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Synthesis of plastic scintillation microspheres: Evaluation of scintillators

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ABSTRACT

The use of plastic scintillation microspheres (PSm) appear to be an alternative to liquid scintillation for the quantification of alpha and beta emitters because it does not generate mixed wastes after the measurement (organic and radioactive). In addition to routine radionuclide determinations, PSm can be used for further applications, e.g. for usage in a continuous monitoring equipment, for measurements of samples with a high salt concentration and for an extractive scintillation support which permits the separation, pre-concentration and measurement of the radionuclides without additional steps of elution and sample preparation. However, only a few manufacturers provide PSm, and the low number of regular suppliers reduces its availability and restricts the compositions and sizes available.

In this article, a synthesis method based on the extraction/evaporation methodology has been developed and successfully used for the synthesis of plastic scintillation microspheres. Seven different compositions of plastic scintillation microspheres have been synthesised; PSm1 with polystyrene, PSm2 with 2,5-Diphenyloxazol(PPO), PSm3 with p-terphenyl (pT), PSm4 with PPO and 1,4-bis (5-phenyloxazol-2-yl) (POPOP), PSm5 pT and (1,4-bis [2-methylstyryl] benzene) (Bis-MSB), PSm6 with PPO, POPOP and naphthalene and PSm7 with pT, Bis-MSB and naphthalene.

The synthesised plastic scintillation microspheres have been characterised in terms of their morphology, detection capabilities and alpha/beta separation capacity. The microspheres had a median diameter of approximately 130 μm. Maximum detection efficiency values were obtained for the PSm4 composition as follows 1.18% for ^{3}H, 51.2% for ^{14}C, 180.6% for ^{90}Sr/^{90}Y and 76.7% for ^{241}Am. Values of the *SQP*(*E*) parameter were approximately 790 for PSm4 and PSm5. These values show that the synthesised PSm exhibit good scintillation properties and that the spectra are at channel numbers higher than in commercial PSm. Finally, the addition of naphthalene modifies the shape of the pulses produced by alpha and beta particles leading to better alpha/beta separation.

1. Introduction

Liquid scintillation counting (LSC) [1,2] is the most often used technique for the measurement of beta and alpha emitters in environmental samples [3] and in highly active samples [4] that are produced by nuclear power plants, in research centres, or in hospitals. LSC is a simple and very well established technique; however, the use of LSC in some specific applications such as continuous measurements or measuring of samples with high salinity is problematic. Moreover, the measurements with liquid scintillators generate a mixed waste that has both radioactive and organic properties [5] and a special regulation is devoted to their disposal [6]. This regulation causes special difficulties for the centres in which large amounts of mixed waste are generated [7–9].

The use of plastic scintillation microspheres (PSm) appears to be an alternative to liquid scintillation to solve some of the problems associated with its use. PSm are a solid solution of fluorescent solutes in a polymeric solvent and have a diameter that can vary from tens of micrometres to a few millimetres. Since the polymer is completely polymerised, PSm have no reactivity and are neither flammable nor toxic. Moreover, as they are solid, PSm can be separated from the radioactive sample by filtration after the measurement and no mixed waste is produced [10,11]. Since the composition of PSm is similar to that of liquid scintillators, the scintillation mechanism is also similar. However, considerable differences are observed for weak beta emitters (e.g. ^{3}H) and alpha emitters (when microspheres of high diameter are used) since the particles lose energy in the aqueous phase before reaching the scintillator [12].

In addition to the routine determination of radionuclides, specific applications of PSm, which take advantage from its characteristics, are continuous monitoring of radionuclides in fluid streams [13,14]; measurement of samples with a high salt content that can produce instability (phase separation) when

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measured by LSC [15]; usage as a selective extractant scintillation support (PSm resin) in which the radionuclides can be separated and pre-concentrated in a column-vial that can be measured later without additional steps of elution and sample preparation [16–19].

PSm are a relatively new material, and there are only a few manufacturers providing them [20,21]. However, due to the low number of regular suppliers, it is difficult to purchase PSm and only a few compositions and diameters of the microspheres are available. For this reason, the development of procedures for the synthesis of PSm could be of interest not only to regularly provide PSm for the different applications but also to synthesise PSm with new compositions which can be used to solve important radioanalytical challenges.

Among the different procedures described in the literature for the synthesis of polymeric microspheres [22–24], the most important are drop disruption using microwaves [25,26], polymerisation [27–29] and evaporation/extraction [30,31]. The advantage of evaporation/extraction is that it can be easily implemented in a laboratory and that there are no reactions during the synthesis. Therefore, the components in the PSm are known, which avoids possible quenching effects. In addition, this technique is well described in the literature and is commonly used in the pharmaceutical industry to produce formulations in which the active compound is encapsulated within a biodegradable polymeric matrix. This method is based on the mixture of an organic solution, in which the polymer and the active compounds are dissolved, with a large volume of an aqueous solution with an emulsifier dissolved. After mixing both solutions, microdroplets of the organic solvent are formed in the aqueous solution and are stabilised by the presence of the emulsifier. Then, the aqueous solution extracts slowly the organic solvent of the droplets and at the same time the extracted organic solvent is evaporated from the aqueous solution (which is in contact with the air). After a period of time, the organic solvent is completely extracted from the droplets, and the polymer, with the active compound encapsulated, becomes solid in form of a microspheres and precipitates.

The first objective of this work was to adapt the evaporation/extraction method for the preparation of PSm by using polystyrene as the polymeric solvent and a series of scintillation fluorescent solutes as the active compounds. The scintillation solutes considered in this paper are a selection of those that are commonly described in the literature [32]. p-Terphenyl (pT) and 2,5-diphenyloxazol(PPO) were used as primary solutes and were combined with 1,4-bis(5-phenyloxazol-2-yl) (POPOP) and (1,4-bis [2-methylstyryl] benzene) (Bis-MSB) as secondary solutes [4]. Naphthalene was also evaluated as a secondary solvent, since it has been described in the literature as a component that is capable of enhancing alpha/beta discrimination capabilities of organic scintillators [33–34]. The second objective was to evaluate the capabilities of the differently synthesised PSm and the influence of each component (primary solute, secondary solute, primary solvent and secondary solvent).

2. Experimental

2.1. Reagents

Polystyrene (molecular weight of 250000 g/mol) was purchased from Acros Organics (Geel, Belgium). Fully hydrolysed polyvinylalcohol was obtained from Merck (Schuchardt OHG, Germany). Naphthalene (synthesis reagent), 2,5-diphenylozaxol (scintillation reagent) and dichloromethane (liquid chromatography solvent, 99.9% purity) were purchased from Merck (Darmstadt, Germany). p-Terphenyl and 1,4-bis(2-methylstyryl) benzene (both of scintillation grade) were supplied by Fluka Analytical (Buchs, Switzerland). 1,4-bis(5-phenyloxazol-2-yl)benzene (scintillation grade) was supplied by the Montedison Group, Division Chimica (Milan, Italy).

The radioactive samples were prepared in 6 mL Pico Prias polyethylene vials (PerkinElmer) from the following active stock solutions: A ^{3}H solution ($^{3}H_2O$) with a concentration of 3941(138) Bq/g prepared from a standard of 69.84(244) kBq/g provided by Eckert–Ziegler (Berlin, Germany) in deionised water; a ^{14}C solution (in form of labelled glucose) of 114.6(29) Bq/g prepared from a standard of 44.70(112) kBq/g from Amersham International (Buckinghamshire, UK) in a carrier solution containing 50 μg/g of glucose and 1 mg/g of formaldehyde in deionised water; a $^{90}Sr/^{90}Y$ active stock solution (Sr^{2+} and Y^{3+}) of 37.22(28) Bq/g prepared from a standard of 4.071(31) kBq/g from Amersham International in 0.1 HCl as carrier solution; a ^{241}Am solution (Am^{3+}) of 185.5(19) Bq/g prepared from a standard of 55.44(55) kBq/g supplied by Amersham International in 0.5 M HCl deionised water solution.

2.2. Instruments

The samples were centrifuged using an AJ2-HS centrifuge (Beckman-Coulter Inc., Brea, USA) and sonicated using an Ultrasons-P ultrasonic bath of 40 kHz (JP Selecta, Abrera, Spain).

The radioactive samples were measured using a 1220 QUANTULUS liquid scintillation spectrometer (PerkinElmer) equipped with logarithmic amplification, a multichannel analyser (4096 channels distributed into four segments of 1024 channels), alpha/beta discrimination and background reduction by means of an active guard detector.

The size distribution of the plastic scintillation microspheres was determined using an LS 13 320 single-wavelength laser diffraction particle size analyser (Beckman-Coulter Inc., Brea, USA).

Secondary-electron images were obtained using a Stereoscan S-360 scanning electron microscope.

2.3. Synthesis procedure

PSm were synthesised using the evaporation/extraction method. This synthesis method was adapted to our purposes as follows: 100 mL of dichloromethane containing 10 g of polymer and the corresponding amount of the fluorescent solutes and naphthalene were carefully poured into a 3 L glass that contained 2 L of an aqueous solution of 20 g of polyvinylalcohol in deionised water. The organic/aqueous mixture was continuously stirred with a magnetic stirrer at 16.7 Hz to ensure the formation of a heterogeneous mixture of organic droplets in an aqueous solvent. The mixture was stirred for 5 h to allow the extraction and evaporation of the organic solvent. After this period, the microspheres were separated by filtration and then washed with ethanol and deionised water. Finally, the PSm were dried in an oven at about 40 °C.

Seven different compositions of PSm (from PSm1 to PSm7) were synthesised to evaluate the influence of each component in the scintillator. Table 1 summarises the amount of fluorescent solute and naphthalene added in each synthesis. Each synthesis was performed in triplicate.

In cases of PSm1, PSm2, PSm3, PSm4 and PSm5, the microspheres were mixed in a plastic container and homogenised by shaking. In cases of PSm6 and PSm7, the obtained microspheres from each synthesis were stored separately to evaluate the reproducibility of the synthesis method. After determining the particle size and measuring a tritium sample, the PSm6 and PSm7 were homogenised using the same procedure.