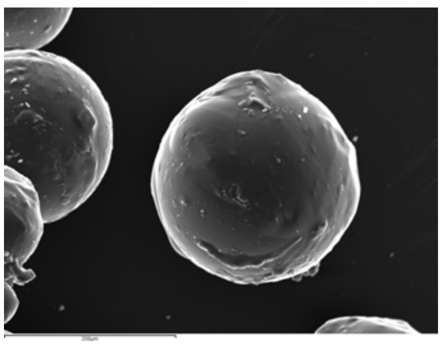


Plastic Scintillating resin (PSresin)

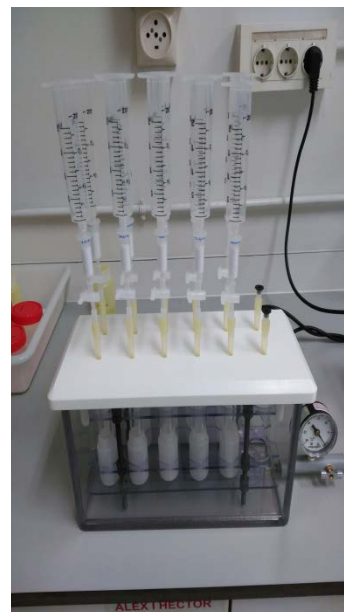
Selective Radionuclide determinations - PSresin

Plastic Scintillating resins – Extractive Scintillating resins.

. **PSresin**: separation step + measurement preparation



PSresin



Selective Radionuclide determinations - PSresin

Plastic Scintillating resins – Extractive Scintillating resins.

. **PSresin**: separation step + measurement preparation

. Time reduction

. Reagents and man power reduction

. Waste reduction

. Development in progress

. Cost ?

Selective Radionuclide determinations - PSresin

Preparation approaches.

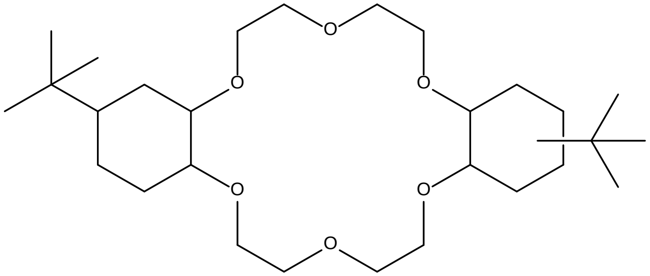
. Approaches to incorporate the selective capability:

- **Immobilization**: selective extractant (solvent) coating the PSm or CPS.
- **Imprinted polymers**: selective cavity on the PSm or CPS
- **Covalent bounding**: selective extractant bounded on the PSm or CPS surface.

-

Selective Radionuclide determ - Applications

Immobilization.



^{90}Sr in Water

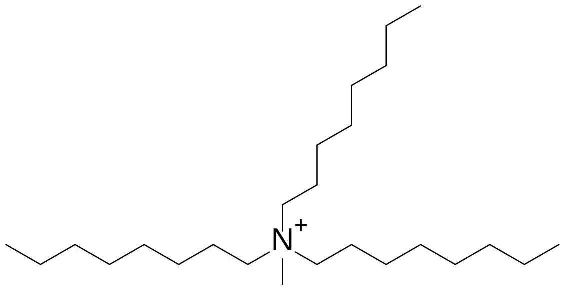
Extractant: 4,4'(5')-di-t butylcyclohexane 18-crown-6 1M Octanol

Separation conditions: $LiNO_3$ 6 M

	Act (dpm)	Act calc (dpm)	Error (%)
Drinking water	8.02	8.18	1.94
	7.77	7.66	-1.44
	7.66	7.54	-1.51
Sea Water	7.88	8.06	2.29
	8.00	7.80	-2.56
	7.70	8.01	4.09
River Water	7.86	7.84	-0.28
	7.75	7.60	-1.94
	7.77	7.72	-0.61

Selective Radionuclide determ - Applications

Immobilization.



Radiotracer $S^{14}CN$ in oil reservoir.

Extractant: Aliquat 336

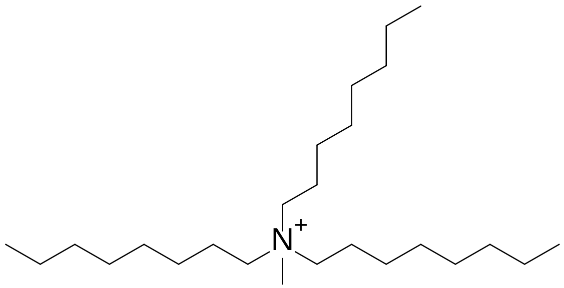
Separation conditions: water

Sample	Conductivity (mS cm^{-1})	TOC (mg L^{-1})	Activity (Bq L^{-1})	
			PS resin	IFE
1	52.1 ± 0.1	13.6 ± 0.3	2.89 ± 0.14	2.98 ± 0.09
2	51.5 ± 0.2	18.4 ± 0.3	2.01 ± 0.04	2.21 ± 0.06
3	50.8 ± 0.2	22.4 ± 0.7	1.00 ± 0.09	1.02 ± 0.07
4	51.3 ± 0.1	39.2 ± 0.6	1.42 ± 0.02	1.36 ± 0.05
5	51.5 ± 0.2	18.4 ± 0.7	2.66 ± 0.08	2.76 ± 0.08

Selective Radionuclide determ - Applications

Immobilization.

<u>^{99}Tc in water and urine.</u>



Extractant: Aliquat 336

Separation conditions: HCl 0.1M

Sample	Activity (dpm L^{-1})	Activity Calc (dpm L^{-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
Urine	0,43	0.44	2,4
Urine	0,46	0,42	-6.5

Selective Radionuclide determ - Applications

Immobilization.

^{210}Pb in water.

Extractant: 4,4'(5')-di-t butylcyclohexane 18-crown-6 1M Octanol

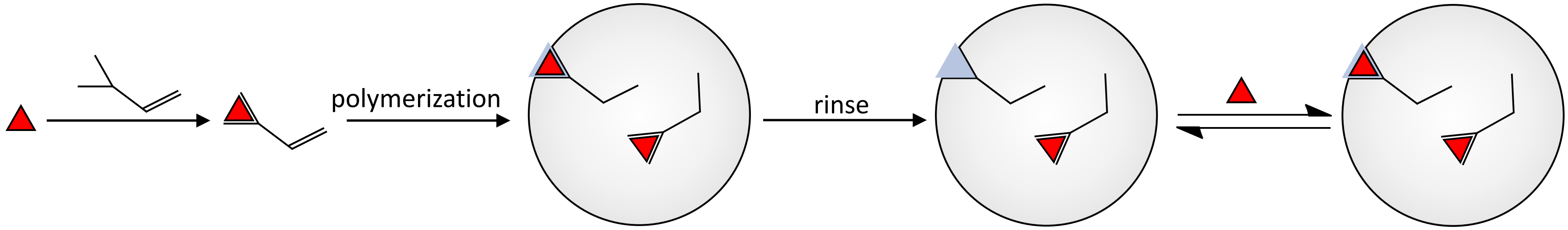
Separation conditions: HNO_3 2M

Sample	Activity (dpm/mL)	Activity Calc (dpm/mL)	Deviation (%)
Ebro river	10,1	10,8	-7,0
	10,1	11,0	-9,2
	10,1	9,8	3,6
Subterranean water	10,9	11,7	-7,0
	11,4	11,4	0,2
	11,4	11,8	-4,1
Congost river	11,0	11,4	-4,2
	10,4	10,7	-3,3
	11,4	11,3	0,7

Selective Radionuclide determinations

Imprinted.

Synthesis in presence of a template.



-Selectivity based on steric impediment

- No breakthrough volume

- Use of generic extractants

In progress: PSresin ^{63}Ni

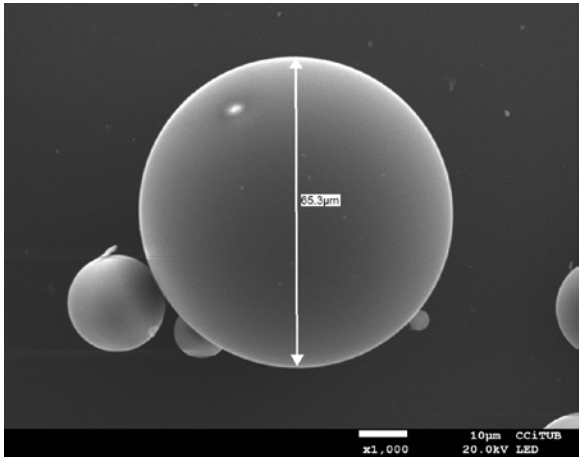
Selective Radionuclide determinations

Imprinted.

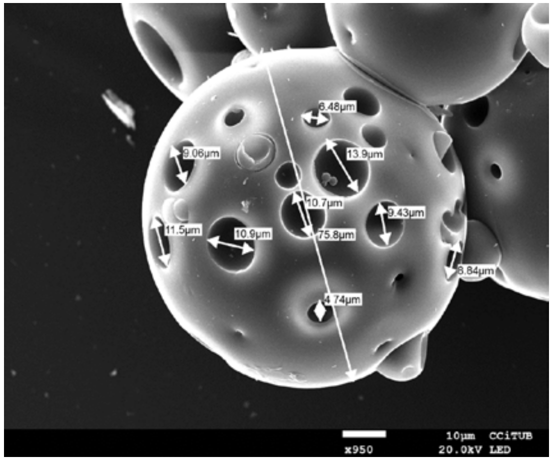
Synthesis in absence of template.

Polymer Free Volume – Porosity

SEM



PSm



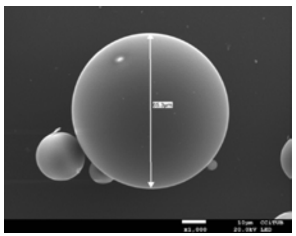
PSm-Porous

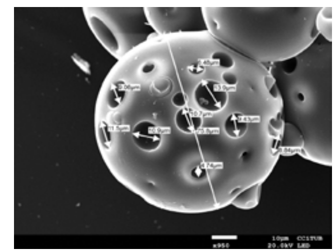
Selective Radionuclide determinations

Imprinted.

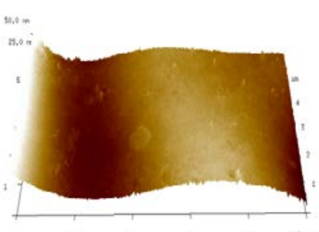
Synthesis in absence of template.

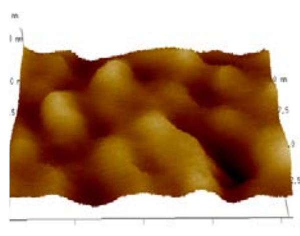
SEM



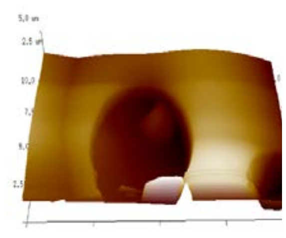


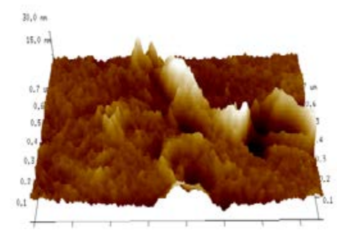
AFM

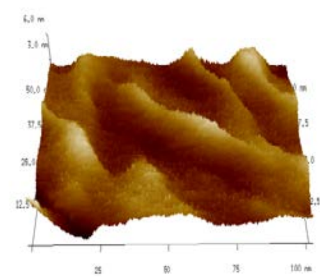




PSm







PSm-Porous

In progress: ^{222}Rn

Selective Radionuclide determinations

Covalent Bounding.

Selective extractant bounded on the PS surface.

- No breakthrough volume

Studies **in progress**:

- CPS - ^{233}U
- CPS – ^{63}Ni

Selective Radionuclide determ - Applications

Automation.

-Routine analysis improves by using automated systems.

- Inclusion of PSresin cartridges fits this approach

Summary and Future challenges.

Summary.

- Alpha and Beta emitters can be determined by PS (Low beta emitters)
- Calibration by using Quenching Parameters
- Alpha/ Beta discrimination is possible.
- Selective determinations are possible

- Selective Plastic Scintillating Resins.

: Procedures of extractant incorporation

Summary and Future challenges.

Future challenges.

- Selective Plastic Scintillating Resins.
  - . Procedures of extractant incorporation
  - . Controlled porous materials
- New Plastic Scintillating formats.
  - . Foils
  - . Monolites
- Automation.
- New application fields.
  - . Routine control
  - . Medical
  - . Decommissioning
  - . Emergency situation

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Thanks for your attention.