



Original Research Paper

Influence of preparation parameters on the synthesis of plastic scintillation microspheres and evaluation of sample preparation



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ARTICLE INFO

Article history:

Received 30 April 2015

Received in revised form 18 March 2016

Accepted 25 April 2016

Available online 6 May 2016

Keywords:

Plastic scintillation microspheres

Mixed waste

Organic solvent evaporation/extraction

Radioactivity

Liquid scintillation

ABSTRACT

Plastic scintillation microspheres (PSm) are solid dispersions of fluorescent solutes encapsulated in a polymeric matrix; they are used to measure β and α decay of radionuclides. Since organic solvent evaporation/extraction methods have been successfully employed to produce PSm, this work evaluates the influence of different parameters (i.e., polystyrene (PS) and polyvinyl alcohol (PVA) concentrations, temperature, stirring speed and the organic/aqueous phase ratio) on the final size of the PSm; and the relationship between this final size and the radiometric capacities of the PSm in relation to emitters of both beta (^3H , ^{14}C and $^{90}\text{Sr}/^{90}\text{Y}$) and alpha (^{241}Am) radiation.

The results show that when the concentration of PVA is increased, the size of the PSm decreases; meanwhile, an important decrease in particle size is also achieved when the PS concentration is decreased. For almost all the parameters evaluated, the resultant PSm were smoothed and spherical. However, when temperature was increased, the particle size increased and the PSm eventually became amorphous and porous. The observed decrease in particle size correlated with an increase in radiation detection efficiency and a movement in the positioning of the spectra at lower energy values.

We also evaluated the reproducibility of the vial preparation for ^3H measurements and confirmed that small variations in the quantity of PSm and preparation of different vials by different experimenters did not influence the radiometric capacities.

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1. Introduction

Plastic scintillation microspheres (PSm) are composed of a polymeric matrix encapsulating a couple of fluorescent solutes [1]. They were developed to measure emissions of beta and alpha radiation, based on the same principles as those of liquid scintillation counting (LS), but with the advantage of being solid and inert materials. Therefore, when measuring with PSm, the generation of mixed waste (organic and radioactive waste) is avoided. Moreover, among other applications, PSm can be used as a selective extractive scintillation support [2] in continuous radionuclide monitoring [3], to measure the properties of salty samples while avoiding phase separation [4].

Different methods have been employed to produce polymeric microspheres for different applications (e.g., controlled drug release, inks, cosmetics, pigments and chemical reagents) [5]. Organic solvent extraction/evaporation has been widely used and it is one of the most appropriated techniques, because it is capable

of producing microspheres in a safe, economic and simple way; and because it allows control of the size distribution and morphology of the PSm [6]. This method has been successfully employed to obtain PSm with different compositions [1,7].

When using organic solvent evaporation/extraction, the particle size distribution and morphology of the PSm depend on different variables which influence the evaporation of the organic solvent and the formation of the initial embryonic droplets. Some of these variables are: the polymer concentration, the proportion of surfactant used in the aqueous phase, the organic/aqueous phase ratio and the stirring speed.

When measuring with PSm, the detection efficiency is highly dependent on their size [7]. Therefore, the organic extraction/evaporation formulation (i.e., polymer and emulsifier concentration, and organic/aqueous phase ratio) and process parameters (i.e., temperature and stirring speed) are evaluated in order to establish their influence on the size and morphology of the resulting PSm, and ultimately on their radiometric capacities (i.e., detection efficiency and spectrum position). This allows determining which parameters need to be controlled to obtain microspheres of a desired diameter.

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From the point of view of radiometrics, another highly important parameter is the vial preparation reproducibility, since it has an impact on the uncertainty associated with the activity assigned to a measured sample. So, it is worth evaluating the reproducibility related to sample preparation when performing radiometrics using PSm obtained by organic solvent extraction/evaporation.

This work has two main objectives. On the one hand, to evaluate different formulation and process parameters in the production of PSm, in order to obtain PSm batches with different sizes which can be used for the measurement of radioactivity, depending on the purpose. On the other hand, to evaluate the effects of sample preparation on the reproducibility of the measurements. To evaluate the reproducibility, the parameters studied were: the quantity of PSm added to the vial for a fixed volume of aqueous sample; and the influence of the experimenter on this step (vial preparation by different experimenters).

2. Materials and methods

2.1. Materials

Polystyrene (PS; molecular weight of 250,000 g mol⁻¹) was purchased from Acros Organics (Geel, Belgium). Fully hydrolysed polyvinylalcohol, 2,5-diphenyloxazol (scintillation grade), 2,6-diisopropyl-naphthalene (99% pure) and dichloromethane (99.9% pure) were purchased from Merck (Darmstadt, Germany); while 1,4-bis(5-phenyloxazol-2-yl)benzene (scintillation grade) was supplied by the Montedison Group, Division Chimica (Milan, Italy).

For the radioactivity measurements, Pico Prias polyethylene vials of 6 mL (Perkin Elmer, Massachusetts, USA) were used to prepare the samples, with the following active stock solutions: ³H solution (HTO) with a concentration of 3.94(7) kBq g⁻¹ in deionized water prepared by weight from a standard of 69.8(12) kBq g⁻¹; C-14 (labelled glucose) of 114.6(1) Bq g⁻¹ prepared from a standard of 2212(27) Bq g⁻¹ from Amersham International (Buckinghamshire, UK) in a carrier solution of 50 µg g⁻¹ of glucose and 1 mg g⁻¹ of formaldehyde in deionized water; ⁹⁰Sr/⁹⁰Y active stock solution (Sr²⁺ and Y³⁺) of 37.2(3) Bq g⁻¹ prepared from a standard of 4.07(3) kBq g⁻¹ from Amersham International in 0.1 M HCl; and finally, ²⁴¹Am solution (Am³⁺) of 185(2) Bq g⁻¹ prepared from a standard of 924(9) kBq g⁻¹ supplied by Amersham International in 0.5 M HCl and deionized water.

For the reproducibility of the measurements related to vial preparation, a plastic spoon (Tescoma-Italy) with capacity of 1 tbsp (15 mL) was employed to add the PSm to polyethylene vials of 20 mL (Perkin Elmer).

2.2. Instruments

A “Macrotronic” centrifuge and an “Ultrasons-P” ultrasonic bath (both from JP Selecta, Abrera, Spain) were used to centrifuge and sonicate the measurement vials, respectively.

The radioactive samples were measured using a 1220 QUANTULUS liquid scintillation spectrometer (Perkin Elmer) equipped with logarithmic amplification, a multichannel analyser (4096 channels distributed into four segments of 1024 channels) and background reduction through an active guard detector.

The scanning electron microscopy (SEM) images were obtained using a “JSM-7100F Field Emission Scanning” electron microscope. The samples were attached using double-coated adhesive tape and coated with gold by a sputtering coater.

An “LS 13 320 Coulter” single-wavelength laser diffraction particle size analyser (Beckman-Coulter Inc., Brea, USA) was used to determine the size and size distribution of the plastic scintillation microspheres.

2.3. Preparation of the plastic scintillation microspheres

PSm were synthesized using organic solvent/extraction evaporation described in the work of Santiago et al. [7]. Briefly, the process involved the preparation of an organic phase in which the PS, the naphthalene or 2,6-diisopropyl-naphthalene (DIN) and the fluorescent solutes were dissolved in dichloromethane (DCM). Then, the organic phase was added to an aqueous phase composed of deionized water containing polyvinyl alcohol (PVA). When the phases were in contact, an organic/aqueous emulsion was formed and, with the help of continuous stirring, micro droplets and subsequently embryonic microspheres were formed. The organic solvent was extracted and evaporated causing the microspheres to harden. The PSm were collected by filtration, washed with ethanol and water, and finally dried in the oven to remove residual organic solvent, at 40 °C for 20 h.

Fifteen different sets of conditions were used in the synthesis (Table 1) resulting in PSm1 to PSm15. In all cases, the synthesis was performed in triplicate. All the syntheses were composed of PS, PPO, POPOP and naphthalene; except PSm12 and PSm15, in which the naphthalene was replaced by DIN, since it is a less toxic compound which also acts as a pulse delayer. PSm1 was adopted as the reference to compare the other PSm to.

The influence of the stirring speed was evaluated by synthesizing at 16.7, 8.3 and 13.3 Hz. To study the influence of the emulsifier concentration, PVA concentrations of 1%, 2% and 5% (w/v) with regard to the aqueous phase, were used. Meanwhile, the influence of polymer concentration was evaluated using proportions of 10%, 5% and 2.5 % (w/v) PS.

The effect of the organic/aqueous phase ratio (O:W) was studied by using 2000 mL of aqueous phase for each experiment, and adding an increasing amount (100, 200 or 400 mL) of organic phase containing PS, PPO, POPOP and naphthalene for each synthesis. Finally, the influence of temperature was evaluated by keeping the aqueous phase of the synthesis at 20 °C, 35 °C or 50 °C, during the PSm formation process.

After gaining a clear understanding of the influence of these parameters on the final shape and dimensions of the microspheres, PSm13, PSm14 and PSm15 were produced by adjusting more than one of the parameters.

2.4. Radioactivity measurements

2.4.1. Sample preparation

2.4.1.1. Evaluation of radiometric capacities. The measurement samples were prepared by adding 1.5 g of the PSm and 0.75 mL of the counting solution (active or blank solution) to a 6 mL polyethylene

Table 1
Different parameters employed for PSm synthesis.

Synthesis	PS (g)	DCM (mL)	Temperature (°C)	O:W	PVA (%)	Stirring speed (Hz)
PSm1	10	100	20	1:20	1	16.7
PSm2	10	100	20	1:20	1	8.3
PSm3	10	100	20	1:20	1	13.3
PSm4	10	100	20	1:20	2	16.7
PSm5	10	100	20	1:20	5	13.3
PSm6	10	200	20	2:20	1	16.7
PSm7	10	400	20	4:20	1	13.3
PSm8	20	200	20	2:20	1	16.7
PSm9	40	400	20	4:20	1	13.3
PSm10	10	100	35	1:20	1	16.7
PSm11	10	100	50	1:20	1	16.7
PSm12	10	100	20	1:20	1	16.7
PSm13	30	300	20	3:20	6	11.67
PSm14	30	600	20	6:20	6	11.7
PSm15	25	250	20	2.5:20	1	10.0

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