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Synthesis of plastic scintillation microspheres: Alpha/beta discrimination

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HIGHLIGHTS

- Plastic scintillation microspheres for α/β discrimination have been synthesised.
- The energy transfer process in PSm with different compositions has been investigated.
- The α/β discrimination capabilities of two commercial detectors have been evaluated.
- 2% and 0.5% of misclassifications for β and α radionuclides have been achieved respectively.

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ABSTRACT

Plastic scintillation microspheres (PSm) have been developed as an alternative for liquid scintillation cocktails due to their ability to avoid the mixed waste, besides other strengths in which the possibility for alpha/beta discrimination is included. The aim of this work was to evaluate the capability of PSm containing two combinations of fluorescence solutes (PPO/POPOP and pT/Bis-MSB) and variable amounts of a second organic solvent (naphthalene) to enhance the alpha/beta discrimination. Two commercial detectors with different Pulse Shape Discrimination performances (Quantulus and Triathler) were used to evaluate the alpha/beta discrimination. An optimal discrimination of alpha/beta particles was reached, with very low misclassification values (2% for beta particles and 0.5% for alpha particles), when PSm containing PPO/POPOP and between 0.6 and 2.0 g of naphthalene were evaluated using Triathler and the appropriate programme for data processing.

1. Introduction

The accurate and precise determination of the activity of samples in which alpha and beta type signals are mixed currently represents a challenge in the field of radiation detection. This challenge exists for the detection of neutron and gamma activities (Flaska and Pozzi, 2007; Gamage et al., 2011; Klein and Neumann, 2002; Zaitseva et al., 2012) and for the quantification of mixtures of alpha- and beta-emitting radionuclides in different types of samples from natural or artificial origins and from different fields (Dávila Rangel et al., 2002; Happel et al., 2004; Kleinschmidt, 2004; McKlveen and McDowell, 1984; Pates et al., 1998; Salonen, 1993, 1997; Sanchez-Cabeza and Pujol, 1995; Wierczinski et al., 1996). In all these cases, the solution proposed for the determination is the use of organic scintillators combined with the discrimination between the signals generated based on the different temporal distribution of pulses (i.e. pulse shape discrimination (PSD)) because in this way, complex separations can be avoided (Bagán et al., 2011).

When measured with organic scintillators, the signals generated by alpha and high-energy beta particles appear in the same energy region of a multichannel analyser even though the energy of alpha particles is approximately five times higher than that of the beta particles. This signal overlap is because the alpha particles have higher linear energy transfer than the beta particles; therefore, the passage of the alpha particles through the scintillator leads to a greater specific ionisation of solvent molecules; this ionisation does not ultimately result in the production of photons. Moreover, the proportion of excited triplet states is also higher for the alpha particles than for the beta particles, in which the proportion of singlet excitations is higher. The recombination of two triplet states leads to the relaxation of states and the emission of photons. This process is delayed in time relative to the relaxation of singlet excited states. The measurement of the delayed component of the photon emission of alpha particles is the basis for the pulse shape discrimination technique described by various authors (Birks, 1964; Brooks, 1979; L'Annunziata, 2013; McDowell and McDowell, 1991; Moebius and Moebius, 2012) and implemented in commercial detectors. In commercial detectors, the energy and

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amplitude of each pulse are measured. Depending on the electronics implemented, the signals can be classified with regard to a discrimination parameter as alpha or beta in two dimensional spectra of counts as a function of energy (Quantulus or Tricarb detectors), or the signals can be classified with regard to their energy and duration in a three-dimensional spectrum (Triathler and Hidex SL300 detectors).

The use of liquid scintillators (LSs) combined with pulse shape discrimination has been widely applied to the quantification of mixtures of alpha and beta radionuclides and demonstrates low misclassifications if the appropriate scintillator is used, if the calibration process is realistic and if the electronic setup is optimised correctly. However, measurement with liquid scintillators presents an important drawback, which is the generation of mixed waste (Hsu and Krieger, 1991; Tahnassian et al., 1991); this type of waste deserves special regulations for its disposal because of its characteristics, radioactive and hazardous (EPA, 2001, 2006). The use of plastic scintillation microspheres (PSm), among other configurations that use plastic scintillators (sheets or containers), can be considered to overcome this drawback. PSm are a solid solution of fluorescent solutes in a polymeric solvent and can have a diameter in the range of tens or hundreds of micrometres. Because the polymer is completely polymerised, PSm have no reactivity; thus, PSm are neither flammable nor toxic, and because the PSm are solid, the sample and the scintillator microspheres can be segregated by filtration after the measurement (Tarancon et al., 2002, 2004). Concerning the measurements with PSm, they are very similar to that of liquid scintillators (i.e. preparation, sample volume, vials and detector). PSm are mixed with an aqueous sample to yield a heterogeneous mixture. In this heterogeneous mixture, a particle emitted by a radionuclide must travel through the sample medium until it reaches the surface of the microsphere in which is detected. The detection efficiency for measurements with PSm depends on the diameter of the microspheres and the energy of the radioactive particle. Therefore the detection efficiency is lower to that of liquid scintillation for low-energy beta emitters, slightly lower for alpha and medium-energy beta emitters and similar for high-energy beta emitters (Sanz and Kossert, 2011; Santiago et al., 2013b).

From the perspective of the mechanism, because the composition of PSm is similar to that of LSs, it can be expected that the energy transfer mechanism should be similar. However, the rigid structure of the solid scintillator may affect the relaxation process for the triplet states of the solvent. For example, previous tests have shown that discrimination between beta and alpha particles is possible with commercial PSm (with a commercial detector), but with higher misclassifications than with LSs. However, the limited information about the energy transfer process in organic scintillators, the limited availability of commercial PSm and the limited setup options or commercial detection equipment hide the reasons for the high rate of misclassifications. The objective of this study is to obtain information about the energy transfer process in PSm though the evaluation of the alpha/beta discrimination obtained when using PSm of different compositions.

To this end, PSm of different compositions have been synthesised through an evaporation/extraction method (Santiago et al., 2013a). The synthesised PSm are composed of polystyrene (PS) as the polymeric organic solvent; 2,5-diphenyloxazol (PPO) and *p*-terphenyl (pT) as primary solutes; and 1,4-bis(5-phenyloxazol-2-yl) (POPOP) and 1,4-bis[2-methylstyryl] benzene (Bis-MSB) as secondary solutes. To improve the pulse shape discrimination, various amounts of second organic solvent were added in each synthesis. Of the different compounds described in the literature, naphthalene is well known to be a secondary solvent capable of enhancing discrimination between alpha and beta signals in organic scintillators because naphthalene has a long decay time (i.e. 96 ns) (Hallam and Birks, 1978; Rodriguez Barquero and Grau Carles, 1998; Yang et al., 1990). The addition of naphthalene to the scintillator enhances the formation of excited triplet states; this enhancement leads to an increase in the delayed component of the scintillation pulse. As described above, this increase leads to a greater increase in the pulse duration of alpha signals than beta signals and consequently leads to a better separation of alpha and beta disintegration events. Measurements with PSm of different compositions (i.e. with variable capabilities for alpha/beta discrimination) in commercial detectors with different pulse shape discrimination performances (Quantulus and Triathler) can be used to define some of the aspects that cause the high misclassification in PSm.

2. Experimental

2.1. Reagents

All the reagents used were of analytical or scintillation grade. Polystyrene (PS) (MW 250,000 g/mol) was provided by Acros Organics (Geel, Belgium). Fully hydrolysed poly(vinyl alcohol) (PVA) was purchased from Merck (Schuchardt OHG, Germany). Dichloromethane, naphthalene and 2,5-diphenyloxazol were supplied by Merck (Darmstadt, Germany). 1,4-bis(2-methylstyryl)-benzene and *p*-terphenyl were purchased from Fluka Analytical (Buchs, Switzerland). 1,4-bis(5-phenyloxazol-2-yl)benzene was supplied by the Montedison Group, Division Chimica (Milan, Italy).

Radioactive samples were prepared in 6 mL Pico Prias polyethylene vials (PerkinElmer, USA) from the following active stock solutions: a ^{3}H solution (HTO) with a concentration of 3.94(14) kBq/g in deionised water prepared from a standard of 69.8(24) kBq/g provided by Eckert-Ziegler (Berlin, Germany); a ^{14}C solution (labelled glucose) of 114.6(29) Bq/g prepared from a standard of 44.7(11) kBq/g from Amersham International (Buckinghamshire, UK) in a carrier solution of 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 M HCl; and finally, 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 in deionised water.

2.2. Equipment

An AJ2-HS centrifuge (from Beckman-Coulter Inc., Brea, USA) was used to centrifuge the measurement vials and an Ultrasons-P ultrasonic bath (from JP Selecta, Abrera, Spain) was used to sonicate the vials (40 kHz).

The measurements of radioactive samples were performed with a 1220 Quantulus detector and with a Triathler detector. The 1220 Quantulus liquid scintillation spectrometer (from PerkinElmer, USA) is equipped with logarithmic amplification, a multichannel analyser with 4096 channels distributed into four segments of 1024 channels (four spectra), and it is capable of alpha–beta discrimination. Background reduction is achieved by a combination of passive shielding and active shielding based on a guard detector. The Triathler liquid scintillation spectrometer (from Hidex, Turku, Finland) is a single-sample detector equipped with one photomultiplier, a multichannel analyser with 2048 channels (one spectrum of 64 energy channels and 32 time channels) and has alpha–beta discrimination capabilities.

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

Secondary-electron images of the PSm were obtained with a Stereoscan S-360 scanning electron microscope.