



A new method based on selective fluorescent polymers (PSresin) for the analysis of ^{90}Sr in presence of ^{210}Pb in environmental samples

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ABSTRACT

^{90}Sr is of major concern in emergency and environmental control plans. It is one of the main fission products in nuclear facilities and is a high-energy beta emitter that presents chemical properties similar to those of calcium. ^{90}Sr is commonly detected using methods based on liquid scintillation counting (LSC) following a chemical separation to remove potential interferences. However, these methods generate mixed wastes (hazardous and radioactive). In recent years, an alternative strategy using PSresins has been developed. For ^{90}Sr analysis with PSresins, ^{210}Pb is the main interferent that should be considered, as it is also strongly retained in the PSresin. In this study, a procedure was developed involving a precipitation with iodates to separate lead from strontium before the PSresin separation. Moreover, the method developed was compared with well-established and routinely used methods based on LSC, revealing that the new method produced equivalent results in less time and with less waste generation.

1. Introduction

Nuclear energy currently accounts for up to 11.5% of global electricity production (Schneider et al., 2022). This energy source offers the advantage of being carbon dioxide (CO_2) emission-free, making it a valuable tool in the strategy against climate change. Additionally, it is a cost-effective source of energy. However, it carries the risk of environmental contamination, particularly in the event of accidents or uncontrolled spills during nuclear power plant (NPP) operations and decommissioning, which can result in the release of radionuclides into the environment. To mitigate the potential damage caused by such incidents, efficient environmental monitoring is crucial. Among the pure beta-emitting radionuclides that could contaminate the environment, ^{90}Sr (E_{max} : 545.9 keV) is of particular interest in environmental measurements because it is one of the main ^{235}U fission products and may remain in the environment for a longer time due to its long half-life ($T_{1/2}$: 28.80 years) (Bé et al., 2016). The danger of ^{90}Sr stems from its high mobility, migrating from rivers and soils into food chains. It can contaminate products like milk, as it shares physicochemical properties with calcium and can be absorbed into the body. Once ingested, it becomes a source of radiation in the bones. The Spanish normative, following European directives and international recommendations, has set the limit of ^{90}Sr in drinking water at 4.9 Bq/L (REAL DECRETO 3,

2023).

Historically, ^{90}Sr analysis has been a matter of concern due to the need to separate out interferences prior to beta counting. Various methods have been described in the literature for ^{90}Sr analysis, with the main difference being the strategy followed to separate out the most common interferences (Vajda and Kim, 2010). One of the most used methods is the one recommended by the International Atomic Energy Agency (IAEA). It involves the separation of strontium from interferences, mainly calcium but also lead, yttrium or actinides, by exploiting the different solubility of the respective nitrates, chromates and hydroxides using fuming nitric acid and chromate as the precipitating agents (IAEA et al., 1989; Tayeb et al., 2015; Johnson et al., Pecora). This method is laborious, and to achieve good separation, the precipitations need to be repeated several times. The methods in the literature often include a preliminary precipitation step (for separation or sample concentration) followed by other separation strategies. Chobola et al. (2006) recommended first preconcentrating the strontium in an alkaline medium by precipitating with carbonates, whereas Maxwell and Culligan (2009) suggested coprecipitation of strontium along with calcium using phosphate. Several methods suggest the use of extraction chromatography for ^{90}Sr isolation. Extraction chromatography or solid-phase extraction follows the same principles as solvent extraction, but the compounds that interact selectively with the target element are impregnated in a

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solid support (i.e. resin) and placed in a chromatographic column. As an example, is the case of the Sr-Resin developed by Eichrom Technologies (Eichrom Technologies, 2014) and based on the work of Horwitz et al. (1991). This extraction chromatography resin contains a crown ether, 4, 4'-(5'')-di-*t*-butylcyclohexano-18-crown-6 (DtBuCH18C6), that specifically retains strontium through a complexation in a strong nitric media solution, effectively removing interfering cations. After elution, the strontium can be measured using a liquid scintillation counter or a proportional counter (Triskem International, 2015).

Although the pretreatment methods for Sr analysis are robust and several applications have been established, they do have certain weaknesses. For example, lengthy procedures can be a problem in emergency situations. Furthermore, measuring ^{90}Sr by liquid scintillation generates a significant amount of mixed liquid waste (hazardous and radioactive). Proper management of this kind of waste requires specific treatment procedures. Moreover, the use of hazardous reagents such as fuming nitric acid and chromatates poses risks for the analyst. In this context, new methods are being developed to reduce procedure length, waste generated and the use of dangerous reagents. One promising approach involves the use of plastic scintillation resins (PSresins).

PSresins are produced by immobilizing a selective extractant, which is specific for a certain radionuclide, onto the surface of plastic scintillation microspheres (Coma et al., 2019; Torres et al., 2022; Giménez et al., 2021). These PSresins, when packaged in a solid-phase extraction (SPE) cartridge, offer several advantages. Firstly, they integrate the separation and measurement process into a single step, eliminating the need for liquid scintillators and thus reducing the generation of mixed wastes. Furthermore, it reduces the number of procedure steps by eliminating the requirement for elution or processing of the measuring sample. Moreover, the use of fuming nitric acid to remove interferents is avoided.

This approach has been already applied for radiostrontium (Bagán et al., 2011) using 4,4'-(5'')-di-*t*-butyldicyclohexano-18-crown-6 in 1-octanol (Sr-PSresin) as the extractant (Sáez-Muñoz et al., 2018). However, it has been observed that there are other elements, such as lead, that are also retained in the column and cannot be eluted. In fact, that same PSresin can be used to measure ^{210}Pb (Lluch et al., 2016), a naturally occurring low beta-emitting radionuclide that could be present in environmental samples. When both ^{210}Pb and ^{90}Sr are measured with the PSresin, the ^{210}Pb spectrum overlaps with part of the ^{90}Sr spectrum when the measured immediately after separation (Fig. 1). This overlap persists throughout the whole spectrum when secular equilibrium was achieved after 21 days due to the ingrowth of ^{210}Bi . Therefore, quantification of ^{90}Sr can only be performed at $t = 0$ in the region above channel 450, where the influence of ^{210}Pb is minimal, or at 21 days if all the Pb has been completely removed from the loading sample. Removal of Pb is crucial to avoid quantification errors and false positive results. Precipitation methods can be effective in achieving separation if one of

the elements (target or interferent) precipitates quantitatively. In the case of extraction chromatography, successful separation can be achieved if the target or the interferent is retained or eluted quantitatively during loading, cleaning or elution. With the PSresin, as the target radionuclide must remain in the column for later measurement, the interferent (Pb) cannot be retained during loading or cleaning stages. Since Pb has a higher affinity for the crown ether than Sr, a selective precipitation is necessary before column separation to prevent the loading and retention of ^{210}Pb in the PSresin.

This study presents a novel analytical method for the measurement of ^{90}Sr in environmental samples, even in the presence of ^{210}Pb , utilizing PSresins. The proposed method demonstrates successful quantification through the utilization of optimal windows and a selective pretreatment procedure involving the precipitation of strontium before passing it through the PSresin. A comprehensive comparison of this new method with various standard methods currently in use has been conducted.

2. Experimental

2.1. Reagents and solutions

All the reagents used were of analytical grade and double deionized water was used. Lead and strontium standards (10000 mg/L) were from Inorganic Ventures (Christiansburg, USA). Iron solution of 5 mg/L was prepared with iron nitrate (III) supplied by Sigma Aldrich (Burlington, MA, USA). Nitric acid (69%), ammonia (25%) and oxalic acid were supplied by PanReac (Castellar del Vallés, Spain). Crown ether, 4,4'-(5'')-di-*t*-butyldicyclohexano-18-crown-6, 1-octanol, sodium iodate, di-ammonium hydrogen phosphate, potassium iodate and calcium nitrate were supplied by Sigma Aldrich (Burlington, MA, USA). A ^{210}Pb active stock solution of 160 Bq/g (4.8) was prepared from a standard of 35.5 kBq/g (1.1) (CEA/DAMRI, Gif-Sur-Yvette CEDEX, France) with 22 years of ingrowth, while a $^{90}\text{Sr}/^{90}\text{Y}$ active stock solution of 38.45 Bq/g (0.29) was prepared from a standard of 4071 Bq/g (31) in a solution of strontium (100 $\mu\text{g/g}$) and yttrium (100 $\mu\text{g/g}$) in 0.1 M HCl (Amersham International, Buckinghamshire, England).

Sr-PSresin was prepared following a procedure developed in (Bagán et al., 2011) using plastic scintillation microspheres of 60 μm (Santiago et al., 2013) and the crown ether. Sr-Resin in 2 mL cartridges were supplied by Triskem International (Rennes, France).

Empty SPE cartridges (2 mL) and frits were supplied by Triskem International (Rennes, France). 20 mL polyethylene vials and the Gold XR liquid scintillation cocktail were purchased from PerkinElmer (Waltham, USA).

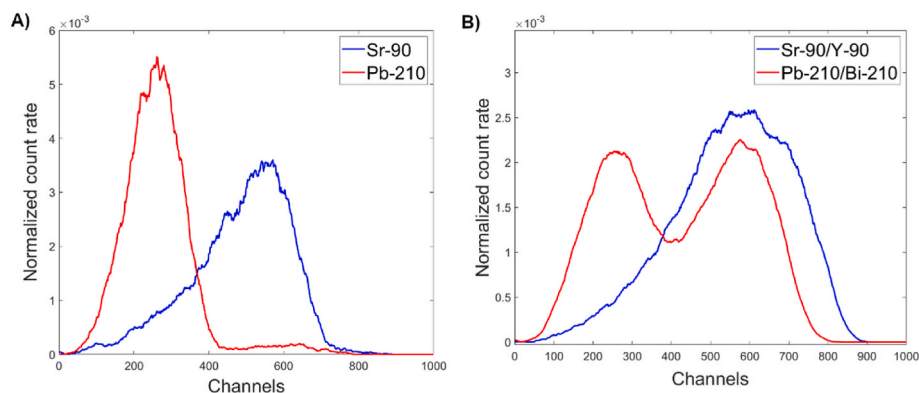


Fig. 1. ^{210}Pb (red) and ^{90}Sr (blue) normalized spectra in the PSresin at time 0 (A) and with ingrowth daughters at time >21 days (B). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Samples

The samples analyzed for method comparison were:

- River water sample

Spiked river water samples were prepared by adding known amounts of ^{210}Pb and $^{90}\text{Sr}/^{90}\text{Y}$ standards to river water obtained from the Ebro River in Ascó (Tarragona, Spain). The samples were filtered through a 0.45- μm filter before being spiked. Two activity levels were prepared: 4.9 Bq/L and 0.49 Bq/L.

- MAPEP water samples

Two interlaboratory samples from the MAPEP program were used: MAPEP-16-MaW34, with a ^{90}Sr activity range of 5.65–10.48 Bq/L, and MAPEP-10-MaW22 without strontium. The samples were diluted 1:10.

- CSN Interlaboratory water sample (CSN sample)

An interlaboratory sample from the Consejo Seguridad Nuclear (CSN) with a ^{90}Sr activity of 4.1 Bq/L (0.2) was used. This sample contains other radionuclides, with ^{57}Co (4.7 Bq/L), ^{60}Co (3.1 Bq/L), ^{134}Cs (3.8 Bq/L), ^{238}Pu (0.41 Bq/L), ^{226}Ra (0.62 Bq/L), ^{210}Pb (0.62 Bq/L) and ^{228}Ra (1.12 Bq/L) being the most relevant.

2.3. Apparatus

A Quantulus 1220 liquid scintillation spectrometer (PerkinElmer, Waltham, USA) with logarithmic amplification, a multichannel analyzer (MCA) (4096 channels distributed in four segments of 1024), alpha/beta discrimination and background reduction via an active guard were used for the scintillation measurements.

The analysis of stable strontium and lead for yield determination was undertaken using an OPTIMA 8300 ICP-OES detector (PerkinElmer, Waltham, USA) or an ELAN-6000 ICP-MS detector (PerkinElmer, Waltham, USA) from the Technological and Scientific Centres of the University of Barcelona (CCIT-UB).

2.4. Procedures

2.4.1. Preparation of the Sr-PSresin cartridges

Sr-PSresin cartridges (Coma et al., 2019) were prepared by filling a 2 mL SPE cartridge with 1.4 g of Sr-PSresin into. The cartridges were sealed with a filter and a stopper. To ensure PSresin homogenization, the cartridges were placed in a vacuum chamber, and 10 mL of water were passed through each one at a flow rate of 1 mL/min. Prior to loading the sample onto the cartridge, each column was vortexed for 3 min at 3000 rpm.

2.4.2. Study of preliminary precipitation methods previous to PSresin separation

A preliminary study was conducted to investigate the necessary pretreatment for separating Pb and Sr before passing through the PSresin was performed. The aim was to identify the precipitation method that yielded optimal results for the purpose of the paper. For this study, four samples were prepared in 25 mL conical tubes, each containing 5 mg of lead and 5 mg of strontium. Later, both metals were measured in the different solutions obtained using ICP-OES to confirm if the separation was achieved and to determine the separation yield.

- Separation of lead and strontium by oxalate precipitation

3 g of oxalic acid and 2 g of calcium nitrate were added to the samples. The mixture was placed in a water bath at 45 °C for 15 min. NH_3 was added until the pH ranged between 4 and 6.5, leading to the

precipitation of strontium. The tubes were centrifuged at 5000 rpm for 5 min to separate the precipitate from the supernatant where lead should remain. The precipitate was further treated with 8 M nitric acid and placed in a water bath for 45 min at 45 °C for solubilization.

- Separation of lead and strontium by chromate precipitation

4.85 g of potassium chromate and 0.4 g of barium nitrate were added to the samples. The mixture was placed in a water bath for 1 h at 45 °C to maximize the solubilization of strontium chromate. Nitric acid was then added to the samples until the pH reached a range between 3 and 5.5, measured with a pH-meter. Within this pH interval, lead precipitates while strontium remains in solution. The samples were centrifuged for 5 min at 5000 rpm. The supernatant was separated and adjusted with ammonia until the pH ranged between 8 and 10, causing strontium to precipitate. To facilitate coprecipitation of strontium, 0.2 g of barium, in the form of barium nitrate, was added during this step. The tubes were centrifuged once again and the strontium precipitate was separated from the supernatant. The precipitate was treated with nitric acid and placed in a water bath at 45 °C for solubilization.

- Separation of lead and strontium by iodate precipitation

1 g of sodium iodate and 0.41 g of calcium nitrate were added to the samples. The mixture was then placed in a water bath for 15–20 min at 45 °C. The solution was adjusted, if necessary, to a pH range of 1 and 8 using nitric acid to facilitate the precipitation of lead. Afterward, the samples were centrifuged for 5 min at 5000 rpm. The supernatant, where strontium should remain, was separated from the solid. The solid, containing only lead, was dissolved with nitric acid and put in a water bath for 10 min.

- Separation of lead and strontium by hydrogen phosphate and citrate precipitation

0.125 g of di-ammonium hydrogen citrate and 0.25 g of di-ammonium hydrogen phosphate were added to the samples. The mixture was then neutralized to pH 7. As a result, the solution became cloudy, indicating the formation of lead phosphate, and was left to stir for 10 min. Subsequently, the solution was filtered, and the resulting solution was adjusted to a pH of 10, causing the formation of a suspended strontium precipitate. The mixture was allowed to sit for 30 min without stirring before the tubes were centrifuged. The supernatant was separated from the precipitate. The solid precipitate, containing only strontium, was dissolved with nitric acid.

2.4.3. Methods for ^{90}Sr analysis

The performance of the PSresin method was compared with two methods already employed in our laboratory for the analysis of ^{90}Sr . The detailed procedures for each method are described next.

- Extraction chromatography-LSC (EC-LSC)

A 100 mL aliquot of the interlaboratory water sample from the CSN was spiked with 5 mg of a strontium solution and evaporated to dryness. The resulting solid was reconstituted with 10 mL of 3 M nitric acid. Sr-Resin TrisKem cartridges were then placed in a vacuum chamber and conditioned with 20 mL of 3 M nitric acid at a flow rate of 1 mL/min. Subsequently, 10 mL of the sample were passed through the cartridges at a flow rate of 2 mL/min, followed by two elutions. The first involved 10 mL of a 3 M nitric acid/0.05 M oxalic acid solution (1 mL/min) to remove Pu(IV), Np(IV), Zr(IV) or Ce(IV), which could be retained by Sr-Resin. The second elution utilized 10 mL of 8 M nitric acid to remove any remaining oxalic acid and ensure complete removal of K^+ and Ba^{2+} . Finally, the strontium retained in the cartridges was eluted with 30 mL of 0.05 M nitric acid. The resulting solution was evaporated to dryness

and reconstituted with 20 mL of 0.2 M nitric acid. 8 mL of this final sample were mixed with 12 mL of scintillation cocktail (Ultima Gold XR) and measured in a Quantulus detector. The final sample was also analyzed by ICP-OES to determine the amount of stable strontium present. The ICP-OES results were used to calculate the strontium recovery by comparing the amount of stable strontium initially added to each sample. Three replicate samples were analyzed.

- Successive precipitations-LSC (SUC-LSC)

1 L of the river water sample spiked with ^{90}Sr was analyzed. The sample was filtered through a fiberglass filter (1.6 μm porous size). To the filtered solution, 56 mg of stable strontium was added, followed by heating and stirring. Subsequently, 1 mL of 25% ammonia and 20 g of ammonium carbonate were added. After the solution reached room temperature, it was filtered through a fiberglass filter (1.6 μm porous size). The resulting precipitate was redissolved with 8 M nitric acid (10 mL) and double deionized water (10 mL). To this solution, 50 mL of fuming nitric acid were added, and another filtration step was performed using fiberglass filter with a porous size of 1.6 μm . The precipitate was redissolved in 20 mL of double deionized water. The process of isolating the precipitate and redissolving it was repeated after the addition of 60 mL of fuming nitric acid. Following this, 0.5 mL of a stable barium solution (10 mg/L) were added, followed by 4 M ammonia to achieve a pH of 5–5.2 and 1.5 mL of an ammonium acetate buffer solution (pH 5.2). The solution was heated to boiling and 0.5 mL of a 1.5 M sodium chromate solution were added. After cooling the solution, it was filtered once again using a fiberglass filter (1.6 μm porous size). Subsequently, 1 mL of 25% ammonia and 20 g/L ammonium carbonate were added to the filtered solution. The mixture was heated and filtered again using a fiberglass filter (1.6 μm porous size) once it reached room temperature. The solid obtained was redissolved in 10 mL of 4 M nitric acid and 20 mL of water. To this solution, 1 mL of a 6% hydrogen peroxide solution and 0.5 mL of a 5 mg/L iron (III) solution were added. The solution was boiled for 10 min, followed by 15 mL of 25% ammonia to achieve a pH of between 9 and 10. After cooling to room temperature, another filtration step was carried out using a fiberglass filter (1.6 μm porous size), with the solid washed with diluted ammonia before the addition of ammonium carbonate to the filtered solution. The solution was heated, before cooling it down and filtering it through a fiberglass filter (1.6 μm porous size). The resulting precipitate was redissolved with 40 mL of 0.2 M nitric acid. The solution was then evaporated to dryness and reconstituted with 20 mL of 0.2 M nitric acid. For measurements, 8 mL of the final sample solution were mixed with 12 mL of the Ultima Gold XR liquid scintillation cocktail and analyzed using a Quantulus detector. In addition, the final sample was analyzed using ICP-OES to determine the concentration of stable strontium present, enabling the calculation of recovery. Only one replicate was analyzed.

- PSresin method

This method consisted of two steps: the precipitation of strontium using phosphate and iodate, followed by final separation with the PSresin. The selection of the pretreatment was based on the results obtained from the preliminary study (sections 3.4.2 and 4.1).

Samples containing known activity of ^{90}Sr and ^{210}Pb were prepared in beakers. 1 g of sodium iodate as the precipitating agent and 0.41 g of calcium nitrate were added to the samples. The beakers were boiled for 15 min and then centrifuged for 5 min at 5000 rpm. The supernatant was decanted, and 0.5 g of di-ammonium hydrogen phosphate was added. Ammonia was added until a pH of 10 was reached, resulting in the formation of a strontium precipitate. This step is crucial to remove other matrix interferences that are not separated during the iodate precipitation. The mixture was centrifuged again, and the supernatant was decanted. The remaining solid was dissolved in 11.5 mL of 8 M nitric acid. Subsequently, 10 mL of this solution were passed through the PSresin

cartridge. Fig. 2 illustrates the procedure diagram.

PSresin cartridges were connected to a vacuum box, and the pressure was adjusted to 5 inHg. They were then conditioned with 2 mL of 8 M nitric acid. Next, 10 mL of the sample were passed. Afterward, two rinses with 2 mL of 8 M nitric acid and two rinses with 2 mL of 6 M lithium nitrate were performed. Finally, the cartridges were left for 5 min at 20 inHg to remove any remaining solution between the PSresin particles. The PSresin cartridges were placed in a 20 mL polyethylene scintillation vial for measurement. The solution that passed through the PSresin was collected in a 50 mL conical tube to determine the yield.

2.5. Measurements

All the measurements with the Quantulus detector were performed in the low coincident bias and “ ^{14}C ” configuration.

The samples were measured immediately after separation to prevent ^{90}Y ingrowth, using 3 cycles of 20 min with 10 min for the SQP(E) parameter. The river water samples, having an activity of 0.49 Bq/L, and the MAPEP samples were measured in 15 cycles of 20 min, with 10 min for the SQP(E). Blank samples were measured using the same time durations.

The samples were measured after 21 days for 12 h, with 10 min for the SQP(E).

The ICP-OES samples were prepared by diluting a certain amount of solution with 1% nitric acid to achieve a maximum concentration of 5 mg/L of Sr or Pb. The fractions measured included solutions from the preliminary study that might contain lead or strontium, samples from the different steps of the separation procedure, eluted solutions from the PSresin cartridge and the Sr-Resin as well as the initial samples and standards.

2.6. Data treatment

The spectra obtained from the scintillation measurements were smoothed using the Savitzky–Golay algorithm, with an average window of 21 points and a first-degree polynomial. The smoothing process was applied within the range channels 1 to 1024. The net spectrum was obtained by subtracting the spectrum of the corresponding blank solution. The detection efficiency spectrum was obtained as the ratio between the net counts in each channel and the activity in the PSresin cartridge.

The uncertainty values quoted correspond in all cases to the standard deviation of replicate measurements.

The optimal windows were determined using in-house program built in Matlab 2019 (Mathworks, Natick, Massachusetts, USA). The program calculated the figure of merit (Eff^2/Bkg) for several channel windows and identifies the region with the highest FM value.

The Medusa/Hydra free software (Royal Institute of Technology, Stockholm, Sweden) was used to simulate the chemical equilibrium and plot the logarithm of the concentration against pH variation (1–14) for the different precipitating agents investigated. The simulations were conducted using a 100 mL volume containing 5 mg of Sr and 5 mg of Pb, with the precipitating agents present at a concentration of 1 M.

3. Results and discussion

The work was divided into two sections. The first section aimed to investigate various precipitation pre-treatments to selectively remove Pb from Sr prior to passing the sample to the PSresin. In the second section, the final procedure, including precipitation, separation, and measurement of Sr using the PSresin, was validated by comparing it with established reference methods.

3.1. Preliminary lead separation studies

The initial phase involved investigating different precipitation pre-

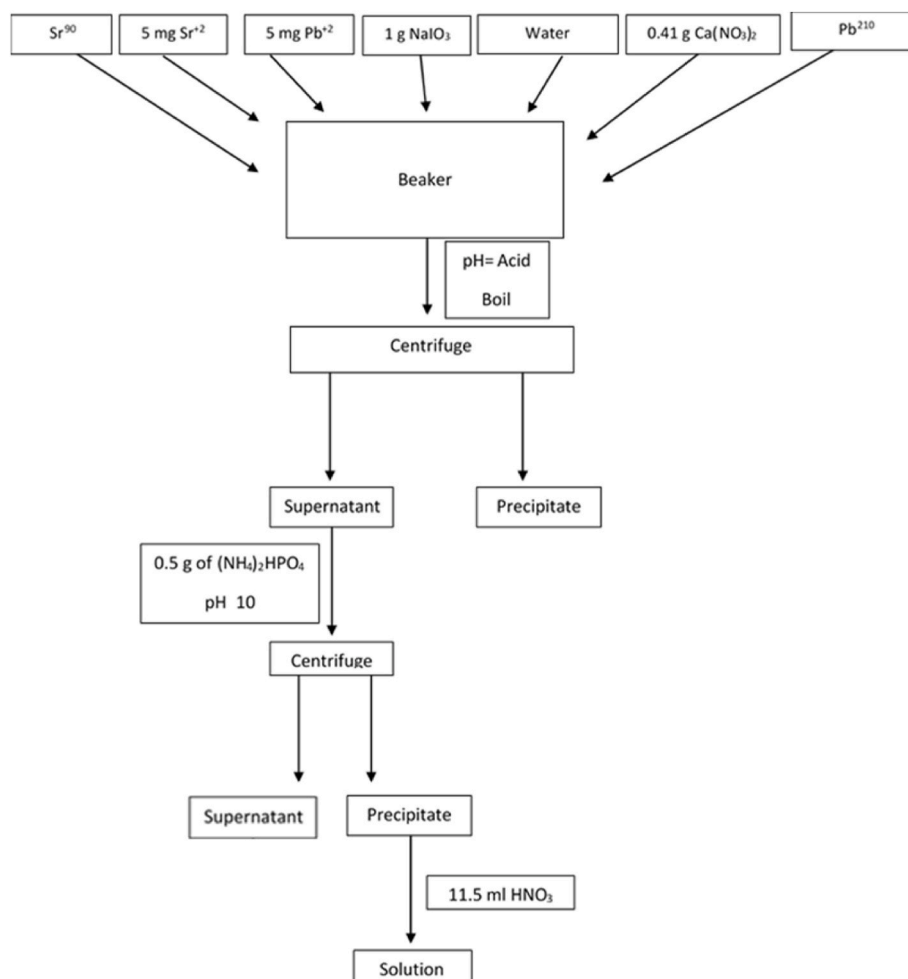


Fig. 2. Pre-treatment involving the use of iodate and phosphate to precipitate strontium.

treatments in which Pb could be removed selectively from Sr. The selection of methods was based on their descriptions in the literature and the results obtained from the software Medusa. Four different precipitation methods were evaluated, namely oxalate, hydrogen phosphate plus citrate, chromate or iodate. Table 1 shows the recovery of Sr and Pb in the solution after the application of each procedure to four replicate samples.

The hydrogen phosphate plus citrate method demonstrated a separation efficiency of 59% (11) of Sr, carrying with only 6% (8) of Pb being carried along. However, this method was quite irreproducible, as indicated by the standard deviations and the RSD values associated with it. This is not, in fact, a problem for Sr, but it poses a concern for Pb, as there is a probability that Pb may reach the PSresin cartridge. In one of the replicates, 18% of Pb remained in the solution. Due to the lack of reproducibility, this method was not selected for further use.

The chromate proved effective in separating Sr, with almost no Pb remaining in the solution. It resulted in the lowest concentration of Pb in

the strontium fraction compared to other methods. However, the yield of Sr was too low and the method displayed low reproducibility. Moreover, the use of chromate is not recommended due to its toxicity. However, the main reason for discarding this method was the yellow solution, which would produce color quenching when loaded into the PSresin cartridge, thereby decreasing the detection efficiency.

In the iodate method, a recovery of 72% (2) for Sr and only 5% (1) of Pb was achieved. On first sight, this method was more reproducible than the phosphate method, with better recovery rates. However, it was observed that in the initial acidic medium, both metals precipitated upon the addition of iodate, contradicting the indications from the Medusa diagrams which suggested only Pb would precipitate. By adding 8 M nitric acid, only strontium iodate dissolved, effectively separating Sr from Pb. Despite this discrepancy, this iodate method could be optimal for the separation of Sr from Pb.

Finally, precipitation with oxalate did not result in a satisfactory separation as both metals were precipitated and dissolved together, without achieving the desired selectivity.

Among the four methods, precipitation with iodates was selected. Even with that, the precipitation of Pb and Sr was temperature-dependent, as strontium iodate could be redissolved in boiling water (Sunderman and Townley, 1960). Therefore, separation using this method was not consistently satisfactory.

Bearing in mind the results from the preliminary study and the available literature, a final procedure was developed (experimental section 3.4.3) that was suitable for use with the Sr-PSresin. In this procedure, the precipitation of Sr from the sample was carried out using iodate and calcium as a coprecipitating agent, along with the boiling of

Table 1

Recovery of strontium and lead from the sample after applying the precipitation procedure, expressed as the mean plus standard deviation in brackets. 4 replicates were done for each method.

Method	Sr %	Pb %
Oxalate	83 (2)	103 (4)
Hydrogen phosphate + citrate	59 (11)	6 (8)
Chromate	31 (15)	0.65 (0.03)
Iodate	72 (2)	5 (1)

the sample. Increasing the temperature resulted in an increase in the solubility of Sr, allowing it to remain in solution while lead iodate precipitated. After removing the lead iodate precipitate, Sr was precipitated using hydrogen phosphate in a basic medium and subsequently dissolved in 8 M nitric acid for passage through the PSresin. This method was proven successful in achieving a nearly complete recovery of Sr, with only 3% of Pb remaining (Table 2), effectively eliminating any potential matrix interference. Furthermore, the method demonstrated good reproducibility.

The absence of ²¹⁰Pb in the PSresin was verified by examining the spectra obtained from cartridge measurements (Fig. 3). It was observed the absence of any peak within the energy channel range of 100–400. This confirmed that there was no presence of ²¹⁰Pb in the PSresin.

Once the method development was complete, the detection efficiency for ⁹⁰Sr in the PSresin was determined by analyzing three replicate standard samples of 10 mL. The integration window was selected following the study of the figure of merit, which involved choosing the window with the highest difference between the ²¹⁰Pb and ⁹⁰Sr spectra. To achieve this, the spectrum of a standard sample of ²¹⁰Pb was utilized as reference for the blank, while the spectrum of the ⁹⁰Sr standard served as the sample. This approach generated a channel range where the influence of ²¹⁰Pb on ⁹⁰Sr was minimal. Table 3 presents the detection efficiency values immediately after separation and after a 21-day period in the optimal window.

Concerning the selected optimal windows, it is important to note that immediately after separation, the contribution of Pb to the counting rate was minimal, as indicated by the absence of any signal from ²¹⁰Pb above 450 (Fig. 1). However, at equilibrium, there was a noticeable overlap with ²¹⁰Bi, highlighting the need for effective separation of ²¹⁰Pb from ⁹⁰Sr.

The complete method was initially validated by applying it to two different interlaboratory samples (MAPEP-16-MaW34 and MAPEP-10-MaW22). Table 4 shows the results obtained for both samples. For the MAPEP-16-MaW34 sample, the results obtained fell within the acceptable range for both time zero and secular equilibrium. Regarding the MAPEP-10-MaW22 sample, the results obtained were satisfactory because the sample did not contain ⁹⁰Sr and the count rate registered was below the limit of detection.

3.2. Validation through method's comparison

The method validation was performed by comparing the PSresin method with the two most common methods for ⁹⁰Sr analysis:

- EC-LSC method was compared with the PSresin method using a water sample with medium ⁹⁰Sr activity that also contained other radionuclides.
- The SUC-LSC method was compared with the PSresin method using a river water sample spiked with a very low activity of ⁹⁰Sr.

3.2.1. EC-LSC vs the PSresin method

100 mL of an interlaboratory water sample from the CSN with a theoretical ⁹⁰Sr activity of 4.1 Bq/L (0.2) (CSN sample) and containing several interferences was analyzed following two different procedures: (1) The EC-LSC method (Triskem International, 2015) (Triskem International, 2023) and (2) The PSresin method with Pb separation

Table 2
Recovery of Sr and Pb by precipitating with iodate before precipitating with hydrogen phosphate. Three replicates were performed.

Sr (%)	90 (4)
Pb (%)	3 (1)

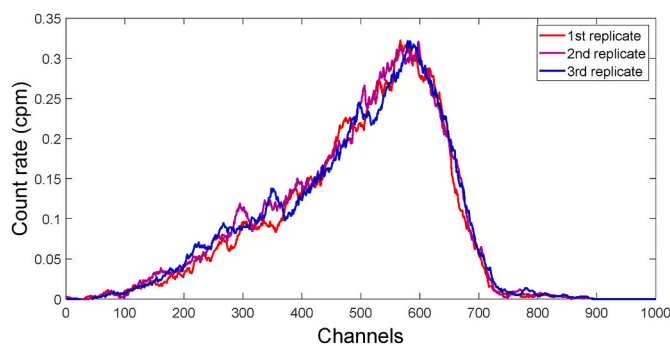


Fig. 3. Spectra obtained with the PSresin after the precipitation with iodates.

Table 3

Detection efficiency for ⁹⁰Sr at separation (t = 0) and after 21 days (t > 21 days) in the full and optimal windows. Three 100 mL replicate standard samples were analyzed.

t = 0		t > 21 days	
Full (1:1024)	Optimus (450:632)	Full (1:1024)	Optimus (517:875)
86 (4)	51 (3)	179 (8)	126 (6)

Table 4

Quantification of ⁹⁰Sr in MAPEP samples. Three replicates were performed.

	Activity (Bq/L)		
	t = 0	t > 21 days	Acceptance range 2019
MAPEP-16-MaW34	7.2 (0.7)	5.64 (0.5)	5.65–10.48
MAPEP-10-MaW22	<0.37 Bq/L	<0.20 Bq/L	Not present

(PSresin). Three replicate samples were analyzed by each method. The results obtained are summarized in Table 5.

The Sr recoveries varied for each method, but they were all acceptable as they were higher than 50%, which can be considered the minimum value acceptable to keep the variability associated to the yield determination in an acceptable range. The PSresin method achieved a high recovery, indicating that the precipitation with iodate and phosphate was nearly quantitative. In addition, the PSresin method efficiently removed almost all the Pb, with only 6% (2) remaining in the sample. In contrast, The EC-LSC method yielded lower recoveries, possibly due to the step of Sr elution, where some Sr might have remained retained in the Sr-Resin cartridge.

Regarding the determination of ⁹⁰Sr activity, the EC-LSC method consistently yielded accurate and reproducible results. In contrast, the PSresin method for immediate measurements produced slightly higher values for ⁹⁰Sr activity, which were still within the acceptance range when taking into account the measurement variability. After 21 days, the bias in the PSresin method was corrected, resulting in values that closely approached both the theoretical activity and the values obtained

Table 5

Results obtained in the analysis of CSN sample with medium activity containing interferences using the EC-LSC and PSresin methods. Three 100 mL replicate samples were analyzed.

	Recovery (%)		Activity of ⁹⁰ Sr (Bq/kg)		Background signal (cpm) (optimal window)
	Sr	Pb	t = 0	t > 21 days	
EC-LSC	69 (2)	/	3.9 (0.2)	4.09 (0.08)	4.2 (0.2)
PSresin	87.6 (0.4)	6 (2)	4.6 (0.6)	4.1 (0.1)	0.18 (0.03)

through the EC-LSC method. The results demonstrated the viability of the method by using the PSresin, since none of the other radionuclides present in the sample, including ^{210}Pb , were detected. Finally, the results and variability of the EC-LSC and PSresin methods were equivalent at 21 days.

In view of this, measurements performed at each time point serve different purposes. Immediate measurements offer a quick and initial estimate of the ^{90}Sr activity level in a sample, while measurements after 21 days provide more accurate and precise values of ^{90}Sr activity, but with a longer waiting time.

3.2.2. SUC-LSC vs the PSresin method

For this comparison, a river sample of a large volume (1 L) fortified with a lower activity level (0.4 Bq/L of ^{90}Sr) was used. As the sample volume was quite large, an additional step of carbonate precipitation was introduced. Therefore, the matrix effect in the PSresin method was first studied by analysing 4 samples of increasing volume (100, 250, 500 and 1000 mL), all containing the same level of ^{90}Sr activity (0.4 Bq). The obtained results (Table 6) showed that the quantification was accurate and no matrix effect on the scintillation properties was observed.

After confirming the absence of a matrix effect, the analysis of 1 L river water samples spiked with 0.4 Bq of ^{90}Sr was conducted using two different methods: the PSresin method (three replicates) and the SUC-LSC method, which involved successive precipitations and LSC (one replicate). Both methods yielded optimal results, as it can be seen in Table 7. At $t = 0$, the SUC-LSC method had lower bias, although the bias for the PSresin method was still acceptable for a preliminary analysis. In this regard, the PSresin method was notably faster and less laborious with a total processing time of 5–6 h compared to the 20 h for the SUC-LSC method. Moreover, if we pay attention to the measurements conducted at secular equilibrium ($t > 21$ days), both methods showed the same bias, indicating that the PSresin method can provide the same results for an environmental sample as the reference procedure SUC-LSC, but with a shorter and less laborious method as well as the possibility of processing more than one sample at the same time.

3.2.3. Quality parameter comparison

As the final step in comparing the methods, the values of various quality parameters were assessed, including background, detection efficiency, limit of detection, and analysis time. These parameters were compared and summarized in Table 8.

In terms of the background signal, the LSC methods had higher values compared to the PSresin method. The LSC methods require mixing the sample (8 mL) with a scintillation cocktail (12 mL), resulting in a total volume of 20 mL in the counting vials. In contrast, the PSresin method only requires the presence of the PSresin cartridge (1.4 g of the PSresin) with the retained ^{90}Sr in the counting vial. This dissimilarity in the sample volume and scintillation material makes the LSC method more prone to generating extra background signals through interactions with external radiation. Moreover, the optimal window in the PSresin method is smaller compared to the LSC method, which also affects the registered background signals.

This, in fact, also explains the differences in the detection efficiencies. While both methods presented similar values in the total window, the PSresin method employed an optimal window designed to

Table 6

Bias in the quantification of the river water samples with increasing volume (0.4 Bq/L).

Volume	$t = 0$	$t > 21$ days
	Bias (%)	Bias (%)
100 mL	8.9	6.6
250 mL	6.8	-5.2
500 mL	8.0	0.4
1000 mL	4.7	-1.1

Table 7

Results for the spiked river water samples at environmental levels. One replicate sample was analyzed by SUC-LSC and three with PSresin.

Method	Sr recovery (%)	Bias (%)	
		$t = 0$	$t > 21$ days
SUC-LSC (n = 1)	80.3	1.0	3.5
PSresin	63.3	4.7	-1.1
PSresin	81.3	12.8	-8.3
PSresin	75.5	12.7	-1.9

Table 8

Summary of the quality parameters of the methods applied.

	Efficiency		Background (cpm)	LoD (Bq/L)	Time of analysis (hours)
	$t = 0$	$t > 21$ days			
EC-LSC	96.5	193 (1)	4.1	0.081**	6-7
SUC-LSC	(0.4)			0.068**	20
PSresin	51* (3)	126* (6)	0.3	0.027**	5-6

* Optimum windows detection efficiency

** (1 L and 1 h counting time)

minimize the potential contribution of ^{210}Pb . As a result, a smaller window excluding the first 400 channels was using decreasing the value of detection efficiency.

The combination of these parameters, along with the yield, led to the LoD values calculated following the curie's expression (Currie, 1968). As shown in Table 8, the PSresin method presented a lower limit of detection compared to the other methods. Nevertheless, all methods have LoD values clearly below the values required by the Spanish regulation (0.4 Bq/L).

Finally, the PSresin method appeared to be as fast as the EC-LSC method for samples with high and medium activity levels. For samples with low activity, the PSresin method was significantly faster than the SUC-LSC method. In this sense, the addition of the Pb precipitation step introduces some time delay that is compensated by the simplification of the separation process in the column.

4. Conclusion

A new procedure for ^{90}Sr analysis involving the removal of ^{210}Pb interference has been developed. This procedure incorporates a selective precipitation step with iodates and subsequent redissolution in boiling water, resulting in a high recovery rate of 90% for while minimizing the presence of Pb to only 3%. This makes the quantification of ^{90}Sr possible in samples containing low amounts of ^{210}Pb . Moreover, the procedure has demonstrated its reliability by avoiding false positive results, since the interlaboratory sample MAPEP-10-MaW22, which does not contain ^{90}Sr , was analyzed correctly.

For samples with medium and high activity that contain interferents, the proposed method has demonstrated satisfactory performance when compared to the most commonly used method EC-LSC. The quantification is acceptable and the limit of detection is lower for the same time of analysis.

For samples with low activity and high volume, the PSresin method can reach lower detection limits than the SUC-LSC method with highly reproducible results. While the accuracy of the PSresin method is acceptable, the SUC-LSC method gives better results in this regard. The PSresin method has the advantage of shorter analysis time (5–6 h for the PSresin method vs 20 h for the SUC-LSC method) and uses fewer harmful reagents. Finally, the PSresin method generate less waste, avoiding the production of mixed waste associated with LSC analysis.

CRedit authorship contribution statement

I. Giménez: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **J. Rotger:** Validation, Investigation, Formal analysis, Data curation. **E. Apellániz:** Investigation, Formal analysis. **H. Bagán:** Writing – review & editing, Supervision, Methodology, Conceptualization. **J. Tent:** Visualization, Supervision, Methodology. **A. Rigol:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **A. Tarancón:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

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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