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Simultaneous determination of ^{210}Pb and ^{90}Sr and ^{210}Po isolation in sludge samples using a plastic scintillation resin

J. Martínez [a], M. de los Cobos [a], A. Peñalver [a], A. Tarancón [b,c], I. Giménez [c], H. Bagán [c], C. Aguilar [a,b,*], F. Borrull [a]

[a] Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili Unitat de Radioquímica Ambiental i Sanitaria, Consorci d'Aigües de Tarragona (CAT), Ctra. Nacional 340, Km. 1094, 43895, L'Ampolla, Tarragona, Spain
[b] Serra Hunter Professor, Generalitat de Catalunya, Barcelona, Spain
[c] Department of Chemical Engineering and Analytical Chemistry, Universitat de Barcelona, Diagonal 645, 08028, Barcelona, Spain

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ABSTRACT

This study describes a new and fast method for separating ^{210}Po from ^{210}Pb and ^{90}Sr, before simultaneously measuring the individual activities of the latter two radionuclides using a plastic scintillation resin (PSresin) in sludge samples taken from a drinking water treatment plant. This method speeds up the analysis process significantly by simultaneously measuring ^{210}Pb and ^{90}Sr in a single step. The method is reproducible and has a relative standard deviation of less than 25% for ^{210}Pb, ^{210}Po and ^{90}Sr. The method was satisfactorily validated with an intercomparison sample and applied to sludge samples from a drinking water treatment plant. The minimum detectable activities for 0.9 g of sludge are 5.5 Bq/kg and 8 Bq/kg for ^{210}Pb and ^{90}Sr respectively when measured for 180 min, and 0.5 Bq/kg for ^{210}Po when measured for 5000 min.

1. Introduction

The drinking water treatment plant (DWTP) located in L'Ampolla (Tarragona) collects water from the Ebro River and distributes it across the province of Tarragona. Besides the influence of the terrain's lithology (Martínez et al., 2021b), the main radioactive influences in the lower basin of the Ebro River are the dicalcium phosphate (DCP) production plant, a naturally occurring radioactive material (NORM) industry, and a nuclear power plant (NPP) (Palomo et al., 2010). Generally, the gross alpha and gross beta levels in the water that feeds the DWTP are not significantly high (Palomo et al., 2010) and therefore, the water distributed to the population following the treatment processes comply with Spanish Royal Decree 314/2016 (RD 314/2016, 2016). However, some of the radionuclides that are present in the water stream at very low concentrations can be concentrated in the sludge, generated as a by-product of the different water treatment processes in the DWTP (Peñalver et al., 2020). This matrix can be useful for assessing the presence of some radionuclides that would otherwise be very difficult to measure directly in water samples due to their low levels.

In previous studies focused on determining the presence of different radionuclides in sludge produced by the DWTP, our laboratory found that the main gamma-emitting radionuclides were ^{4} K, ^{7}Be and ^{238}U and ^{232}Th and their decay chain daughters (Palomo et al., 2010). Also, among the descendant isotopes of ^{238}U, the beta emitter ^{210}Pb (Mola et al., 2014) and the alpha emitter ^{210}Po were also determined, with average activities of 37 ± 5 Bq/kg (Fonollosa et al., 2015). The presence of the previously mentioned radionuclides is mainly linked to the lithology of the river basin (Martínez et al., 2021b). Moreover, the presence of some artificial beta radionuclides such as ^{63}Ni and ^{55}Fe (with average activities of 45.5 Bq/kg and 112 Bq/kg respectively) (Fonollosa et al., 2016) as well as ^{90}Sr (with an average activity of 55 Bq/kg) (Mola et al., 2014) was determined and in this case, their origin could be attributed to the NPP located upstream of the aforementioned DWTP.

In general, determining radionuclides requires radiochemical sample pretreatments, which tends to be a complex, tedious and lengthy process (Grate and Egorov, 2003). However, methods that are able to provide a fast response are needed, particularly for emergency situations. Among all the radionuclides we determined in previous studies in sludge samples from the DWTP in L'Ampolla, the present study focuses on determining ^{210}Pb, ^{210}Po and ^{90}Sr due to their radiotoxicity and because they

* Corresponding author. Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili Unitat de Radioquímica Ambiental i Sanitaria, Consorci d'Aigües de Tarragona (CAT), Ctra. Nacional 340, Km. 1094, 43895, L'Ampolla, Tarragona, Spain.
E-mail address: carme.aguilar@urv.cat (C. Aguilar).

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are common radionuclides in natural waters, especially those influenced by NPPs in the case of ^{90}Sr presence (International Atomic Energy Agency, 1963). In this regard, the literature reports several methods using an extraction chromatographic Sr resin to isolate one or even two of these three radionuclides prior to their measurement, in different kind of matrices. Vajda et al. (1997) proposed the sequential analysis of ^{210}Pb and ^{210}Po using this resin and since then, it has usually been the method of choice for isolating these radionuclides in environmental matrices (Kong et al., 2021a; Şahin and Özbay, 2021; Vreček and Benedik, 2002). Given that the time it takes to complete the analysis is one of the most critical considerations when emergency situations arise, our laboratory recently developed a rapid method to sequentially separate ^{210}Pb, ^{210}Po and ^{90}Sr in water samples (Martínez et al., 2021a), as these are targeted radionuclides that must be analysed in drinking water according to Spanish Royal Decree 314/2016 (RD 314/2016, 2016). In this regard, the literature also mentions some other examples also focused on accelerating and optimising the analytical methodology (Fons-Castells et al., 2017a; Mola et al., 2014). Some approaches based on automating the separation procedure, such as those reported by Mola et al. (2014), focused on the determination of ^{90}Sr and ^{210}Pb in DWTP sludge through lab-on-valve multisyringe flow injection analysis (LOV-MSFIA). This has been proven to be a good alternative to traditional radiochemical methods as it reduces reagent consumption and minimises the amount of resin used, and the effluents generated. Other approaches use mathematics to simultaneously and quickly determine the individual activities of different radionuclides present in a given sample (Bagán et al., 2011a; Fons-Castells et al., 2017a,b), as well as some that simplify the conventional separation and sample preparation.

In recent years, a new family of extraction resins with scintillating properties has been developed by the University of Barcelona, named plastic scintillation resin (PSresin) (Barrera et al., 2016; Giménez et al., 2021). This new type of resin is capable of selecting each radionuclide being studied, as it is composed by selective extractants. In this regard, a PSresin for strontium determination was designed as an analogy of the Sr resin (TrisKem) and the plastic scintillator microspheres were coated in DtBuCH18C6 in 1-octanol. The use of this PSresin offers different advantages to Sr resin, such as reducing the time, labour and reagents needed for analysis, unifying chemical separation and sample measurement so they can be completed in one step, and directly measuring radionuclides using liquid scintillation counting (LSC). In the few last years, the PSresin for strontium has been used to determine ^{210}Pb, ^{89}Sr and ^{90}Sr. Lluch et al. (2016) take advantage of its high selectivity for ^{210}Pb to develop a method to determine this radionuclide by combining separation and measurement preparation into a single step, thus reducing the reagents required for analysis and the amount of organic waste generated. In the same vein, Sáez-Muñoz et al. (2019, 2018) report two rapid methods for determining the individual activities of ^{89}Sr and ^{90}Sr in aerosol filters and vegetation using deconvolution methods and total radiostrontium (^{89}Sr+^{90}Sr) in milk. Both are robust and reproducible methods that could be used in emergency situations given the significant reduction in time needed for analysis.

In view of this, this study's main objective is to develop a novel method capable of determining the individual activities of ^{210}Po, ^{210}Pb and ^{90}Sr in sludge samples by using a PSresin. To achieve this, we will isolate the ^{210}Po, with its subsequent alpha measurement, then simultaneously measure the ^{210}Pb and ^{90}Sr attached to the resin using direct scintillation counting. This method would significantly reduce the time needed to analyse the individual activities of ^{90}Sr, ^{210}Pb and ^{210}Po while also reducing the number of reagents used in comparison with the methods previously described.

2. Materials and methods

2.1. Reagents and materials

All reagents were of analytical or reagent grade. Hydrochloric acid (37%) was supplied by Merk (Darmstadt, Germany), nitric acid (65%) was supplied by AvantorTM (Gliwice, Poland), lithium nitrate (>95%) was supplied by Chem-Lab NV (Zedelgem, Belgium), strontium nitrate (>99%) was supplied by Fluka Chemie (Buchs, Switzerland), lead nitrate (>99%) was supplied by Probus (Spain) and scintillation cocktail Optiphase HiSafe 3 was supplied by PerkinElmer™ (Waltham, USA). Ultrapure water was obtained from a Purification System Milli-Q Reference. The silver disks onto which ^{210}Po was autodeposited were supplied by Goodfellow (Huntingdon, United Kingdom), the twelve-hole vacuum box were supplied by TrisKem International (France). The prepacked PSresin cartridges (1.5 g of PSresin in 2 mL solid-phase extraction cartridges) were provided and produced by the Department of Chemical Engineering and Analytical Chemistry of the University of Barcelona. They are composed of 60 μm plastic scintillation microspheres coated by DtBuCH18C6 in 1-octanol in a proportion PSm: extractant of 1:1/8 and prepared as the authors previously described (Bagán et al., 2011b). A twelve-position vacuum box from TrisKem International (Rennes, France) was used.

The following stock solutions were used to prepare the calibration samples. A ^{210}Pb stock solution of 1545.93 (31.86) Bq/kg in a 3 M HNO_3 medium was prepared from a standard of 0.58 (0.01) Bq/mg and a ^{90}Sr stock solution of 1764.98 (33.73) Bq/kg in a 3 M HNO_3 medium was prepared from a standard of 0.123 (0.001) Bq/mg, both provided by Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT) (Spain). A ^{209}Po stock solution of 4989 (748) Bq/kg was prepared from standard of 100 Bq/mL provided by Eckert & Ziegler (United States). The values in brackets refer to the standard uncertainty.

2.2. Certified reference materials and samples

To validate the method, a certified reference material obtained from an intercomparison exercise organised by the Spanish Nuclear Council (CSN) was used (CSN/CIEMAT-05). The certified reference material was made from wood ash and contained ^{90}Sr and ^{210}Pb with the following respective reference activities, 91.2 ± 1.4 Bq/kg and 102.0 ± 7.4 Bq/kg. This sample also contained ^{210}Po, the activity of which was considered equal to ^{210}Pb as they were in secular equilibrium.

The presence of ^{90}Sr, ^{210}Pb and ^{210}Po was also evaluated in a sludge sample from the DWTP located in L'Ampolla. This was a mixture of single samples collected once a week over the course of a month in a polyethylene bottle.

It is important to highlight that the certified reference material and the real sample analysed (sludge) are not similar in terms of composition. Even that, and due to the lack of a certified sludge containing the three radionuclides under study, the wood ash reference material has been chosen to validate the present method taking into account the possible limitations using this approach.

2.3. Equipment and software

^{90}Sr and ^{210}Pb were measured using a 1220 Quantulus™ LS counter supplied by PerkinElmer™ (Waltham, USA), which was operated using the software WinQ version 1.3. The data obtained was viewed and treated using Matlab R2020b. Alpha measurements were performed using an Octête plus™ alpha detector supplied by Ortec (Oak Ridge, United States) and the data obtained was viewed using Maestro. Analysis of stable elements were performed with a 7500ce inductively coupled plasma mass spectrometer (ICP-MS) and octopole reaction system supplied by Agilent (Santa Clara, United States), as well as an optima 8300 ICP-OES spectrometer supplied by PerkinElmer™. A Digital Orbital Shaker supplied by Heathrow Scientific (Vernon Hills, United States) was used to shake the vials for the batch experiments. The samples were digested using a Speedwave® Four microwave digestion system with built-in, non-contact temperature and pressure measurement supplied by Berghof (Germany).

2.4. Procedure

2.4.1. Batch studies

First, it was necessary to determine the optimal composition and molarity of the acid solution in order to condition and load the sample onto the PSresin for the radionuclides being studied. The procedure used was as follows. First, 1 mL of solution containing 0.1 mL of Sr^{2+} and Pb^{2+} solutions (10,000 ppm, respectively) and 0.5 mL of ^{209}Po (5000 Bq/L) at the appropriate HNO_3 and HCl mixture molarity (final concentrations of 3 M and 1 M, respectively) was mixed with 1 mg of PSresin. The vials were shaken with an orbital shaker for 24 h and the resulting solution was filtered using a syringe and 0.45 μm cellulose filter. The Sr^{2+} and Pb^{2+} present in the acidic phase were determined by ICP (OES and MS), while ^{209}Po activity was determined by LSC.

2.4.2. Final analytical procedure

A sample pretreatment method based on a microwave digestion was chosen according to previous studies performed in our laboratory (Fonollosa et al., 2015; Mola et al., 2014). Calcination was avoided to prevent the volatilisation of ^{210}Po (Thakur and Ward, 2020). For this purpose, 0.9 g of sludge were transferred into a vessel with 15 mL of a mixture of HNO_3:HCl (3:1), 1 mL of Pb^{2+} and Sr^{2+} solutions (1000 ppm, respectively) and 2 mL of ^{209}Po (19 ± 2 Bq/kg). Microwave digestion was then performed for 30 min by increasing the temperature from 0 to 140 °C over 5 min, and then to 175 °C over 25 min. The vessel was kept in the fridge overnight to prevent losing polonium. The next day, the sample was filtered using a 45 μm pore size syringe filter to remove any potential insoluble particles. The soluble part was then evaporated until it was dry at a controlled temperature of 80 °C and then finally redissolved to a final volume of 20 mL with a mixture of HNO_3 and HCl with a final concentration of 3 M and 1 M, respectively.

The sequence for isolating and preconcentrating ^{90}Sr, ^{210}Pb and ^{210}Po was performed following the steps described in Table 1.

First, the resin was pre-conditioned with 2 mL of the acidic solution (3 M HNO_3 and 1 M HCl). Then, 20 mL of digested sample was loaded into the cartridge.

Next, ^{210}Po was eluted with two fractions of 10 mL of 8 M HNO_3 and the cartridge was rinsed with 4 mL of 6 M $LiNO_3$ to reduce/avoid chemiluminescence when it came to measurement, due to the presence of nitric acid in the cartridge as it showed good results in other studies on PSresin (Sáez-Muñoz et al., 2018, 2019). The ^{210}Po present in each eluate was autodeposited on a silver disk. Soon after, autodeposition was performed for 3 h at 85 °C in an 80 mL 2 M HCl solution, containing 0.1 g of ascorbic acid (to reduce Fe^{3+} and avoid its interference during the deposition process), whilst being continuously stirred, and then counted using an alpha spectrometer (Fonollosa et al., 2015; Martínez et al., 2021a). Then, the PSresin was directly measured for 3 h with a 1220 Quantulus™ LS counter as soon as the separation was performed to minimise the growth of daughter radionuclides from ^{210}Pb and ^{90}Sr. Elution fractions and waste were analysed by ICP to evaluate possible losses of ^{90}Sr and ^{210}Pb. The retention efficiency of ^{210}Pb and ^{90}Sr was evaluated by the determination of stable Pb and Sr by ICP-OES and ICP-MS, respectively, and calculated by determining the initial concentration and final concentration after PSresin isolation. The ^{210}Po overall method recovery was evaluated by determining the initial and final activity of ^{209}Po by alpha spectrometry.

The developed method shares some similarities with a previously published method in our laboratory (Martínez et al., 2021a) focused on the fast separation and determination of the same radionuclides in water. However, and even the similarities, the presented reported strategy here constitutes a further step in which new developed resins are employed. The use of these resins is related to greener strategies as these minimise the waste generation and unifies separation and measure steps.

Table 1
Sequential conditions for ^{210}Po separation and for ^{90}Sr and ^{210}Pb measurement using the PSresin.

Step	Description	Solvent	Volume [mL]	Targeted radionuclide
I	Conditioning	3 M HNO_3 + 1 M HCl	2	–
II	Sample loading	3 M HNO_3 + 1 M HCl	20	–
III	^{210}Po elution	8 M HNO_3	2 × 10	^{210}Po
IV	PSresin rinse	6 M $LiNO_3$	4	–

2.4.3. Calibration

Three replicates of deionised water samples with known amounts of ^{90}Sr and ^{210}Pb (150 Bq/kg) were processed with a PSresin as described in section 2.4.1. They were measured in the liquid scintillator counter in order to calibrate the detection efficiencies for each appropriate window (for ^{90}Sr, a window between channels 375 and 650 and for ^{210}Pb, a window between channels 125 and 325). Also, two replicates deionised water samples containing a mixture of ^{90}Sr and ^{210}Pb with different ratios (1:1, 1:2 and 2:1) were processed to optimise the windows setting. In all cases, 0.5 mL of stable Sr^{2+} and Pb^{2+} solutions (10,000 ppm respectively), were added to determine the retention efficiency.

2.4.4. Data treatment

The retention efficiency (%R) of each radionuclide was calculated for each step of the separation using equation (1):

$$Retention\ efficiency\ (\%R) = \frac{\left(mg\ tracer_{sample} - mg\ tracer_{waste}\right)}{mg\ tracer_{sample}} \times 100 \quad (1)$$

where: the mass of the tracer (mg), both in the waste and in the sample, were determined by ICP-OES in case of stable Pb and by ICP-MS in case of stable Sr.

Equation (2) was used to determine the activity of ^{90}Sr:

$$Activity\ 90_{Sr} = \frac{90_{Sr}\ CPM_{375-650} - \ blank\ CPM_{375-650}}{60\ x\ sample\ amount\ x\ R\ x\ Eff_{375-650}\ x\ f} \quad (2)$$

where: the ^{90}Sr CPMs (counts per minute) of the sample and those corresponding to the blank were measured in a window between channels 375 and 650, the sample amount (kg), the detection efficiency ($Eff_{375\text{-}600}$) is 0.658 (0.1) and R is ^{90}Sr's retention efficiency of the sample (both given as a unit fraction), and f is the decay correction factor.

To determine the activity of ^{210}Pb, the corresponding ^{90}Sr CPMs interfering in ^{210}Pb's window (between channels 125 and 325) must be calculated first using equation (3):

$$CPM_{^{90}Sr\ in\ 125-325} = CPM_{^{90}Sr} \times Eff_{125-325} \times R \quad (3)$$

where: the detection efficiency ($Eff_{125\text{-}325}$) is 0.195 and R is ^{90}Sr's retention efficiency of the sample (both given as a unit fraction).

The activity of ^{210}Pb was calculated by subtracting the interfering ^{90}Sr CPMs to the total CPM measured in ^{210}Pb's window using equation (4):

$$Activity\ 210_{Pb} = \frac{210_{Pb}\ CPM_{125-325} - 90Sr\ CPM_{125-325} - \ blank\ CPM_{125-325}}{60\ x\ sample\ amount\ x\ R\ x\ Eff_{125-325}\ x\ f} \quad (4a)$$

where: the ^{210}Pb CPMs, the ^{90}Sr CPMs and those corresponding to the blank were measured in a window between channels 125 and 325, the sample amount (kg), the detection efficiency ($Eff_{125\text{-}325}$, ^{210}Pb's windows) is 0.601 (0.1) and R is ^{210}Pb's retention efficiency of the sample (both given as a unit fraction), and f is the decay correction factor.

3. Results and discussion

The following section discusses the optimisation processes that were performed to retain ^{90}Sr, ^{210}Pb and ^{210}Po in the resin when loading the sample, and to selectively elute ^{210}Po. It also describes calibrating the detection efficiency of ^{90}Sr and ^{210}Pb. Finally, it presents the validation of the method using reference material, as well as its applicability to real samples.

3.1. Batch study of ^{90}Sr, ^{210}Pb and ^{210}Po in PSresin

Initially, the acidic conditions used to condition and load the sample (10 mL of 3 M HNO_3) in the PSresin were the same as those used in one of our previous studies based on a sequential separation of ^{90}Sr, ^{210}Pb and ^{210}Po in drinking water samples using a Sr resin (TrisKem) (Martínez et al., 2021a). Despite the analogy between both resins, those conditions do not work with PSresin. The results were unexpected. Low retention of ^{210}Po was found when loading the sample (22%) while ^{210}Pb and ^{90}Sr were retained well (99% for both radionuclides). To improve ^{210}Po's retention, a batch study was performed. The acidic solutions to condition and load samples (a mixture of 3 M HNO_3 and different concentrations of HCl in the range from 1 to 5 M) were selected after looking for advice in various studies. It should be noted that the studies we consulted are only based on Sr resin (TrisKem) because of their similarities and the lack of information and methods using PSresin. In this regard, some reported strategies demonstrate that ^{210}Po and ^{210}Pb are well retained in Sr resin at moderately low concentrations of HCl, while these conditions for retaining ^{90}Sr in the resin are not favourable (Vajda et al., 1997). However, when using HNO_3:HCl mixtures at ratios of above 50:50%, the retention of ^{90}Sr radionuclide improved considerably (McLain et al., 2018). Although, as far as we know, in the reported literature there is no data related to ^{210}Pb and ^{210}Po's retention in HNO_3:HCl mixtures in Sr resin. In general, the retention of the aforementioned radionuclides in Sr resin is characterised in pure mineral acids.

The results obtained from this study are shown in Fig. 1, where the percentages of retention for each radionuclide at a mixture of 3 M HNO_3 and different concentrations of HCl from 1 to 5 M can be observed. It shows that ^{210}Po presented a slight decrease in retention when a higher hydrochloric acid concentration was used. For this radionuclide, a retention value of 96% was obtained for an HCl concentration of 1 M and approximately 80% at an acid concentration of 5 M. This is in line with the bibliographic review by Thakur and Ward (2020) who reported that the retention of polonium is high across a range of HCl molarities, with 2 M HCl being the most typical Sr resin load solution.

As regards lead and as shown in Fig. 1, this element presented a significant decrease in retention when a higher hydrochloric concentration was used. For this radionuclide, a retention value of 99% was obtained for an HCl concentration of 1 M and approximately 5% at an acidic concentration of 5 M. These results are in line with some studies stating that this radionuclide is retained well in HCl (0.1–2 M) and Sr resin (Eichrom Technologies, 2021; Kong et al., 2021b).

^{90}Sr was retained well when a lower hydrochloric concentration was used. A retention value of approximately 88% was obtained for an HCl concentration of 1 M. However, the affinity of ^{90}Sr with PSresin as well as Sr resin reaches maximum values at between 3 and 8 M HNO_3 (Dianu and Dobrin, 2020), as is the case in the present study.

Finally, considering all the results and retention percentages for the three radionuclides involved in this study, the mixture chosen to load the sample and condition PSresin in the separation procedure was the 3 M HNO_3 and 1 M HCl final molarities mixture. This was a compromise between all the values obtained and thus ensured the optimal retention of each radionuclide in the PSresin. Therefore, mixed nitric and hydrochloric acid matrix are useful to perform separations in PSresin.

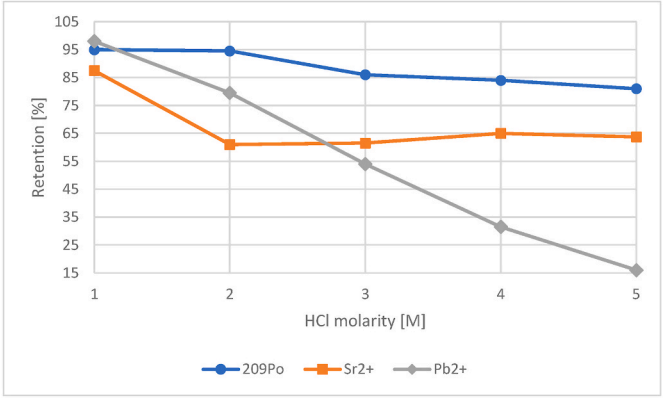

Fig. 1. % of ^{209}Po, Sr^{2+} and Pb^{2+} retention in PSresin using a mixture composed by different HCl concentrations and 3 M HNO_3 in a batch experiment.

3.2. Optimisation of separation parameters to avoid interferences

Before measuring ^{90}Sr and ^{210}Pb in PSresin using liquid scintillation counting, potential interferences present in the sample must be removed as they could influence the separation and measurement of the radionuclides (Barrera et al., 2016; Giménez et al., 2021; Kocadag et al., 2013; Sáez-Muñoz et al., 2018). For example, if ^{210}Po cannot be completely stripped from PSresin, it could interfere with the quantification of ^{90}Sr and ^{210}Pb as it appears approximately between channels 300 and 600 (Kim et al., 2008; Lluch et al., 2016). To achieve this, an optimisation of the necessary volume of 8 M HNO_3 was carried out, which is the most common acidic media used in the literature to strip ^{210}Po from Sr resin (Hurtado-Bermúdez et al., 2017). Using this elution media means that ^{90}Sr and ^{210}Pb do not coelute with ^{210}Po. The first is retained well in nitric acid concentration by the Sr resin (Triskem International, 2015) and ^{210}Pb elutes with 0.06 M ammonium oxalate (Martínez et al., 2021a; Mola et al., 2014).

Different volumes of 8 M HNO_3, ranging from 8 to 20 mL, were used to try to perform the quantitative elution of polonium. As shown in Fig. 2, 60% of ^{210}Po was eluted by using 8 mL of 8 M HNO_3, which increased to approximately 100% when 20 mL was used. The latter, therefore, has proven to be the optimum volume to quantitatively elute almost all polonium retained in PSresin, thus avoiding radiochemical interferences when measuring ^{90}Sr and ^{210}Pb using LSC. Moreover, a PSresin rinse with 4 mL of $LiNO_3$ was also applied to reduce and avoid chemiluminescence.

3.3. Calibration of ^{90}Sr and ^{210}Pb detection efficiency

The next step was to measure both the ^{90}Sr and ^{210}Pb retained in the resin by using a LSC spectrometer. When performing this quantification

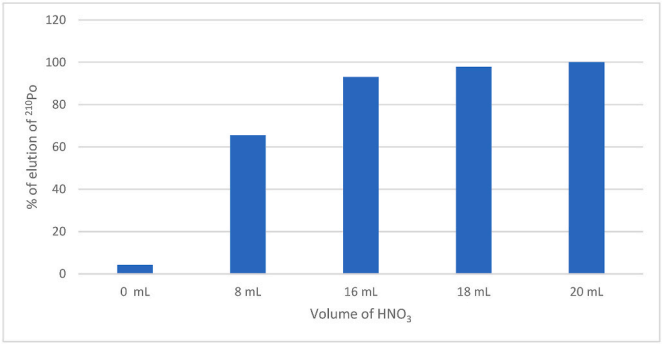

Fig. 2. % of ^{210}Po elution with different 8 M HNO_3 volumes.

and as shown in Fig. 3, it is important to consider that the spectra of both radionuclides overlap in some regions, which can cause activities to be overestimated. Different methods for LSC spectra deconvolution that avoid overlapping are found in the literature (Sáez-Muñoz et al., 2019), and among them, partial least squares (PLS) have been used to determine alpha and beta emitters in mixtures (Fons-Castells et al., 2017a). In this case, Fons-Castells et al., 2017a apply a multivariate calibration method using PLS regression to avoid overlap in the spectra between ^{228}Ra and ^{210}Pb. In the present study and in order to avoid or minimise ^{90}Sr and ^{210}Pb spectra overlapping, we used a calibration model by windows. It involved a two-window approach, one for ^{90}Sr and one for ^{210}Pb. Data from the standards was used to select the optimum count windows, compromising between the detection efficiency for each radionuclide, as follows.

Individual standards (^{90}Sr and ^{210}Pb) were processed following the procedure explained in section 2.4.1. The corresponding CPMs and retention efficiencies could be obtained from the PSresin measurement. The CPMs of the individual standard of ^{90}Sr were measured in ranges of more than 100 channels between channels 300 and 650. The detection efficiency was measured for each window using equation (4).

$$Detection\ efficiency\ (\%Eff) = \frac{CPM_{sample} - CPM_{blank}}{DPM_{theoretical} \times R} \times 100 \quad (4b)$$

The ^{90}Sr CPMs were calculated for each mixture of standards (^{90}Sr + ^{210}Pb) using the previously calculated detection efficiencies and the calculated CPMs were compared with the theoretical values using equation (5) to evaluate the error of the method (%). The optimal window was considered the one for which detection efficiency led to the lower error in the CPM calculations.

$$\%\ Error = \frac{CPM_{Calc} - CPM_{theoretical}}{CPM_{theoretical}} \times 100 \quad (5)$$

The same procedure was performed for the individual standards between channels 0 and 350 to determine both ^{90}Sr and ^{210}Pb's detection efficiency in ^{210}Pb's window. The respective CPMs of ^{210}Pb and ^{90}Sr in the mixtures of standards were calculated, and their errors were calculated using equation (5). As shown in Table 2, the optimum windows were from channels 375 to 600 to quantify ^{90}Sr, and from channels 125 to 325 to quantify ^{210}Pb. The related optimal detection efficiencies shown are in line with those obtained in studies in the literature determining ^{90}Sr and ^{210}Pb using PSresin (Bagán et al., 2011b; Lluch et al., 2016).

The calibration procedure was validated by quantifying three water samples containing different ratios of ^{90}Sr and ^{210}Pb (1:1, 1:2 and 2:1). The deviations obtained when quantifying ^{90}Sr and ^{210}Pb are shown in Table 3. The relative bias of ^{90}Sr and ^{210}Pb is less than 15% in all three cases, so the approach can be used to quantify ^{90}Sr and ^{210}Pb simultaneously in one sample. It is important to note that when the concentration of ^{90}Sr is two times higher than the concentration of ^{210}Pb, the relative bias percentage of the latter is high (14.1%). This is due to the fact that there is more ^{90}Sr interfering in channels 150 to 325 and ^{210}Pb activity could be overestimated. Therefore, the present mathematical method is a useful tool for determining individual ^{90}Sr and ^{210}Pb in emergency situations, taking into account that ^{210}Pb activities could be overestimated when there are higher levels of ^{90}Sr in the sample due to how it can interfere in the ^{210}Pb spectra.

Table 2
Optimal spectrum windows for each radionuclide and their related detection efficiency.

	Window (Channels)	Optimal detection efficiency (%)
^{90}Sr	375–600	65.8
^{210}Pb	125–325	60.1
Interfering ^{90}Sr		21.1

Table 3
Relative bias in the determination of ^{90}Sr and ^{210}Pb in water samples with different activity ratios.

Ratio ^{90}Sr:^{210}Pb	^{90}Sr Relative bias (%)	^{210}Pb Relative bias (%)
1:1	−1.1	6.7
1:2	6.4	4.6
2:1	−0.85	14.1

3.4. Method validation and application to real samples

The developed method was validated by analysing certified reference material (CSN/CIEMAT-05) made from wood ash. The sample contained ^{90}Sr and ^{210}Pb, with 91.2 and 102 Bq/kg of dry mass, respectively, at the time of separation. ^{210}Pb and ^{210}Po were in secular equilibrium. As shown in Table 4, the mean values of the three replicates obtained generally agreed with the certified values, as Z-score (<1) indicates. Regarding the accuracy of the measurements, the average relative standard deviation of each radionuclide is low (<10%) with the exception of ^{90}Sr, which shows a deviation that is higher than expected. This could be related to the variation of ^{90}Sr PSresin retention due to changes in the acid molarity mixtures used for the resin conditioning and sample loading. In this regard, it is worth mentioning the published work of McLain et al. (2018) who reported that mixtures of HNO_3 and HCl can evolve to their decomposition into volatile gaseous products

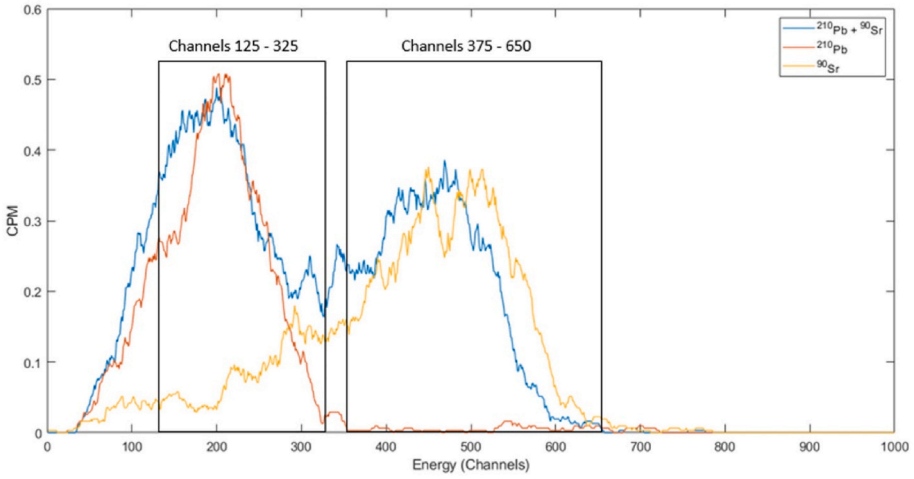

Fig. 3. Spectra of ^{210}Pb, ^{90}Sr and ^{210}Pb/^{90}Sr measured with a PSresin of spiked water samples by LSC.

Table 4
Validation results obtained in three replicates (n = 3) of the CSN/CIEMAT-05 intercomparison sample.

Sample	Radionuclide	Certified value (Bq/kg)	Mean measured activity of the present study (Bq/kg)	RSD (%)	Z-score
CSN/CIEMAT-05	^{210}Po	102.0 ± 7.4	101.5 ± 5.0	7	0.57
	^{210}Pb	102.0 ± 7.4	100.7 ± 9.3	1	−0.07
	^{90}Sr	91.2 ± 1.4	107.8 ± 8.3	22	0.91

Uncertainties are expressed at k = 2.

and their initial concentration can decrease and this can influence on the retention of the radionuclides.

After the validation procedure, the method developed in this study was applied to three replicates of a sludge sample from the DWTP located in L'Ampolla. The results obtained are displayed in Table 5.

It shows that ^{210}Pb presented an averaged activity (n = 3) of 23.9 ± 4.9 Bq/kg. This sludge sample was also analysed using gamma spectrometry to compare the ^{210}Pb results with those obtained in the present study, obtaining a result of 21.2 ± 4.9 Bq/kg, which, by value comparison, indicates a satisfactory performance of the method in terms of lead quantification. This radionuclide was previously quantified using a LOV-MSFIA automated method in our laboratory, which obtained activities in a range of 38–63 Bq/kg (Mola et al., 2014). It is important to note that the results obtained in the present study are slightly lower than those obtained by Mola et al. (2014) in sludge samples from the same DWTP collected in 2014. The variability of these results could be due to seasonal changes in the Ebro River system, behaviour that has been observed in other natural radionuclides (Martínez et al., 2021b).

As regards ^{90}Sr, the average activity obtained is 17.8 ± 5.3 Bq/kg. This activity is lower than that obtained in a previous study performed in our laboratory (34–78 Bq/kg) (Mola et al., 2014). As DWTP sludge concentrates radionuclides present in the influent (from the Ebro River) at the DWTP, it can be concluded that the presence of ^{90}Sr in the sludge could be related to the normal operational radioactive liquid discharges found in the Ebro River from Ascó NPP, located upstream, as reported by the Spanish Nuclear Council (CSN) (P. Martínez et al., 2021).

^{210}Po presented an activity of 25.5 ± 4.9 Bq/kg, which is comparable with ^{210}Pb activity because both were in secular equilibrium. Fonollosa et al. (2015) determined the presence of polonium in this DWTP's sludge years ago, by means of sample digestion and direct autodeposition onto silver disks, in the range of 31–42 Bq/kg. It is a particle-reactive radionuclide that tends to be associated more with the particulate phase and consequently is found concentrated in sludge (Fonollosa et al., 2015). According to UNSCEAR (2008), the obtained activity values are quite comparable to the ^{210}Po activities expected in normal soils and it seems that the DCP production plant located upstream does not have any influence.

Table 5 also shows the minimum detectable activity (MDA) calculated in the present study using the Currie approach (Currie, 1968) in a sample of 0.9 g. The current method shows improvements in the MDAs of ^{90}Sr and ^{210}Pb compared to other methods reported in the literature (Mola et al., 2014; Qiao et al., 2017). Mola et al. (2014) developed an automated method based on LOV-MSFIA using Sr resin and LSC, where the MDAs for ^{90}Sr and ^{210}Pb were 15 and 13 Bq/kg respectively for a sludge sample of 0.5 g that was measured for 500 min. On the other hand, Qiao et al. (2017) report a MDA for ^{90}Sr of 10.4 Bq/kg by analysing 1 g of soil and measuring it for 2400 min through ^{90}Y. In the case of ^{210}Po, the MDA obtained remains in the same order of magnitude as the conventional methods used in our laboratory (0.15 Bq/kg for 0.3 g of sample and measured for 5833 min) (Fonollosa et al., 2015). They are also in line with the MDA value obtained by El Afifi and Borai (2006) (0.28Bq/kg), who determined ^{210}Po by using Sr resin, a 0.3–0.7 g soil sample after measuring it for 1440 min.

4. Conclusions

This study has successfully developed a fast and novel method to determine ^{210}Po, ^{210}Pb and ^{90}Sr using a PSresin by selectively retaining the three radionuclides, eluting ^{210}Po and subsequently measuring it by alpha spectrometry, while measuring the ^{210}Pb and ^{90}Sr retained in the PSresin by LSC. The optimal loading medium was found to be a mixture of 3 M HNO_3 and 1 M HCl and the optimal elution method for ^{210}Po was 20 mL of 8 M HNO_3. As the PSresin combines the steps involving separation and measurement, less time is needed for analysis. Finally, the mathematical method proposed and tested to determine ^{90}Sr and ^{210}Pb simultaneously provided good results.

The method was successfully validated by analysing reference material and obtaining activities statistically similar to the reference values. It was then applied to a real sludge sample from the DWTP located in L'Ampolla (Tarragona).

In conclusion, it has been shown to be a successful method for determining the aforementioned radionuclides in rapid-response situations.

Table 5
Results obtained from the analysis of a sludge sample from the DWTP.

Sample	Radionuclide	Mean measured activity of the present study (Bq/Kg)	RSD (%)	MDA (Bq/kg)
DWTP sludge	^{210}Po	25.5 ± 4.9	12	0.5[a]
	^{210}Pb	23.9 ± 4.9	5	5.5[b]
	^{90}Sr	17.8 ± 5.3	30	8[b]

Uncertainties are expressed at k = 2.
N.A. not applicable.
[a] MDA calculated for 5000 min of measurement time.
[b] MDA calculated for 180 min of measurement time.

CRediT authorship contribution statement

J. Martínez: Writing – original draft, Validation, Methodology, Investigation, Conceptualization. **M. de los Cobos:** Writing – original draft, Validation, Methodology, Investigation. **A. Peñalver:** Writing – review & editing, Methodology, Conceptualization. **A. Tarancón:** Writing – review & editing, Investigation, Conceptualization. **I. Giménez:** Methodology. **H. Bagán:** Writing – review & editing, Investigation, Conceptualization. **C. Aguilar:** Writing – review & editing, Supervision. **F. Borrull:** Writing – review & editing, Supervision.

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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References

Bagán, H., Tarancón, A., Rauret, G., García, J.F., 2011a. Mixture quantification using PLS in plastic scintillation measurements. Appl. Radiat. Isot. 69, 898–903. https://doi.org/10.1016/j.apradiso.2011.02.039.

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

Barrera, J., Tarancón, A., Bagán, H., García, J.F., 2016. A new plastic scintillation resin for single-step separation, concentration and measurement of technetium-99. Anal. Chim. Acta 936, 259–266. https://doi.org/10.1016/j.aca.2016.07.008.

Currie, L.A., 1968. Limits for qualitative detection and quantitative determination: application to radiochemistry. Anal. Chem. 40, 586–593. https://doi.org/10.1021/ac60259a007.

Dianu, A.M., Dobrin, R.I., 2020. Separation and quantification of 90Sr from ion-exchange resin radioactive waste: methods and techniques of analysis. Radiochim. Acta 108, 627–640. https://doi.org/10.1515/ract-2019-3213.

Eichrom Technologies, 2021. Sr resin [WWW Document]. URL. https://www.eichrom.com/eichrom/products/sr-resin/. (Accessed 3 February 2021).

El Afifi, E.M., Borai, E.H., 2006. Performance characteristics of sequential separation and quantification of lead-210 and polonium-210 by ion exchange chromatography and nuclear spectrometric measurements. J. Environ. Qual. 35, 568–574. https://doi.org/10.2134/jeq2005.0223.

Fonollosa, E., Nieto, A., Peñalver, A., Borrull, F., Aguilar, C., 2016. Determination of artificial beta-emitters in sludge samples. J. Radioanal. Nucl. Chem. 309, 1077–1085. https://doi.org/10.1007/s10967-016-4705-9.

Fonollosa, E., Peñalver, A., Aguilar, C., Borrull, F., 2015. Polonium-210 levels in different environmental samples. Environ. Sci. Pollut. Res. 22, 20032–20040. https://doi.org/10.1007/s11356-015-5158-3.

Fons-Castells, Jordi, Oliva, J., Tent-Petrus, J., Llauradó, M., 2017a. Simultaneous determination of 226Ra, 228Ra and 210Pb in drinking water using 3M Empore™ RAD disk by LSC-PLS. Appl. Radiat. Isot. 124, 83–89. https://doi.org/10.1016/j.apradiso.2017.03.016.

Fons-Castells, J., Tent-Petrus, J., Llauradó, M., 2017b. Simultaneous determination of specific alpha and beta emitters by LSC-PLS in water samples. J. Environ. Radioact. 166, 195–201. https://doi.org/10.1016/j.jenvrad.2016.04.035.

Giménez, I., Bagán, H., Tarancón, A., García, J.F., 2021. PSresin for the analysis of alpha-emitting radionuclides: comparison of diphosphonic acid-based extractants. Appl. Radiat. Isot. 178 https://doi.org/10.1016/j.apradiso.2021.109969.

Grate, J.W., Egorov, O.B., 2003. Automated radiochemical separation, analysis and sensing. In: L'Annunziata, M.F. (Ed.), Handbook of Radioactivity Analysis, second ed., pp. 1129–1164. https://doi.org/10.1016/B978-012436603-9/50019-3.

Hurtado-Bermúdez, S., Mas, J.L., Villa-Alfageme, M., 2017. A sequential determination of 90Sr and 210Po in food samples. Food Chem. 229, 159–164. https://doi.org/10.1016/j.foodchem.2017.02.077.

International Atomic Energy Agency, 1963. A basic toxicity classification of radionuclides [WWW Document]. Tech. Reports Ser. no. 15. URL. https://inis.iaea.org/collection/NCLCollectionStore/_Public/24/072/24072024.pdf. (Accessed 5 February 2020).

Kim, C.K., Martin, P., Fajgelj, A., 2008. Quantification of measurement uncertainty in the sequential determination of 210Pb and 210Po by liquid scintillation counting and alpha-particle spectrometry. Accred Qual. Assur. 13, 691–702. https://doi.org/10.1007/s00769-008-0437-z.

Kocadag, M., Musilek, A., Steinhauser, G., 2013. On the interference of 210Pb in the determination of 90Sr using a strontium specific resin. Nucl. Technol. Radiat. Protect. 28, 163–168. https://doi.org/10.2298/NTRP1302163K.

Kong, X., Yin, L., Ji, Y., 2021a. Simultaneous determination of 210Pb and 210Po in seafood samples using liquid scintillation counting. J. Environ. Radioact. 231 https://doi.org/10.1016/j.jenvrad.2021.106553.

Kong, X., Yin, L., Ji, Y., 2021b. Simultaneous determination of 210Pb and 210Po in seafood samples using liquid scintillation counting. J. Environ. Radioact. 231 https://doi.org/10.1016/j.jenvrad.2021.106553.

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

Martínez, J., de los Cobos, M., Peñalver, A., Aguilar, C., Borrull, F., 2021a. A fast strategy to sequentially separate and determine 90Sr, 210Pb and 210Po in water samples using Sr resin. J. Radioanal. Nucl. Chem. 331, 629–637. https://doi.org/10.1007/s10967-021-08093-0.

Martínez, J., Peñalver, A., Aguilar, C., Borrull, F., 2021b. Role of lithology in the presence of natural radioactivity in drinking water samples from Tarragona province. Environ. Sci. Pollut. Res. 28, 39333–39344. https://doi.org/10.1007/s11356-021-13470-z.

Martínez, P., Luque, S., Ortiz, A., Sánchez, B., Trinidad, J., Rey, C., Muñoz, M., 2021. Programas de vigilancia radiológica ambiental. Resultados 2019.

McLain, D.R., Liu, C., Sudowe, R., 2018. Using Sr Resin with mixed acid matrices. J. Radioanal. Nucl. Chem. 316, 485–490. https://doi.org/10.1007/s10967-018-5778-4.

Mola, M., Avivar, J., Nieto, A., Peñalver, A., Aguilar, C., Ferrer, L., Cerdà, V., Borrull, F., 2014. Determination of 90Sr and 210Pb in sludge samples using a LOV-MSFIA system and liquid scintillation counting. Appl. Radiat. Isot. 86, 28–35. https://doi.org/10.1016/j.apradiso.2013.11.123.

Palomo, M., Peñalver, A., Aguilar, C., Borrull, F., 2010. Impact of industries in the accumulation of radionuclides in the lower part of Ebro river (Catalonia, Spain). Radioprotection 45, 459–475. https://doi.org/10.1051/radiopro/2010032.

Palomo, M., Peñalver, A., Aguilar, C., Borrull, F., 2010. Radioactivity evaluation of Ebro river water and sludge treated in a potable water treatment plant located in the South of Catalonia (Spain). Appl. Radiat. Isot. 68, 474–480. https://doi.org/10.1016/j.apradiso.2009.11.071.

Peñalver, A., Baciu, T., Borrull, F., Aguilar, C., 2020. Possible factors influencing the accumulation of different radionuclides in sludge from a drinking water treatment plant located in Southern catalonia between 2002 and 2018. Water. Air. Soil Pollut. 231 https://doi.org/10.1007/s11270-020-04491-4.

Qiao, J., Salminen-Paatero, S., Rondahl, S.H., Bourgeaux-Goget, M., Roos, P., Lagerkvist, P., Strålberg, E., Ramebäck, H., 2017. Inter-laboratory exercise with an aim to compare methods for 90Sr and 239,240Pu determination in environmental soil samples. J. Radioanal. Nucl. Chem. 314, 813–826. https://doi.org/10.1007/s10967-017-5385-9.

RD 314/2016, 2016. Real Decreto 314/2016, de 29 de julio, por el que se modifican el Real Decreto 140/2003, de 7 de febrero, por el que se establecen los criterios sanitarios de la calidad del agua de consumo humano, el Real Decreto 1798/2010, de 30 de diciembre, por el que, vol. 183. Boletín Oficial del Estado, Madrid, p. 30 de julio de 2016.

Sáez-Muñoz, M., Bagán, H., Tarancón, A., García, J.F., Ortiz, J., Carlos, S., Martorell, S., 2019. Rapid methods for radiostrontium determination in aerosol filters and vegetation in emergency situations using PS resin. J. Radioanal. Nucl. Chem. 322, 1397–1408. https://doi.org/10.1007/s10967-019-06779-0.

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

Şahin, M., Özbay, D.Ş., 2021. A study on 210Pb and 210Po levels in different tobacco types produced in Turkey and the estimation of the committed effective dose. J. Radioanal. Nucl. Chem. 329, 45–50. https://doi.org/10.1007/s10967-021-07684-1.

Thakur, P., Ward, A.L., 2020. 210Po in the environment: insight into the naturally occurring polonium isotope. J. Radioanal. Nucl. Chem. 323, 27–49. https://doi.org/10.1007/s10967-019-06939-2.

Triskem International, 2015. Sr resin. Product Sheet [WWW Document]. URL. https://www.triskem-international.com/scripts/files/5f463447ad4026.94629022/PS_SR-Resin_EN_160927.pdf. (Accessed 3 February 2021).

United Nations Scientific Committee on the Effects of Atomic Radiation, 2008. UNSCEAR 2008 Report on Sources and Effects of Ionizing Radiation, UNSCEAR 2008 Report to the General Assembly, with Scientific Annexes, vol. I. UNSCEAR.

Vajda, N., LaRosa, J., Zeisler, R., Danesi, P., Kis-Benedek, G., 1997. A novel technique for the simultaneous determination of 210Pb and 210Po using a crown ether. J. Environ. Radioact. 37, 355–372. https://doi.org/10.1016/S0265-931X(95)00059-J.

Vreček, P., Benedik, L., 2002. Determination of 210Pb and 210Po in sediments, water and plants in an area contaminated with mine waste. Mine Water Environ. 156–159.