

Plastic scintillators and related analytical procedures for radionuclide analysis

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Abstract This article is a general overview of the potential capacities of plastic scintillators in radionuclide activity determination. Plastic scintillation (PS) behaves as liquid scintillation does, but with some differences related to the solid state of plastic scintillators. These differences are the base of some drawbacks and some advantages, related to the use of PS. This article describes how these capacities are affected by PS composition, sample preparation, scintillation mechanisms and quenching calibration procedures. It also describes the capabilities for alpha and beta emitter determination and discrimination through the use of PS microspheres and PS resins and their application to different types of samples and radionuclide determination.

Keywords Plastic scintillators · Scintillating extractive resins · Plastic scintillating resins · Radionuclides

Introduction

The first paper published on scintillation was probably “*Scintillation counting with solutions*” by H. Kallmann in 1950 [1]. Other articles followed [2, 3], a few of which focused specifically on plastic scintillators, such as the study by F. D. Brooks in 1960 “*Pulse shape discrimination in a plastic scintillator*” [4]. However, the book by J.

B. Birks “*The Theory and Practice of Scintillation Counting*”, published in 1964 [5], can be considered the consolidation of scintillation as a potential technique for real and extensive use in laboratories to determine radionuclides in all kind of samples. In that book, Birks describes both liquid and plastic scintillation at the same level; however, their evolution in the following decades was quite different.

The potential of liquid scintillation was concentrated on beta-emitter radionuclide determinations favoured by the development of liquid scintillation counters (later spectrometers) and liquid scintillation cocktails [6–8]. Needs and interests converge on the development of nuclear activities together electronics and companies producing counters. Easy sample preparation and large numbers of applications described using the technique contributed to the spread of liquid scintillation [9].

Applications of plastic scintillation focused on the field of large area detectors [10–12], dosimetry [13–15], scintillation proximity assays [16] and more recently, neutron detection [17–19]. These fields developed later and their applications are important but reduced on number. Recently, interest in the application of plastic scintillation to radionuclide activity determination has increased, probably due to the fact that it avoids mixed waste production [20–23] and its capacity to integrate separation and detection processes.

This article presents a general overview of the capacities of plastic scintillation in radionuclide activity determination, based on our experience. This overview will include Plastic Scintillators composition and sample preparation; scintillation mechanisms, including the different types of quenching and the consequences on alpha/beta discrimination capacities; calibration; and different examples of direct and selective detection of alpha and beta emitters.

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Composition

The composition of Plastic Scintillators (PS) is totally equivalent to that of liquid scintillation cocktails. PSs are solids that include a polymeric solvent and both primary and secondary scintillators, such as the classical PPO, POPOP, p-T or bis-MSB. Fluor molecules remain encapsulated inside the PS solid [24].

For water insoluble PSs, the solvents include linear polymeric chains based on styrene or vinyltoluene [25]. For PSs that are insoluble in organic and aggressive media, the polymer has to include a cross linker, as divinylbenzene, to create a three-dimensional structure [26]. The addition of the cross linker decreases the scintillation yield.

Liquid scintillation may also include a secondary solvent, as naphthalene or disopropilnaphthalene, to produce a temporal delay in the emission signal distribution. This addition is especially interesting for PS composition, to improve its capacity for alpha/beta signal discrimination [27].

PSs are solids that could be produced in any form. The most common for radionuclide determination in solution are microspheres (PSm), foils (PSf) and pellets (Fig. 1). Detection capacities depend, among other variables, on their size. Orientative values could be: for PSm, diameters of 10–300 μm , for PSf, widths of 50–100 μm , and for pellets, 3 mm. There are few suppliers for the production of the different compositions and formats [28, 29].

Sample preparation and reuse of PS

In plastic scintillation, sample preparation for measurement also follows the same steps as in liquid scintillation. A vial is filled with the appropriate amount of PSm and the active solution is added; finally, the vial content is homogenized using a shaking procedure such as a Vortex (Fig. 2). This last step is the main difference with regard to sample



Fig. 2 Scintillation vial filled with the PSm and the active solution ready to be measured

preparation for liquid scintillation and it makes plastic scintillation a bit longer.

The relationship PSm:sample solution is important for optimum detection conditions. The solution level should not be above the PSm level, because emissions in that part would not be detected; or below it, because the excess PSm would increase the background unnecessarily. As an example, for PSm of 60 μm diameter, the recommended proportion is 1.5 g:0.625 mL, irrespective of the vial volume.

The measurement procedure in liquid scintillation counters is performed in a totally equivalent way to that in liquid scintillation samples, including the use of external standard sources to determine quenching parameters.

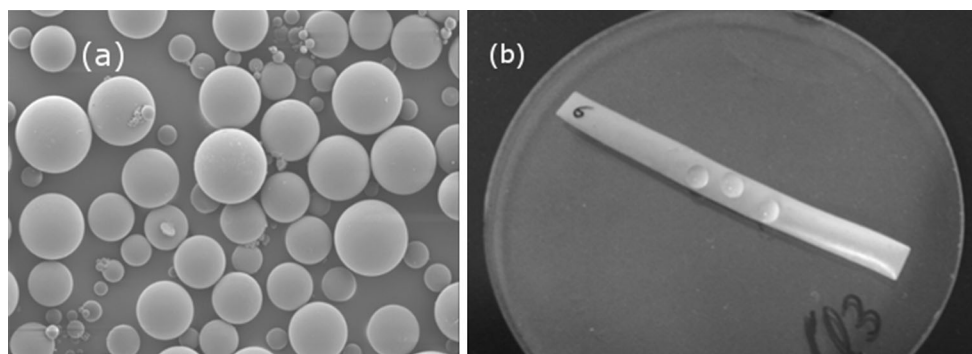


Fig. 1 **a** Secondary electron microscope images for the PSm obtained using a scanning electron microscope; **b** visible image of a PSf

Once measurements have been completed, sample solution and PSM can be segregated by filtration avoiding the production of mixed waste and allowing sample recovery and PSM reuse.

For most radionuclides, cleaning procedure is easy by simply washing the PSM with a solution of citric acid, 0.1 M and pH = 3 (for instance, in a flask and by shaking the mixture in an end-over-end system for 24 h) [30]. For some isotopes, such as americium, citric acid has to be substituted by 1 M hydrochloric acid. The main drawback of reuse is the time consumed in the washing process.

A comparison of the capacities of plastic and liquid scintillation is summarized in Table 1.

Mechanism

The transmission of the energy corresponding to the emitted particles to produce a final cascade of detectable photons follows a similar process in both liquid and plastic scintillation. The only difference is two additional quenching interferences: particle quenching and optical quenching.

The general process of energy transmission is shown in Fig. 3.

In a vial including an active sample solution and PSM, the beta or alpha particle emitted in the middle of the sample solution must pass through this phase for some distance before reaching the scintillator material. Once the PSM are reached, energy is transmitted and finally the fluorescent molecule emits the corresponding photons. The photons must then pass through a heterogeneous medium, changing from plastic to solution media on several occasions, before being detected by the photomultiplier tube. This series of successive changes of refraction index produces the corresponding optical processes of reflexion, refraction, dispersion and absorption that may reduce the number of photons finally detected.

Ionization, colour and chemical quenching are the three best-known processes that decrease the scintillation yield in a liquid scintillation detection process [31]. These are also present in plastic scintillation [32].

In both cases, ionization quenching, which is the reduction in the number of radiation-excited scintillation cocktail molecules as a consequence of ionization generated by the nuclear radiation with the associated reduction in photon intensity [9] depends on the scintillator/solvent composition and it represents a constant decrease for a defined measurement medium.

Colour quenching is also clearly an interference process when the sample medium shows some absorbance in the wavelength of the photons emitted by the scintillator [33]. Meanwhile, chemical quenching is related to interference in the solvent–solvent, solvent–scintillator or scintillator–scintillator energy transmission process that other, mainly electronegative, compounds present in the sample solution may produce.

Taking into account that this transmission process happens in the interior of the PS once the particle has reached its surface, it is reasonable to have some doubts about the extent of chemical quenching in plastic scintillation. The experimental results show that plastic scintillation is affected by chemical quenching just as liquid scintillation is [34]. This could be related to the fact that PS materials are quite “porous” and some of the compounds responsible of chemical quenching could penetrate the spaces in the polymer chains, at least close to the surface where transmission is initiated, and produce interference.

Particle quenching is related to the path that the emitted particle follows before arriving at the PS surface [33, 35]. Along that path, interactions with the medium decrease the energy of the less energetic emissions that finally are not detected (Fig. 4).

The length of the path increases as the diameter of the PSM does and consequently, the larger the PSM used, the lower the radionuclide detection efficiency.

Table 1 Advantages and disadvantages of plastic and liquid scintillation techniques

Liquid scintillation	Plastic scintillation
Large number of scintillation cocktail suppliers	Limited number of suppliers and composition
Easy sample preparation	More expensive than LS cocktails
	Additional homogenization step in sample preparation
Instability due to phase separation in samples with high salinity	No phase separation
No particle or optical quenching	Importance of particle and optical quenching
	Lower detection efficiency for low energy beta emitters
Not reusable	Easy separation and reusability of the PSM
Production of mixed wastes	Does not produce mixed waste
	Capable of for selective determinations or continuous measurements

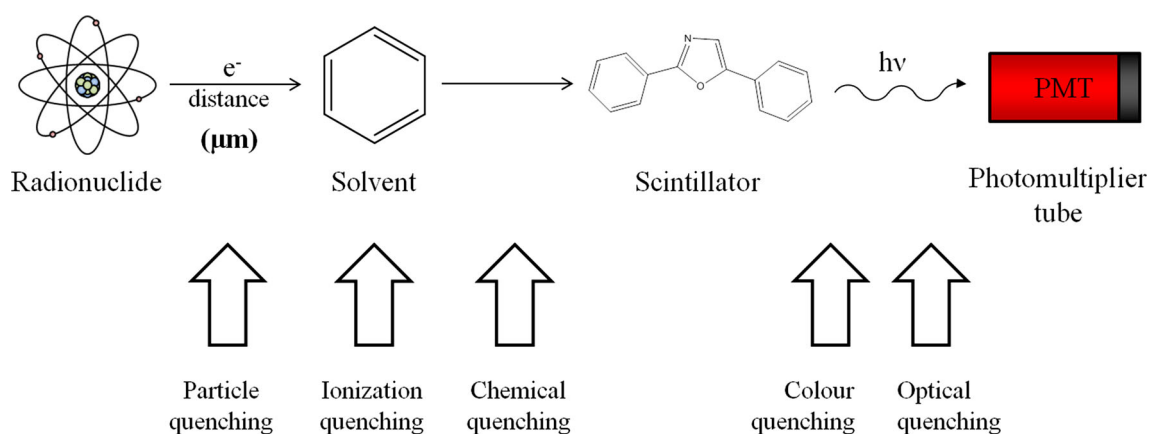


Fig. 3 Scintillation process detection scheme with the different quenching processes that affect it

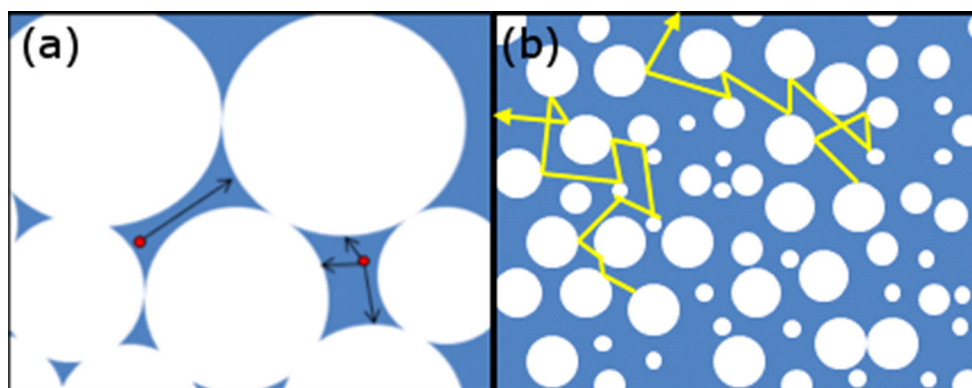


Fig. 4 Scheme of the PSm in solution showing: **a** particle quenching, where black lines represent the path of the particles emitted by the radionuclide (red circle); and **b** optical quenching, where yellow lines represent the path of the photons emitted by the PSm. (Color figure online)

Optical quenching is at the opposite extreme of the detection process [35]. This quenching is a consequence of the successive changes of refractive index encountered by the photons before they exit the vial. The number of solution-PS changes increases as the diameter of the PSm decreases. The consequence in this case is that detection efficiency decreases together with PSm size.

Thus, in terms of detection efficiency, particle and optical quenching act in opposite directions and a compromise is required with regard to the diameter of the PSm (or the structural organization of the sample solution and PS materials when foils or pellets are involved). Our experience has taught us that a convenient diameter range for PSm is 10–300 μm ; in this range, PSm detection efficiencies for most alpha and beta emitters are similar to those for liquid scintillation, except for low-energy beta emitters such as ^3H .

This is probably the main drawback of using PSm: the low detection efficiency for ^3H . For a low activity level and

short counting time, liquid scintillation is the recommended option.

Values of detection efficiency for different radionuclide and quenching calibration procedures are given in the following sections.

Detection capacities of plastic scintillators

PSs are sensitive to gamma, beta and alpha emissions, but only beta and alpha show detection efficiency values and spectra that are adequate for direct activity determination in solution samples at environmental activity levels.

Gamma and neutron detectors made of PSs are also used, but for other purposes that are beyond the scope of this overview.

Detection efficiencies of PSs depend mainly in their shape (microspheres or foils) and how they interact with the sample.

Plastic scintillators in the form of microspheres (PSm)

Beta emitters can be detected and quantified by plastic scintillation. Detection efficiencies corresponding to the measurement of aqueous solutions of these radionuclides using 20 mL polyethylene vials and PSm made of polystyrene + PPO + POPOP of diameters 15–150 μm are shown in Table 2. Spectrum distributions can be observed in Fig. 5.

From the table, it can be seen that detection efficiencies for high- and medium-energy beta emitters ($^{90}\text{Sr}/^{90}\text{Y}$ and ^{14}C) are maximal at around a 60 μm diameter, and similar to the values obtained in liquid scintillation [35].

For ^3H , the values are clearly lower, as pointed out previously, mainly due to particle quenching. In spite of this decrease, detection is possible and can be used if activity is not very low. Some proposals, such as the use of pellets by E. Furuta, may increase the efficiency, but with some restrictions on the volume of the sample [36].

The effect of particle quenching becomes lower as the energy of the radionuclide increases. Thus, detection efficiency remains almost constant for $^{90}\text{Sr}/^{90}\text{Y}$, whereas it decreases from 75 to 45% for ^{14}C .

For all three radionuclides, spectrum distributions are similar and located approximately at the same energy position as for the corresponding results obtained by liquid scintillation. These positions are evidence of similar scintillation yields for PSs and liquid scintillation cocktails, and allow similar integration procedures to be applied for activity quantification.

Alpha emitter detection by PSs is also possible. Table 3 shows detection efficiencies for two alpha emitters of different energy (^{241}Am at 5552 keV; and ^{236}U at 4573 keV) using PSs of polystyrene + PPO + POPOP.

It is worth noting that, as in the case of beta emitters, detection efficiency decreases with the decrease of the energy of the particle emitted and with the increase of the PSm diameter. Both variations are related to particle quenching, as already mentioned. Detection efficiencies for PSm of 60 μm or smaller are high and equivalent to

the values obtained by liquid scintillation since the mean path of alpha particles in water is around 50 μm (Table 4).

Spectrum distributions of the isotopes ^{241}Am and ^{236}U are shown in Fig. 6. The distributions are similar in shape, quite broad, and energy is in the same position as that obtained by liquid scintillation except for the tail at low energies. The origin of these low-energy signals is not clear, but it could be related to the distance between the emission point and PS and how this affects the energy of the alpha particle. When the diameter of the PSm is reduced (Fig. 7), the tail disappears and the spectrum is more similar to that obtained by liquid scintillation.

When the solution is evaporated to dryness onto PSm, the distance to the scintillator is greatly reduced for some of the alpha emissions, whereas for other, the density of the medium that they have to cross is also reduced significantly. Consequently, detection efficiency increases to values close to 100% and the spectrum band at low energies disappears while the peak at high energies becomes more sharp (Table 5; Fig. 8).

Plastic scintillators in the form of foils (PSF)

In this case, two scenarios can be described: when the radioactive solution is deposited on one foil or when the radioactive solution is placed between two foils. Values of detection efficiency for the situations for a beta emitter (^{36}Cl) and an alpha emitter (^{241}Am) are shown in Table 6.

It can be seen that in the case of one foil, the efficiency is less than 100%, since there are particles that are emitted in the opposite direction to that of the foil. Detection efficiency is higher than 50% probably due to the fact that some of radionuclide have penetrate a little inside the foil. However, detection efficiencies are high and make measurement viable. When the solution is enclosed between two foils, efficiency increases and almost all events are detected.

Detection efficiency calibration

The different quenching processes that may reduce signal detected in plastic scintillation have been discussed previously. These effects on detection efficiency can be calibrated following the same procedures applied in liquid scintillation: the use of experimental quenching parameters or following computation methods.

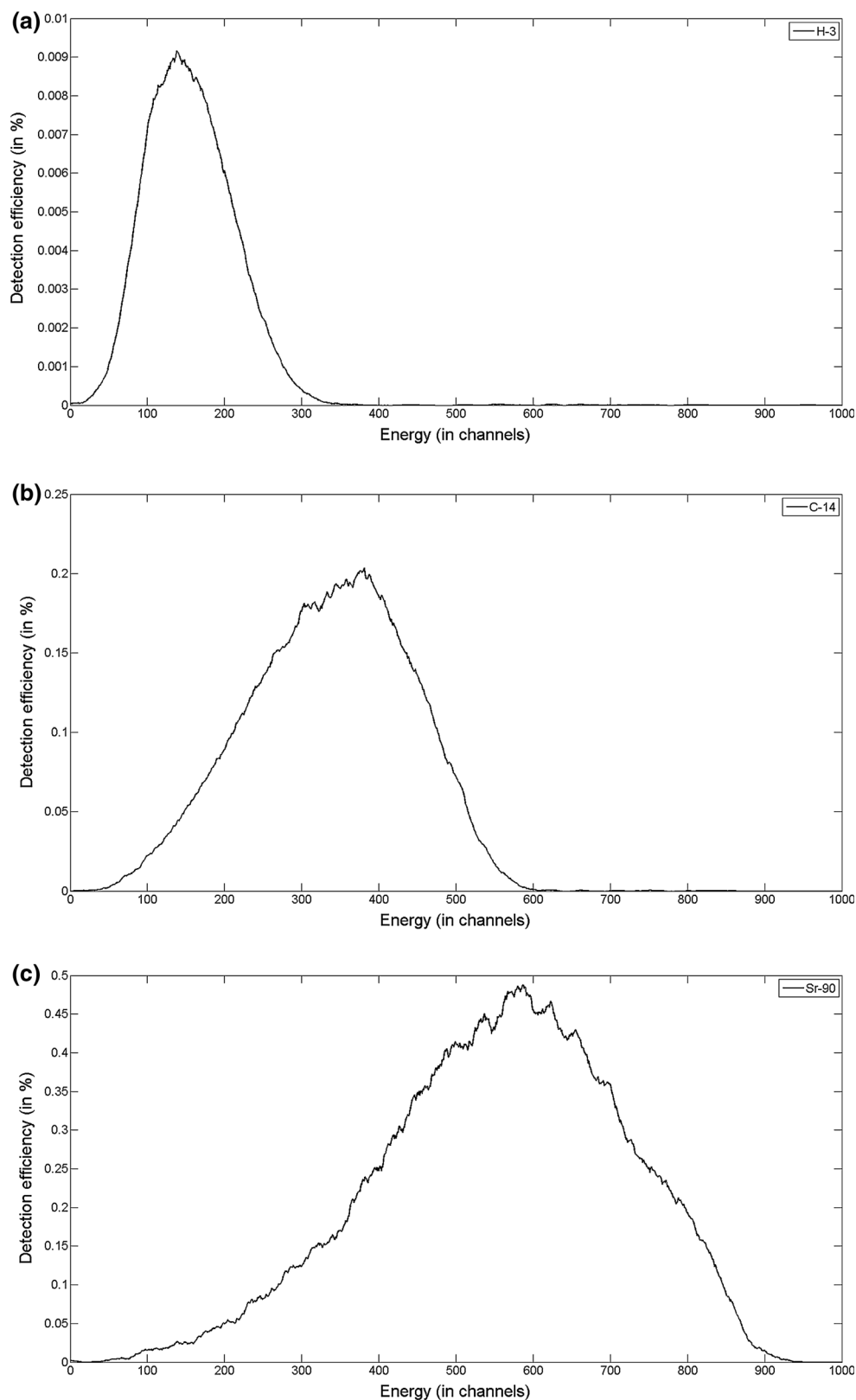
Experimental quenching calibration

In plastic scintillation calibration, the quenching parameters used are the same as in liquid scintillation [33]. Most

Table 2 Detection efficiencies of three beta emitter radionuclides (^3H , ^{14}C and $^{90}\text{Sr}/^{90}\text{Y}$), measured using PSm of different diameter

Particle size (μm)	^3H (%)	^{14}C (%)	$^{90}\text{Sr}/^{90}\text{Y}$ (%)
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

Fig. 5 Detection efficiency spectra of three radionuclides: **a** ^3H , **b** ^{14}C and **c** $^{90}\text{Sr}/^{90}\text{Y}$ measured using PSm with a diameter of $60\ \mu\text{m}$



of them are derived from the spectrum obtained from the Compton electrons produced by an external gamma source.

Colour and chemical quenching effects are calibrated using a series of standards of known activity and increasing the amount of the corresponding interfering compound. For

Table 3 Detection efficiencies of two alpha radionuclides (^{241}Am and ^{236}U) measured using PSm of different diameter

Particle size (μm)	^{241}Am (%)	^{236}U (%)
106	52	37
327	45	29
416	35	24

Table 4 Detection efficiencies of ^{241}Am measured using PSm of different diameters

Particle size (μm)	^{241}Am (%)
17	102.9
32	99.7
57	95.2
79	85.5
145	67.3

colour quenching, Fig. 9 shows the decrease of detection efficiency for ^{36}Cl and the SQP(E) parameter for increasing amounts of methyl orange. It can also be observed that the spectra shift to low energies as a consequence of the quenching effect.

Similar changes are produced by chemical quenching: the detection efficiency of ^3H decreases encompassed within SQP(E) values when the amount of nitromethane in the solution increases (Fig. 10).

In contrast to this chemical and colour quenching, particle quenching shows totally different behaviour. As can be observed in Fig. 11a, the position of the ^3H spectra remain almost constant despite changes in the

concentration of Barium Chloride; whereas in Fig. 11b, the relationship between detection efficiency and salt concentration is clear. According to the constant spectrum positions, the values of the SQP(E) parameter also remains constant at 671 ± 3 . This behaviour suggests that particle quenching totally avoids that the emitted particle was detected. As a consequence of this result, the classical quenching parameters, such as SQP(E), cannot be used to model the detection efficiency variation and they must be substituted for parameters related to concentration and easily determined as density.

Optical quenching effects are also different from those observed for colour and chemical quenching.

In this case, there is an apparent contradiction between detection efficiency and quenching parameter values (Table 7). Thus, whereas ^{36}Cl detection efficiency decreases when PSm size increases, the associated SQP(E) values and the spectra distribution location (Fig. 12) follow the opposite trend, achieving higher values. This behaviour is explained by the combined effect of particle quenching and optical quenching. Particle quenching produces a decrease in the detection efficiency when the path through the solution before reaching the PSm increases. In contrast, optical quenching is a consequence of the multiple refraction index changes along the path of the photons. Thus, higher PSm diameters increase particle quenching (reducing detection efficiency) but reduce optical quenching (increasing the number of photons from each pulse and the SQP(E) value).

In summary, colour and chemical quenching can be calibrated in plastic scintillation as in liquid scintillation by

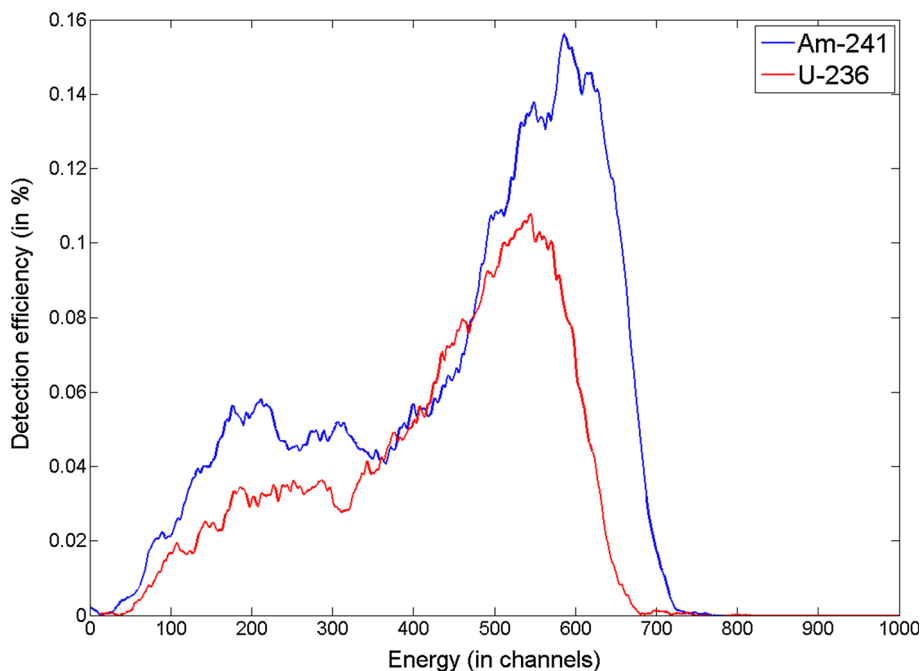
Fig. 6 Detection efficiency spectra of ^{241}Am and ^{236}U measured using PSm with a diameter of $106 \mu\text{m}$. (Color figure online)

Fig. 7 Net count rate spectra of ^{241}Am measured using PSm with different diameters. (Color figure online)

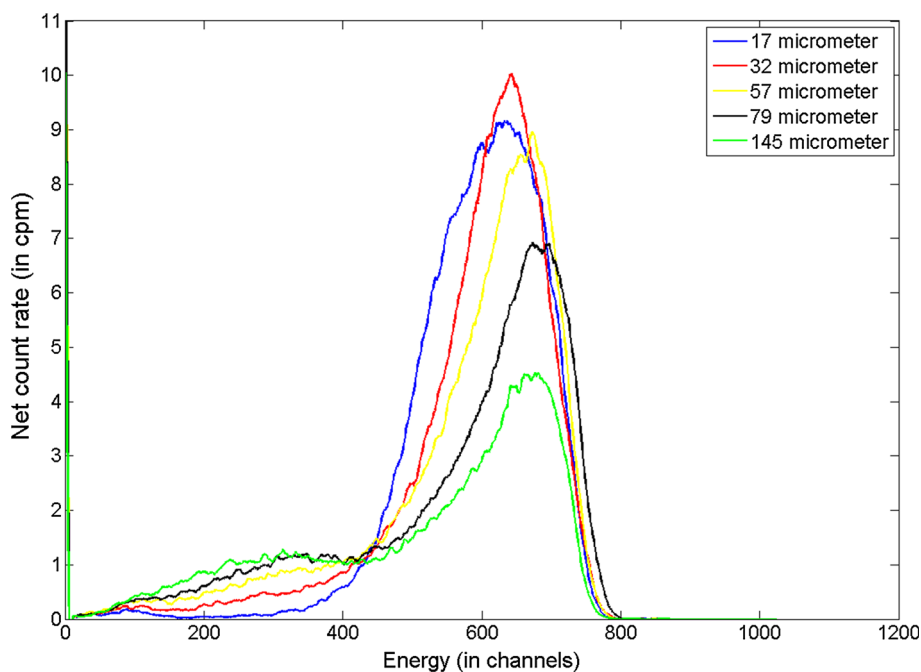


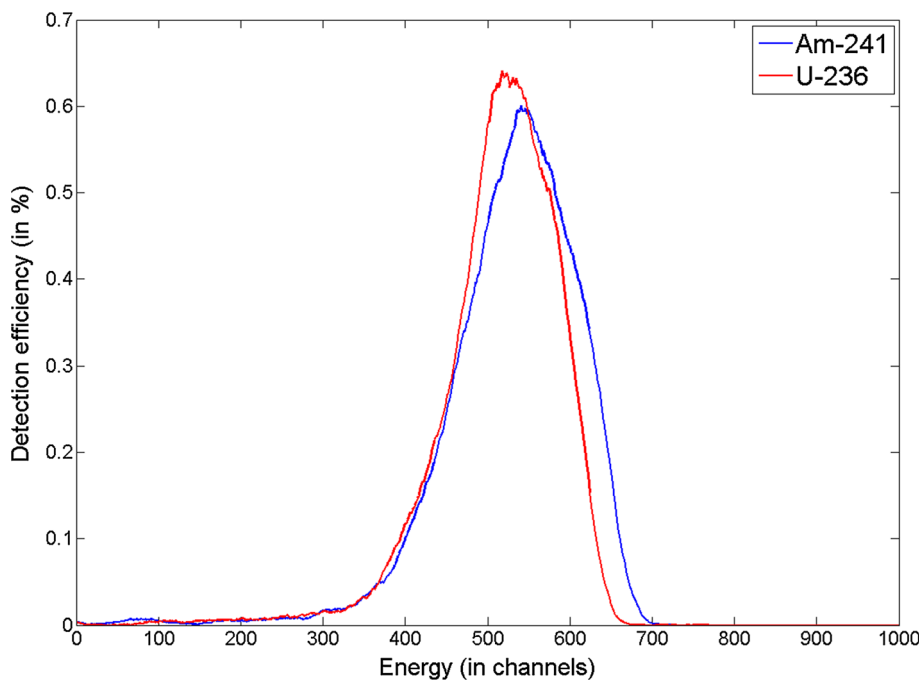
Table 5 Detection efficiencies of two alpha radionuclides (^{241}Am and ^{236}U) measured using PSm of different diameter evaporating the solution to dryness

Particle size (μm)	^{241}Am (%)	^{236}U (%)
106	102	95
327	103	99
416	103	98

Table 6 Detection efficiencies for two different isotopes (^{36}Cl and ^{241}Am) when the radioactive solution is placed onto the surface of one foil or between two foils

Isotope	One foil	Two foils stuck
^{36}Cl	63 (5)	95 (4)
^{241}Am	87 (4)	100 (5)

Fig. 8 Detection efficiency spectra of ^{241}Am and ^{236}U measured using PSm with a diameter of $106\ \mu\text{m}$ and evaporated to dryness. (Color figure online)



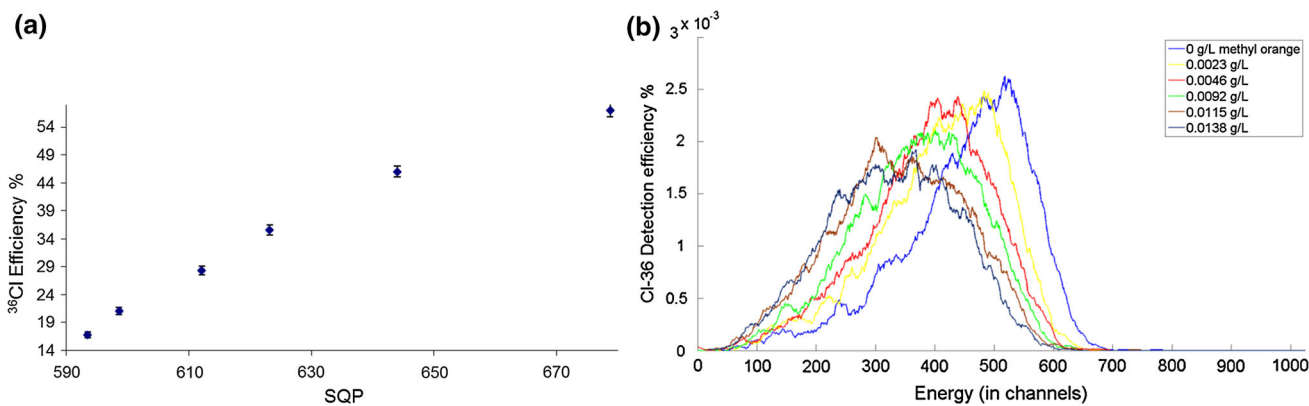


Fig. 9 Effect of colour quenching on the measurement of ³⁶Cl: **a** detection efficiency value as a function of SQP(E) value; and **b** spectrum shift with increase of colour quencher (methyl orange). (Color figure online)

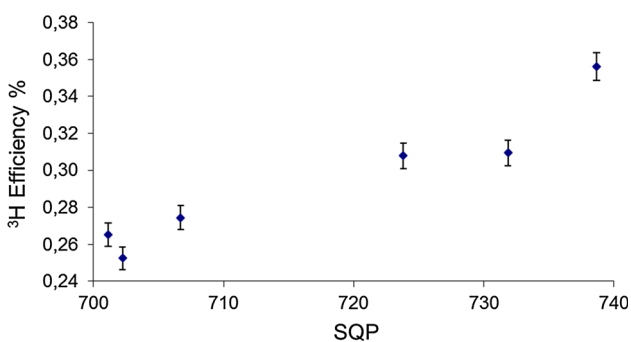


Fig. 10 Detection efficiency as a function of SQP(E) value when chemical quenching increases

using quenching parameters based on the use of an external standard source, whereas particle quenching can only be corrected for by using the solution density as a quenching parameter.

Optical quenching can be considered constant whenever the samples and calibration standards are prepared under the same conditions.

Table 7 Detection efficiency and SQP(E) value obtained in the measurement of ³⁶Cl with two different diameters of PSm

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

Computation calibration methods

Several attempts have been made in all radioactivity analytical techniques to develop computational models capable of simulating the detection process. Such simulations have not only been useful to provide better understanding of the physical phenomena associated with detection, but they have also been applied to determine, in combination with certain experimental data, the detection efficiency of detection systems. This is the case, in liquid scintillation, of the Ciemat-Nist and the TDCR methods [37–40].

The application of these methods to PSm measurements requires a good description of the scintillation phenomena and of the particular geometry of the PSm-solution system.

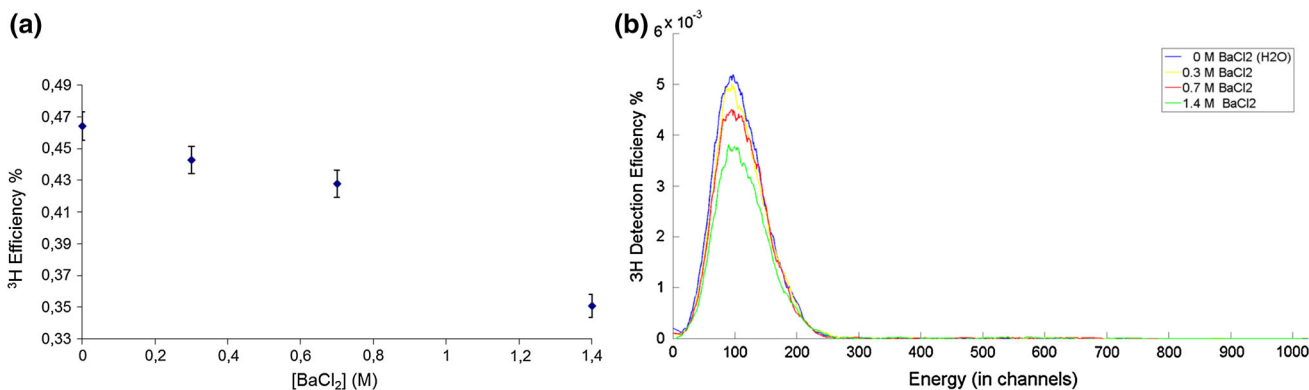
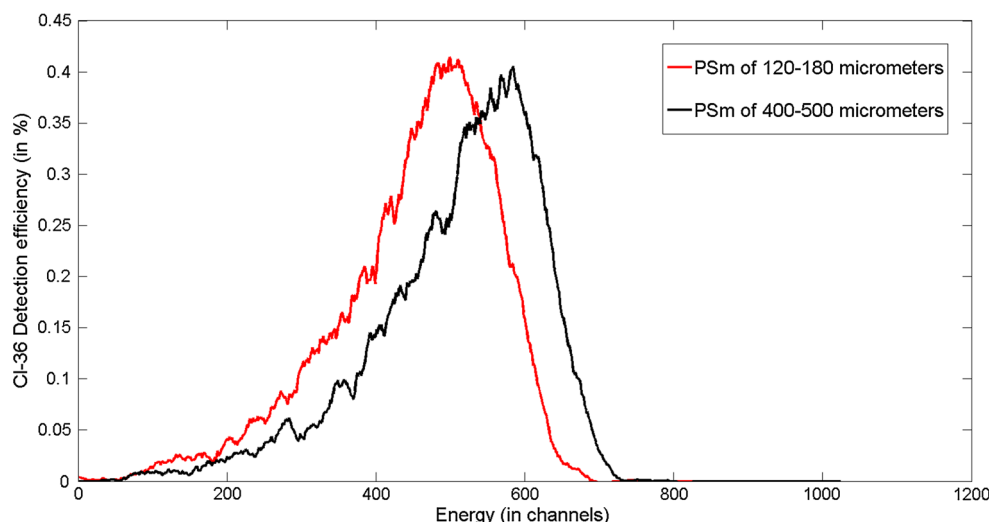


Fig. 11 Effect of particle quenching on the measurement of ³H: **a** detection efficiency as a function of BaCl₂ concentration; and **b** spectrum shift with increase of particle quencher (BaCl₂). (Color figure online)

Fig. 12 Detection efficiency spectra of ^{36}Cl measured with two diameters of PSm: 120–180 μm and 400–500 μm . (Color figure online)



In an initial approach, a TDCR counter was used to determine the activity of several pure beta emitters using the same strategy as in liquid scintillation [41]. The results obtained showed a very high deviation from the reference value for low-energy beta emitters (Table 8). This was due to the fact that triple double detection efficiency (TDCR) computation methods used the theoretical beta spectrum and assumed that all beta particles interacted with the scintillator. This is valid for liquid scintillation, but in PSm measurements, not all beta particles reach the scintillator due to particle quenching and, as consequently, the energy distribution of the beta particles that reach the scintillator is different, especially for low-energy beta emitters. Therefore, the strategy used was to develop several geometries that simulate the system PSm-solution system and compute, through Monte Carlo simulation using the Penelope software, which was the energy distribution of spectra that achieves the scintillator (Fig. 13) and the probability of achieving the microspheres (Table 8). It can be seen how

the original spectrum and the spectrum that arrive at the scintillator are different. To take into account this behaviour, a tracer radionuclide, ^{63}Ni , was used to fit the correct geometry. The application of this model allows the activity of the rest of the radionuclide to be quantified successfully with a deviation lower than 3%.

In a second approximation, the Ciemat-Nist method was used to quantify several beta emitters using a Quantulus 1220. Moreover, a very-low-energy beta emitter was used (^3H) to stress the robustness of the method [34]. The data provided by the Monte Carlo simulation with the Penelope software (efficiency and spectrum) was input into the Micelle2 code to compute the detection efficiencies and perform the activity quantifications. The results showed errors lower than 10% for ^{63}Ni and lower than 3% for the rest, ^3H included (Table 9). These results demonstrate that Monte Carlo simulation of particle quenching was adequate.

Table 8 Values of TDCR parameter, detection efficiency, deviation, probability that 50% of the particles reach a microsphere and deviation with corrections for the different isotopes studied

Isotope	TDCR value	Detection efficiency (%)	Deviation (%)	P_{reach} (%)	Deviation (%) with geometry correction and ^{63}Ni tracer
^{63}Ni	0.871	8	−89.8	10.2	−
^{35}S	0.961	37	−60.0	39.9	0.2
^{33}P	0.976	55	−41.1	57.4	2.5
^{45}Ca	0.978	52	−43.0	57.4	−0.6
^{99}Tc	0.978	61	−34.8	64.6	1.0
^{36}Cl	0.991	88	−8.3	91.2	−0.5
$^{90}\text{Sr}/^{90}\text{Y}$	0.993	−	−9.3	182.0	0.8
^{32}P	0.999	97.3	−0.8	97.9	1.3
^{90}Y	0.998	97.6	−2.1	97.9	0.1

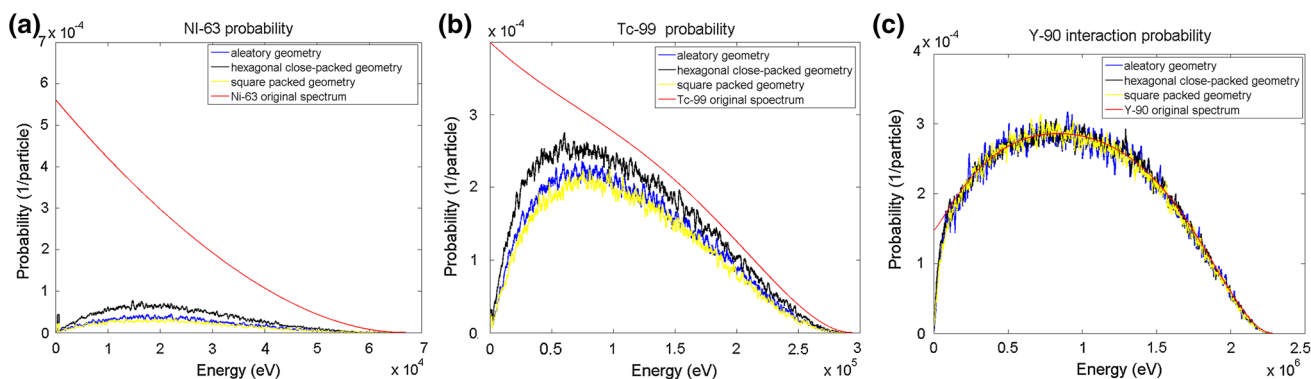


Fig. 13 Electron emission spectra (dotted line) and reduced spectra for three different PSm packing geometries for ⁶³Ni (a), ⁹⁹Tc (b) and ⁹⁰Y (c). (Color figure online)

Table 9 Results obtained in the activity calculation of ⁶³Ni, ¹⁴C, ³⁶Cl and ⁹⁰Sr/⁹⁰Y solutions using the Ciemat-NIST method

Isotope	Deviation (%)
⁶³ Ni	-8.8
¹⁴ C	-1.9
³⁶ Cl	0.4
⁹⁰ Sr/ ⁹⁰ Y	-0.9

Alpha/beta discrimination

Alpha and beta emissions can be discriminated in liquid scintillation [42, 43]. Alpha particles produce more triplet excited states than beta particles during energy transfer to the scintillation cocktail. This situation leads to a temporal pulse distribution that is longer for alpha than for beta emissions and this is used for discrimination purposes.

This difference is not so important in plastic scintillation, probably due to the non-radiative transmission of the energy through the polymer chains that decreases the local concentration of triplet states [4, 44, 45].

The different behaviour of liquid and plastic scintillation for alpha and beta classification can be observed in Fig. 14,

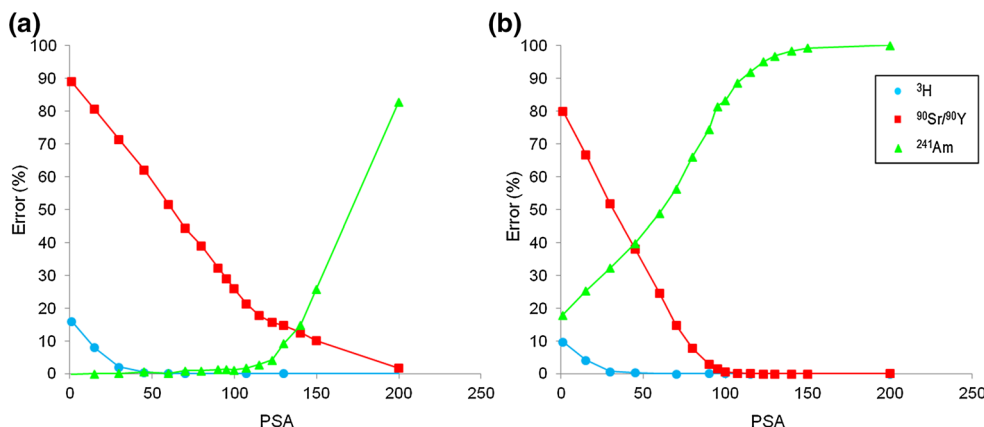
where misclassification for ³H, ⁹⁰Sr/⁹⁰Y and ²⁴¹Am are represented for different pulse shape analysis (PSA) parameters. PSm composition is polystyrene + PPO + POPOP (120–150 μm) [46]. The higher misclassification of plastic scintillation measurements at low PSA values is related to the low-energy tails observed in the alpha spectrum (see Figs. 6, 7).

It has been reported that the addition of a secondary solvent produces a delay in the emissions [47]. In Fig. 15 it is possible to observe this effect in PSm including polystyrene + naphthalene + PPO + POPOP (120–150 μm). Both alpha and beta pulses are delayed and the final compromise in the PSA value leads to a reduction of misclassification to values slightly higher than those achieved with plastic scintillation [27].

The use of detectors with 3D spectrum capacities (intensity, energy and duration time) allows the results for PSm of the mentioned composition to be improved. The addition of a secondary solvent rotates the pulse time distribution in the opposite, anticlockwise direction, but more for alphas than for betas (Fig. 16).

Looking at this behaviour it is clear that pulse duration depends on the energy of the emission and that the use of a

Fig. 14 Misclassification error as a function of the PSA value for a liquid scintillation and b plastic scintillation



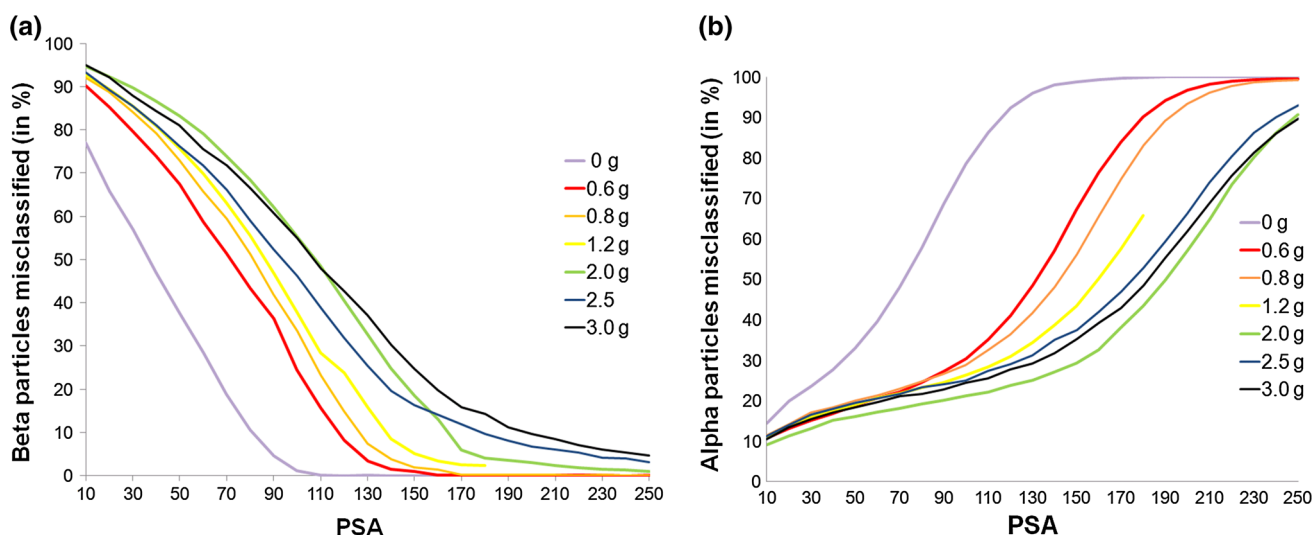


Fig. 15 Misclassification of synthesized PSm using a Quantulus detector when the secondary solvent (naphthalene) content increases for the measurement of: **a** beta particles ($^{90}\text{Sr}/^{90}\text{Y}$) and **b** alpha particles (^{241}Am).

The amount of naphthalene is that used for 10 g of polystyrene. (Color figure online)

Fig. 16 Misclassification of synthesized PSm using a Triathler detector when the secondary solvent (naphthalene) content increases for the measurement of: **a** beta particles ($^{90}\text{Sr}/^{90}\text{Y}$) and **b** alpha particles (^{241}Am). The amount of naphthalene is that used for 10 g of polystyrene. (Color figure online)

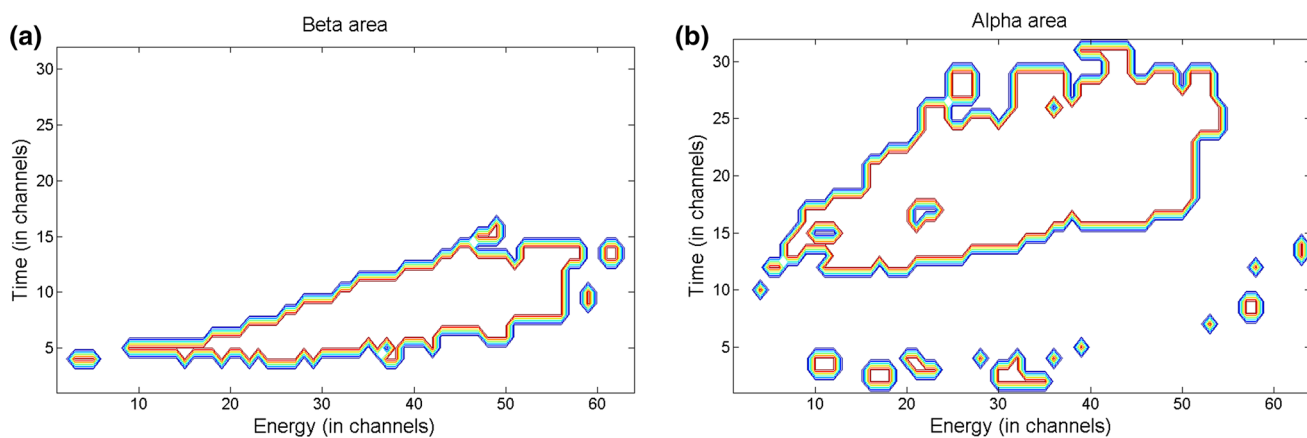
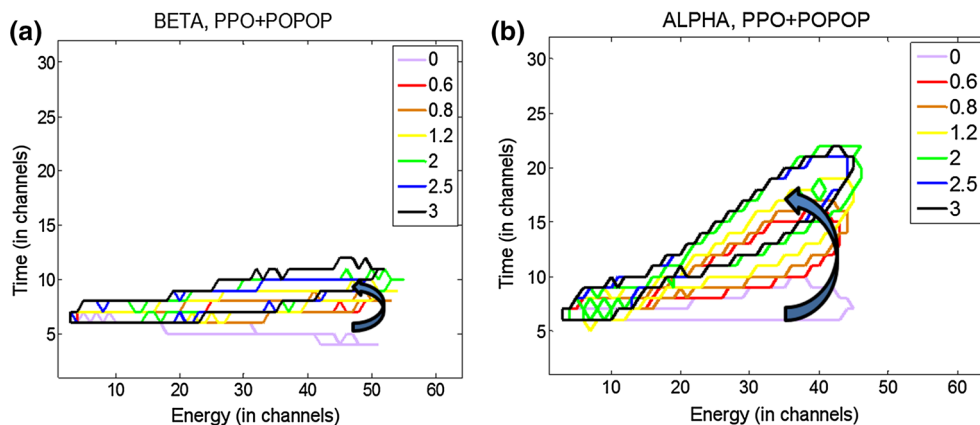


Fig. 17 Perimeter of the alpha (^{241}Am) and beta ($^{90}\text{Sr}/^{90}\text{Y}$) regions defined for PSm containing 2.0 g of naphthalene, and PPO and POPOP as primary and secondary fluorescent solutes

constant discrimination value is not the best option to separate the two distributions. When integrated areas of the 3D distributions are selected by using algorithms that take

into account this dependence, the discrimination capacities of plastic scintillation (and probably liquid scintillation) improve significantly, as can be observed in Fig. 17. There,

for the beta emitters ($^{90}\text{Sr}/^{90}\text{Y}$) misclassification is lower than 2% with a detection efficiency of 90%, and for alpha emitters (^{241}Am) it remains under 1% with a detection efficiency of 25%.

Plastic scintillating resins: extractive scintillating materials

One of the most important drawbacks of scintillation techniques is their lack of selectivity as a consequence of the energy distribution of the beta and alpha emissions, and of the limited resolution and quenching interferences in the scintillation techniques.

With regard to liquid scintillation, plastic scintillation introduces a solid platform into the measurement vial useful to implement separation procedures.

Plastic scintillating resins (PSr)—extractive scintillating materials take advantages of this possibility to include, associated with the PS, an extractive material that allows the selective separation and determination of defined radionuclides [48–50].

This approach unifies into a single step the processes of separation and sample preparation for measurement, introducing some advantages such as reductions of time for sample processing, the manpower required and waste production. Among the disadvantages, it is worth mentioning that development of PSr is still in progress and few are commercially available, and that the cost could be higher than that of non scintillating extractive resins.

Composition and preparation approaches

PSr—extractive scintillating materials are composed of a solid support of PS microspheres coated with an extractant that is selective for the radionuclide of interest. To prepare these resins, several strategies can be applied: immobilization, impregnation, imprinted polymers and covalent bonding.

The most common strategy used to prepare the PSr is immobilization. In this strategy, the scintillating support is suspended in a volatile solvent, usually methanol, in which the selective extractant is dissolved. The methanol is slowly evaporated to deposit the extractant as quite a homogeneous and thin layer on the support (Fig. 18). This strategy has the advantages of being an easy process, easy to scale-up and capable of depositing a large amount of extractant and therefore obtaining a high capacity [51]. However, the resin stability depends on the extractant solubility in the sample solution and therefore PSr can present some breakthrough volume and, at the moment, are only suitable for aqueous samples [52]. Among others, this approach has been used to prepare a resin selective for ^{90}Sr ,

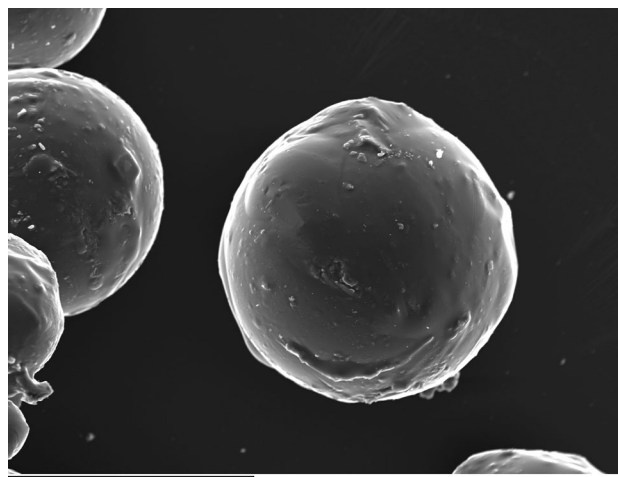


Fig. 18 Secondary electron microscope images for the PSr for ^{90}Sr containing the optimized proportion of extractant obtained using a scanning electron microscope

to analyse water samples using a crown ether as the selective extractant.

Another strategy similar to the previous one is impregnation [51]. In this case, the support is suspended in a solution of the extractant and shaken for several hours to allow the absorption of the extractant onto the support. Later, the excess of extractant is removed by filtration and the resin is rinsed. This strategy has the advantages of being even easier than the previous one, but it also presents the same drawbacks together with the fact that it uses large amounts of extractant for the preparation and also that it is more difficult to control the conditions of the resin preparation. This approach has been used to prepare a resin selective for Sn for analysis of ^{126}Sn in radioactive wastes using tributyl phosphate as the extractant.

Other approaches can be adopted to prepare PSr; more are still in development. Among them are imprinted polymers [53, 54]. In this strategy, a non-selective extractant, with capacity to be polymerized and to complex the stable isotope of the radionuclide of interest (called template), is added to the monomer solution and polymerized together with the other components of the PS support. The stable isotope is removed from the polymer leaving a cavity that is selective for the radionuclide of interest, due to its sterical hindrance characteristics and the disposition of the complexing groups. In some cases, the disposition of the polymer chains during the preparation in the absence of any template makes the support selective for some radionuclides such as radon; something that can be called a template-less imprinted polymer. In general, the imprinting strategy has the advantages of (i) not using selective extractants and therefore selective resins can be produced from generic complexant molecules, (ii) not having breakthrough volume and (iii) being suitable for

different kinds of samples, included in organic or aggressive media. However, to apply this strategy, a stable isotope of the radionuclide needs to be used because large amounts of template are needed to produce the polymer and not all of the template can be removed from the polymer, increasing the background count rate of the PSr if the isotope used was radioactive. Also, the production of imprinted polymers for small molecules, such as metals, is tricky and several conditions and compositions need to be studied to produce the resin.

A final strategy is to covalently bond the selective extractant to the PS support. In this approach, different reactions are applied to functionalise the PS support with the selective extractant. In this way, the resin obtained has no breakthrough volume, but still uses selective extractants, with specific groups capable of reacting, to prepare the PSr. Additionally, the quantity of extractant that can be bonded to the PS support is smaller than in the case of immobilization and therefore it yields less capacity for the PSr [55]. This approach has been used to prepare an extractive scintillating polymer for the determination of ^{233}U using phosphonic acid as the extractant.

Protocol of use

Once the PSr is prepared, its use is very similar to any other separation resin. First, the PSr is packaged inside a column or a cartridge. Then, the column or cartridge is connected to a vacuum chamber or a peristaltic pump to allow the solutions to flow through it. The column or cartridge is first conditioned with the adequate medium, next, the sample is passed through and finally it is rinsed with the required medium. In the case of cartridges, just 2 ml of solution is enough to rinse and condition them. Finally, the column or cartridge is emptied of solution, disconnected and directly measured in any scintillation counter (Fig. 19).

Applications

Radionuclide quantification

The use of PSm as a routine alternative to the liquid scintillation cocktails has had limited success, probably due to the additional homogenisation step in the sample preparation process and because mixed waste production is not considered an important issue in practical terms.

However, PSs play an interesting role for specific determinations where liquid scintillation cocktails are not stable. For example, the determination of radiotracers in oil reservoirs that involves the activity determination in samples in highly salty matrices as could also be the case of other samples from biochemical studies.



Fig. 19 Cartridge of PSr placed in an adapter ready to be measured

The study of radiotracers was performed in collaboration with the Institute for Energy Technology (IFE, Norway) and the objective was to determine the activity of ^{14}C (in the form of S^{14}CN^-) in samples, after a separation process involving high concentrations of NaClO_4 [56]. The samples showed phase separation when they were mixed with liquid scintillation cocktails.

The samples were affected by particle and colour quenching and a double calibration using SQP(E) and density quenching parameters (Fig. 20) was applied. In the Fig. 20a, the double quenching effect can be observed: spectrum shifting (colour quenching) and area decrease in the same position (particle quenching).

The analysis of blind samples provided totally comparable results: IFE-LS: 4.23 dpm g^{-1} versus UB-PS: $4.32 (0.02) \text{ dpm g}^{-1}$ and IFE-LS: 0.55 dpm g^{-1} versus UB-PS $0.59 (0.04) \text{ dpm g}^{-1}$.

Plastic scintillation resins: extractive scintillating materials

Different PSr were prepared to resolve several analytically complex scenarios.

The first PSr developed was for the determination of ^{90}Sr in water samples. In this case, the PS support was coated with a crown ether dissolved in 1-octanol as the selective extractant. Different parameters were optimized such as the separation media or the extractant proportion.

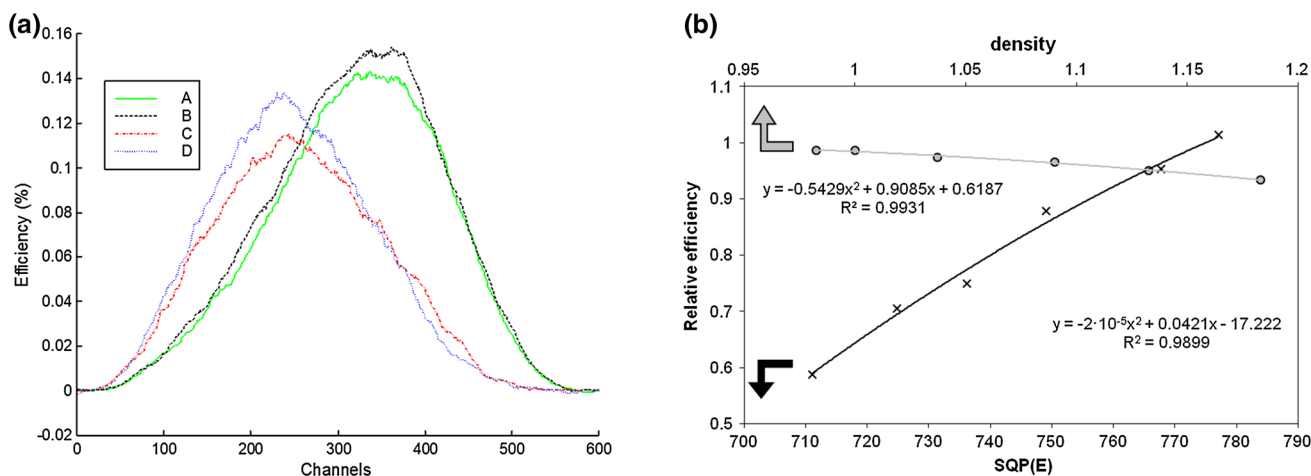


Fig. 20 Combined effect of colour and particle quenching on the detection efficiency shown in: **a** detection efficiency spectra for extreme values of NaClO_4 and bromocresol green concentrations, A: 2.8 M of NaClO_4 and 0 g L^{-1} of bromocresol green, B: 0.0 M of

NaClO_4 and 0 g L^{-1} of bromocresol green, C: 2.8 M of NaClO_4 and 1.04×10^{-2} g L^{-1} of bromocresol green, D: 0.0 M of NaClO_4 and 1.04×10^{-2} g L^{-1} of bromocresol green; **b** relative efficiencies as a function of SQP(E) and solution density. (Color figure online)

The limit of detection for 10 ml of sample was 0.46 Bq L^{-1} with a quantitative retention. The resins were applied to the quantification of drinking, sea and river water samples with relative determination errors lower than 4% in all cases [57].

This same resin was also applied to develop a new procedure for emergency quantification of radiostrontium in milk. In this case, the column recovery and the effect of the different milk types and pre-treatment procedures were studied. The total time of the procedure was 5 h (including milk pre-treatment) and the resin presented good reproducibility and recovery (65%). The method was validated with the analysis of reference materials gave errors lower than 2%. Also, the PSr was applied to the quantification of different kinds of milk samples containing ^{90}Sr and ^{89}Sr , obtaining relative biases lower than 7% in practically all cases when total activity was determined.

A second part of the study of oil radiotracers performed with the IFE was to apply a PSr for the separation and analysis of the S^{14}CN^- radiotracer. In this case, the samples were seawater containing residues of oil without any previous separation step involving perchloride as in the previous example. In this case, Aliquat-336 was selected as the selective extractant. The samples were decanted and filtered and then passed through the columns without further treatment. For 100 mL of sample, the detection limit was 0.08 Bq L^{-1} and the retention was quantitative. The quantification of blind samples showed good agreement with the activities determined by the IFE using their method. Also the quantification errors for the spiked oil radiotracer samples were lower than 5% [58].

For the determination of ^{99}Tc in water and urine, a new PSr was developed. In this case, Aliquat 336 was used as

the selective extractant. First, the PSr production was evaluated showing good reproducibility of the preparation and storage stability. Also, common interferences, radioactive and non-radioactive, were evaluated and showed little influence on the ^{99}Tc measurement. The PSr showed a detection limit of 0.36 Bq L^{-1} when 10 ml of sample was analysed and quantitative retention. Finally, the resin was applied to the measurement of seawater and urine samples showing quantification bias lower than 8% in all cases [59].

An additional resin was developed for the measurement of ^{210}Pb , using a crown ether dissolved in 1-octanol as the selective extractant. In this case, the amount of extractant was optimized as well as the optimum separation medium being selected, showing a complete separation from its daughter products, ^{210}Bi and ^{210}Po , with a retention of 91%. This PSr was applied to the measurement of underground and river water samples with errors lower than 9% in all cases [60]. Additionally, this same resin was applied to the development of a dating procedure for bronze sculptures (Benin) using the decay of ^{210}Pb isotope. The study proved the analytical viability of the method in terms of column performance and amount of sample required.

^{222}Rn analysis

Another potential application of PSs, in the form of microspheres or foils, is the absorption and detection of ^{222}Rn . Polymers have been widely described to be capable of absorbing ^{222}Rn very efficiently. They can be considered template-less imprinted polymers. This capacity, together with the scintillation properties of the PSs, makes them attractive for the concentration and detection of ^{222}Rn in

several types of samples. PSs in the form of microspheres present very high surface areas, if compared to PS in the form of blocks or sheets. This fact enhances the absorption capacities of the scintillators.

In the test performed, PSm were exposed to an atmosphere with a known ^{222}Rn activity for a controlled period of time. Later, the PSm filled a 20 mL glass vial and were measured in a commercial counter. The results showed a decrease in the count rate which presented very good correlation with the decay of ^{222}Rn . The detection efficiency was 314% (a maximum of 500% due to ^{222}Rn and its progeny could be expected) and the spectrum presented several broad bands (Fig. 21), compared to that of liquid scintillation with polycarbonate pellets to absorb ^{222}Rn . These results can be attributed to optical quenching when a 20 mL vial filled with PSm is measured and can be highly improved in terms of efficiency and spectrum shape by the use of a thinner glass vial.

Regarding the absorption capacities of the PSm, the partition coefficients between the microspheres and the ambient medium (K) are 4.95 ± 0.54 in air and 37.2 ± 1.9 in water [61]. Comparing these results with other polymers, PSm present an acceptable capacity for ^{222}Rn absorption, but lower than polycarbonates; and the absorption and desorption process is very fast. These properties make PSm very promising for use in fast systems of ^{222}Rn detection, for example in soil–gas samples.

Finally, the diffusion model permits us to determine that PSm of 90 μm diameter should be the most appropriate for ^{222}Rn absorption, since all the volume of the microsphere will be filled with ^{222}Rn and no excess polymer or ^{222}Rn will be present.

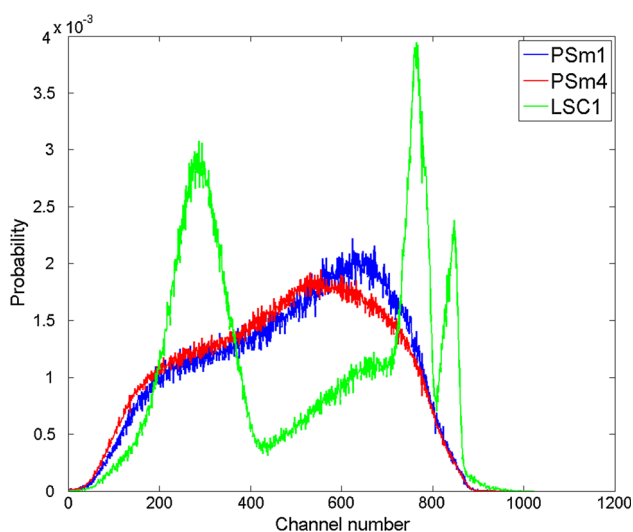


Fig. 21 Detection efficiency spectra for the measurement of ^{222}Rn , measured using two PSm samples (PSm1 and PSm4) and liquid scintillation. (Color figure online)

Sensors and automatic analysis

PSs and PSr—extractive scintillating materials may have several applications due to their specific capacities.

Continuous detection of alpha and beta emitters in a fluid (aqueous or non-aqueous stream) using liquid scintillation requires a homogeneous mixture of the sample and scintillation cocktail in the measurement cell. This mixture is sometimes unstable and the procedure continually consumes the cocktail and continuously produces mixed waste.

The use of PSs in the cell would be a good option to improve the stability of the measurements, but would probably decreasing the detection efficiency achieved.

This approach is already applied in some chromatography detectors and also in some sensors for water activity determination in environmental analysis [62–69].

Automatic analysis is a continuous demand as a consequence of the increasing amount of radiochemical analysis performed. Many proposals for commercial equipment have been introduced onto the market in the last few years [70, 71].

The introduction of PSs in measurement cells or PSr cartridges in the separation scheme may be an important improvement for reducing the resources required for the different determinations.

Challenges

Plastic scintillation is not a new field in scintillation research but its application for radionuclide determination opens new challenges for the future.

Within this research field, it would be interesting:

- to know more about the scintillation mechanism in PSs;
- to continue developing new plastic scintillating formats such as foils or monoliths;
- to develop procedures for the preparation of selective scintillating and controlled porous materials.

In the application field, more studies would help:

- to implement new options for automatic analysis designs or continuous monitoring systems;
- to apply the developments to many areas of analysis such as routine monitoring, emergencies, decommissioning, medical uses and so on.

Conclusions

Plastic scintillation is becoming a useful technique for radionuclide analysis and determination, with some advantages and drawbacks.

Plastic scintillation is capable of determining alpha and beta emitting radionuclides and to perform alpha/beta discrimination based on pulse shape analysis. Among its limitations, the most important is the low detection efficiency for low-energy beta emitters and secondarily, the requirement for an additional step in sample preparation. Among the advantages, sample and scintillator can be segregated after measurement and mixed waste production is thus avoided.

One important potential contribution of PSs to radionuclide analysis is the possibility of developing selective plastic scintillating materials taking advantage of their solid state. This possibility offers a great opportunity for future work on radionuclide determination, because it opens the way for several potential improvements in the design of analytical procedures and new fields of application.

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