



Analysis of isotopes of plutonium in water samples with a PSresin based on aliquat-336

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ABSTRACT

There is a necessity to have techniques capable to perform rapid determinations of specific radionuclides with the aim to provide fast response in emergency situations where a large number of samples need to be measured in a short time. Plastic Scintillation Resins (PSresins) raises as an adequate tool to achieve this purpose and in the present study a methodology to determine plutonium using a PSresin based on Aliquat-336 was developed. Different sample treatments have been studied under acidic conditions with an emphasis on valence adjustment treatment to achieve an effective retention within the PSresin. Under 3 M nitric acid conditions and an iron sulphamate (II) + nitrite valence adjustment, quantitative retention and 100% detection efficiency were achieved. The retention of the different interferences evaluated (²³⁸U, ²³⁰Th, ²⁴¹Am, ²¹⁰Pb and ⁹⁹Tc) was low and therefore they do not interfere significantly in the determination of plutonium, except for ⁹⁹Tc. Finally, a stable tracer to calculate the PSresin separation yield was studied, revealing that gold is suitable for this purpose. This procedure was applied to the analysis of spiked sea and river water samples, obtaining errors lower than 10% in their quantification.

1. Introduction

Plutonium isotopes are used in the military industry, in nuclear reactors for energy production, and nuclear reprocessing industry. Plutonium isotopes are present in the environment at very low activities. The majority is the result of nuclear weapon testing performed mainly during 1950–1960. Nuclear accidents (i.e., Chernobyl (1986), Thule (1968) or the Systems for Nuclear Auxiliary Power generator (1964)) and isolated releases from reprocessing plants have made a small contribution (Qiao et al., 2009). Plutonium isotopes, as well as other transuranic isotopes, are considered among the most radiotoxic elements and as a consequence effective environmental monitoring is required to protect ecosystems from their potential release. Moreover, plutonium isotopes are considered one of the main threats in terrorist attacks and therefore we need methods of analysis, in terms of sample treatment and detection, that would be capable of providing a fast response in emergency situations (Dolique et al., 2019; Kim et al., 2015; Landstetter et al., 2015; Lemons et al.; Qiao et al., 2011).

All plutonium isotopes are artificial and the most commonly found are ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, and ²⁴¹Pu. All these radionuclides are alpha emitters except ²⁴¹Pu, which is a low beta energy emitter. They can only be measured using techniques capable of detecting low penetration

particles, such as alpha spectrometry and scintillation. A chemical treatment is required to isolate plutonium from other radionuclides for scintillation detection, and to isolate plutonium from most of the other components of the sample (i.e., several stable cation, anion and organic compounds) in alpha spectrometry to avoid attenuation of the alpha particles (Vajda and Kim, 2010), (Hou and Roos, 2008). Plutonium presents a rich chemistry and depending on the complexity of environmental samples, its determination can be quite challenging, involving long and tricky sample treatments. Separation can be achieved using a variety of strategies including co-precipitation, solvent extraction, and ion-exchange or extraction chromatography with different extractants (Qiao et al., 2009), (Hou and Roos; Liu et al., 2016a; Vajda and Kim, 2010).

Alpha spectrometry is the technique most used to quantify plutonium isotopes. It has the lowest detection limit thanks to an extremely low background, although the preparation of alpha sources is time consuming and not suitable for fast or emergency uses. Liquid scintillation can also be used for plutonium analysis since it has acceptable detection limits and sample preparation for measurement is easy. However, no specific information about each specific isotope is obtained and mixed wastes (hazardous and radioactive) are produced. An alternative to these techniques, especially suited for fast analysis in

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emergencies, is based on the use of Plastic Scintillators in the form of resins (PSresins). A PSresin is a plastic scintillation microsphere (PSm) coated with a selective extractant. When packed in a solid phase extraction cartridge it allows the combination of separation through extraction chromatography and measurement through scintillation within 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 also reduces the number of reagents required, since elution steps are no longer required, thus also avoiding the generation of mixed wastes derived from the use of liquid scintillation cocktails. The development of a method of analysis of plutonium isotopes with PSresin will therefore provide a new tool for the analysis of plutonium that will be of interest in emergency situations, where sample treatment has to be simplified and more than one sample needs to be treated simultaneously.

In this work, the PSresin proposed for the retention of plutonium isotopes is based on a quaternary aliphatic amine (known as aliquat-336). This PSresin has been studied in detail previously for the analysis of ^{99}Tc (Coma et al., 2019), (Barrera et al., 2016) but may also be used for plutonium since several methods using extraction chromatography with this extractant have been described (Horwitz et al., 1993; Kumar et al., 2013; Lemons et al., Liu et al., 2016a,b, Maxwell et al., 2014, 2015; Maxwell and Culligan, 2006; Varga et al., 2007). In these methods, the oxidation state is adjusted to Pu(IV) after a preconcentration process since this is the valence at which retention of plutonium is highest. The medium of the loading solution can be nitric acid (2–4 M) (Liu et al., 2016b), (Lemons et al., 2017b) or hydrochloric acid (9 M) (Varga et al., 2007), (TrisKem International, 2015). To adapt these procedures to include the use of a PSresin three issues need addressing. First, the valence adjustment treatment and loading and cleaning media for optimum scintillation measurement of plutonium with the PSresin in the column need to be established. Second, as plutonium is not eluted from the resin, the potential retention of interferents needs to be evaluated and minimized with cleaning steps. Finally, a non-radioactive element with analogous behaviour to plutonium under the treatment conditions is needed for tracing the yield of the separation, since if a plutonium radiotracer is used it would interfere with the scintillation signal coming from the plutonium isotopes in the sample.

2. Experimental

2.1. Reagents

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), nitric acid (69%), L(+)-ascorbic acid ($\leq 99\%$) and hydrogen peroxide (30%) were from Panreac (Castellar del Valles (Barcelona), Spain); hydrochloric acid (37%), methanol ($\leq 99.9\%$ for HPLC), hydroxylammonium chloride ($\leq 90\%$), amidosulphuric acid, aluminium nitrate nonahydrate, aliquat-336 and dichloromethane (99.9%) 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). Standards of tin (1000 ppm), cerium (1000 ppm), gold (1000 ppm) and samarium (1000 ppm) from Inorganic Ventures (Christiansburg, USA) were used. Europium (III) chloride hydrate and ammonium molybdate were provided by Alfa Aesar (Heysham, United Kingdom).

$A^{238}\text{U}$ active stock solution of 2.22 (0.03) Bq/g was prepared from a standard of 101.34 (1.18) Bq/g from Eckert and Ziegler (Berlin, Germany). $A^{241}\text{Am}$ active stock solution of 47.4 (1.2) Bq/g in 0.5 M HCl was prepared from a standard of 55.44 (1.3) kBq/g and $a^{238}\text{Pu}$ active stock solution of 46.3 (1.4) Bq/g was supplied by GE Healthcare-Amersham International (Buckinghamshire, England). $A^{230}\text{Th}$ active stock solution of 2.38 (0.03) Bq/g was prepared from a standard of 23.59 (0.27) Bq/g from the National Institute of Standards and Technology (NIST) (Gaithersburg, USA). $A^{226}\text{Ra}$ active stock solution of 4.0 (0.1) Bq/g in

HNO_3 was prepared from a standard of 1986 (62) kBq/g supplied by Ciemat (Madrid, Spain). $A^{210}\text{Pb}$ active stock solution of 160 (5) Bq/g was prepared from a standard of 35.5 (1.1) kBq/g provided by CEA/DAMRI (GIF-SUR-YVETTE CEDEX, France).

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

Plastic scintillation microspheres were prepared as described previously (Santiago et al., 2013).

PSresin were prepared by coating PSm with aliquat-336 as described previously (Barrera et al., 2016).

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.

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

2.3. Procedures

2.3.1. Separation and measurement of plutonium solutions in the PSresin

One gram of the PSresin was packed in a 2-mL SPE cartridge from Triskem International (Rennes, France). The cartridge was placed in a vacuum chamber connected to a pump and 10 ml of deionized water were passed through it at a flow rate of 1 mL/min (around 3–5 inHg). Afterwards, the cartridges were shaken for 180 s at 50 Hz in an IKA MS3 digital vortex (Merck, Darmstadt, Germany) for homogenization.

Standard were prepared in polyethylene vials by adding 72 μL of ^{238}Pu standard and the corresponding medium up to 11 mL. The activity of the sample was around 3.33 Bq. Some samples were passed through the column without a valence adjustment treatment. Others were passed through after applying a valence adjustment treatment. Two different treatments were evaluated. One consisted of adjusting the valence with hydroxylamine and sodium nitrate and the other one was based on the adjustment with iron sulphamate (II), ascorbic acid and sodium nitrite (Liu et al., 2016b), (Lemons et al., 2017b), (Varga et al., 2007), (TrisKem International, 2015). Mediums evaluated were HCl 9 M, HNO_3 3 M and HNO_3 0.5 M. The addition of $\text{Al}(\text{NO}_3)_3$ 0.5 M to the HNO_3 3 M solutions was also evaluated (Maxwell et al., 2014).

To perform the sample analysis, the PSresin cartridge was placed in a vacuum box connected to a vacuum pump. The cartridge was first conditioned with 2 mL of the sample medium. Afterwards, 10 mL of the sample solution were passed through the cartridge. The flow was around 1 mL/min, which corresponds to a pressure of 3–5 inHg. Once the sample was loaded, two rinses with 2 mL of the loading sample medium were performed, followed by two rinses with 2 mL of 9 M HCl and two rinses with 2 mL of 0.5 M HNO_3 . Finally, to ensure the dryness of the cartridge, the pressure was increased to 15–20 inHg for 10 min after removal of solution.

The solutions eluted after passing through the sample and rinsing the cartridge (referred to as “waste”) were collected in Corning (New York, USA) 50-mL conical tubes.

Once the separation process was complete, the PSresin cartridge was placed in a 20-mL polyethylene vial with no further operations (PerkinElmer, Massachusetts, USA) and measured in the scintillation counter.

The waste was also measured by liquid scintillation to determine the proportion of plutonium that was not retained. For this, 1 mL of the waste was mixed with 19 mL of liquid scintillator (Optiphase hifase 3) in a 20 mL polyethylene vial. The vials were shaken for 180 s in the vortex at 60 Hz to homogenize the mixture. Standard samples were prepared using this cocktail:sample proportion to determine the detection efficiency of Pu in the LSC measurements.

Blanks were prepared by adding deionized water instead of the plutonium standard.

2.3.2. Evaluation of the interferent's retention in the PSresin

To determine the retention of possible interferents within the PSresin, other radionuclides (^{nat}U and daughters, ^{230}Th , ^{241}Am , ^{226}Ra and daughters, ^{99}Tc , ^{210}Pb and daughters) were tested under the optimum sample treatment conditions. The quantity of each radionuclide added to each sample is meant to achieve 3.33 Bq in a final volume of 11 mL of the sample. The rinsing media used were the same as mentioned above. Each interferent was analysed separately and the columns and wastes obtained after the loading and cleaning steps were measured as described earlier.

2.3.3. Search for stable elements chemically analogous to plutonium

The elements evaluated as potential chemical analogues of plutonium in the optimum conditions of separation were: europium; molybdenum; samarium; tin; cerium; and gold. Solutions of 1 mg of the different elements in 11 mL of final volume were passed through the PSresin in the optimum conditions of separation and the waste obtained after loading and each rinsing step was collected in different 50 mL conical tubes and analysed by ICP-MS to evaluate the retention of those elements within the PSresin. Dilutions from the sample and the collected wastes were diluted to a final concentration of HNO_3 1% or HCl 1% depending on the original medium of the waste.

2.3.4. Analysis of spiked water samples

Spiked river water and seawater samples with 10 Bq/L were analysed to determine the viability of applying the final method to the analysis of Pu isotopes in environmental samples. Seawater was collected from *Platja de Sant Miquel* in Barcelona on November 28, 2020 and river water was collected from the Ebro River where it passes through *Flix* on February 24, 2012. Samples were filtered using filter paper before analysis. Non-spiked (blank) and samples spiked with 10 Bq/L of ^{238}Pu were analysed.

Three sample treatments were applied to 100 ml of sample: evaporation to dryness and redissolution with 4 mL 8 M nitric acid and 1 mL 30% hydrogen peroxide plus evaporation until dryness; partial evaporation until 1 mL volume and redissolution in 8 M nitric acid with 4 mL and evaporation until less of 1 mL without arriving dryness; evaporation to dryness and redissolution with a 3:2 mixture of concentrated nitric acid and hydrochloric acid (aqua regia) and evaporation to dryness. In all procedures, the dried sample is redissolved in 3 M nitric acid plus 0.5 M aluminium nitrate. Afterwards, valence adjustment with iron sulphamate was performed.

2.4. 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 standard samples and 5 h for spiked water samples. Liquid scintillation samples of the wastes were measured for 1 h. The external quenching parameter (SQP(E)) was measured for 10 min in each vial. The measurement vials were stored in the dark for 2 h before counting.

2.5. Data treatment

Data obtained from the Quantulus detector was treated using MATLAB (The Mathworks, Natick, Massachusetts (USA)) computing software. Spectra were softened using the Savitzky Golay algorithm with an average window of 10 points for each side and a polynomial of 1st degree for improving graphical representation.

The detection efficiency was calculated as the ratio between the net count rate (as counts per minute) measured by the detector and the activity in the PSresin column as disintegrations per minute. The yield

(proportion of radionuclide retained within the PSresin) was calculated as the proportion of activity in the column relative to the activity in the sample (in disintegrations per minute). Activity in the column was obtained from the difference between the activity of the sample and the activity in the wastes measured by LS. Activity in the wastes was calculated considering a detection efficiency value of 100% obtained in the measurement of standard solutions. In the case of stable metals, the same concept was applied, using the amount of stable metal measured by ICP-MS in the sample and in the waste.

3. Results

Aliquat-336 has been widely reported as capable of retaining Pu isotopes and therefore the aliquat-336-PSresin already developed by the authors for ^{99}Tc (Barrera et al., 2016) could be used for Pu isotope analysis since alpha emitters are also efficiently detected with plastic scintillators in the form of microspheres. Nevertheless, the most appropriate chemical pretreatment and separation conditions for direct measurement of the Pu retained on the PSresin needed to be determined, including the evaluation of the non-retention of potential interferents. Moreover, the efficiencies needed to be high and reproducible and the spectrum shape acceptable. However, the main challenge was developing a strategy to trace the separation process without the use of the classical plutonium tracer (i.e. ^{242}Pu) since it may interfere with the scintillation signal. Finally, the full procedure proposed was evaluated for the analysis of river and seawater samples.

3.1. Plutonium separation conditions

According to the retention of plutonium on aliquat-336 in acid medium described in the literature (TrisKem International, 2015), the media in which plutonium retention is highest are hydrochloric acid 9 M and nitric acid from 0.5 to 4 M, 3 M being the most commonly used (Maxwell et al., 2014), (Maxwell et al., 2015), (Liu et al., 2016b).

Plutonium retention on aliquat-336 not only depends on the loading medium, but also on the oxidation state, which needs to be adjusted before passing through the column (Maxwell and Culligan, 2006). To achieve the Pu (IV) oxidation state, which is the state with the highest retention, several redox reactions have been described in the literature (Qiao et al., 2009), (Vajda and Kim, 2010), (Maxwell et al., 2015), (Liu et al., 2016b). Nevertheless, the fastest and most effective way to achieve this state is to reduce Pu to Pu (III) and then oxidize it to Pu (IV) which is the most common procedure used in LSC. In order to achieve this objective in the analysis with PSresin, two different strategies were tested by analysing standard samples in order to find the procedure with less quenching effect on the PSresin. The first valence adjustment applied involved the use of hydroxylamine as a reducing agent and sodium nitrate as an oxidizing agent. This strategy was studied under loading conditions of 9 M hydrochloric acid, obtaining a brown coloured solution and effervescence. The percentage retention of plutonium in the PSresin cartridge was 96.2% and the detection efficiency was 96.7%. Even though these results were good, the spectrum (Fig. 1) was shifted to low energies channels. This was also consistent with the SQP(E) parameter, which was 616.

The low SQP(E) value means that a high quenching effect occurred due to the reaction of Cl^- with NO_2^- under a high concentration of HCl and the formation of brown coloured species that did not disappear, even after strong agitation (as happens with NO_2^-). Therefore, the spectrum was wider and shifted to lower energies.

The shape of the spectrum is not ideal for quantifying plutonium with PSresin since it can lead to deviations in the determination of the detection efficiency if quenching increases. The same valence adjustment method was performed in a 3 M nitric acid loading medium but did not work properly, leading to a plutonium retention of around 60%. This is because hydroxylamine reacted with the nitric acid instead of plutonium, not achieving the initial reduction of plutonium.

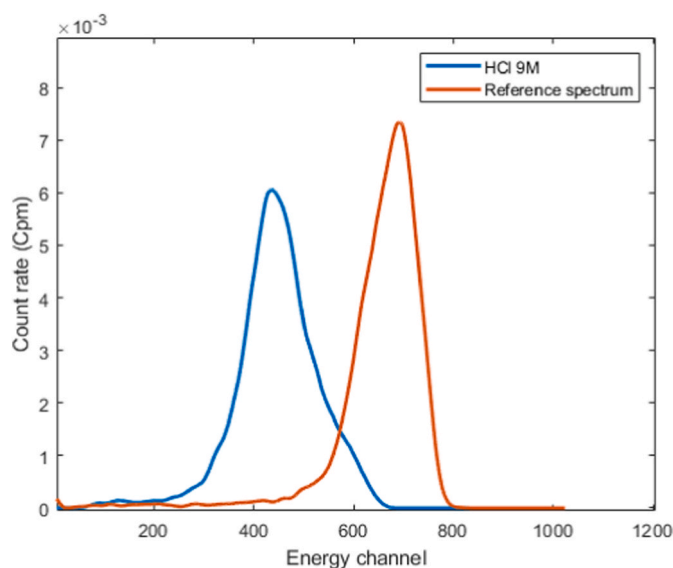


Fig. 1. Normalized spectra obtained in the analysis of ^{238}Pu with PSresin using hydroxylamine/sodium nitrite treatment in HCl 9 M and a plutonium reference spectrum measured with the PSresin.

The second adjustment was based on the use, in the following order, of: iron (II) sulphamate as a reducing agent; ascorbic acid to reduce the Fe (III) to Fe (II) and to ensure that all the plutonium species have been reduced to Pu(III); sodium nitrite (Liu et al., 2016b). This valence adjustment method was applied in two different media: HNO_3 3 M and HNO_3 3 M with $\text{Al}(\text{NO}_3)_3$ 0.5 M. $\text{Al}(\text{NO}_3)_3$ 0.5 M is usually employed because it confers stability to the separation process and can be useful in future sample treatments based on phosphate precipitation (Maxwell et al., 2014).

The retention of plutonium in the PSresin cartridge was quantitative and detection efficiency was optimal under both media (Table 1). SQP (E) values were very similar for both media, with slightly low to normal values (i.e. around 780) due to blue colouration on the column caused by the presence of residues of iron (II) sulphamate. As the values were acceptable, successive cleaning steps with HCl 9 M and HNO_3 0.5 M media were performed. Slight colour changes were seen during cleaning. When HCl 9 M was passed through, the column took on a green colouration that was lost during the HNO_3 0.5 M cleaning step, leaving the column colourless, unlike in the treatment with hydroxylamine, which had a positive impact on scintillating measurement as colour quenching did not affect the resulting spectrum. This was reflected in the spectrum position, which was narrower and located at higher energies (Fig. 2). Treatment with or without the presence of $\text{Al}(\text{NO}_3)_3$ 0.5 M did not lead

Table 1

Yield, detection efficiency and SQP(E) obtained after in each step in the analysis of ^{238}Pu with PSresin using iron (II) sulphamate/sodium nitrite treatment in HNO_3 3M media without and including $\text{Al}(\text{NO}_3)_3$ 0.5 M

		Without $\text{Al}(\text{NO}_3)_3$ 0.5 M	With $\text{Al}(\text{NO}_3)_3$ 0.5 M
Yield (%)	Loading (3 M HNO_3)	100	100
	1st cleaning (9 M HCl)	98	97
	2nd cleaning (0.5 M HNO_3)	96	96
Efficiency (%)	Loading (3 M HNO_3)	96	98
	1st cleaning (9 M HCl)	94	97
	2nd cleaning (0.5 M HNO_3)	91	97
SQP(E)	Loading (3 M HNO_3)	680	684
	1st cleaning (9 M HCl)	676	676
	2nd cleaning (0.5 M HNO_3)	679	671

to significant differences. Thus, $\text{Al}(\text{NO}_3)_3$ was incorporated into the separation process.

Five replicate standard samples were analysed under the optimum conditions to evaluate reproducibility of plutonium retention, detection efficiency and spectrum position in the PSresin cartridge. Values of yield, efficiency and SQP(E) obtained (Table 2) demonstrated that retention yield was almost quantitative, that all particles emitted were detected and that the columns still showed slight colouration, which slightly reduced the SPQ(E) values. The reproducibility was good since the relative standard deviation was around 5%.

However, as shown in Fig. 3 the spectra position of the five samples varied slightly. This could be because of colour quenching or changes in the retention pattern of Pu within the PSresin due to the influence of the components present in the solution or generated in the valence adjustment. Nevertheless, integration between channels 350 and 800 would cover all signals from Pu. Therefore, it can be concluded that this method leads to high and reproducible plutonium retentions and detection efficiencies.

3.2. Study of interferent's retention

Samples can contain other radionuclides apart from plutonium, the presence of which could interfere in its determination. For this reason, an estimation of the retention of those radionuclides with a high probability of being found in an environmental sample was needed. These radionuclides include natural radionuclides such as ^{238}U (in equilibrium with ^{234}Th , ^{234}Pa , ^{234}U), ^{230}Th and ^{210}Pb (in equilibrium with ^{210}Bi and ^{210}Po) and artificial radionuclides such as ^{99}Tc and ^{241}Am .

Samples were prepared individually for each radionuclide and analysed by applying the optimum sample treatment. Once the separation process was complete, the count rate obtained from the column and the wastes from each step was used to determine the amount of radionuclide retained in the PSresin cartridge. The results are shown in Tables 3 and 4.

The retention of each interferent, once the separation process was complete, was very low (below 4%), with the exception of ^{99}Tc , which was almost completely retained in HCl media, and is slightly retained in HNO_3 media. Nevertheless, the presence of ^{99}Tc cannot be considered usual in environmental samples and moreover the position of its spectrum (from the 0 to 650 channels) was sufficiently different to that of Pu to allow its identification in the spectrum and also Pu determination. The majority of the interferents were not retained in the 3 M HNO_3 and 0.5 M $\text{Al}(\text{NO}_3)_3$ media, with the exception of ^{230}Th , which was eluted in the 9 M HCl cleaning step. Therefore it can be concluded that the media selected can be used for column cleaning and decontamination from interferences, which could be improved further by performing cleaning steps with higher volumes of HNO_3 3 M and $\text{Al}(\text{NO}_3)_3$ 0.5 M and HCl 9 M. Thus, Pu can be quantified using aliquat-336 PSresin.

3.3. Stable tracer for Pu

Once we had demonstrated that the method developed allows Pu retention while separating it from other possible interferents, we had to find a tracer to allow accurate quantification of retention when measuring a real environmental sample. ^{242}Pu is usually employed for this purpose in alpha spectrometry analysis as it is not found in natural samples. However, a radioactive tracer cannot be added when scintillation techniques are used since its signal will overlap with the signal of the other Pu isotopes in the sample. For radionuclides like ^{90}Sr or ^{210}Pb , the stable element can be used to trace the progress of separation since its concentration is measured by ICP or other techniques before and after column separation. Nevertheless, there is no stable isotope for Pu and therefore, a stable element that may act as an analogue of Pu in the separation conditions is needed.

Stable elements that were taken into consideration were those with at least one of the following characteristics: a similar chemistry to Pu;

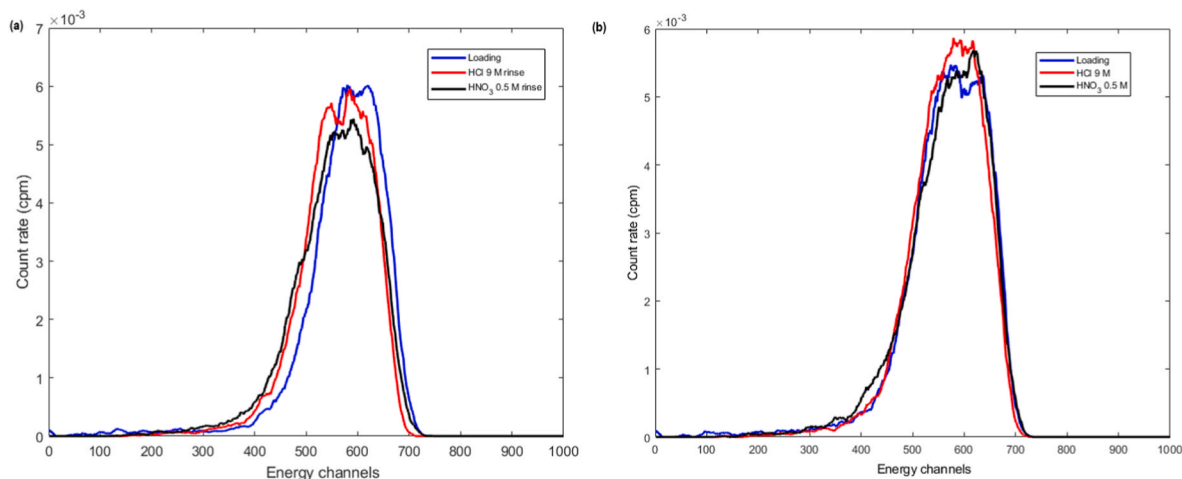


Fig. 2. Spectra obtained in the analysis of ²³⁸Pu with PSresin using iron (II) sulphamate/sodium nitrite treatment in HNO₃ 3M media (A) without and (B) with Al (NO₃)₃ 0.5 M.

Table 2

Yield, detection efficiency and SQE(E) in the analysis of five replicate standard samples of ²³⁸Pu with PSresin. Mean values and standard deviation.

Yield (%)	98(5)
Efficiency (%)	100(6)
SQP(E)	722(9)

Table 4

Proportion of the total activity eluted in each phase in relation to the 100% eluted.

Radionuclide	% not retained in loading step + eluted with HNO ₃ and Al (NO ₃) ₃	% eluted with HCl 9 M	% eluted with HNO ₃ 0.5 M
²³⁸ U and daughters	78.4	16.1	5.4
²³⁰ Th	1.2	92.2	6.6
²¹⁰ Pb and daughters	84.2	15.5	0.4
²⁴¹ Am	100	0	0
⁹⁹ Tc	93.8	4.8	1.6

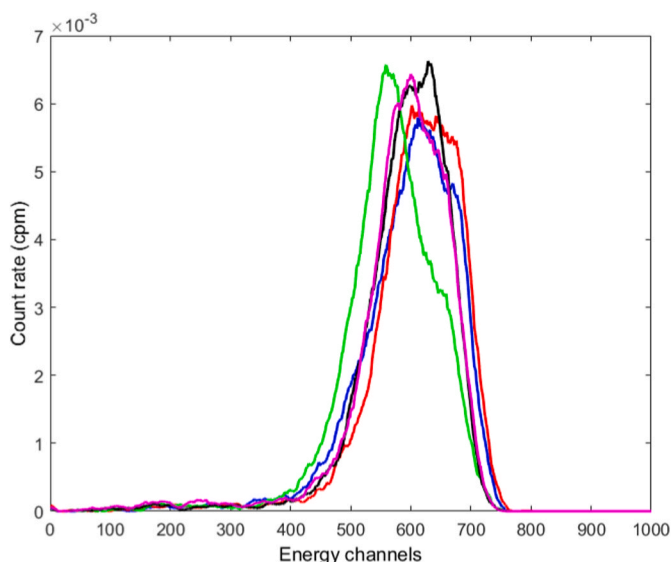


Fig. 3. Spectra obtained in the analysis of five replicate standard samples of ²³⁸Pu with PSresin.

Table 3

Proportion of interferent radionuclides retained in the PSresin.

Radionuclide	Activity (Bq)	% Retained
²³⁸ U and daughters	3.33	2.0
²³⁰ Th	3.32	3.6
²¹⁰ Pb and daughters	3.35	3.6
²⁴¹ Am	4.48	1.0
⁹⁹ Tc	3.32	11.2

Table 5

Proportion of stable element eluted in each step of the PSresin separation.

	Eu (%)	Mo (%)	Sn (%)	Ce (%)	Sm (%)	Au (%)
Effluent of the Loading (3 M HNO ₃ + 0.5 M Al(NO ₃) ₃)	54	97.3	75.4	100	100	0
Effluent of the 1st cleaning (9 M HCl)	0	0.3	19.3	0	0	0
Effluent of the 2nd cleaning (0.5 M HNO ₃)	46	2.4	5.3	0	0	0

The above results indicated that the presence of Cl^- in the solution might stabilize gold as $[\text{AuCl}_4]^-$. For this reason, the medium used when gold was added was a 5:4 mixture of 3 M HNO_3 and 0.5 M $\text{Al}(\text{NO}_3)_3$ with 1 M HCl . The use of this medium permitted gold stabilization, avoiding its precipitation during valence adjustment. It must be noted that during the valence adjustment when ascorbic acid was added, a pink-orange solution was obtained. That was due to the formation of gold nanoparticles, an amorphous formation of metallic gold that was further dissolved when sodium nitrite was added.

Results obtained in the analysis of standard samples containing plutonium and gold as the tracer (0.75 mg) (Table 6) showed that retention was quantitative (for Pu measured by LS and Au by ICP-MS) which demonstrates that the change in the medium did not change the retention of plutonium in the PSresin cartridge and that Au can be used as a tracer.

Regarding the detection efficiency Table 6 shows that it was slightly lower when gold was retained in the PSresin cartridge, although values were highly reproducible. The SQP(E) values were similar to those obtained without using gold, however, the spectra obtained (Fig. 4) showed a shift to low energy channels due to the presence of gold.

This movement of the spectra was associated with the presence of a yellow ring on the top of the PSresin caused by the gold that was retained, leading to colour quenching. It is important to highlight the discrepancy between the SQP(E) values (indicative of low quenching) and the spectrum position (indicative of high quenching). This is because SQP(E) considers the end of the spectrum produced by the Compton electrons. Compton electrons are produced within the PSresin bed, which includes areas without colour quenching (almost all the PSresin) and areas with high colour quenching (the top of the cartridge). There are several scintillation emissions that do not suffer colour quenching and therefore the SQP(E) value is not affected by the yellow ring on the top of the vial. In contrast, if Pu is retained in a similar position to that of gold (at the top of the PSresin bed) scintillation emissions generated by Pu would be affected by colour quenching when measured and consequently the spectrum would shift to low energies. The fact that spectra is shifted to low energies but a small proportion is still placed at high energies, suggest that most of the plutonium is placed at the same position as gold and a small proportion is in a less quenched area (with fewer or without gold). These results, then, confirmed the similar behaviour of Pu and Au in the PSresin.

With the aim of reducing the effect of the Au ring on the scintillation measurements, the addition of lower amounts of gold (i.e. 0.1 mg, 0.25 mg and 0.5 mg) was studied. The resulting detection efficiencies (Table 7) and spectra positions (Fig. 5) confirmed that both depend on the amount of gold the sample is spiked with, since efficiency decreases and the spectrum moves to low energies and becomes broader when increasing amounts of gold are added.

Despite this behaviour, the results show that low amounts of gold (below 0.25 mg) do not cause a loss of detection efficiency and therefore this amount was selected and used as a stable tracer for plutonium measurement.

3.4. Analysis of spiked water samples

100 mL of two different spiked water samples (river water and

Table 6

Yield, detection efficiency and SQP(E) obtained in the analysis of standard samples containing gold as the tracer.

	Yield Au (%)	Detection efficiency (%)	SQP
Blank with Au	98.8	–	696
Active without Au	–	94	724
Active with Au (1st replicate)	99.3	88	719
Active with Au (2nd replicate)	99.5	88	705
Active with Au (3rd replicate)	99.7	88	706

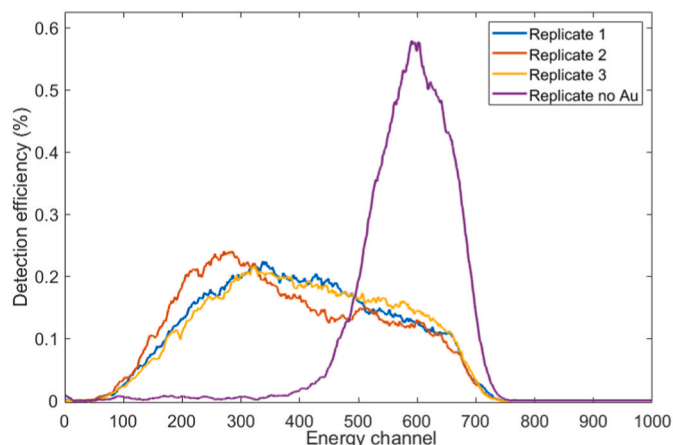


Fig. 4. Spectra obtained in the analysis of standard samples containing 0.75 mg of gold as the tracer. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 7

Values of detection efficiency versus mg of gold

Amount of Au (mg)	Detection efficiency (%)
0.1	94.5
0.25	95.1
0.5	90.9
0.75	87.9

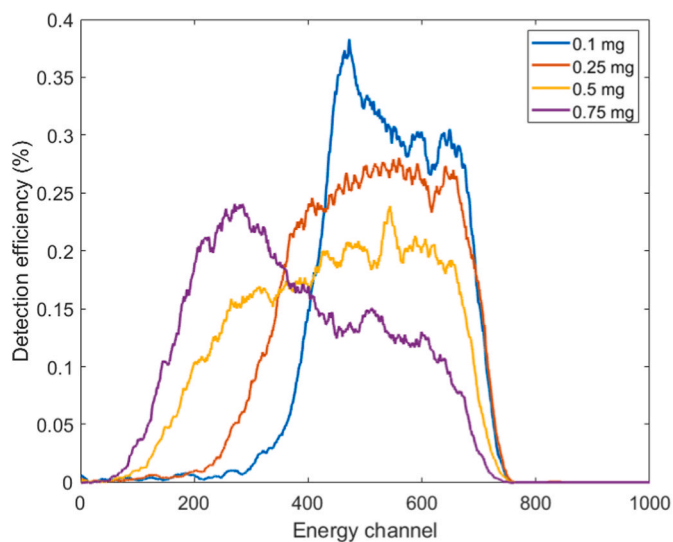


Fig. 5. Spectra obtained in the analysis of samples containing different amounts of Au.

seawater) were analysed with the aim of determining which pretreatment is needed and whether the full method could be applied to environmental samples of differing composition (i.e. mineral salts, organic matter, ...).

The first sample pretreatment evaluated consisted of evaporation to dryness and the treatment of the residue with 8 M HNO_3 and H_2O_2 30% to ensure organic matter destruction. Following a second evaporation to dryness, the samples were reconstituted in HNO_3 3 M and $\text{Al}(\text{NO}_3)_3$ 0.5 M. The results obtained were satisfactory since retention of Pu within the PSresin in the column was quantitative and the quantification error was low: 1.3% for seawater and below 0.5% for river water. Moreover, SQP(E) values were high, at 714 and 717 for seawater and river water

respectively, and the spectrum appeared well positioned and defined (Fig. 6A and B).

Having shown that the method developed is not affected by the sample matrix, the same samples were analysed but with the addition of gold as a tracer (0.25 mg). In this case, the results were not satisfactory in terms of gold recovery since gold remained precipitated during the reconstitution of the sample after the last evaporation step. Therefore, this pretreatment was discarded since it was valid for Pu but not for Au.

In order to find a pretreatment condition compatible with the addition of gold, two different approaches were considered: preconcentration without evaporation to dryness to avoid gold precipitation and aqua regia treatment of the evaporation residue to allow gold redissolution.

For the blank and active samples of river and seawater treated without full evaporation, it was shown that the retention of gold was quantitative, as well as the retention of plutonium, the retention of which was confirmed by the measurement of the eluted solutions by liquid scintillation. However, the presence of incompletely digested organic matter affected the position of the spectra (Fig. 6C and D), which were partially located below channel 200. As a consequence, the quantification error was high (31% for river water and 14% for seawater) due to the fact that the presence of organic matter causes quenching that modifies the detection efficiency.

Pretreatment with aqua regia was more satisfactory, with the spectra obtained being in a similar position to the standard sample spectrum

(Fig. 6E and F). Moreover, the recovery was high and quantification error was below 10% for both water matrices. To confirm the viability and reproducibility of the aqua regia treatment, two more replicates were performed under the same conditions (Table 8). The yield obtained was high in all cases and quantitative in most of them. Again, plutonium quantification had errors below 10%, which demonstrates that spectrum position was adequate and that the detection efficiency obtained in standard samples (95%) can be used for the quantification of samples. Moreover, the results confirmed that gold works well as a tracer of

Table 8

Yield and quantification deviation obtained in the analysis of spiked river water and seawater samples treated through evaporation to dryness and aqua regia redissolution.

Sample	Yield (%)	Quantification error (%)
River water (blank)	99.3	
River water (1st replicate)	92.2	9
River water (2nd replicate)	99.4	6
River water (3rd replicate)	99.9	8
Seawater (blank)	72.9	
Seawater (1st replicate)	76.6	-4
Seawater (2nd replicate)	99.9	-4
Seawater (3rd replicate)	99.9	10

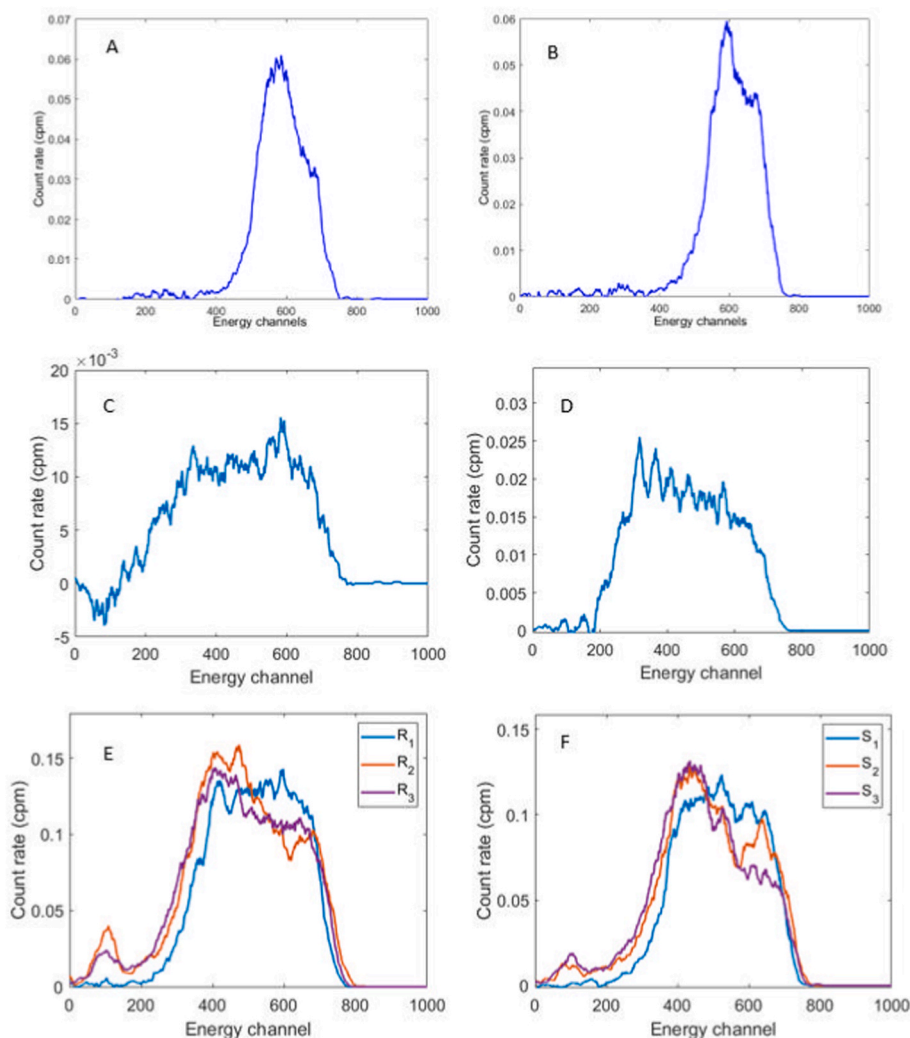


Fig. 6. Spectra obtained in the analysis of spiked river water and seawater samples treated through evaporation to dryness (A river; B sea). Spectra obtained in the analysis of spiked river water and seawater samples treated through incomplete evaporation to dryness (one replicate) (C river; D sea) and aqua regia redissolution (three replicates) (E river; F sea).

plutonium due to the fact that, in those cases where the retention of plutonium in the PSresin cartridge was not quantitative, this retention was correctly evaluated through the measurement of gold, as well as in those with quantitative retention of plutonium.

It should be pointed out that there was a small amount of luminescence between energy channels 0 to 200. However, the associated increase in counts had no effect on quantification since the integration window was between channels 200 and 1024.

Finally, the minimum detectable activity was calculated with Curie's expression being 0.073 Bq/L, taking into consideration a sample volume of 100 mL, a background value of 1.20 cpm and 3 h of measurement.

4. Conclusions

Pu determination using PSresin was found to be effective, with optimal separation from other interferents found in environmental samples. As a consequence, the rapid determination of Pu is possible while avoiding the generation of mixed wastes. The need to perform adequate valence adjustment under acidic conditions to achieve Pu (IV) as the overall oxidation state was demonstrated. Samples in HNO₃ 3 M and Al(NO₃)₃ 0.5M with the addition of iron sulphamate(II), ascorbic acid and sodium nitrite gave the optimal results. A complete separation process was established, showing good reproducibility of results. The application of this method to real environmental samples showed good results when nitric acid and hydrogen peroxide pretreatment were performed and no gold was used.

For quantifying the retention of plutonium, it was shown that gold behaves in an analogous way to plutonium, enabling its use as a tracer. In this scenario, HCl 1 M is needed in the loading solution to stabilize gold and avoid its reduction to metallic gold and its precipitation. Under such conditions, the amount of Pu in seawater and river water samples was determined with quantification errors below 10%. The use of gold as a tracer was shown to be successful since even the samples with no quantitative retention of Pu were quantified correctly thanks to the gold correction. Nevertheless, it should be pointed out that gold and plutonium have different chemistry, and therefore this phenomenological similar behaviour observed in the treatment and separation conditions described should be contrasted with other quality control processes (e.g. periodic measurement of spiked samples). Moreover, this phenomenological similitude should be checked again when changes on the procedure or in the nature of the sample took place.

This study was therefore successful at developing a new methodology to achieve Pu isotope quantification without the use of alpha spectrometry as the detection technique, allowing its determination within 1.5 h of separation plus 3 h of measurement with a limit of detection low enough for emergency situations.

CRedit authorship contribution statement

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

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