PSresin for the analysis of alpha-emitting radionuclides: Comparison of diphosphonic acid-based extractants

I. Giménez [a], H. Bagán [a], A. Tarancón [a,b,c,*], J.F. García [a,c]

[a] *Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, Marti i Franqués, 1-11, ES, 08028, Barcelona, Spain*
[b] *Serra-Húnter Programme, Generalitat de Catalunya, Barcelona, Spain*
[c] *Institut de Recerca de l'Aigua, University of Barcelona, Spain*

1 . A B S T R A C T

The analysis of radionuclides is complex, with high economic and time costs. For this reason, there is a need to develop new methods and strategies to reduce these costs. One important group in the analysis of radionuclides is the actinides, which are the main constituents assessed in the total gross alpha together with radium and radon test used to measure radioactivity in drinking water. Moreover, in nuclear dismantling processes, the possible spread of the released radionuclides has to be controlled, which is measured by many techniques, depending on the radionuclides, through scintillation. This work presents a new method to analyse actinides using plastic scintillation resins (PSresins) packed in a solid-phase extraction cartridge. The proposed method combines chemical separation and sample measurement into a single step, reducing the effort, time and reagents required for analysis as well as decreasing the amount of waste generated. The PSresins compared in this study contained three selective extractants based on methylenediphosphonic acid with different radicals, which has a high affinity for tri-, tetra-, and hexavalent actinides in dilute acids. These extractants were immobilised on plastic scintillation microspheres at a ratio of 1/1:6, producing a retention and detection efficiency of 100% for ^{241}Am, ^{230}Th, Uranium and ^{238}Pu. The retention and detection efficiency were 20% and 100%, respectively, for ^{210}Po and low for ^{226}Ra.

1. Introduction

The analysis of radionuclides is complex, with high economic and time costs. This is very evident in decommissioning and environmental monitoring, for which the obtention of appropriate information requires as much analysis as possible. In such situations, the assessment of global or screening parameters may be of help to avoid the use of selective procedures for each radionuclide. For example, the gross beta and alpha parameters are used to measure radioactivity in water intended for human consumption, which are assessed in order to avoid the specific analysis of several alpha and beta emitters if the parametric values do not exceed the limits (España, 2016).

One of the radionuclides group of major concern in radioactivity analysis is the actinides, which include some natural alpha emitters commonly found in natural waters and artificial alpha emitters that indicate nuclear contamination, accidents or terrorist attacks. The quantification of these actinides, regardless of whether alpha spectrometry or liquid scintillation is used, requires previous chemical separation to avoid radiochemical or non-radiochemical interferences. This separation can be achieved through precipitation, liquid-liquid extraction with organic solvents like tributyl phosphate (TBP), or anion-exchange chromatography (M.F. L'Annunziata, 2007). These procedures are usually laborious, long and tedious, and also generate waste. Therefore, they have been replaced by extraction chromatography through solid-phase extraction (SPE) (Horwitz et al., 1993; Zagyvai et al., 2017). This strategy, using a suitable selective extractant in a resin and an appropriate medium, can result in a very good selective extraction of the target radionuclide from the rest of the interferences. Resins that use octyl phenyl diisobutyl carbamoyl methyl phosphine oxide (CMPO) dissolved in TBP as an extractant on an inert support can sorb americium, plutonium and uranium in 1–3 M nitric acid (Triskem, 2015a). The resins based on dipentyl pentylphosphonate show high affinity for uranium(VI) and some tetravalent actinides, such as thorium, neptunium and plutonium, in a nitric acid medium (Triskem, 2015b). Resins based on N,N,N′,N′-tetra-*n*-octyldiglycolamide can sorb americium in 5 M hydrochloric acid and actinium in 1–3 M nitric acid while radium is eluted. Finally, resins based on bis(2-ethylhexyl) methanediphosphonic acid have a high affinity for several alpha emitters (Chiarizia et al., 2007; Rim et al., 2016) and their use has been proposed for the assessment of the total gross alpha parameter (Navarro et al., 2004) due to their high affinity for actinides in 0.1 M hydrochloric acid.

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* Corresponding author. Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, Marti i Franqués, 1-11, ES, 08028, Barcelona, Spain.
  E-mail address: alex.tarancon@ub.edu (A. Tarancón).

For a fast and simple analysis of alpha-emitting radionuclides, scintillation techniques should be taken into consideration since they combine simplicity with good detection limits. Plastic scintillation resins (PSresins), which are plastic scintillation microspheres (PSm) coated with a selective extractant packed in an SPE cartridge, combine the extraction process and measurement into a single material (Bagán et al., 2011; Coma et al., 2019; Lluch et al., 2016; Sáez-Muñoz et al., 2018). This not only simplifies the analytical method, but it also reduces the number of reagents required, since elution steps are no longer required, and avoids the generation of mixed wastes (hazardous and radioactive) derived from the use of liquid scintillation cocktails (L'Annunziata, 2020; Jay et al., 2020; Tarancón et al., 2021). Extractive scintillating resins has also been used for on-line monitoring of radionuclides (Egorov and O'Hara J. W. 2006; A. F. Seliman et al., 2013; A. F. Seliman et al., 2017).

PSresins have already been mainly developed for the measurement of beta-emitting radionuclides such as ^{90}Sr and ^{99}Tc. In this paper, different PSresins for the selective measurement of alpha-emitting radionuclides have been developed and compared, providing a new methodology for the measurement of alpha emitters that requires less time and fewer reagents. Scintillating resins were tested tested previously for uranium but also for americium, and plutonium (Duval et al. 2016, Duval et al., 2019; Hughes and DeVol, 2003; Roane and DeVol, 2002, 2005). The extractants used in this study are based on diphosphonic acid derivatives (Fig. 1), which have attracted a lot of interest due to their effectiveness as a complexing reagent for metal ions, showing high sorption capacities for actinides that make the stripping of the sorbed actinides difficult (Griffith-Dzielawa et al., 2000; Horwitz et al., 1997; McAlister et al., 2001; Rim, 2013; Rim et al., 2016). This property is of special interest in PSresin measurements since the analyte is not eluted from the resin during analysis.

The interaction between the extractant and the radionuclide is mediated by a diphosphonic group (Rim, 2013; Rim et al., 2016). Therefore, the interaction is expected to be the same for the three extractants assessed in this study. However, a modification of the radicals in the extractant could lead to a better assessment of steric impedance or polarity that could affect the retention capacities of the resin and the quenching effects, which have a direct impact on the detection efficiency and the resolution of the spectrum. These improvements via modifications in the radical chain would benefit the scintillating capacities of the PSresin, thereby improving the detection of scintillation and the discrimination of beta and alpha emitters through pulse shape analysis.

For that reason, the aim of this work was to study different extractants for the extraction of alpha-emitting radionuclides to find the most suitable one for the synthesis of PSresins.
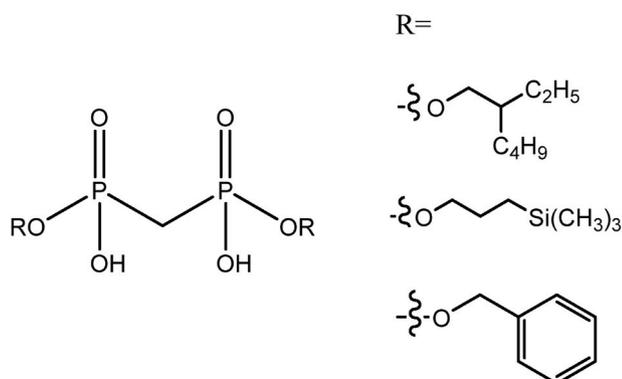
2. Experimental

2.1. Reagents and solutions

All the reagents used were of analytical grade. Polystyrene (PS) (MW 250.000 g/mol) was supplied by Acros Organics (Geel, Belgium). Fully hydrolysed polyvinyl alcohol (PVA), 2,5-Diphenyloxazole (PPO), 2,6-diisopropylnaphthalene (DIN) (99% pure), benzyl alcohol, tetrahydrofuran (max. 0.005% H_2O), 3-(trimethylsilyl)-1-propanol (97%) and dichloromethane (99.9% pure) were supplied by Merck (Darmstadt, Germany). 1,4-bis(5-phenyl-2-oxazolyl) benzene (POPOP) was purchased from Carlo Erba Reagents (Chaussée du Vexin, France). Methylenediphosphonic acid (99+%), 2-ethylhexanol and N,N'-dicyclohexylcarbodiimide (DCC; 99%) were supplied by Alfa Aesar (Kendal, Germany).

A ^{90}Sr/^{90}Y active stock solution of 38.45 (0.29) Bq/g was prepared from a standard of 4071 (31) Bq/g in a water solution of strontium (100 µg g^{-1}) and yttrium (100 µg g^{-1}) in 0.1 M HCl (Amersham International, Buckinghamshire, England). A natural purified uranium (^{238}U+^{235}U+^{234}U) active stock solution of 2.22 (0.03) Bq/g was prepared from a standard of 101.34 (1.18) Bq/g (Eckert and Ziegle, Berlin, Germany) with 11 years of ingrowth. A^{238}Pu active stock solution of 46.30 (1.4) Bq/g was supplied by GE Healthcare-Amersham International (Buckinghamshire, England). A^{230}Th active stock solution of 2.38 (0.07) Bq/g was prepared from a standard of 23.59 (0.27) Bq/g (National Institute of Standards and Technology (NIST), Gaithersburg, USA). A^{241}Am active stock solution of 47.4 (1.2) Bq/g in 0.5 M HCl was prepared from a standard of 55.4 (1.3) kBq/g (GE Healthcare-Amersham International, Buckinghamshire, England). A^{226}Ra active stock solution of 4 (0.12) Bq/g in HNO$_3$ was prepared from a standard of 1.986 (61.5) KBq/g (Ciemat, Madrid, Spain). A^{210}Pb active stock solution of 160 (4.8) Bq/g was prepared from a standard of 35.5 (1.06) KBq/g (CEA/DAMRI, Gif-sur-Yvette, France). The values in brackets refer to the standard uncertainty.

The OptiPhase Supermix liquid scintillation cocktail from PerkinElmer (Waltham, USA) was used for the liquid scintillation measurements.

2.2. Apparatus

A Quantulus liquid scintillation spectrometer (PerkinElmer, Waltham, USA) with logarithmic amplification, a multichannel analyser (MCA) (4096 channels distributed in four segments of 1024), alpha/beta discrimination and background reduction by an active guard was used for the scintillation measurements.

Secondary electron images were obtained using a JSM-7100F JEOL (Tokyo, Japan) scanning electron microscope at the Scientific and Technological Centres of the University of Barcelona (CCiTUB).

The analysis of stable isotopes was performed using an OPTIMA 8300 ICP-OES detector (PerkinElmer, Waltham, USA) or an ELAN-6000 ICP-MS detector (PerkinElmer, Waltham, USA).

A Varian Mercury 400 MHz nuclear magnetic resonance (NMR) system (Oxford, England) was used to confirm the structures of the molecules synthesised.

2.3. Procedure

2.3.1. Preparation of PSresins

PSm were prepared through the extraction-evaporation method, as previously reported (Santiago et al., 2013). Briefly, 250 mL of a solution of polystyrene, diisopropylnaphthalene and the fluors (PPO and POPOP) in dichloromethane were mixed with 2 L of a 1% PVA aqueous solution and stirred for 24 h at 11.6 Hz. The microspheres formed were recovered by filtration and dried in an oven at 40 °C for 24 h.

Three PSresins based on methanediphosphonic acid and with three different radicals were prepared: EH-PSresin; SI-PSresin and BZ-PSresin.

R=

Fig. 1. Core structure of the extractant studied and the different radicals.

The different extractants were prepared in a similar way, as previously reported for bis(2-ethylhexyl)methanediphosphonic acid (Griffith-Dzielawa et al., 2000; Horwitz et al., 1997; McAlister et al., 2001). Briefly, a 60-ml mixture of THF with methanediphosphonic acid and 2-ethylhexanol (EH-PSresin), benzilic acid (BZ-PSresin) or 3-(trimethylsilyl)-1-propanol (SI-PSresin), depending on the PSresin being prepared, was purged with N_2 and refluxed. Afterwards, an 80-ml solution of DCC in THF was added dropwise. This was left to react for 1 day.

PSresins were prepared by coating the surface of the microsphere with the respective extractant, according to previous studies. A mixed solution of the extractant in isopropanol was stirred with PSm for 45 min and then incubated in a rotary evaporator for 2 h to remove the solvent (Bagán et al., 2011).

2.3.2. PSresin extraction and measurement

One gram of the corresponding PSresin was packed in a 2-mL SPE cartridge (length: 3.2 cm; internal diameter: 1 cm; external diameter: 1.2 cm) from Triskem International (Rennes, France). The cartridge was placed in a vacuum chamber connected to a pump and 10 ml of deionised water was passed through it at a flow rate of 1 ml/min, around 5 inHg. Afterwards, the cartridges were shaken for 180 s at 50 Hz in an IKA MS3 digital vortex (Merck, Darmstadt, Germany) for homogenisation.

Samples were prepared by adding a known amount of the radioactive stock solution and 0.5 M hydrochloric acid made up to 11 ml. The activity added was around 7.5 Bq for ^{241}Am and 3.3 Bq for ^{230}Th, natural uranium, ^{238}Pu, ^{210}Po and ^{226}Ra. Blank samples were prepared by adding deionised water instead of the radioactive stock solution. The ^{90}Sr/^{90}Y sample solution was prepared in 2 M nitric acid and with an activity of around 10 Bq. All solutions were prepared by weight.

The ^{226}Ra sample was subjected to ultrasound for 10 min to remove ^{222}Rn before its passing through the PSresin cartridge.

To perform the sample analysis. The cartridge was first conditioned with 2 ml of 0.5 M HCl. Afterwards, 10 ml of the sample solution were passed through the cartridge. The flow must be around 1 ml/min, which corresponds to a pressure of 3 inHg. Once the sample was loaded, two rinses with 2 ml of 0.5 M HCl or 2 M HNO$_3$ (in the case of the ^{90}Sr/^{90}Y sample) were performed. Two additional rinses with 2 ml of 6 M lithium nitrate were undertaken for the ^{90}Sr/^{90}Y sample to avoid the chemiluminescence caused by nitric acid.

To ensure the dryness of the cartridge, the pressure was increased to 15–20 inHg for 10 min.

The solutions eluted after passing the sample and rinsing the PSresin cartridge, effluent or effluent solutions, were collected in Corning (New York, USA) 50-ml conical tubes.

Once the extraction process was completed, the cartridge with the PSresin was placed in a 20-mL polyethylene vial and measured in the scintillation counter.

PSresin cartridge effluent were also measured by liquid scintillation to determine the amounts of radionuclides that were not retained. A 6-ml aliquot of effuent was added to a 20-ml polyethylene vial along with 14 ml of the scintillation cocktail. The vials were shaken for 180 s in the vortex at 60 Hz to homogenise the mixture. Blanks were prepared by adding deionised water instead of the effluent solution.

2.3.3. Retention profile of stable metals

Two samples containing 1000 mg L^{-1} of europium(III) and iron(III), respectively, were prepared in 0.5 M HCl. 50 mL of each solution were passed through the cartridge with PSresin and 2-ml fractions of the effluent solution were collected in separate conical tubes to evaluate how is the retention profile of Eu and Fe in the PSresin and to make and estimation of the PSresin capacity. Fractions containing iron(III) were analysed by ICP-OES, whereas ICP-MS was used for those containing europium(III).

2.3.4. Breakthrough volume

400 ml of a 0.5 M-HCl solution were passed through a PSresin cartridge in which ^{241}Am was previously retained. The PSresin cartridge effluent were collected in fractions of 40 ml in a 50-ml conical tube. Each fraction was measured by liquid scintillation, as described before.

2.3.5. Measurement conditions

A "low" coincident bias and a "high-energy" multichannel analyser configuration were used for the scintillation measurements. The counting time for the measurement of the PSresin cartridges was 1 h for ^{241}Am and 3 h for the other radionuclides. LS samples were measured for 1 h. The external quenching parameter (SQP(E)) was measured for 10 min for each vial. The measurement vials were stored in the dark for 2 h before counting, except those containing the ^{226}Ra and ^{210}Po samples that were directly measured after separation to avoid the ingrowth of daughter isotopes.

Alpha/beta discrimination through pulse shape analysis was performed by analysing the PSresin cartridges for 25 min at PSA values of 50, 75, 100, 115, 125, 130, 135, 140, 145, 150, 175, 200, 225 and 250.

2.3.6. Data treatment

The NMR spectra were integrated with the MestReNova software (Mestrelab, Santiago de Compostela, Spain). All the spectra acquired from the scintillation measurements were smoothed using the Savitzky–Golay algorithm with an average window of 21 points, delimiting the range of the windows from 1 to 1024. A net spectrum was obtained by subtracting the spectrum of the equivalent blank solution. The detection efficiency spectrum was obtained as the ratio between the net counts in every channel and the activity in the PSresin cartridge. The detection efficiency was calculated from the integration of the detection efficiency spectrum at the selected energy channel range.

3. Results and discussion

The study of the PSresins was performed in four stages. First, the PSresins were prepared, which included the synthesis of the extractants and the coating of the PSm. Second, the retention and detection efficiencies and the quenching effects for the analyses of several alpha and beta emitters were assessed. Third, the capacity and retention profile were evaluated with stable elements and, fourth, the alpha/beta discrimination capabilities were evaluated.

3.1. PSresin preparation

The correct synthesis of the extractants was confirmed with NMR spectroscopy. The ^{1}H NMR (MD$_3$OD) signals obtained were:

- EH-PSresin: δ 0.9 (t, 12 H), 1.20 (m, 14 H), 1.47 (m, 4 H), 2.46 (t, 2 H), 3.99 (m, 4 H)
- BZ-PSresin: δ 2.46 (t, 2 H), 4.5 (s, 1 H), 4.9 (s, 4 H), 7.35 (m, 10 H)
- SI-PSresin: δ 0.01 (s, 18 H), 0.53 (m, 4 H), 1.67 (m, 4 H), 2.46 (t, 2 H), 3.99 (m, 4 H)

Three different PSresins were prepared by coating PSm presenting a median diameter of 60 μm with the corresponding extractant. The extractants used were: bis(2-ethylhexyl)methanediphosphonic acid (EH-PSresin), bis(trimethylsilylpropanyl)methanediphosphonic acid (SI-PSresin) and bis(benzylyl)methanediphosphonic acid (BZ-PSresin).

The scanning electron microscopy images (Fig. 2) showed that most of the resins maintained their spherical shape. Furthermore, there were almost no agglomerates present due to the possible softening caused by the solvent used (isopropanol), which could partially dissolve the polystyrene surface of the microspheres after the long contact time. Moreover, it was ensured in a preliminary study that the exposure time conditions in which the immobilisation was performed, were not enough to soften or dissolve the PSm, ensuring that any change observed in the surface could be attributed to the correct immobilisation of the extractant. This indicates that the amount of solvent used for the
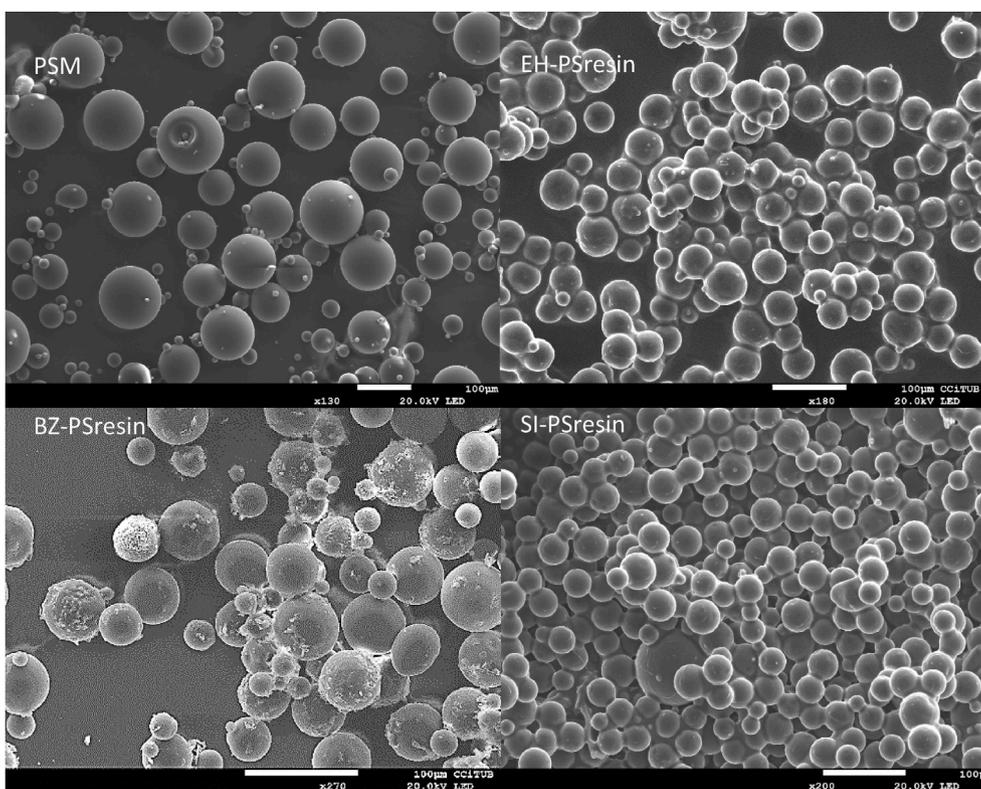
Fig. 2. Secondary electron images for the different PSresins obtained using a scanning electron microscope. EH-PSresin (R = 2-ethylhexyl); BZ-PSresin (R = benzyl); SI-PSresin (R = 3-(trimethylsilyl)-1-propyl).

immobilisation and the time of exposure to it were adequate. The images confirmed that the immobilisation of the extractant on the surface of the scintillation support was performed correctly. The PSm, is the virgin resin, the support without any extractant on it, showing how smooth and plain is the surface, whereas the PSresins had small folds (EH-PSresin), scales (BZ-PSresin) or crystals (SI-PSresin) on the surface, confirming the presence of a superficial layer of the extractant and the presence of extractant between PSm which enhance the retention of the target radionuclide. This difference in appearance was also the first indication of the differences between the PSresins.

Moreover, EH-PSresin and SI-PSresin showed a homogeneous distribution of the extractant on their surface whereas BZ-PSresin does not. These results indicate that the proportion of the PSm:extractant used was adequate at least for EH-PSresin and SI-PSresin. Furthermore, there were some physical differences between them in this regard, since EH-PSresin was stickier than the other two resins.

3.2. Extraction and scintillation detection capabilities

The study was performed using solutions prepared in 0.5 M HCl. This medium was chosen because it was already used in the separation methods involving the non-scintillating diphosphonic acid-based resins (Eichrom, 2014) given the very strong retention of actinides in it.

3.2.1. Background

The background values for the different PSresins were quite similar (0.91 (0.12) cpm, 0.79 (0.11) cpm and 1.14 (0.14) cpm for EH-PSresin, BZ-PSresin and SI-PSresin, respectively). This was expected since all the compounds used for the PSm were organic and the main difference between the PSresins was the radicals of the different extractants, which should not affect the background values.

3.2.2. Americium-241

The first radionuclide that was studied was [241]Am since the most

stable valence state of americium is (III), which is the one with the highest affinity for diphosphonic acids (Chiarizia et al., 2007). Therefore, it can be assumed that the retention and detection efficiency for the other alpha-emitting radionuclides should be similar to or lower than those for americium.

[241]Am showed very high retention in EH-PSresin and SI-PSresin, whereas only half of the total americium was retained in BZ-PSresin (Table 1).

The different retention behaviour of BZ-PSresin could be due to the effect of the benzyl group of the lateral chains of the extractant. This group is more polar and more voluminous than the other two, which could affect access and the interaction between the disphosphonic group and the radionuclide in the medium.

The detection efficiency was high for the americium retained in all three PSresins and all the disintegrations are detected. These results are in according to those obtained previously with PSm of 60 μm in similar measurement conditions since all alpha particles are capable to hit the PSresin without being attenuated by the medium (Tarancón et al., 2017). However, the SQP(E) values for BZ-PSresin were lower than those for EH-PSresin and SI-PSresin, which were comparable and similar to those of other PSresins and PSm. Although the SQP(E) for BZ-PSresin indicated that there was not a great quenching effect, the spectrum obtained was broad and shifted to low energies compared to those obtained for EH-PSresin and SI-PSresin, which were not affected by any

Table 1
Retention and detection efficiency for Am-241 in each PSresin. EH-PSresin (R = 2-ethylhexyl); BZ-PSresin (R = benzyl); SI-PSresin (R = 3-(trimethylsilyl)-1-propyl).

	Yield (%)	Detection efficiency (%)	SQP(E)
EH-PSresin	>99.5	100	781
BZ-PSresin	48.4	100	736
SI-PSresin	>99.5	100	779

quenching effect (Fig. 3). This effect is presumed to be associated with the presence of an aromatic ring of the benzyl substituent, which can interfere in the energy transfer process along the polymer chain of the scintillator, causing a decrease in the number of photons emitted by the scintillator.

The broad spectrum obtained with BZ-PSresin will probably hamper alpha/beta discrimination, as well as cause overlapping of the peaks of other potential radionuclides that could be present in a real sample. This and the low retention led to BZ-PSresin being discarded as a candidate for a scintillation resin in subsequent studies.

3.2.3. Plutonium, thorium and uranium

EH-PSresin and SI-PSresin were used for the analysis of plutonium (^{238}Pu), thorium (^{230}Th) and natural uranium (^{238}U+^{235}U+^{234}U) standards in 0.5 M HCl. A quantitative retention of ^{238}Pu, ^{230}Th and natural uranium was observed in both PSresins (Table 2), which indicated an optimum interaction between the radionuclides and the extractant, showing no significant differences between them. The valence state in which the analysis was performed was plutonium (IV), thorium (IV) and uranium (VI).

Regarding the scintillation properties, the detection efficiency for ^{238}Pu and ^{230}Th was close to 100%, as expected from the previous analysis of americium. In the case of uranium (^{238}U + ^{235}U + ^{234}U), all the disintegrations were detected, including the short-live decay products in equilibrium, ^{234}Th and ^{234}Pa, which are both high energy beta-emitting radionuclides. As it has been explained in the reagents section, the uranium solution used is a standard from a natural source that has been purified in order to exclude long half-live time radionuclides. Nevertheless, there are also the short half live-time radionuclides formed very fast after purification which are also retained. For that reason, the calculation of the efficiency was done considering the sumatorium of all the uranium isotopes present plus the contribution of ^{234}Th and ^{234}Pa. The detection efficiency and retention were the same for both PSresins. Fig. 4 shows the normalised spectrum for each radionuclide, which was obtained by dividing the count rate spectrum by the total the spectrum area, for SI-PSresin as an example.

Despite organic scintillation is not a technique suited for spectroscopy studies, from a qualitative point of view we can observe that there was a certain correlation between the spectrum position and the energy of the radionuclides studied. Uranium spectrum is the sum of the contribution of ^{238}U and ^{234}U, being their respective energies of 4.27 MeV (^{238}U) and 4.86 MeV (^{234}U), as well as the contribution of the short-
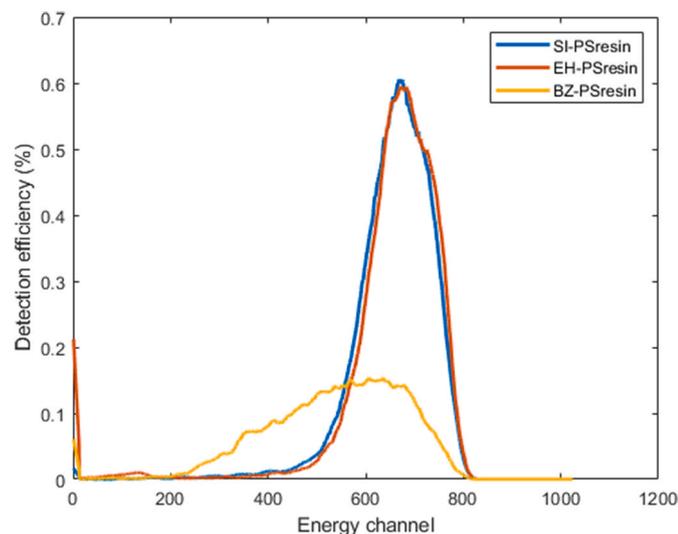
Table 2

Retention and detection efficiency for each type of resin for ^{241}Am, ^{238}Pu, uranium and ^{230}Th. EH-PSresin (R = 2-ethylhexyl); BZ-PSresin (R = benzyl); SI-PSresin (R = 3-(trimethylsilyl)-1-propyl).

	EH-PSresin		SI-PSresin	
	Detection efficiency (%)	Retention (%)	Detection efficiency (%)	Retention (%)
^{241}Am	100 (1)	>99.5	100 (1)	>99.5
^{238}Pu	97.6 (0.6)	>99.3	97 (3)	>99.3
natural U	100 (2)	>98.6	95.9 (0.8)	>98.6
^{230}Th	98 (2)	>97.9	98 (4)	98.2 (0.6)
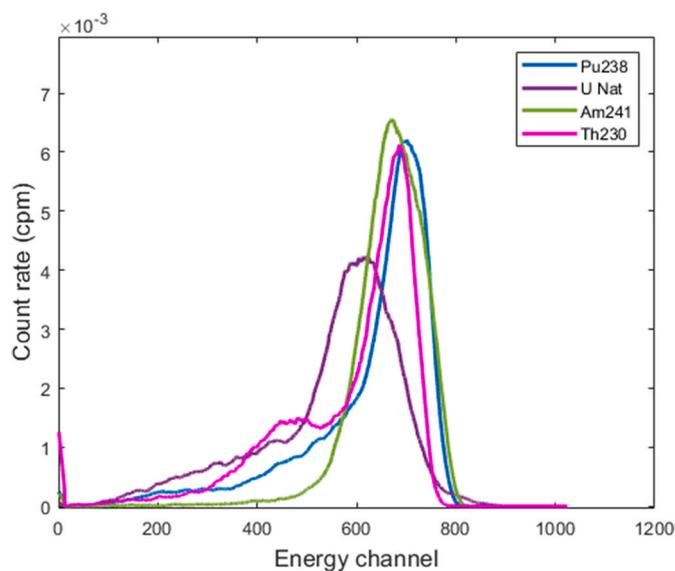
Fig. 4. Normalised spectra for each radionuclide.

lived beta decay products. The spectrum for uranium is located at lower energy channels compared to ^{230}Th due to the ^{238}U contribution which make the spectrum broader together with the presence of the short-lived beta decay products. The spectrum for ^{230}Th, with an energy of 4.77 MeV similar to ^{234}U, is located in the high energy range of the spectrum of the natural uranium, which correspond to the ^{234}U contribution. However, they were not at higher energy than americium. The spectrum for americium, which had an energy of 5.48 MeV, appeared at higher energy channels and showed the narrowest peak of all of them. Lastly, the spectrum for ^{238}Pu, with an energy of 5.59 MeV, appeared at the highest energy channels. Moreover, the shape of the spectrum depended on other factors such as differences in the position and retention inside the PSresin cartridge, which would explain the different shapes of the spectra for ^{241}Am and ^{238}Pu since the former was sharper.

No differences were observed in the spectra for EH-PSresin and SI-PSresin (Supplementary Material), demonstrating the similarity of the two extractants used to synthesise the resins.

3.2.4. Polonium and radium

Since both resins presented a very good retention of the actinides, their behaviour regarding other common alpha emitters of interest, such as ^{226}Ra and ^{210}Po, was studied.

Retention of polonium was assessed through the measurement of a solution in which ^{210}Pb, ^{210}Bi and ^{210}Po were in secular equilibrium. The spectra obtained (Fig. 5A for the PSresin and 5B for the PSresin cartridge effluent) confirmed the total retention of ^{210}Bi in both PSresins since the peak was broad and located at high energies. By contrast, in the effluent solutions, two clear peaks were identified, one broad peak at low energies corresponding to ^{210}Pb and one sharp peak at high energies

Fig. 3. Detection efficiency spectrum of Am-241 in each PSresin. EH-PSresin (R = 2-ethylhexyl); BZ-PSresin (R = benzyl); SI-PSresin (R = 3-(trimethylsilyl)-1-propyl).
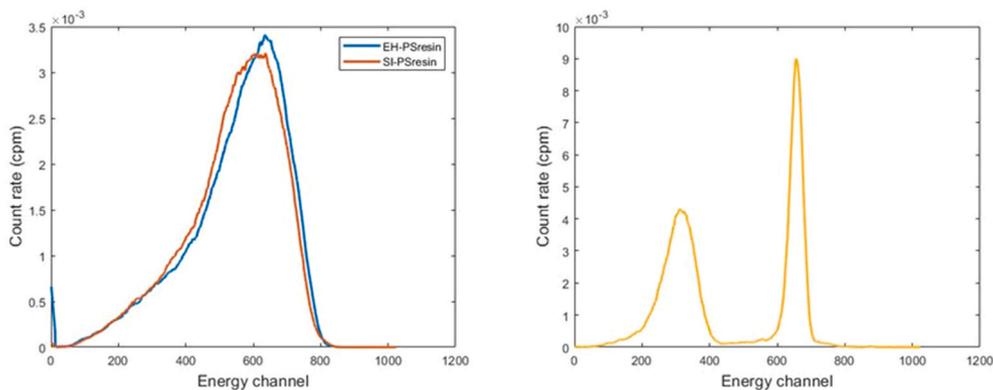
Fig. 5. Normalised spectra of ^{210}Pb, [210]Bi and [210]Po in the: (A) EH-PSresin and SI-PSresin cartridges; and (B) effluent solution measured through LS.

corresponding to [210]Po. This behaviour can be explained by the fact that the oxidation state of bismuth, III, is the one with the highest affinity for this type of diphosphonic acid-based resin in this medium. The retention of polonium was estimated to be around 20%, considering that all bismuth is retained and a 100% detection efficiency in the measurement by LS. No significant differences between the two PSresins were found.

As with uranium, the study of radium was affected by the presence of decay products despite the previous removal of [222]Rn before the separation in the PSresin. For this reason just a qualitative analysis of the retention behaviour has been done.

The spectra for [226]Ra obtained for EH-PSresin and SI-PSresin (Fig. 6A) were similar, with a broad band indicating that some beta emitters, mainly bismuth radionuclides, were retained in the PSresin cartridge. The spectrum obtained in the measurement of the effluent solution (Fig. 6B) by liquid scintillation indicated that the alpha emitter was weakly retained in both PSresins. In this case, it can be concluded that neither resin presented a good retention of [226]Ra in the medium selected, although they presented a good retention of bismuth ([214]Bi) confirming the results obtained previously for the ^{210}Pb/[210]Bi/[210]Po solution.

3.3. Breakthrough volume

Breakthrough volume was studied by the analysis of the PSresin cartridge and the PSresin cartridge effluent after passing 400 mL of 0.5 M HCl through a cartridge which already contained retained [241]Am (Table 3).

No differences were observed after passing 400 mL of 0.5 M HCl in terms of retention, detection efficiency and the SQP(E) value for any of the radionuclides and PSresins studied. This, therefore, confirmed that the extractant was strongly adhered to the PSm and the retention of the radionuclide was also very strong.

Table 3
Retention, detection efficiency and the quenching parameter before and after the passing of 400 mL of 0.5 M HCl.

		*Retention (%)		Detection efficiency (%)		SQP(E)	
		Before	After	Before	After	Before	After
[241]Am	EH-PSresin	>99.5	>99.5	102	102	777	776
	SI-PSresin	>99.5	>99.5	103	104	783	773

*Calculated with the detection limit.

As shown in Fig. 7, the spectrum shifted slightly to lower energy channels after the passing of 400 mL of HCl. This shift can be attributed to a change in the retention pattern along the cartridge, which make the distribution of the radionuclide less homogenous and gave the radionuclide access to areas with worst light emission properties. In spite of that, PSresin demonstrate to be resistant to the pass of 400 mL. For that reason, in case of having a volume sample of several milliliters, the calibration of the detection efficiency and spectrum position might be done under the same condition (same volumes and media for the standards and samples), because as it has been seen, a huge volume of rinse solution or sample modifies the retention pattern along the cartridge.

3.4. Capacity and retention of stable metals

The study of how some stable isotopes are retained in PSresins is of interest as this not only indicates the capacity of the PSresins, but it also provides information about potential stable tracers or stable interferences.

Iron(III) was studied since it is an element commonly found in real samples and its predominant valence state, III, shows affinity for diphosphonic acid-based resins. Europium(III) was also studied as it may
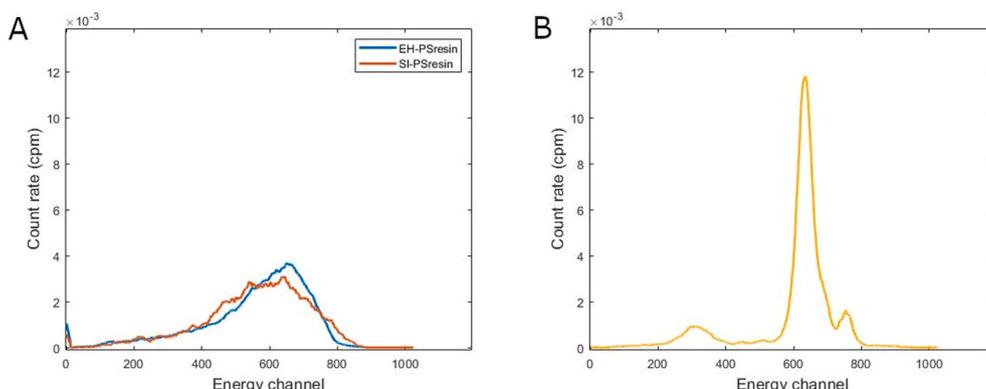
Fig. 6. Normalised spectra of [226]Ra in the: (A) EH-PSresin and SI-PSresin cartridges; and (B) effluent solutions measured through LS.
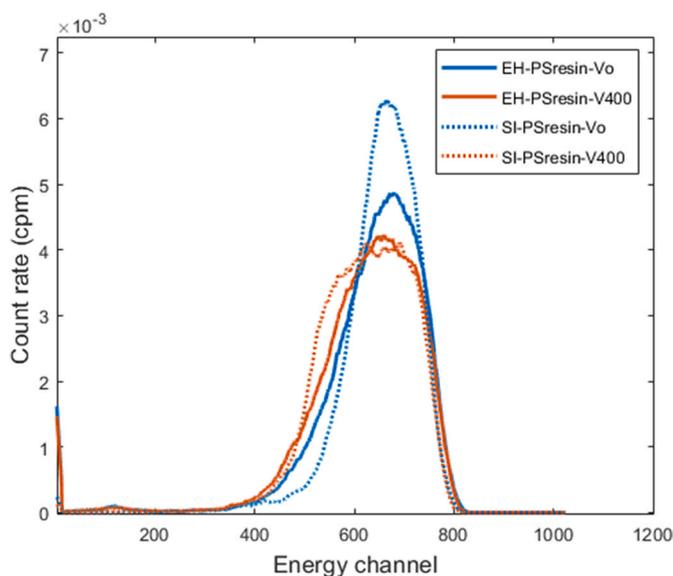
Fig. 7. Normalised spectra for EH-PSresin (continuous line) and SI-PSresin (dashed line) for ^{241}Am. Vo corresponds to the initial spectrum and V400 corresponds to that obtained after passing 400 mL of 0.5 M HCl.

also have a high affinity for the resin and it might be used as a tracer in the extraction process of actinides given its extremely low concentration in samples. Since U, Th, Pu and Am have not stable isotopes, in order to trace its retention in the PSresin in a sample, an element with similar behaviour to them (an analogue) can be used to quantify the yield of the retention. In this situation through a mass balance between the amount of europium spiked in the sample and the amount it is found in the PSresin cartridge effluent, we could know the amount of the analogous radionuclide that has been retained in the PSresin cartridge because all behave similarly in terms of retention into this PSresin. Nevertheless, for its application in real samples, it must be studied further how a non-simple matrix sample could affect the retention and behaviour in the PSresin cartridge of the different actinides and europium.

Both resins for the two elements studied presented similar behaviour since retention profile (supplementary material) and maximum amount of metal retained in each resin (Table 4) are similar. The maximum amount of metal retained was achieved after passing around 2 mg of iron (III) through both resins. For europium (III), EH-PSresin presented a slightly higher capacity than SI-PSresin. This capacity of each resin was relatively low. These results indicated that trivalent metals can become an important interferent in terms of retention, particularly iron(III), which is commonly found in real samples. However, this can be overcome by reducing iron(III) into iron(II) with ascorbic acid. Moreover, despite the relatively low capacities, europium could be used as a stable tracer in the analysis of radionuclides since it is normally not found in real samples and spiking with a low amount (less than 1 mg) would be enough.

However, the low capacity could be improved by increasing the amount of extractant used for the preparation of both PSresins.

3.5. Alpha/beta discrimination

The results obtained in the analysis of the different alpha emitters showed that diphosphonic acid-derived resins were also capable of

Table 4
Capacity of EH-PSresin and SI-PSresin to retain iron(III) and europium(III).

	EH-PSresin	SI-PSresin
Fe (mg/g PSresin)	2.06	1.88
Eu (mg/g PSresin)	2.78	2.13

retaining some beta emitters (e.g., ^{90}Y in 2 M HNO$_3$). It was therefore worth evaluating the ability of PSresins to discriminate between signals produced by alpha and beta particles, taking advantage of the principle that beta pulses are faster than alpha pulses in organic scintillators. To evaluate alpha/beta discrimination, a ^{90}Sr/^{90}Y solution in 2 M HNO$_3$ (where ^{90}Y is the beta emitter retained in the PSresin), as well as ^{241}Am and ^{238}Pu solutions in 0.5 M HCl, were passed through a PSresin cartridge and measured at different values of the pulse shape discriminator parameter, PSA, of the Quantulus detector.

Fig. 8 shows the alpha and beta misclassification errors obtained at different PSA values. Both EH-PSresin and SI-PSresin showed similar behaviour (slightly better for EH-PSresin) regarding beta discrimination, with a wrong classification at low PSA values and correct classification at values above 175. For alpha discrimination, a similar behaviour was observed for americium, but not for plutonium, where the misclassification differed slightly, being higher in EH-PSresin than in SI-PSresin. The different behaviour for ^{241}Am and ^{238}Pu can be attributed to the different shapes of the spectra (Fig. 4), since ^{238}Pu had a queue at low energies that tended to be classified as beta. The different behaviour of ^{238}Pu in EH-PSresin and SI-PSresin regarding ^{241}Am can be attributed to factors such as the retention pattern, which can introduce variability in the scintillation process being this variability higher for Pu than for Am.

The values of misclassification at the crossing points are shown in Table 5.

The results demonstrated that alpha/beta discrimination was possible using a compromise PSA value to obtain information about the activity derived from beta and alpha emitters.

4. Conclusions

A method for synthesising PSresins to analyse actinides using three diphosphonic acid-based extractants was successfully developed. All three PSresins showed a smooth and homogeneous immobilisation of the extractant. Among the three PSresins, the ones with a 2-ethylhexyl (EH-PSresin) and 3-(trimethylsilyl)-1-propanyl (SI-PSresin) radical chain showed quantitative retention of ^{241}Am, 100% detection efficiencies and no quenching effects, with their spectrum located at high energies. By contrast, the PSresin developed with an extractant containing a benzylic radical chain had a low retention of ^{241}Am and presented a broad spectrum located at low energies. This behaviour was attributed to the steric effects generated by the benzylic radical that affected the interaction between the radionuclide and the extractant as well as the chemical quenching effects caused by the benzyl radical.

EH-PSresin and SI-PSresin presented very similar behaviour in the quantitative retention of ^{241}Am, ^{238}Pu, ^{230}Th and ^{NAT}U. Regarding other common alpha emitters such as ^{210}Po and ^{226}Ra, their retention was not quantitative and more studies are required to identify the medium in
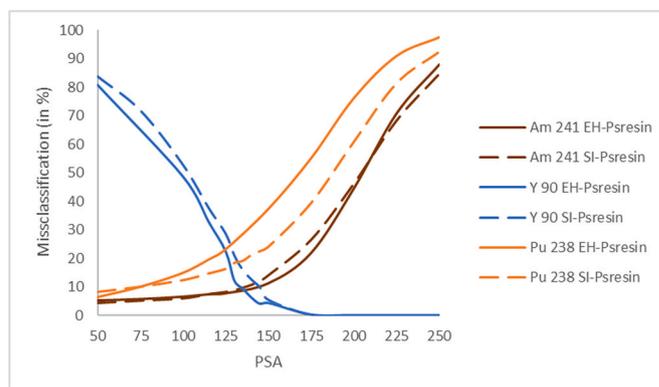
Fig. 8. Alpha and beta classification at different PSA values with EH-PSresin (continuous line) and SI-PSresin (dashed line) for ^{241}Am and ^{238}Pu as the alpha emitters and ^{90}Sr/^{90}Y as the beta emitter.

Table 5

Misclassification error for each PSresin in the crossing points and for the different radionuclides.

	EH-PSresin			SI-PSresin		
	crossing PSA point	Beta (%)	Alpha (%)	crossing PSA point	Beta (%)	Alpha (%)
[241]Am	150	6	11	150	5	14
[238]Pu	125	22	30	135	16	19

which these alpha emitters would be retained in order to develop a method for calculating the gross alpha.

The PSresins also showed high retention of beta emitters such as Bi (III) and Y(III), which could lead to the development of applications based on the analysis of these radionuclides.

The capacity of EH-PSresin and SI-PSresin was established to be around 2 mg for Fe(III) and 2.5 mg for Eu(III). Despite the low capacities, these can be used for tracing purposes since the natural concentration of Eu is very low. Moreover, capacity can be improved by increasing the amount of the extractant coating the PSm or by using porous PSm.

Taking everything into consideration, EH-PSresin and SI-PSresin behaved equally in terms of retention yield, detection efficiency, quenching, capacity and alpha/beta discrimination. Both are promising new PSresins that could be used to develop new methods for the total gross alpha test or in actinide analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apradiso.2021.109969.

References

Bagán, H., Tarancón, A., Rauret, G., García, J.F., 2011. Radiostrontium separation and measurement in a single step using plastic scintillators plus selective extractants. Application to aqueous sample analysis. Anal. Chim. Acta 686, 50–56. https://doi.org/10.1016/j.aca.2010.11.048.

Chiarizia, R., Horwitz, E.P., Rickert, P.G., Herlinger, A.W., 2007. Acids. Part 1. P,P''-Di(2-Ethylhexyl) methanediphosphonic acid. Solvent Extr. Ion Exch. 14, 773–792. https://doi.org/10.1080/07366299608918368.

Coma, A., Tarancón, A., Bagán, H., García, J.F., 2019. Automated separation of 99Tc using plastic scintillation resin PSresin and openview automated modular separation system (OPENVIEW-AMSS). J. Radioanal. Nucl. Chem. 321, 1057–1065. https://doi.org/10.1007/s10967-019-06659-7.

Duval, Christine E., Devol, Timothy A., Husson, Scott M., 2016. Extractive scintillating polymer sensors for trace-level detection of uranium in contaminated ground water. Anal. Chim. Acta 947. https://doi.org/10.1016/j.aca.2016.09.029. Elsevier Ltd: 1–8.

Duval, C.E., Hardy, teven Pellizzeri, DeVol, Timothy A., Husson, Scott M., 2019. Phosphonic acid and alkyl phosphate-derivatized resins for the simultaneous concentration and detection of uranium in environmental waters. React. Funct. Polym. 137, 133–139. https://doi.org/10.1016/j.reactfunctpolym.2019.01.015.

Egorov, O.B., O'Hara, J.W., M.J., J.W.G., 2006. Equilibration-based preconcentrating minicolumn sensors for trace level monitoring of radionuclides and metal ions in water without consumable reagents. Anal. Chem. 78, 5480–5890.

Eichrom, 2014. Gross Alpha Radioactivity in Water Analytical Procedure, pp. 1–4.

España, 2016. Real Decreto 314/2016. In: BOE-A-2016-7340, vol. 183. Boletin Oficial del Estado, pp. 53106–53126.

Griffith-Dzielawa, J.A., Barrans, R.E., McAlister, D.R., Dietz, M.L., Herlinger, A.W., 2000. Synthesis and characterization of di-[3-(trimethylsilyl)-1-propylene] alkylenediphosphonic acids. Synth. Commun. 30, 2121–2132. https://doi.org/10.1080/00397910008087391.

Horwitz, E.P., Chiarizia, R., Dietz, M.L., Diamond, H., Nelson, D.M., 1993. Separation and preconcentration of actinides from acidic media by extraction chromatography. Anal. Chim. Acta 281, 361–372. https://doi.org/10.1016/0003-2670(93)85194-O.

Horwitz, E.P., Chiarizia, R., Dietz, M.L., 1997. DIPEX: a new extraction chromatographic material for the separation and preconcentration of actinides from aqueous solution. React. Funct. Polym. 33, 25–36. https://doi.org/10.1016/S1381-5148(97)00013-8.

Hughes, L., DeVol, T.A., 2003. On-line gross alpha radiation monitoring of natural waters with extractive scintillating resins. Proc. tenth Symp. Radiat. 505, 435–438. https://doi.org/10.1016/S0168-9002(03)01115-X.

Jay, W., Grate, M.J., Egorov, O.B., 2020. Automated radiochemical separation, analysis, and sensing. In: Handbook of Radioactivity Analysis, vol. 2. Eliesever, Amsterdam, pp. 821–879.

L'Annunziata, M.F., 2007. Radioactivity. Introducction and History. Eliesever Science B.V., Amsterdam.

Lluch, E., Barrera, J., Tarancón, A., Bagán, H., García, J.F., 2016. Analysis of 210Pb in water samples with plastic scintillation resins. Anal. Chim. Acta 940, 38–45. https://doi.org/10.1016/j.aca.2016.08.004.

L'Annunziata, M.F., 2020. Flow-cell radionuclide analysis. In: Handbook of Radioactivity Analysis, vol. 2. Eliesever, Amsterdam, ISBN 9780128143971, pp. 729–820.

McAlister, D.R., Dietz, M.L., Chiarizia, R., Herlinger, A.W., 2001. Metal ion extraction by silyl-substituted diphosphonic acids. I. P,P'-di[3-(trimethylsilyl)-1-propylene] methylene- and ethylenediphosphonic acids. Separ. Sci. Technol. 36, 3541–3562. https://doi.org/10.1081/SS-100108348.

Navarro, N., Rodriguez, L., Alvarez, A., Sancho, C., 2004. Rapid determination of alpha emitters using Actinide resin. Appl. Radiat. Isot. 61, 287–291. https://doi.org/10.1016/j.apradiso.2004.03.023.

Rim, Jung H., 2013. Development of Novel Method for Rapid Extract of Radionuclides from Solution Using Polymer Ligand Film. The Pennsylvania State University, state collage.

Rim, J.H., Armenta, C.E., Gonzales, E.R., Ünlü, K., Peterson, D.S., 2016. Evaluating bis(2-ethylhexyl) methanediphosphonic acid (H2DEH[MDP]) based polymer ligand film (PLF) for plutonium and uranium extraction. J. Radioanal. Nucl. Chem. 307, 2327–2332. https://doi.org/10.1007/s10967-015-4444-3.

Roane, J.E., DeVol, T.A., 2002. Simultaneous separation and detection of actinides in acidic solutions using an extractive scintillating resin. Anal. Chem. 74, 5629–5634. https://doi.org/10.1021/ac026050z.

Roane, J.E., DeVol, T.A., 2005. Evaluation of an extractive scintillation medium for the detection of uranium in water. J. Radioanal. Nucl. Chem. 263 (1), 51–57. https://doi.org/10.1007/s10967-005-0011-7.

Sáez-Muñoz, M., Bagán, H., Tarancón, A., García, J.F., Ortiz, J., Martorell, S., 2018. Rapid method for radiostrontium determination in milk in emergency situations using PS resin. J. Radioanal. Nucl. Chem. 315, 543–555. https://doi.org/10.1007/s10967-017-5682-3.

Santiago, L.M., Bagán, H., Tarancón, A., Garcia, J.F., 2013. Synthesis of plastic scintillation microspheres: evaluation of scintillators. Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip. 698, 106–116. https://doi.org/10.1016/j.nima.2012.09.028.

Seliman, A.F., Helariutta, K., Wiktorowicz, S.J., Tenhu, H., Harjula, R., 2013. Stable and selective scintillating anion-exchange sensors for quantification of 99TcO4- in natural freshwaters. J. Environ. Radioact. 126, 156–164. https://doi.org/10.1016/j.jenvrad.2013.07.025.

Seliman, A.F., Bliznyuk, V.N., DeVol, T.A., 2017. Development of stable extractive scintillating materials for real-time quantification of radiostrontium in aqueous solutions. J. Radioanal. Nucl. Chem. 314, 743–751. https://doi.org/10.1007/s10967-017-5420-x.

Tarancón, A., Bagán, H., García, J.F., 2017. Plastic scintillators and related analytical procedures for radionuclide analysis. J. Radioanal. Nucl. Chem. 314 (2), 555–572. https://doi.org/10.1007/s10967-017-5494-5.

Tarancón, A., Bagán, H., García, J.F., 2021. Plastic scintillators in environmental analysis. In: Hamel, M. (Ed.), Plastic Scintillators. Topics in Applied Physics, vol. 140. Springer, Cham.

Triskem, 2015a. PRODUCT SHEET TRU Resin.

Triskem, 2015b. PRODUCT SHEET UTEVA Resin.

Zagyvai, M., Vajda, N., Groska, J., Molnár, Z., Bokori, E., Szeredy, P., 2017. Assay of actinides in human urine by rapid method. J. Radioanal. Nucl. Chem. 314, 49–58. https://doi.org/10.1007/s10967-017-5363-2.