

Rapid determination of ^{210}Pb and ^{210}Po in water and application to marine samples

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ABSTRACT

Measurement of radionuclides in marine samples, specifically radioactive pairs disequilibrium, has gained interest lately due to their ability to trace cutting edge biogeochemical processes. In this context, we developed a fast, direct method for determining ^{210}Pb and ^{210}Po water through the use of ultra low-level liquid scintillation counting and alpha-particle spectrometry respectively and through Eichrom Sr resins for the Po-Pb separation. For ^{210}Pb analysis, the method uses stable lead as a yield tracer measured by a robust ICP-MS technique, and ^{210}Po is determined through self-deposition using the conventional ^{209}Po yield tracer. The improvements of the method over other techniques are: a) the analysis can be completed within 6 days, simplifying other methods, b) very low limits of detection have been achieved – 0.12 and 0.005 mBq L⁻¹ for ^{210}Pb and ^{210}Po , respectively – and c) most of the method could be carried out in on-board analysis. We applied the method to different aqueous samples and specifically to marine samples. We determined ^{210}Pb and ^{210}Po in the dissolved fraction of Mediterranean Sea water and an estuary at the South-West of Spain. We found that it can be successfully employed to marine samples but we recommend to i) use a minimum of 20 L water to measure the ^{210}Pb in the dissolved phase by LSC and lower volumes to measure total concentrations; ii) wait for ^{210}Pb and ^{210}Bi in secular equilibrium and measure the total spectrum to minimise the limit of detection and improve accuracy.

1. Introduction

In the last decades, radionuclides from the uranium decay chains have been widely used as tracers of a variety of processes in the marine environment – e.g. Ra-isotopes for groundwater discharge into the coastal ocean [1], ^{210}Pb sediment chronology [2] ^{238}U - ^{234}Th for export fluxes of particles from the upper ocean [3] or ^{231}Pa - ^{230}Th for the ocean circulation [4]. Specifically, the disequilibrium between the radioactive pairs ^{234}Th - ^{238}U ($T_{1/2}=24$ days) and ^{210}Pb - ^{210}Po ($T_{1/2}=138$ days) have been widely used in the marine environment to study scavenging rates [5,6], carbon export fluxes [7] and more recently e.g. [8–10] carbon export efficiency [10,11]. In the past ten years the alpha emitter ^{210}Po has regained considerably interest, due to its different biogeochemical behaviour compared to the beta emitter ^{234}Th – e.g. different adsorption and desorption rates [12] and bioaccumulation within the

cells [13] – . Furthermore, its longer half-life allows ^{210}Pb - ^{210}Po disequilibrium to penetrate deeper into the ocean, as it will take longer than for ^{234}Th - ^{238}U to reach the equilibrium parent-daughter. Hence using this radioactive pair it is possible to explore biogeochemical processes that take place not only in the euphotic zone but deeper and that are mainly related to the operation of the biological carbon pump in the ocean [14,15].

The concentrations of ^{210}Po and ^{210}Pb in the dissolved fraction in seawater samples range from 1 to 3 Bq m⁻³ [16] and are typically similar. The accuracy and precision in their determination is crucial, since the disequilibrium between them greatly affects their use to estimate, for instance, C export fluxes. A widespread technique, due to its very low background and precision, is the measurement of both ^{210}Po and ^{210}Pb by alpha spectrometry after its spontaneous deposition on a silver disc [17,18]. This technique requires an initial deposition to measure initial ^{210}Po , and a second one within several months, to evaluate ^{210}Pb concentration after allowing ^{210}Po to grow from ^{210}Pb . Therefore, two additional ^{210}Po self-deposition onto silver plates had to be fulfilled. The main disadvantage of this technique is that at least six months must be

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elapsed for sufficient ^{210}Po activity to grow from ^{210}Pb [18]. And most important, there must be a total elimination of polonium from the solution after the first ^{210}Po deposition; otherwise initial polonium tracer will lead to inaccuracies in ^{210}Pb evaluation [18].

Liquid scintillation counting (LSC) techniques could be also used, since they have the advantage that parallel measurements of both isotopes can be conducted without the need of waiting for more than 6 months for the ingrowth of ^{210}Po , as it is required in alpha spectrometry. However, the limits of detection of non-optimised LSC methods can sometimes be one order of magnitude higher than those typical of α -spectrometry (i.e. $10^{-1} \text{ Bq m}^{-3}$) [19]. The concentration of ^{210}Po and ^{210}Pb in the dissolved fraction in seawater samples ranges from 1 to 3 Bq m^{-3} [20]. Besides, ^{210}Po and ^{210}Pb concentrations are in many cases very close. A competitive alternative to α -spectrometry technique implies optimising the minimum detectable activity of the LSC method, while keeping the radiochemical method as simple as possible.

The use of Liquid Scintillation Counting (LSC) for ^{210}Pb analysis is a well-known technique that could be used as an alternative in order to avoid the disadvantages mentioned above. For the ^{210}Pb analysis, lead co-precipitation with sulphates [21–23] or oxalates [24] is a common and simple extraction method. However these methods are only suitable for ^{210}Pb measurement and an additional step should be added for polonium separation and measurement.

The behaviour of crown ether based Sr resins for the extraction of lead was first presented by [24–27]. In [24] a method of lead chromatographic extraction using crown ether selective Pb resin was also discussed. However, the recovery of polonium using this technique is very low ($< 25\%$). The method of chromatographic extraction of lead and polonium using Eichrom Sr resins was developed by [28] to measure ^{210}Pb and ^{210}Po in organic, sediment and soil samples. In [29] an initial step of lead and polonium pre-concentration through iron hydroxide precipitation it was added to be applied to the measurement of seawater samples.

Here we present a fast, competitive, method based on the use of crown ether Sr resin for the measurement of ^{210}Pb and ^{210}Po in seawater samples. The method is a step forward in order to shorten the initial method proposed by [28], since some steps of the procedure are simplified (i.e. no Fe removal through solvent extraction). We evaluate the capacity of this simplified method to adequately isolate lead from polonium with high recoveries, assessing the crossover contamination during column separation. Accuracy and precision of the method is also discussed. We consider that the radiochemical procedure is simple and fast enough to compete with the α -spectrometry method based on a two-step deposition of polonium.

2. Experimental procedure

2.1. Sampling

Water samples from different origins for the optimisation of the method were employed. Spiked MilliQ water was used to study the performance of the resin in lead and polonium separation and also to determine the accuracy of the method. Samples were prepared adding 1 mL of ^{210}Pb standard solution to 0.5 L MilliQ water. The standard solution was purchased from German PTB.

The dissolved fraction in different aqueous matrices was analysed to determine the ability of the method to analyse very low levels of ^{210}Pb and ^{210}Po . Dissolved ^{210}Pb and ^{210}Po in filtered superficial seawater samples from the Mediterranean Sea, collected at the Institut de Ciències del Mar (ICM) in Barcelona were measured. Three batches of aliquots of 30 L in June 2008 (three

aliquots), August 2008 (three aliquots) and November 2008 (five aliquots) were collected.

In order to study the capabilities of the separation method in different marine matrices, estuarine samples were analysed. Estuarine water samples of 0.5–2.5 L collected in February 2007 from the Odiel and Tinto rivers (SW of Spain) were filtered through 0.45 μm pore size Millipore filters.

2.1.1. ^{210}Po and ^{210}Pb isolation procedure

The radiochemical procedure starts with a preliminary concentration of lead and polonium from the water matrix through co-precipitation with iron hydroxides, followed by the chromatographic extraction of lead and polonium using Eichrom prepackaged Sr resins. The steps of the radiochemical procedure are shown in Fig. 1. In detail:

Step 1. Pre-treatment of water samples.

After collection and filtration, each sample was acidified with HNO_3 to $\text{pH} < 3.5$ for preservation and to avoid adsorption of elements onto the carboy walls of the container bottles. Afterwards, Fe^{3+} (200 mg) and known amounts of internal tracers (0.1 Bq ^{209}Po and 3.5–8.5 mg of stable Pb^{2+}) were added to assess chemical yields. Samples were left for at least 24 h to allow for homogenisation. The potential contamination of ^{210}Pb and ^{210}Po from stable Pb, which was prepared by dilution of $\text{Pb}(\text{NO}_3)_2$, was evaluated by analysing blanks of the procedure (Table 1).

Step 2. Preconcentration of lead and polonium.

NH_4OH was added to the samples to raise the pH up to 8.5 and obtain a complete precipitation of $\text{Fe}(\text{OH})_3$, which produces the co-precipitations of lead, polonium and actinides, leaving radium and other elements in solution. Most of the supernatant was discarded by syphoning and centrifugation of the resulting volume to further concentrate the precipitate.

Step 3. Conditioning of the sample.

The iron hydroxides precipitates were evaporated to dryness and dissolved using 10 mL of HCl 37%. Samples were taken again to dryness three times to eliminate residual nitrate ions and the final residue was dissolved in 10 mL of 2 M HCl.

Step 4. Separation of lead and polonium using prepackaged Sr resin.

The Sr resin column was pre-conditioned with 10 mL 2 M HCl before loading the sample and $2 \times 20 \text{ mL}$ 2 M HCl was used to wash the beaker and elute Bi, Fe and actinides [25] (Fraction #1). Lead and Polonium were retained in the column [28]. Polonium was eluted by adding $2 \times 20 \text{ mL}$ 6 M HNO_3 (Fraction #2). Thorium is retained in the column in this step, whereas uranium would be eluted together with polonium [26] but would not interfere in polonium deposition onto silver discs. Finally, lead was eluted by adding $2 \times 20 \text{ mL}$ 6 M HCl (called Fraction #3).

Finally, the column was washed by adding 10 mL of 6 M HNO_3 (Fraction #4), 10 mL of 6 M HCl (Fraction #5) and 10 mL of 2 M HCl, before preservation in 2 M HCl.

Step 5. Preparation of the sources.

The polonium strip solution was taken to dryness and dissolved in 1 mL HCl 37%. This step was repeated three times and the residue was finally dissolved in 50 mL 1 M HCl. Polonium in 1 M HCl was spontaneously deposited onto silver discs at about 80°C during 6 h [19]. A few milligrams of ascorbic acid before plating prevents from deposition of potential iron traces on the silver disc. The deposition separates polonium from other potential contaminants and allows the subsequent measurement by alpha spectrometry.

Afterwards, the solution (6 M HCl) was taken to dryness and dissolved in 8 mL EDTA in 0.1 M NH_3 . The suitability of this final step is discussed in the next section. The solution was transferred to a teflonated polyethylene vial and 12 mL of scintillation cocktail Optiphase Hisafe 3 were added, vigorously shaking the resulting

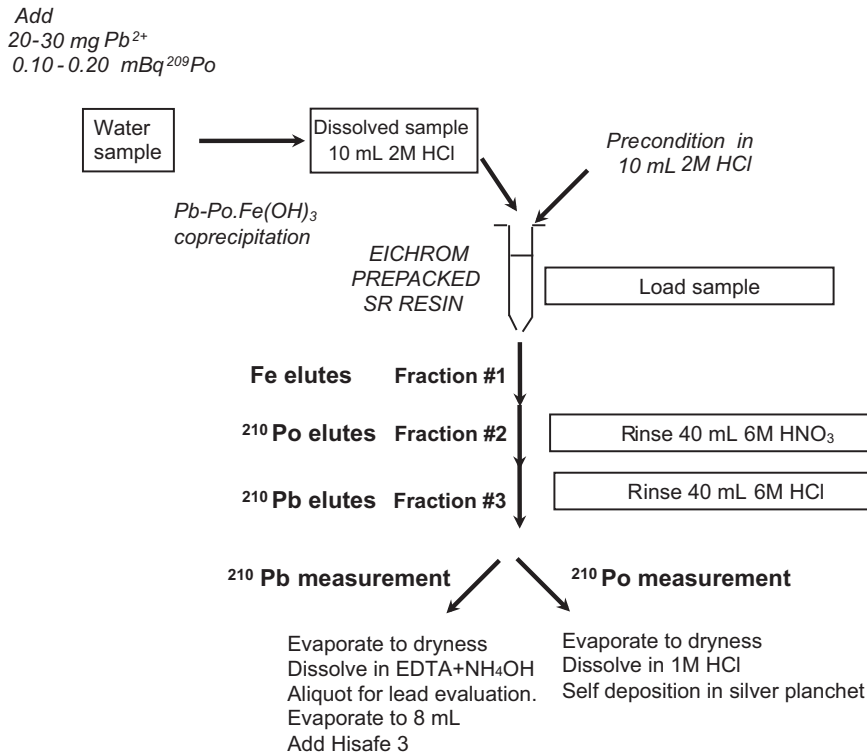


Fig. 1. Radiochemical procedure for ²¹⁰Pb and ²¹⁰Po isolation using prepacked Sr resin columns.

Table 1
Counting efficiency, background counting rates and counting rate of the average of three reagent blank samples. The Figure of Merit (FOM) and Minimum Detectable Activity (MDA) are calculated. Values from [29] obtained using a TriCarb detector are also included [29]. Counting times were 600 min in all cases.

Window	Radionuclide	LSC detector	Efficiency	Background (cpm)	Blank sample (cpm)	FOM ϵ^2/B (cps ⁻¹)	MDA (Bq m ³)	Sample volume (L)	Ref
5–60 keV	²¹⁰ Pb	Quantulus	0.717 ± 0.009	0.672 ± 0.034	0.802 ± 0.037	46	0.12	30	This work
5–1160 keV	²¹⁰ Pb, ²¹⁰ Bi	Quantulus	1.790 ± 0.008	1.779 ± 0.055	1.840 ± 0.056	108	0.08	30	This work
1–40 keV	²¹⁰ Pb	Tri-Carb	0.919 ± 0.028	3.350 ± 0.020		15	0.32	20	[29]

sample to ensure homogeneity. We assessed the chemical yield of Pb by taking an aliquot from Fraction #3 that was measured by ICP-MS.

2.2. Measurement and instrumentation

The measurement of ²¹⁰Po and ²⁰⁹Po emissions was done using two α -spectrometry arrays (Alpha Analyst, Canberra) at the University of Sevilla (CITIUS). Each dual chamber is equipped with two Passivated Implanted Planar Silicon (PIPS) detectors.

²¹⁰Pb was measured by using a Quantulus 1220 low-background scintillation spectrometer at the University of Sevilla (CITIUS). The counting time was optimised to obtain a MDA below 1 Bq m⁻³ (ca. 600 min). This spectrometer is equipped with a pulse shape analyser (PSA) to achieve separation and simultaneous counting of α - and β -emissions. The PSA threshold level was adjusted to obtain the best separation between α - and β -events. An analysis of the calibration of the PSA system is provided in Section 3.

We tested two measurement procedures. The first one considers only the use of the ²¹⁰Pb spectra (channels 20–350 in Quantulus 1220, i.e. 5–60 keV). The measurement is done 2 h after the sample preparation, although the potential contribution of any ²¹⁰Bi present in the sample at the time of its measurement needs

to be accounted for and is analysed later. In the second method, the counting window includes the spectra of ²¹⁰Pb and its daughter ²¹⁰Bi ($T_{1/2}$ = 5.0 day) in secular equilibrium (channels 20–1024 in Quantulus 1220, i.e. 5–1160 keV). Therefore, the measurements are conducted 20 days after the preparation of the samples. The implications of using one method or the other will be discussed in Section 3.

Counting efficiencies for the two selected windows of energies were obtained from the measurement of several lab-made standards, based on a MilliQ water-scintillation cocktail mix with the same proportions of real samples and spiked with ²¹⁰Pb (0.278 ± 0.005 Bq). Results are shown in Table 1.

Using window setting of channels 20–350, 5–60 keV, ²¹⁰Pb counting efficiency must correspond exclusively to ²¹⁰Pb, with no ²¹⁰Bi, coinciding with the spectrum that will be obtained immediately after the ²¹⁰Pb separation in the resins. Note that this is an additional difficulty when using this window, because to calculate this efficiency the contribution of ²¹⁰Bi must be previously removed from the standard spectrum, see for example [23].

The determination of stable lead was carried out using a Quadrupole ICP-MS (Agilent 7500c) at the University of Sevilla (CITIUS), equipped with a Babington nebulise. Samples were analysed following the EPA 200.8 protocol [30]. Aliquots from seawater collected June 2008 were measured using an ICP-OES

(Perkin Elmer Optima 4300DV) at the Servei d'Anàlisi Química at the Universitat Autònoma de Barcelona.

3. Results and discussion

3.1. Performance of Sr resin

In this work we present a radiochemical simplification of previous methods. In particular, and compared to the method proposed in [29], we have introduced two main changes. On one hand there is no previous purification of iron before the sample it is loaded into the column, avoiding a time-consuming step. On the other hand ^{212}Pb is not used to evaluate the radiochemical yield of lead; instead we have used stable lead. The use of ^{212}Pb ($T_{1/2} = 10.6$ h) as a tracer has the main disadvantage that the radiochemical separation and measurement must be done immediately after the sample collection and using a gamma spectrometer. This is not always possible (i.e. on-board oceanographic vessels) and prevents for preparing batches of numerous samples.

In this section we evaluate how the performance of the resin is affected by the analysis of large volume of seawater (up to 30 L) and the lack of purification of Fe before loading the samples into the Sr column. To co-precipitate polonium and lead from the seawater sample we need to use large amounts of Fe^{3+} (i.e. ca. 150 mg Fe^{3+}). Furthermore, large volumes of seawater, a complex matrix due to its high concentration of salts, are needed to optimise the limit of detection of the technique.

Vajda et al. [28] described one of the first methods for the separation of lead and polonium following the sequence described above. The lead capacity factor k' is $> 10^2$ [27], and it is highly retained in the column in any nitric media. In contrast, k' for

polonium is $< 10^{-1}$, and thus should be completely eluted from the column in nitric media [27]. Then, no significant crossover contamination of both elements is expected. However, variable traces of lead and polonium in the different fractions can change can be found for different conditions of separation, e.g. loaded volume, the type of matrix or the load of solutions highly enriched in iron. We analyse to which extent these factors might appreciably alter the retention and separation capacity of the resin.

The recoveries of lead and polonium in the different fractions of the separation process are shown in Tables 2 and 3. Note that ^{209}Po was used as spike to evaluate the polonium performance through the column, and thus the step of ^{209}Po auto-deposition in the silver disc must be taken into account. A specific experiment using 10 samples was carried out and ^{209}Po plating efficiency was estimated in $(71 \pm 8)\%$.

The total recovery of ^{209}Po and stable lead is also shown in Tables 2 and 3. This recovery is the sum of the recoveries measured in the fractions collected during the separation process (#1 loading, #2 polonium recovery, #3 lead recovery, #4 washing solution for polonium recovery, #5 washing solution for lead recovery). Note that the total recovery does not account for the recovery of the co-precipitation step. In most of the cases the total recovery is not quantitative, indicating that some of the polonium and lead remain in solution after the $\text{Fe}(\text{OH})_3$ precipitation. The incomplete recovery of uranium has been recently analysed and quantified in [31] and it is found that depends on the volume of sea-water analysed and the iron concentration in the sample. A similar analysis should be performed in future studies to analyse the recovery of lead and polonium by $\text{Fe}(\text{OH})_3$ precipitation in large sea-water volumes.

In order to reproduce the real performance of the resin we do not analyse the recoveries given directly by the spikes in the

Table 2

Recoveries of polonium for different samples in several fractions: #1 loading of sample, #2 polonium, #3 lead, #4 cleaning of polonium traces, # 5 cleaning of lead traces. The recoveries presented correspond to the average of the results of the batch normalised to the total recovery, also shown.

Origin	Batch	Polonium recovery in fractions						Number of samples averaged	Comments
		#1 (%)	#2 (%)	#3 (%)	#4 (%)	#5 (%)	Total (%)		
Standard	A	0.7	98	0	0.7	0.6	95	4	Elution 40 mL
0.5 L seawater	B	1.3	97	1	0.4	0.2	79	4	
1.2 L seawater	C	0.3	86	13	0.8	0.1	61	4	
0.4 L Groundwater	D	0.3	69	30	0.5	0.3	86	1	
2 L seawater	E	1.4	99	0	0	0	59	1	
30 L seawater	F	0.9	99	0	0	0	52	3	Elution 30 mL
10 L river water	G	0	100	0	0	0	87	5	
30 L seawater	H	0	100	0	0	0	35	3	
30 L seawater	I	0	100	0	0	0	28	5	

Table 3

Recoveries of stable lead for different samples in several fractions: #1 loading of sample, #2 polonium, #3 lead, #4 cleaning of polonium traces, # 5 cleaning of lead traces. The recoveries presented correspond to the average of the results of the batch normalised to the total recovery, also shown.

Origin	Batch	Lead recovery in fractions						Number of samples averaged	Comments
		#1 (%)	#2 (%)	#3 (%)	#4 (%)	#5 (%)	Total (%)		
Standard	A	62.7	0	37	0	0.0	64.1	4	Elution 40 mL
0.5 L seawater	B	6.2	7.6	82	2.6	1.3	51.8	4	
1.2 L seawater	C	1.1	5.7	86	1.0	6.0	48.2	4	
0.4 L Groundwater	D	2.0	1.1	85	12	0	52	1	
2 L seawater	E	1.7	9.2	89	0	0	61	1	
30 L seawater	F	38.3	9.7	52	0	0	73	3	Elution 30 mL
10 L river water	G	0	0	100	0	0	80	5	
30 L seawater	H	0	0	100	0	0	44	3	
30 L seawater	I	0	0	100	0	0	42	5	

fractions because we need to exclude the losses associated to the incomplete recovery of lead and polonium during the co-precipitation step. For that reason the recoveries of the fractions presented in Tables 2 and 3 are normalised to the total polonium or lead collected in all the steps.

The recoveries of polonium (fraction #2) are over 93% in most of the batches. One batch of four samples (batch C) had an average recovery of 87% and sample D had the lowest recovery, 69%. To verify that the resin successfully retains the polonium, we measured the recovery in the lead fraction #1 and in the fractions #4 and #5, obtained after washing respectively with HNO₃ and HCl 6 M. Polonium recovery ranged from 0% to 1.5% in fraction #1 and was negligible in fractions #4 and #5 (ranged 0–1%).

The method is robust for the polonium separation regardless of the origin of the samples and for 150 mg Fe³⁺. It also works well for large volumes of seawater, as the separation was quantitative in all cases. The method also seems to not be sensitive to changes in the volume of the load solution: we loaded 10, 30 and 40 mL with no significant changes in the polonium recoveries found in the different fractions.

The resin does not perform robustly for the lead recovery. The resin does not retain lead so effectively, and the losses in fraction #1 can be especially high. As expected [32], the sorption of lead by the resin decrease to 40% and 50% when 30 and 40 mL of solution is loaded. However, the resin works well when the loading volume is 10 mL, with recoveries ranging from 80% to 100% in the lead fraction (#3). Contamination of lead into the polonium fraction (Fraction #2) is also significant in some instances (up to 10%). The washing fractions are mostly clean of lead traces.

We conclude that the pre-packed Sr resins perform well for the separation of polonium in seawater, with recoveries over 90% that decrease for seawater. The resin also performs reasonably well for the separation of lead using 30 L seawater and 150 mg of Fe³⁺ and loading the samples in 10 mL, with recoveries over 80%. However it is not recommended to increase the volume of the loading solution, since the recovery of lead decreases drastically. This is because k' of lead in 2 M hydrochloric acid is approximately 100. This guarantees a sufficient retention for lead when loading a 20 mL solution but it does not guarantee an adequate retention for larger volumes.

When the resin performs well (i.e. 10 mL loading solution) the maximum crossover contamination of polonium into the lead fraction and vice versa is negligible. But on some occasions it might be of up to 30% for polonium into lead and to 10% for lead into polonium. This is discussed in Section 3.2.

3.2. Calibration of the measurements and limit of detection

3.2.1. Analysis of potential interferences of ²¹⁰Pb, ²¹⁰Po and ²¹⁰Bi in the measurements

As shown above, the contamination of ²¹⁰Pb in the ²¹⁰Po fraction can be up to 10%. However ²¹⁰Pb and ²¹⁰Bi are beta emitters, so they are not expected to interfere in the ²¹⁰Po measurement using alpha spectrometry. Furthermore, the plating of polonium onto silver discs is a very selective process where polonium is successfully discriminated [19]. The only precaution that must be followed is to conduct the plating immediately after the separation. Otherwise, the decay of the interference of ²¹⁰Pb before the plating step would lead to ²¹⁰Po that would need to be accounted for.

In relation to ²¹⁰Po interferences, ²¹⁰Po would not be present in the ²¹⁰Pb spectrum if ²¹⁰Pb was measured by LSC immediately after separation. But when ²¹⁰Pb and ²¹⁰Bi are in secular equilibrium, significant ingrowth of ²¹⁰Po will occur (i.e. 6% in 20 days). Furthermore, it might be the case that Sr resin does not separate polonium successfully from the lead fraction (occasionally up to

30%). The emissions of ²¹⁰Po and ²⁰⁹Po are collected in the window from 110 keV to 320 keV [23] and the spectrum ²¹⁰Pb-²¹⁰Bi is located in the window from 5 to 1160 keV [23]. Thus, we must use the alpha-beta discrimination system (PSA system) provided by the Quantulus 1220. The PSA system discriminate the counts in two windows for alpha (i.e. polonium) and beta (i.e. lead and bismuth) emissions. In previous calibrations we optimised the PSA system in order to reduce the beta interferences into the alpha window and, more important in this case, to minimise the alpha interferences into the beta window, details can be found in [23,33].

A complete removal of ²¹⁰Bi is necessary to assure the accuracy of ²¹⁰Pb in an immediate measurement. We have not evaluated the performance of the resin regarding ²¹⁰Bi discrimination but Vajda [28] obtained a negligible retention of bismuth using HCl. Besides, in [25] it was established that retention of Bi in the resin for nitric acid elution has a $k' < 0.4$, suggesting that bismuth adsorption is negligible. Using our method we found no contamination of ²¹⁰Bi in the sample, we obtained the same counts after an immediate measurement in the ²¹⁰Bi window (from 60 to 110 keV) and measuring the same window in a background sample.

Even assuming that the separation of ²¹⁰Bi from ²¹⁰Pb is complete, according to their half-lives ten hours after the separation of ²¹⁰Pb from ²¹⁰Bi, ²¹⁰Bi activity produced by direct decay of ²¹⁰Pb is equivalent to 5% of the collected ²¹⁰Pb. A ²¹⁰Pb-²¹⁰Bi spectrum in a LSC counter cannot be easily deconvoluted and the low energy tail of ²¹⁰Bi interferes in the ²¹⁰Pb spectrum. To avoid ²¹⁰Bi interferences the measurement of the sample for LSC counting must be immediate after the separation process or wait 20 days to secular equilibrium. However, note that the immediate counting is not practical for the analysis of a large number of samples, because they could not be processed in batches and a queue for the measurements cannot be prepared.

3.2.2. Optimisation of the limits of detection of the ²¹⁰Pb measurement by LSC

A relatively high beta background that increases the limit of detection is one of the main associated problems with LSC measurements. This disadvantage becomes crucial when analysing samples where ²¹⁰Pb concentration is relatively low, such as seawater (i.e. 1–2 Bq m⁻³).

Background depends on the type of vial. Teflonated polyethylene vials are preferred to glass or PE vials due to their lowest contribution to background and as a compromise between low background and high cost of Teflon vials [34].

As explained before we could use two different windows for the measurement. For the immediate measurement of ²¹⁰Pb, the window 20–350 channels, i.e. 5–60 keV, will be used. When ²¹⁰Pb-²¹⁰Bi secular equilibrium is achieved, it will be used the window 20–750 channels, i.e. 5–1160 keV, that includes both radionuclides.

The background counting rates (cpm) obtained by LSC with the Quantulus 1220 used in this study are shown in Table 1 using teflonated-polyethylene vials.

We analyse in detail the limit of detection provided using both ²¹⁰Pb and ²¹⁰Pb-²¹⁰Bi windows in order to decide which is the best option to minimise the MDA of the ²¹⁰Pb measurement. Background counting rate in the ²¹⁰Pb window is obviously lower than in ²¹⁰Pb-²¹⁰Bi window. However, ²¹⁰Pb counting efficiency is higher in 5–1160 keV window, since it is measuring both ²¹⁰Pb and ²¹⁰Bi. In order to take these two factors into account Figure of Merit (FOM) and Minimum Detectable Activity (MDA) [35] are calculated for both analytical approaches and presented in Table 1.

The complete measurement of the whole spectrum leads to the lowest MDA and the highest FOM. This is confirmed when real samples (see next section) are measured because better precision is achieved when measuring together ²¹⁰Pb and ²¹⁰Bi in secular

equilibrium; This is because background, counts per minute and efficiency values provide lower uncertainties using the complete spectrum window.

The results obtained for the blanks (Table 1) show a ^{210}Pb counting rate of about 3% (window ^{210}Pb - ^{210}Bi) and 17% (window ^{210}Pb) larger than the background counting rate. This contamination is likely due to the presence of ^{210}Pb in the $\text{Pb}(\text{NO}_3)_2$ that was used to prepare the Pb^{2+} solution. It must be taken into account only when ^{210}Pb activities are calculated in real samples in immediate measurements.

These results reinforce the conclusion from previous section that measurement of ^{210}Pb - ^{210}Bi in secular equilibrium is recommended to an immediate measurement.

The MDA and FOM obtained using the method presented in this work can be compared to those obtained by [29], who followed a similar radiochemical method although somewhat more laborious and used a different scintillation counter, Packard Tri-Carb 3170 TR/SL. The success of our method is that we obtain lower limit of detection similar to the one presented in [29] but including a more simple radiochemistry process. Our MDAs are lower either using ^{210}Pb window or ^{210}Pb - ^{210}Bi window for the measurement, but especially in this last case. This is mainly due to the low background counts that are obtained using a Quantulus 1220.

3.3. Applicability of the method

We evaluated the accuracy of the method by measuring the concentration of ^{210}Pb and ^{210}Po in artificial water samples that we produced by spiking MilliQ water with a standard of ^{210}Pb and ^{210}Po in secular equilibrium. The results are shown in Table 4 and correspond to the dissolution (after evaporation to dryness) of the final fraction containing ^{210}Pb using a) HCl 0.1 M and b) EDTA in ammonia medium.

When we used HCl 0.1 M for the redissolution of samples before the ^{210}Pb measurement, we found that the activity was below the spiked one and that was not in agreement with the ^{210}Po measured. These results show that the redissolution of ^{210}Pb using HCl 0.1 M, as suggested in [29] is incomplete. On the contrary, when we used EDTA for the redissolution the measured ^{210}Pb agreed well, within uncertainty, with the spiked ^{210}Pb . Furthermore, measured ^{210}Pb and ^{210}Po were in agreement and this is coherent with the fact that ^{210}Pb and ^{210}Po were in secular equilibrium in the spike solution.

The proposed method was used for the analysis of filtered groundwater samples as part of a national intercomparison exercise organised by University of Barcelona (Table 5). The average ^{210}Po obtained by the laboratories that participated in the exercise is included in Table 5, together with the standard deviation. Our ^{210}Po result coincides within the uncertainty with average ^{210}Po from the intercomparison. ^{210}Pb concentration is not reported in the intercomparison. In our results ^{210}Pb and ^{210}Po are not in secular equilibrium, this is coherent with the higher particle affinity of ^{210}Po compared to ^{210}Pb [36].

Table 4

^{210}Pb and ^{210}Po activities measured in traced samples following two methods for finally dissolution. using (a) 0.1 M HCl and (b) EDTA in ammonia medium. The activity of the added tracer is also displayed.

Sample	Final solvent	Window	^{210}Pb (mBq)		^{210}Pb (mBq) average	^{210}Po (mBq)		^{210}Po (mBq) average	^{210}Po added (Bq)			
a) STD-1	HCl 0.1 M	5–1160 keV	0.24	0.03	0.22	0.03	0.27	0.03	0.268	0.004	0.292	0.002
a) STD-2			0.20	0.02			0.27	0.03				
b) STD-A	EDTA	5–60 keV	3.10	0.06	3.04	0.08	2.89	0.03	2.88	0.02	2.92	0.01
b) STD-B			2.99	0.06			2.86	0.03				
b) STD-A	EDTA	5–1160 keV	2.88	0.06	2.80	0.08	2.89	0.03				
b) STD-B			2.71	0.05			2.86	0.03				

Table 5

^{210}Pb and ^{210}Po activity concentrations in groundwater measured in a national intercomparison ^{210}Po exercise.

Groundwater	A (Bq m^{-3})	$\pm \sigma$ ($\kappa=1$)
^{210}Pb	39	6
^{210}Po	19.6	0.5
^{210}Po Intercomparison average value (n=6)	17	1

Results for ^{210}Pb and ^{210}Po in the dissolved fraction of samples from the Mediterranean Sea are presented in Table 6. These values are the average of the samples collected in the coast of Barcelona, Western Mediterranean. ^{210}Pb and ^{210}Po values in the dissolved fraction in open sea surface waters of the Mediterranean Sea range from 0.4 to 1.8 Bq m^{-3} and from 1 to 1.5 Bq m^{-3} , respectively [37,38]. Our values ranged from 0.35 ± 0.08 to 0.54 ± 0.07 Bq m^{-3} for ^{210}Pb and 0.30 ± 0.08 to 0.38 ± 0.08 Bq m^{-3} for ^{210}Po . They are below the range of the reported values that correspond to open sea waters, but we collected our samples in the coast. And the coastal ^{210}Pb and ^{210}Po concentrations are expected to be lower [39] due to a higher ^{210}Po scavenging when particle concentrations increase in the coast.

In relation to the precision of the measurements, standard deviation of averaged ^{210}Po is 4–10%, and they are in agreement with the uncertainties associated to the aliquots, from 4% to 9%. Standard deviations for averaged ^{210}Pb , from 12% to 22%, are coherent with the individual measurements, with uncertainties from 9% to 25%. ^{210}Pb uncertainties are high, because the values measured are really close to the limit of detection, 0.08–0.12 Bq m^{-3} (Table 1). Uncertainties associated to ^{210}Pb alpha spectrometry in the total fraction are 7–8%. By contrast ^{210}Po alpha spectrometry presents higher uncertainties, 15%, because the measurement of ^{210}Po by alpha spectrometry in seawater depend on the ^{210}Pb measurement and uncertainties propagation takes into account both results.

The uncertainties we obtain following our method correspond to samples with the lowest activity concentrations that can be found in seawater, as they correspond to the dissolved fraction of coastal waters, strongly affected by ^{210}Pb and ^{210}Po particle scavenging.

Finally, we explore the limits of the technique using small volume estuarine samples from Huelva Estuary (SW Spain) and measuring the dissolved fraction. Samples correspond to batches D, E and G from Tables 2 and 3. In this case the volumes ranged from 0.5 L to 2 L. Activity concentration of ^{210}Pb in this area ranges from 1 to 6 Bq m^{-3} [39]; which are values very close to the MDA for ^{210}Pb measurement using our LSC technique (from 1 to 5 Bq m^{-3} for volumes 0.5–2 L). For this reason, uncertainties associated to the measurement were in most of the cases over 30%, and consequently we do not recommend the application of this method to small volume samples. Being 20 L (corresponding to $\text{MDA} \sim 0.15$ Bq m^{-3}) the minimum recommended sample value for measurement.

Table 6
 ^{210}Pb and ^{210}Po activity concentrations in dissolved fraction from sea water samples collected at the Mediterranean coast of Barcelona (NE Spain). 30 L samples were processed. The notation of the batch that was in displayed Table 1 are included. The uncertainties are expressed as absolute and percentage values.

Batch	Collection date	$A (^{210}\text{Pb})$			Average (Bq m^{-3})	$\pm \sigma$ ($\kappa=1$) (%)	$A (^{210}\text{Po})$			Average (Bq m^{-3})	$\pm \sigma$ ($\kappa=1$) (%)
		(Bq m^{-3})	$\pm \sigma$ ($\kappa=1$)	%			(Bq m^{-3})	$\pm \sigma$ ($\kappa=1$)	%		
I	19-06-08	0.28	0.05	16	0.35	22	0.33	0.03	8	0.35	7
		0.35	0.03	20			0.35	0.03	9		
		0.43	0.04	9			0.38	0.03	8		
K	20-08-08	0.59	0.05	9	0.54	12	0.31	0.02	4	0.30	4
		0.47	0.06	13			0.29	0.01	5		
		0.56	0.08	14			0.30	0.02	6		
L	28-11-08	0.39	0.07	17	0.44	15	NM			0.38	10
		NM					0.35	0.02	7		
		0.49	0.09	18			0.40	0.03	7		
		0.37	0.04	16			0.43	0.02	6		
		0.49	0.12	25			0.35	0.02	8		

4. Summary and conclusions

A rapid, direct method has been developed for determining ^{210}Pb and ^{210}Po water using LSC and alpha-spectrometry respectively and through Eichrom Sr resins. There is a previous step of isolation of lead, polonium, actinides and others using coprecipitation with iron hydroxides. After that, the results of this work show that polonium and lead can be strongly bound to Sr resin in hydrochloric acid solution and separated from the other elements by elution with concentrated solutions of nitric and hydrochloric acid respectively. The Sr resin allows separation of ^{210}Pb and ^{210}Po from water samples after loading directly the dissolved, iron enriched, precipitate from samples, thus accelerating the chemical method. The described procedure provides efficient isolation of ^{210}Pb and ^{210}Po from seawater samples and enables their rapid quantitative determination. In addition, this procedure can be applied and used for the isolation of ^{210}Pb and ^{210}Po in seawater samples on board during research cruises before being further analysed in the laboratory.

Stable lead is an appropriate yield tracer measured by a robust ICP-MS technique. The achievements of our method are a) the analysis can be completed within 6 days and b) very low limits of detection have been achieved -0.12 and 0.005 mBq L^{-1} for ^{210}Pb and ^{210}Po , respectively – and uncertainties comparable to α -spectrometry. The best performance of the method is attained when at least 20 L water are used and when ^{210}Pb and ^{210}Bi are measured in secular equilibrium.

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