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Fast analysis of gross alpha with a new plastic scintillation resin

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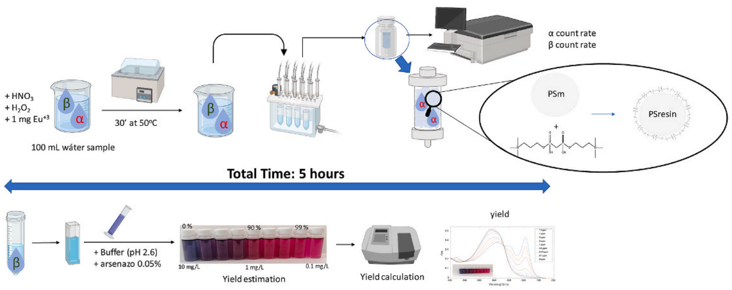
HIGHLIGHTS

- New method to measure gross alpha parameter by using a plastic scintillation resin.
- A quantitative retention and 100% detection efficiencies at pH 2 was achieved.
- Gross alpha parameter was measured in less than 5 h.

GRAPHICAL ABSTRACT



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ABSTRACT

Radionuclides analysis is a complex task, with high time and economic costs. In decommissioning activities and environmental monitoring, it is very evident, in which, to obtain an appropriate information, it is necessary to perform as many analyses as possible. The number of these analyses can be reduced using screening gross alpha or gross beta parameters. However, the currently used methods cannot give an answer as fast as it would be desired and, moreover, more than 50% of the results reported in the interlaboratory exercises fall outside the acceptance range.

This work presents the development of a new material and method to gross alpha activity determination using a plastic scintillation resin (PSresin) in drinking and river water samples. A specific procedure was developed involving a new PSresin (using bis-(3-trimethylsilyl-1-propyl)-methanediphosphonic acid as an extractant) that is selective for all actinides, radium and polonium. Quantitative retention and 100% detection efficiencies were obtained at pH 2 with nitric acid. PSA value of 135 was used for α/β discrimination. Eu was used to determine or estimate retention in sample analyses. The method developed can measure, in less than 5 h from the reception of the sample, the gross alpha parameter with quantification errors comparable or even lower to those obtained with conventional methods.

1. Introduction

Nuclear energy production is gaining increasing awareness due to its lack of CO_2 emissions and its ability to generate electricity without any greenhouse effect [1]. However, possible accidents and radioactive waste generation pose risks for human beings and the environment,

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leading to different controversial opinions about its use. On one side, some countries have chosen to break ties with the generation of electricity through nuclear energy. In these countries, many nuclear facilities have reached their operational lifetime. Consequently, radioactivity measurements have to be performed to check if the wastes generated during this decommissioning process can be classified and treated as radioactive residue or not. On the other side, there are some countries that have chosen to rely on nuclear energy to generate electricity, increasing the number of nuclear power plants. In these countries, radioactivity analyses will become commonplace in the laboratories, mainly for environmental surveillance purposes.

Therefore, radioactivity analyses will continue being something needed in the upcoming years, including the determination of specific radionuclides or screening parameters based on gross activity for the assessment of radioactivity content. In general, screening parameters are used to determine if the samples require an exhaustive analysis of specific radionuclides or can be directly classified as non-radioactive. Avoiding the use of complex, laborious and unnecessary selective procedures. The two most important screening parameters for radioactivity assessment are gross alpha and gross beta which are assessed in several situations such as: the classification of wastes generated in normal operations of a nuclear installation or in the dismantling process; first risk evaluation when a disaster (e.g., a nuclear attack or an accident) occurs; assessment of the indicative dose to determine the potability of drinking water. At first sight, it can be seen that these parameters are important in providing a first indication of presence of radionuclides they must be measured reliably and as quickly as possible.

As said before, water intended for drinking purposes must have radioactivity parametric values that comply with national and international standards before being accepted for human consumption [2,3]. The Euratom Drinking Water Directive established gross alpha parameter as one of those of concern for water monitorization. The current parametric limit is 0.1 Bq L^{-1} [4] and encompasses all the alpha-emitting radionuclides once radon has been eliminated (i.e. actinides plus ^{226}Ra and ^{210}Po).

There are some methods for gross alpha activity measurement in water samples. Most of them conduct the measurement with proportional counter or with liquid scintillation counter (LSC) [5,6]. Normally, the pretreatment consists on an evaporation [7] or a co-precipitation [8,9]. These procedures present some problems such as the potential loss of polonium; sample losses during evaporation of salty samples; or non-quantitative precipitation. Moreover, the measurement of gross alpha activity is affected by different factors such as the response of the detector depending on the alpha-emitting radionuclide energy, the radionuclide used as the standard in the calibration, the time delay between the pretreatment and the measurement, the amount of salt (solid residue) in the water sample, the misclassification between alpha and beta signals, and the quenching correction that might be applied for colored samples in the LSC measurements. Due to that, it is commonly accepted that laboratories can present a deviation up to 30% in their measurements [6,9,10]. However, approximately 60–70% of the results obtained in the interlaboratory exercises fall outside the acceptance range. This is because some of the operational parameters mentioned above, particularly the dependence on the calibration radionuclide and the attenuation due to salt content, have a large impact on the final results and, consequently, large differences between laboratories are observed. For that reason, there is still a need to simplify the gross alpha activity determination using a faster method, but also to reduce the variability of this determination.

This work shows the development of a new material and new method to gross alpha activity determination in drinking and river water samples using a plastic scintillation resin (PSresin). A PSresin is composed of plastic scintillation microspheres (PSm) [11] coated with a selective extractant and then packed in a solid-phase extraction (SPE) cartridge, giving as a result a material that unifies the extraction and measurement step. PSresins have been used previously for ^{90}Sr and ^{99}Tc [12,13]. In the present work, a new PSresin, named α-PSresin using bis-(3-trimethylsilyl-1-propyl)-methanediphosphonic acid was developed. The high retention and detection efficiency of α-PSresin make it suitable for a simplified method to measure the gross alpha activity, which would involve only passing the sample through an SPE cartridge containing the PSresin followed by its measurement. Compared to the classical methods based on proportional counters and liquid scintillation, the PSresin methods present the general advantage of having a lower background, as only 1 g of the scintillator is placed on the counter (instead of the 20 mL of sample and scintillator for LSC), leading to equivalent limits of detection with less counting time. Moreover, sample treatment is reduced as the sample only has to be passed through the PSresin. Another potential advantage would be that the extractant does not retain anions or small cations (i.e., K or Na). This implies that autoabsorption of the alpha particles, as happens in proportional counter, would be avoided, and that ^{40}K would not interfere within the measurements, as happens in LSC, reducing misclassification due to beta particles. Another advantage of the use of PSresin for the gross alpha parameter determination is that polonium would be also detected since there is no evaporation step where it could be lost. Moreover, as the method would be faster and easier, more than one sample could be analyzed at the same time. Finally, compared to LS, as no mixed wastes will be generated, the proposed method would be a “green-chemistry” alternative for the gross alpha parameter determination.

2. Experimental section

2.1. Materials

α-PSresin was prepared by coating plastic scintillation microspheres (PSm) with Bis(trimethylsilylpropanyl)methanediphosphonic acid in isopropanol [14]. Extractant was synthesized using 3-(trimethylsilyl)-1-propanol (97%) and *N*,*N*′-diisopropylcarbodiimide (DIC) (98% purity) from Merck (Darmstadt, Germany) and methylenediphosphonic acid (99+%) from Alfa Aesar (Kendal, Germany). PSm were prepared by using the evaporation/extraction method [11].

Non-radioactive standards used include a 1000 mg L^{-1}europium solution from Inorganic Ventures (Christiansburg, USA). Radioactive standards used were: 38.5 (0.3) Bq/g^{90}Sr/^{90}Y, 46.3 (1.4) Bq/g^{238}Pu, 47 (1) Bq/g^{241}Am; 2.22 (0.03) Bq/g uranium (^{238}U + ^{235}U + ^{234}U); 2.38 (0.07) Bq/g^{230}Th; 4.0 (0.1) Bq/g^{226}Ra; and 160 (5) Bq/g^{210}Pb. Radioactive solutions were supplied by different providers. ^{210}Po was obtained by passing the ^{210}Pb solution (containing in equilibrium ^{210}Bi and ^{210}Po) through an Sr-resin (TrisKem International (Rennes, France)) in a 3-M nitric acid medium (retaining ^{210}Pb and ^{210}Po) and then eluting ^{210}Po with 0.1 M nitric acid.

0.05% arsenazo (III) solution was prepared using a buffer solution of pH 2.6–2.8 that was obtained by mixing monochloroacetic acid and sodium acetate in 100 mL of deionized water.

2.2. Procedures

2.2.1. Retention profile of iron

α-PSresin capacity was determined as the plateau of a retention profile curve. This curve was obtained by measuring the Fe(III) in the 2 mL eluted solutions generated after passing 50 mL of a 1000 mg L^{-1} iron (III) solution through 1 g of α-PSresin. Solution medium was 0.5 M HCl and iron (III) was analyzed with a Optima 8300 ICP-OES equipment (PerkinElmer, Waltham, USA).

2.2.2. Batch study

For the batch study, 0.1 g of α-PSresin was weighed in a 14 mL glass cylindric tub together with 3 mL of the corresponding medium containing 1.4–1.6 Bq of the radionuclide under study (^{241}Am, ^{238}Pu, ^{230}Th, ^{236}U, ^{210}Po and ^{226}Ra). For Sr, Y and Pb, the same study was performed, but with the addition of 0.2 mg of the stable isotope instead of the radioactive. After 24 h of agitation, the resulting supernatant was filtered with disk filters (0.45 μm) and measured together with 2 mL of double-deionized water and 15 mL of OptiPhase Supermix liquid scintillating cocktail in a Quantulus liquid scintillation spectrometer (both from PerkinElmer (Waltham, USA)) for 1 h. In the case of the stable isotopes, the same procedure was followed, but the measurement was performed through ICP-OES in a 1% nitric acid medium.

The media studied were: HNO_3, HCl and H_3PO_4 within the range of 0.5–8 M and at pH 1, 2, 4 and 7.

2.2.3. *Standard sample analysis*

11 mL samples of known activity were prepared by adding to a 20 mL vial the corresponding radioactive solution, water and nitric acid to a final pH 2. Standard samples were measured with the α-PSresin in a 2 mL cartridge using a the twelve-position vacuum chamber (TrisKem International, Rennes, France) and employing the common procedure for separations with PSresins [14].

After the separation, the dried α-PSresin cartridge was counted in the Quantulus to determine the detection efficiency. The α-PSresin was also measured at several PSA values. An aliquot of the collected wastes was also measured by liquid scintillation (6:14 sample:cocktail proportion) to determine the separation yield.

Ra not retained was determined through secular equilibrium with the descendants following the UNE-EN ISO 13164–4_2020 test method [15].

All the standard samples were analyzed in triplicate.

2.2.4. *Sample analysis*

100 mL of sample was acidified with nitric acid up to a pH of 2. Hydrogen peroxide was added to reach a 1% concentration. Moreover, the sample was spiked with 1 mg of europium, which is a tracer for alpha-emitting radionuclides. Next, it was treated for 30 min at 50 °C to assure a correct valence adjustment. The resulting solution was then measured with the α-PSresin.

Six real samples (A21/074, A21/031, A21/044, A21/071, A21/118 and Mreal_1) taken from different places in Catalonia (Spain) and 3 interlaboratory samples (JRC-GAB-1, JRC-GAB-2 and IAEA-TEL-2021-03 (sample 5)) were analyzed. One of the real samples (Mreal_1), which had been fully characterized previously and contained naturally occurring radionuclides, and one of the interlaboratory samples (IAEA-TEL-2021-03 (sample 5)), containing artificial radionuclides, were used to define the optimum PSA value for the measurements. Therefore, both were measured at the most promising PSA values: 135, 150 and 175. The other samples were measured at the optimum PSA value of 135. The real samples were previously measured at the Laboratori de Radioactivitate Ambiental (LRA) of the Universitat de Barcelona using the LSC method [6]. Moreover, for the Mreal_1 a determination of all the alpha emitters found in the sample was also done by the LRA.

2.2.5. *Retention determination*

Two strategies were followed to determine retention: estimation through a visual check and determination with UV–Vis spectrophotometry. Both were based on the formation of a colored complex of Eu with arsenazo (III).

The visual check consisted of taking 10 mL of the effluent solution and adding to it 8 mL of a buffer solution (pH 2.6–2.8) and 1 mL of a 0.05% arsenazo solution. The obtention of a reddish colored solution, similar to that of the arsenazo solution, indicates a retention of Eu higher than 90%, whereas a purple solution indicates that Eu has not been fully retained in the PSresin.

The same solutions were also measured by UV–Vis spectrophotometry at 654 nm. The calibration curve was from 0.1 to 10 mg L^{-1}.

2.2.6. *Scintillation measurement conditions*

The Quantulus detector was configured at low CB and ^{14}C MCA. α-PSresin and effluent solutions were both counted for 1 h.

The PSresin was also measured in the “PSA” configuration at the following PSA values for 15 min each: 50, 75, 100, 115, 125, 130, 135, 140, 145, 150, 175, 200, 225 and 250.

The PSresin used for the real and interlaboratory samples was measured under the optimum PSA for 2 h each. The effluent solutions were measured for 5 h.

2.2.7. *Data treatment*

Scintillation spectra were smoothed with the Savitzky–Golay filter (21 points and a first-degree polynomial). Detection efficiency corresponds to the net count rate divided by the activity retained in the α-PSresin.

Alpha misclassification for the alpha standards corresponds to the percentage of the counts in the beta window (1:1024) divided by the total counts. Beta misclassification for the beta was calculated the percentage of the counts in the alpha window (1025:2048) divided by the total counts.

Gross alpha activity (A in Bq L^{-1}) was calculated with the following equation:

$$A = \frac{\frac{CpmA*Effb-CpmB*Intb}{Effa*Effb-Inta*Intb}}{V*60} \tag{1}$$

where, CpmA the net count rate in the alpha window (in cpm), CpmB the net count rate in the beta window (in cpm), Effa the detection efficiency of the alpha-emitting radionuclides in the alpha window, Effb the detection efficiency of the beta-emitting radionuclides in the beta window, Inta is the misclassification of alphas in the beta window, Intb the misclassification of betas in the alpha window, and V the volume of the sample analyzed (in L).

The combined standard uncertainty was calculated with the following equation using the 20.06.6 version of the wxMaxima free access software:

$$u_c\left(A\left(x_1-x_{2,\ldots}\right)\right)=\sqrt{\sum\left(\frac{\partial A}{\partial x_i}\right)}u\left(x_i\right)^2 \tag{2}$$

where A is the function given in Equation (1), xi the different variables on which the value of A depends, and u (xi) the standard uncertainties of each variable.

The detection limit was established theoretically using the Currie equation [16].

3. Results and discussion

A previous study [17] tested the viability of different extractants in the development of a new PSresin. Bis(trimethylsilylpropanyl)methanediphosphonic acid was chosen as the most promising extractant for the development of a new PSresin to measure gross alpha thanks to the actinides high retention and the good α/β discrimination. The development and optimization of this new PSresin, named α-PSresin, and the fast analysis of water samples is described herewith.

3.1. *α-PSresin optimization*

In order to be able to prepare a PSresin in a bigger scale, the first objective was to improve the synthesis method of the extractant to obtain a purer compound with a high synthesis yield. The main problem was that some sub-products generated during the synthesis (i.e. urea) were partially soluble in organic solvents and water. As consequence, their extraction during the work up was not complete regardless the separation procedure used. Therefore, the synthesis procedure was modified first by changing the reaction solvent from tetrahydrofuran to dichloromethane and the volumes used. On the one hand, the initial volume of solvent in which methanediphosphonic acid and 3-trimethylsilyl-1-propanol were mixed and refluxed was reduced. On the other hand, the solvent volume in which the coupling agent was dissolved was increased, to obtain a diluted solution that promoted the formation of the disubstituted compound. Moreover, dropwise addition over 3 h promoted the disubstitution reaction. It must be also mentioned that *N*, *N*′-dicyclohexylcarbodiimide (DCC) was replaced with *N*,*N*′-diisopropylcarbodiimide (DIC) as the coupling agent. The main reason for this substitution was that the urea derivative compound occurring as a subproduct of the reaction was easier to extract when DIC was used, making the process easier and producing a purer compound. 3-dimethylamino-propyl-ethyl-carbodiimide (EDC) was also tested due to its lower size compared with DIC and DCC. However, the main product obtained was the tetra-substituted compound instead of the desired disubstituted compound. Finally, an N_2 purge was included in all the synthesis steps. As a result, the extractant obtained had a high purity (>95%) if we consider the RMN spectrum and the yield was 70%, in accordance to the acceptable yield previously obtained for a similar kind of molecule [20].

Once the synthesis of the extractant was optimized, the amount of extractant deposited on the PSm surface was studied. Increase on the extractant amount would lead to the increase of the capacity of the column. However, an excess of it, detectable though visual observation in the scanning electron microscopy (SEM), may cause problems in the pass of the solution through the column bed, affecting retention, or even quenching, due to the attenuation of the alpha particles emitted, affecting detection efficiency. Two different proportions of PSm to extractant were tested: 1:1/6 and 1:1/4. Evaluation of the α-PSresins prepared was done by comparing those parameters for both proportions.

Detection efficiency and retention was determined by analyzing with the PSresin a standard sample of ^{241}Am in a medium of 0.5 M HCl. As can be seen in Fig. 1, there were no significant changes in the spectrum position. Retention and detection efficiency were 100% for both proportions.

Therefore, it was confirmed that there was no significant difference between the two proportions tested and that the extractant layer added on the scintillating support did not generate additional particle quenching effects.

The capacity of the resin was also checked in order to know which is the amount of sample that could be passed through the cartridge This is relevant for the analytical purposes of the α-PSresin as capacity determines the possibility of directly passing a large volume of water sample through the resin without any further treatment. This study was performed with iron as it is known that iron is also retained in this extractant [14]. Table 1 shows the capacities obtained for α-PSresin for both proportions and with the old extractant.

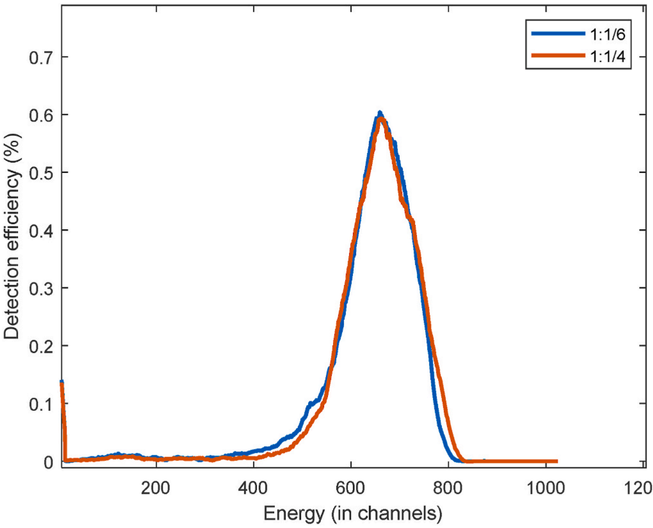

Fig. 1. Comparison of the detection efficiency spectra for different PSm: extractant proportions for a ^{241}Am standard measure.

Table 1
Amount of Fe retained in α-PSresin at two immobilization proportions and with the old extractant.

	1:1/6 PSresin (old extractant	1:1/6 α-PSresin	1:1/4 α-PSresin
Fe retained mg/g PSresin	1.88	4.01	5.81

The optimization of the extractant improved the capacity, which was doubled when comparing the same proportions of the old extractant (1:1/6 PSresin) and the new one (1:1/6 α-PSresin). This confirms that increase on the purity of the extractant lead to more binding active sites. Moreover, it is worth to remark that with a proportion of 1:1/4, the amount of iron retained increased and was around 6 mg. This capacity is big enough ensure a correct water analysis involving the PSresin, taking into consideration the amount of possible stable interfering elements that a river or drinking water could contain (e.g. Fe, Ca), and that the affinity of the extractant for actinides is several orders of magnitude higher than for those elements [17].

Finally, morphology was studied by SEM to evaluate the homogeneity of the recovery. The images obtained with a JSM-7100 F JEOL (Tokyo, Japan) scanning electron microscope from the CCiTUB (Fig. 2) showed that α-PSresin was homogenously coated for both proportions. It might seem that a slight excess of extractant occurred when the proportion of the extractant was increased, as the quantity of extractant in the 1:1/4 proportion seems to be more than the necessary to cover the support and some aggregation takes place. Nevertheless, as the 1:1/4 proportion presented a higher capacity, probably due to this excess of extractant; detection efficiency and recovery were unaffected; no extractant losses were detected; and it did not show problem of solution pass throw the column, it was selected for the subsequent experiments.

3.2. *Batch study of α- and β-emitters*

In order to determine the gross alpha parameter, the retention of all actinides without the retention of the beta emitters, would be desirable. The retention of actinides in bis(trimethylsilylpropanyl)methanediphosphonic acid in 0.5-M HCl was shown to be quantitative in a previous study [17]. However, Ra and Po, both alpha emitters with a natural origin, were not quantitatively retained in this medium. Therefore, a more detailed study of the retention media was performed. The different acid media and their concentrations were chosen based on the previous knowledge on this type of extractants [18–23] and the contact time, 24 h, was selected to ensure enough time for the interaction between the radionuclide and α-PSresin.

The retention curves obtained for several nitric acid concentration is shown in Fig. 3a. The retention profiles obtained with the other acids (HCl and H_3PO_4) were similar and can be checked in detail in the Supplementary Information figures (SI).

In one hand, the retention of all actinides was quantitative in all the concentrations studied which agrees with the very strong affinity of diphosphonic extractants for actinides at different oxidation states described in the literature. On the other hand, the retention of the beta emitters was, in general, low at high acid concentrations, with a small retention of some trivalent beta-emitting radionuclides such as ^{210}Bi or ^{90}Y at HNO_3 8 M. Other alpha emitters, such as polonium and radium, which might be relevant for the measurement of the gross alpha parameter, are not retained at these high acid concentrations, but they are quantitatively retained in low acid concentrations. This means that the extractant is also capable to be linked to divalent elements at low acidic concentrations. As the priority is the retention of all the alpha emitting radionuclides, and the contribution to the scintillation signal of those betta emitter radionuclides retained can be suppressed or corrected through the alpha/beta discrimination analysis, the range of pH between 1 and 7 was studied in more detail (Fig. 3b). In this range, there

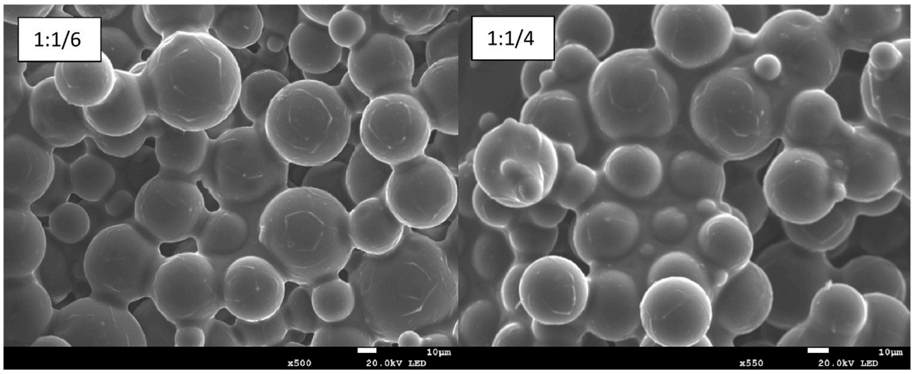

Fig. 2. Comparison of the α-PSresin coating for two different proportions 1:1/6 (left) and 1:1/4 (right) using SEM images.

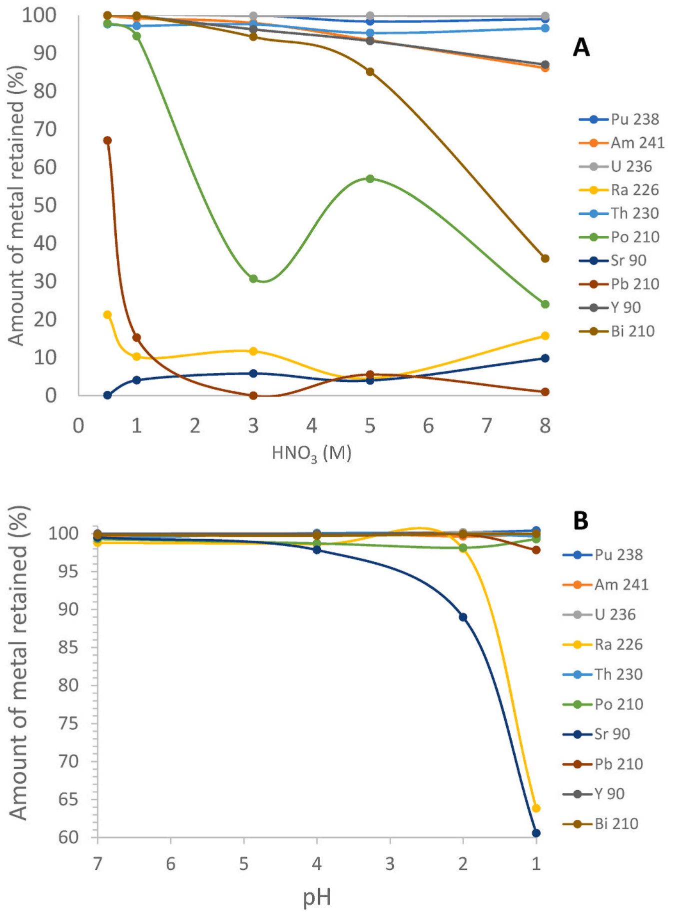

Fig. 3. Results from the batch study. Proportion of metal retention (%) at nitric acid concentrations between 0.5 M and 8 M (A) and at pH values from 1 to 7 (B).

was quantitative retention of radium at pH 2 along with a non-quantitative retention of strontium. Therefore, pH 2 with HNO_3 was chosen as working medium, with the additional advantage that it provided an analytical procedure without the requirement for any further pretreatment, since samples typically arrive acidified at pH 2. It is also important to remark that even in a neutral aqueous medium, without the addition of acid, the retention of all the alpha emitting elements was high.

3.3. *Quality parameters of the α-PSresin in a cartridge*

The retention of alpha emitters in the α-PSresin cartridge can change from the observed in the batch study because it also depends on the contact time or the pass of the solution through the column. Therefore, the α-PSresin cartridge retention of each radionuclide, in the normal working conditions of a column separation, was studied. This also permitted the determination of the detection efficiency under the chosen working medium, pH 2, for each radionuclide.

In the first trials, all the actinides were quantitatively retained, with a detection efficiency of 100%. However, ^{210}Po showed a non-quantitative retention. This was because its valence state was not adjusted to IV. To ensure the oxidation of all polonium into polonium (IV) hydrogen peroxide was added ot the samples (final concentration of 1%) and they were incubated for 30 min at 50 °C in a water bath. The retention and the detection efficiency of each radionuclide found in these conditions can be seen in Table 2.

The study of the retention of radium in the cartridge was possible to be done due to a previous purification [24] of the ^{226}Ra standard in which all the daughter radionuclides (in particular ^{210}Pb and ^{210}Po) were removed, leaving the solution free of other radionuclides [15]. However, it was not possible to quantify the detection efficiency as some subproducts, probably I_2, from the purification process still remained in the solution. Although the amount was small and did not interfere with the retention of radium, it was enough to produce quenching and disturb the spectrum and the determination of the detection efficiency in the α-PSresin. However, taking into consideration that its energy (4.87 MeV) is between that of ^{236}U (4.57 MeV) and ^{238}Pu (5.59 MeV) and leaving aside other parameters that could also affect the measurement such as retention pattern or oxidation state, it could be estimated that ^{226}Ra detection efficiency and spectrum position would be equivalent to that of ^{236}U and ^{238}Pu.

Going back to Table 2, the retention for all the radionuclides studied was quantitative, except for ^{210}Po, which was almost quantitative (97%). Similarly, the detection efficiency for all of them, except for ^{210}Po, was around 100%. The spectrum for each radionuclide is shown in Fig. 4.

Table 2
Quality parameters for each radionuclide (values in brackets shows the standard deviation between triplicates).

	Retention (%)	Detection efficiency (%)
^{241}Am	>99.5[a]	100 (2)
^{238}Pu	>99.5[a]	100.5 (0.8)
^{236}U	>99.5[a]	101 (1)
^{230}Th	>99.5[a]	97.3 (0.2)
^{226}Ra	>99.5[a]	–
^{210}Po	97 (1)	88 (1)

[a] Activity on the effluent solution below LoD.

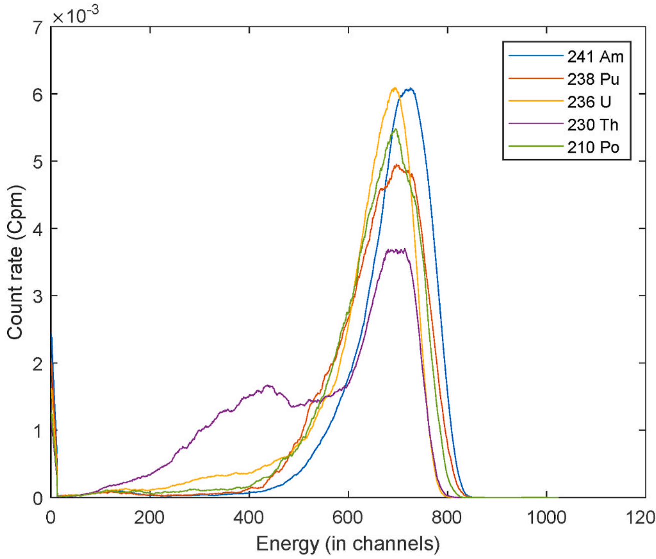

Fig. 4. Normalized count rate spectra for all the alpha-emitting radionuclides measured in the α-PSresin cartridge.

All the spectra appeared at high-energy channels and there were no large differences between radionuclides except for ^{230}Th, which presented a peak at lower energies. One hypothesis to explain this spectra is that, due to its chemistry, Th follows a different retention pattern through the α-PSresin cartridge. This may lead to some precipitation or deposition on the PSm surface [14] during the separation process. As consequence, some attenuation of the alpha particles before reaching the scintillator takes place. Nevertheless, the yield and efficiency for ^{230}Th were also close to 100%.

Regarding the other radionuclides, most of the peaks appeared in a similar position between channels 400 and 850. The small differences can be associated to energy of the α particle, uncertainty of the measurements and differences in the retention pattern on the PSresin [15].

3.4. Alpha/beta discrimination and calibration

As some beta emitting radionuclides could also be retained in the PSresin, their signal could interfere with the one from alpha emitting radionuclides. Therefore, alpha/beta discrimination was studied in order to reduce as much as possible their interference.

Alpha/beta discrimination was studied using ^{90}Sr/^{90}Y in secular equilibrium as a pure beta emitter and ^{241}Am, ^{238}Pu, ^{236}U and ^{210}Po as the alpha-emitting radionuclides, as those present different energies and retention patterns on the PSresin and can therefore have different α/β discrimination behavior. α-PSresin cartridges containing the retained radionuclides were measured using a pulse shape discrimination parameter, measuring at several values of PSA. The aim was to characterize the alpha/beta discrimination capacities of the detection system, as well as to determine which PSA value and which alpha radionuclide were the most suitable to be used as a standard for the calibration of the method. Fig. 5 shows the alpha/beta discrimination for the radionuclides studied.

The misclassification for ^{241}Am was a bit lower than that for the other radionuclides, since it had the thinnest peak and showed a smaller queue at lower energies, as observed in Fig. 4. This improves the classification of particles since low-energy scintillation signals are classified mainly as beta. For the other alpha-emitting radionuclides studied (^{238}Pu,^{236}U and ^{210}Po), the misclassification, as well as the crossing PSA (i.e., the PSA value where alpha and beta misclassifications are equivalent), were similar. Therefore, one of them or a combination of them should be used for the calibration.

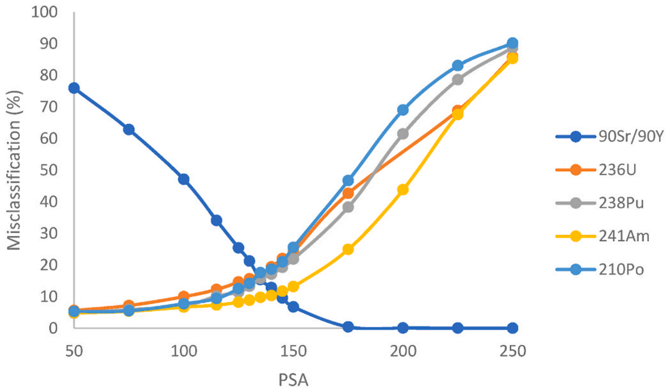

Fig. 5. Misclassification versus the PSA value for ^{236}U, ^{238}Pu,^{241}Am and ^{210}Po.

^{210}Po was rejected for calibration since it needs to be purified from its parent radionuclides (^{210}Pb and ^{210}Bi) before use, making it not suitable, even though the results were good enough. The selection of ^{238}U/^{234}U, probably the most common in natural waters, was not possible for the presence of short-lived daughter beta emitters in equilibrium (i.e. ^{234}Th, ^{234}Pa) that are also retained in the α-PSresin, thus impeding adequate alpha/beta discrimination calibration. Therefore, the mean between ^{238}Pu and ^{236}U were chosen to determine the working PSA.

In order to select the PSA value for the analysis, several factors were taken into account. In one hand, the crossing value of 135 is of interest since alpha and beta misclassifications are compensated. In the other hand, at high PSA values, there will be no interference from the beta-emitting particles in the alpha window, but a lower efficiency of the alpha emitters will be also expected. Therefore, the other PSA values of interest were 150, as the beta misclassification is very low, and 175, because all beta particles are correctly classified and the calculation is simplified. Table 3 shows the alpha and beta misclassification, as well as the detection efficiencies at the different PSA values selected.

These values of detection efficiency and misclassification values were applied in the gross alpha parameter quantification of a real water sample (Mreal_1) and also an interlaboratory sample from IAEA (IAEA-TEL-2021-03 (sample 5)). The objective was to determine which PSA value is the best for the quantification. Mreal_1 is a natural water sample that contains only uranium isotopes at an activity of 1.105 Bq L^{-1}, as provided by the LRA from the Universitat de Barcelona after full characterization by alpha spectrometry. The IAEA-TEL-2021-03 (sample 5) is an interlaboratory sample containing artificial alpha radionuclides. The sample volume was 100 mL and sample treatment only consisted of incubation for 30 min in a water bath at 50 °C after hydrogen peroxide addition to a final concentration of 1%. Moreover, a LSC measurement of the eluted solution was performed to check the retention of all the alpha-emitting radionuclides in the α-PSresin. The values of the quantification deviation at each PSA are shown in Table 4.

For both samples, alpha radionuclides were quantitively retained on the PSresin as no signal was detected on the eluted solutions measured by LSC. The deviations for both samples were lower than 15%

Table 3
Detection efficiency and misclassifications for each PSA studied for the different radionuclides analyzed.

PSA	Detection efficiency (%)				Misclassification (%)			
	^{238}Pu	^{236}U	^{90}Sr	Pu + U	^{238}Pu	^{236}U	^{90}Sr	Pu + U
135	84.2 (3)	82.6 (1)	84.7 (0.1)	85 (4)	16 (3)	17 (2)	12.4 (0.2)	16 (1)
150	78.1 (4)	75.8 (2)	91.9 (0.2)	77 (2)	22 (4)	24 (2)	3.8 (0.2)	23 (2)
175	61.7 (4)	57.3 (0.2)	95.4 (0.1)	59.5 (3)	38 (4)	42.7 (0.2)	0.19 (0.01)	41 (3)

Table 4
Deviation obtained in the quantification of each reference sample at each PSA studied.

PSA	Replicate	Quantification deviation (%)	
		Mreal_1	IAEA-TEL-202-013
135	1	2.0	−14.8
	2	−1.6	6.3
	3	1.6	−10.7
150	1	1.7	−10.9
	2	−7.4	−17.3
	3	−1.4	−11.4
175	1	0.7	−7.2
	2	−10.9	−4.4
	3	3.0	−13.0

irrespective of the PSA value used. These values are highly satisfactory since a deviation of up to 30% [6] is accepted in the gross alpha activity measurement. These results proved that the proposed calibration can be used for both type of sample.

Finally, the deviations were similar for the three PSA studied but slightly lower when using PSA 135. Therefore, PSA 135 was selected for the calibration.

3.5. Retention determination for the alpha-emitting radionuclides

When a separation process is performed, some unknown elements from the sample could modify the retention in the column. Therefore, a tracer has to be used to quantify the retention of radionuclide under analysis. The conventional methods for the gross alpha parameter determination (i.e. LSC or proportional counter) assumed that there are no losses of any of the radionuclides present in the sample when an evaporation or precipitation is performed. It is assumed, for example, that polonium is not lost during evaporation, that all the alpha-emitting radionuclides precipitate or that no splashes take place when the solution is heated until close to dryness.

In this case, using the α-PSresin, the retention of alpha emitters was always quantitative and, therefore, a 100% retention can be assumed in normal conditions. However, the presence of other stable elements in a sample that could be also retained in the α-PSresin, could produce changes in this retention, in particular if their quantity is high. This could be the case of calcium, iron or the organic matter. For a 100 mL sample the amount of iron is lower than the capacity which may be not a problem for the actinide's retention. In the case of calcium, its amount is of the order of the capacity, but it is described that even at high Ca concentrations (0.02–2 M) the retention of actinides in such type of extractants is still very high (k > 1000) and unaffected. Regarding organic matter, it has been checked previously in other works that it has no effect in the retention of other radionuclides in a PSresin. For this reason, an easy way to determine the real retention for each sample was proposed. Nevertheless, the proposed method is intended for drinking or river water samples in which the quantities of elements as calcium or iron, that can be retained in the column, are low enough. In addition, organic matter quantities were not enough to change the retention. The tracer has to be non-radioactive to avoid interfering signals in the PSresin and has to be measurable with a non-radioactive technique (e.g., AAS and IPC).

For the α-PSresin europium was used as the non-radiometric surrogate, since it is retained in the α-PSresin in an analog way to that of the actinides and its presence in natural waters is negligible. Europium can be measured in the effluent solution by ICP-OES and ICP-MS. However, a colorimetric assay, in which retention could be estimated by a visual check or quantified by UV–Vis spectrophotometry, was chosen in this case. The ideas was to make easy the application of this method in any laboratory. To perform this, a method based on a colored complex of europium with arsenazo (III) at a pH of 2.6–2.8 was used [25,26]. The organic ligand, at this pH, presents a pink color, whereas within the presence of europium, the solution turns violet (Fig. 6).

Fig. 6 shows the spectra obtained and the color of the calibration standards and the blank (ordered from 10 to 0 mg L^{-1}). The signal produced by the presence of the europium complex was observed at around 654 nm, while the signal corresponding to the pink color of arsenazo without the presence of europium was observed at 525 nm.

From the point of view of an ultra-fast method, a simple visual check based on the absence of the violet color in the separation effluents could be enough to confirm that europium is not present in them and therefore the retention is quantitative. To validate this approach, a detection limit for visual check must be established. From the color of the vials in Fig. 6, it can be seen that at concentrations of 1 mg L^{-1} or lower the solution becomes pink, making not possible to detect the presence of the violet color of the complex. Considering that the sample volume is 100 mL and the amount of europium added is 1 mg, the expected concentration in the column effluents would be of 10 mg L^{-1} if there is no retention of europium. Therefore, the simple visual check can be used to ensure a retention higher than 90% and to assume a quantitative retention, making a more detailed determination unnecessary since the deviations in the calculations would be acceptable.

However, in those cases that a more accurate determination is desired, an accurate determination could be performed by measuring the spectra using UV-Vis spectrophotometry. The absorbance at 654 nm versus the europium concentration was used for the calibration curve fitting (Fig. 7). The absorbance presented a linear correlation with the concentration of europium between 0.1 and 1 mg L^{-1} which is the region of europium concentration expected for the α-PSresin separation effluents in case of quantitative retention. Taking into account the detection limit of the method, a 0.1 mg L^{-1} concentration in the effluent could be clearly detected with UV–Vis spectrophotometry and therefore a retention higher than 99% could be stablished.

3.6. Real sample analysis

Finally, the method proposed for measuring gross alpha activity was validated by analyzing two samples from the interlaboratory programs organized by the European JRC (JRC-GAB-1 and JRC-GAB-2) and five real water samples from the surroundings of Catalonia. In this last case, the results were compared with the ones given by the LRA of the Universitat de Barcelona obtained with the LSC method.

The gross alpha activity quantification was performed in two ways: by estimation of the retention by a visual check, supposing a scenario of an ultra-fast measurement, and by quantification with UV–Vis spectrometry. Regarding the visual check, the effluents obtained after the passing of the sample through the PSresin presented a clear pink color after the addition of the reagents and, therefore, quantitative retention was assumed for the activity calculation (Table 5). When the retention was calculated by UV–Vis spectrometry, values between 95% and 100% were obtained. Results demonstrate that for this kind of samples the

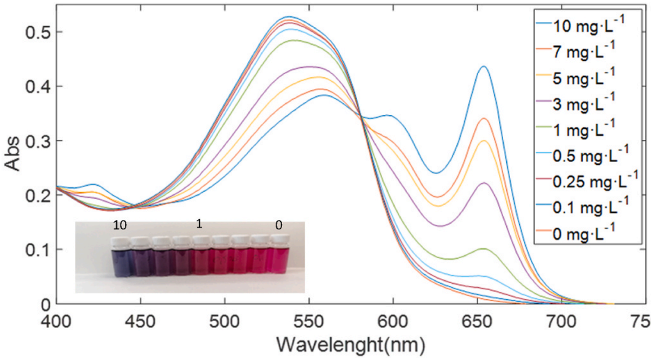

Fig. 6. Standard calibration of the Eu-arsenazo (III) complex measurements with UV–Vis spectrometry.

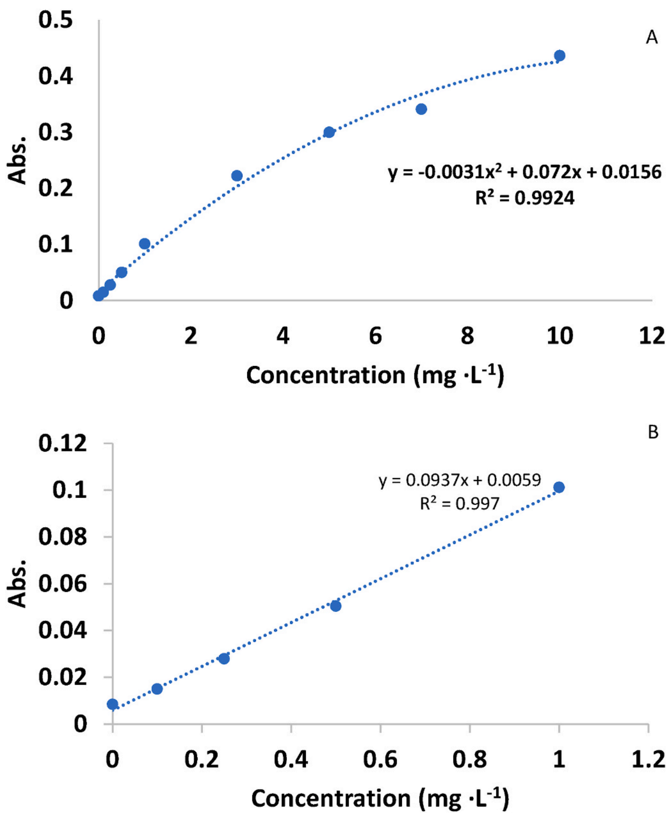

Fig. 7. Calibration curve fitting of absorbance vs concentration of the europium. (A) Complete curve fitting, (B) low-range concentration curve fitting.

Table 5
Retention of europium in each sample that was assessed by a visual check (A) and by UV–Vis spectrometry (B).

Sample	Visual check of color and retention	UV–Vis spectrometry retention
JRC-GAB-1	Pink (100%)	98.3%
JRC-GAB-2	Pink (100%)	99.1%
A21/071	Pink (100%)	98.8%
A21/044	Pink (100%)	97.5%
A21/074	Pink (100%)	95.5%
A21/118	Pink (100%)	99.2%
A21/031	Pink (100%)	95.1%

retention of actinides is almost quantitative and, as expected, potential non-radioactive interferences (e.g., Fe, Ca, organic matter) do not affect their retention.

Focusing on the gross alpha parameter measurement, the results for the two JRC interlaboratory samples analyzed are shown in Table 6.

The results obtained were quite similar to those given as a reference value. Moreover, when the assumption of a 100% retention of alpha-emitting radionuclides was made with the visual check (method A in Table 6), the deviation was low, indicating that the visual check worked correctly. As expected, the deviations obtained with the method determining the real retention of the alpha-emitting radionuclides (method B in Table 6) were slightly lower, suggesting that quantification can be slightly improved if the real retention values are taken into consideration.

The relative uncertainty of the measurement with α-PSresin (expressed as a combined standard uncertainty) was around 10% at this level of activity, which can be considered adequate. The analysis of the different elements contributing to the uncertainty (Fig. 8) showed that the three most important were the alpha count rate, the alpha efficiency and the retention determination. The contribution of the alpha efficiency increased with the increase in sample activity. This is because alpha efficiency, which is the mean of the detection efficiencies for ^{236}U and ^{238}Pu at the PSA value of 135, is independent of sample activity. Furthermore, its variability, RSD, was around 4.9%, which is relatively high as it includes the effect, on the detection efficiency, of the energy of the alpha particles emitted. The contribution of the alpha count rate to the uncertainty depended on sample activity, as observed with the other count rate variables, becoming important as the activity decreased. Finally, the contribution of the retention, with an RSD of 2.9%, was also independent of sample activity and was lower than that of the alpha efficiency.

Finally, the results obtained for the real water samples are shown in Table 7.

Moreover, for the JRC interlaboratory samples, the color was always pink during the visual check, indicating that more than 90% of europium had been retained. The results of the UV–Vis measurements confirmed these findings, showing retentions higher than 95% for all the samples (Table 7). Consequently, there were no significant differences between the results from both strategies.

Therefore, it can be concluded that the α-PSresin is capable to measure the gross alpha parameter with similar results and that the colorimetric UV–Vis determination could be useful in calculating the real retention for each sample. However, if it is requires a fast measurement to assess the gross alpha content of one or more samples, performing a visual check might be a straightforward option.

Regarding the limit of detection it has to be pointed out that the background of the PSresin is lower than that of the LSC due to the use of a lower amount of the scintillating material (1 g in α-PSresin vs 20 mL in the LSC vial). As consequence the minimum activity detection levels required for water monitoring can be achieved in only 2 h of counting time. The minimum detectable activity was 0.025 Bq L^{-1}, considering of 100 mL sample, 0.063 cpm of background and 2 h of measurement.

Comparing the methods proposed with the conventional ones, its main advantage is that it can give reliable results in less time and with a deviation equivalent to the ones obtained in laboratories currently. It is capable to give the result in just 5–6 h since the sample reception, since the conventional methods last up to 24–48 h to give a response since the sample reception.

Moreover, with the method proposed there are no losses of polonium as heating at high temperatures is avoided. Detection is less influence by salt content of the sample as our method has no salt autoabsorption and ^{40}K influence is avoided, leading to an improvement in the quantification. Color quenching is also avoided. If desired, more than one sample can be easily analyzed at the same time depending on the capacity of the vacuum box used (from 4 to 24 positions). Finally, there is also no need for liquid scintillation cocktails for the measurements, thereby reducing the generation of mixed wastes.

4. Conclusions

The preparation of the α-PSresin extractant was successfully

Table 6
Comparison of the results obtained by a visual check (A) and UV–Vis spectrometry (B) versus the reference values.

	Reference value (Bq/L)	PSresin value (Bq/L) (A)	PSresin value + UV–Vis (Bq/L) (B)	Deviation (%) (A)	Deviation (%) (B)
JRC-GAB-1	0.37 (0.01)	0.35 (0.03)	0.35 (0.04)	7.4	5.6
JRC-GAB-2	0.73 (0.02)	0.70 (0.06)	0.71 (0.06)	4.3	3.3

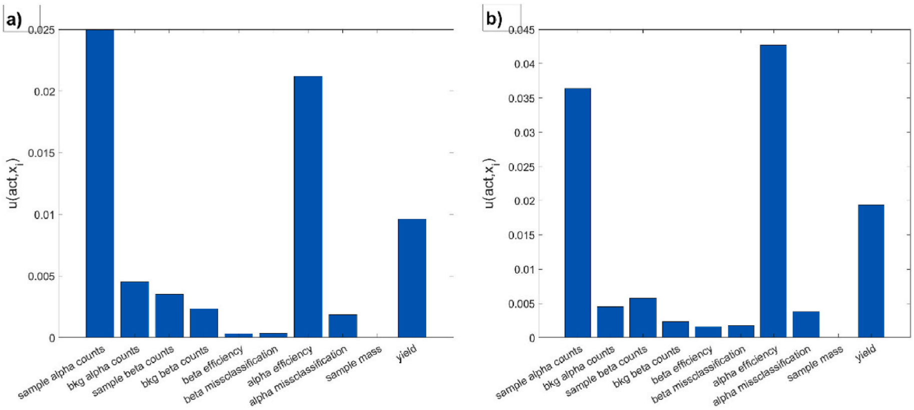

Fig. 8. Analysis of the uncertainty associated with each component for the JRC-GAB-1 (a) and JRC-GAB-2 (b) samples.

Table 7
Comparison of the results obtained with the visual check (A) and by UV–Vis spectrometry (B) versus the values obtained with the LSC conventional method.

	Activity Bq L^{-1}		
Sample	LSC	PSresin (A)	PSresin + UV–Vis (B)
A21/071	< LoD	< LoD	< LoD
A21/044	0.07 (0.02)	0.06 (0.01)	0.06 (0.02)
A21/074	0.53 (0.09)	0.46 (0.04)	0.48 (0.05)
A21/118	0.9 (0.2)	0.65 (0.07)	0.66 (0.07)
A21/031	1.4 (0.3)	1.26 (0.09)	1.3 (0.1)

The activity values obtained were similar to those obtained with the LSC method, with some discrepancies observed only in one sample (A21/118).

optimized, improving yield and purity. The new α-PSresin has a capacity of 5.8 mg, which is suitable for analyzing alpha radionuclides without effect of non-radioactive interferences. Several separation media were studied, which demonstrated that low acid concentrations were the best option for the total retention of alpha-emitting radionuclides (actinides, radium and polonium). pH 2 was selected as optimum medium for the development of a new procedure that can quickly measure the gross alpha parameter.

A new optimal method for measuring gross alpha activity has been developed, reducing the amount of effort and reagents needed compared to currently used methods. This procedure consists of adjusting the sample medium to a pH of 2 with nitric acid, adding H_2O_2 to a final concentration of 1%, heating the solution at 50 °C in a water bath for 30 min, passing the solution through α-PSresin, performing a scintillation measurement of α-PSresin, and estimating or calculating the retention. The procedure avoids potential Po losses, while the retention or loss of alpha particles can be determined. Europium is a good tool for estimating and determining the retention of alpha-emitting radionuclides. The formation of the colored arsenazo-europium complex can be precisely measured with UV–Vis spectrophotometry or estimated by a visual check, enabling an ultra-fast measurement. In the latter case, 100% retention can be assumed if the color of the Eu-arsenazo complex is not obtained. PSA calibration was evaluated with a fully characterized real sample and with an interlaboratory sample, providing satisfactory results at a PSA value of 135.

The whole methodology worked correctly in the analysis of two JRC interlaboratory samples (JRC-GAB-1 and JRC-GAB-2) and 5 real samples. Results obtained were comparable to the references values and to those obtained with the standard LSC method with an equivalent uncertainty.

Finally, the new method developed has a limit of detection of 0.025 Bq L^{-1} with an analysis time of less than 5 h (including sample treatment and measurement), which is much faster than conventional methods today used (around 24–48 h to give a response).

CRediT authorship contribution statement

I. Giménez: Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **H. Bagán:** Software, Resources, Writing – review & editing, Supervision, Funding acquisition. **A. Tarancón:** Software, Formal analysis, Resources, Writing – review & editing, Supervision, Funding acquisition.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aca.2023.340905.

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