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A comparative study of alternative methods for ^{210}Pb determination in environmental samples

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ABSTRACT

The accurate determination of the levels of ^{210}Pb in environmental samples (e.g. atmospheric aerosols, waters, soils, biota, etc.) is essential due to its multiple applications in geochronology, radiation protection, groundwaters flows, air masses movement, etc. For this purpose, it has been developed a novel and thorough study of three alternative radiometric measuring methods of ^{210}Pb activity concentrations in several types of samples. The three selected methods were low-level gamma spectrometry (^{210}Pb), alpha-particle spectrometry (via ^{210}Po), and Cherenkov counting (via ^{210}Bi). This study has been performed in terms of precision, linearity and proportionality as well as spent time, type of matrix, and showing the most appropriate method of measure in each case. Several kinds of samples were analyzed such as atmospheric filters, soils, sediments and phosphogypsum (PG) matrices. These samples contain different ^{210}Pb activity concentrations and were measured by the three techniques carrying out radiochemical procedures when necessary. There were not significant differences in the results obtained for the samples analyzed by the three methods. The major precision was obtained by using alpha-particle spectrometry, but this method is more expensive and time consuming.

1. Introduction

^{210}Pb ($T_{1/2}$ = 22.3 years) belongs to the ^{238}U decay chain. It is supplied into the atmosphere by the decay of ^{222}Rn ($T_{1/2}$ = 3.8 days) that is emanated from the terrestrial surface, which comes from the ^{226}Ra ($T_{1/2}$ = 1600 years) decay contained in rocks and soils (Poet et al., 1972; Tokieda et al., 1996). Most of ^{222}Rn only reaches the troposphere (< 2 km), but it is possible that some ^{222}Rn radionuclides reach the lower stratosphere and, consequently, ^{210}Pb production takes place. Even though its residence time, T_r, in the troposphere is relatively short ($T_r \approx$ several days – 1 month), ^{210}Pb is useful as a tracer for air masses that move regionally.

On the other hand, ^{222}Rn is the main contribution to the environmental radiation exposure (Arinc et al., 2011; Smith-Briggs and Bradley, 1984), and ^{210}Pb and ^{210}Po represent approximately 8 % of the average total internal radiation dose (Marley et al., 1999; UNSCEAR, 1988). For these reasons, a radiological monitoring of these radionuclides is required. Besides that, ^{210}Pb is widely employed in geochronology of recent sediments (< 200 years), as young organic and mineral current sedimentary systems. Thus, there are many studies on ^{210}Pb on dating peats, lake sediments and soil profiles, among others, were accomplished (Appleby and Oldfieldz, 1983; Barsanti et al., 2020; Carrazana et al., 2016; De Vleeschouwer et al., 2010). For this reason, it is also very useful to accurately determine ^{210}Pb. In addition, it is necessary to point out that ^{210}Pb is very used in the evaluation of residence times for atmospheric aerosols.

Furthermore, ^{210}Pb and its progeny (^{210}Bi and ^{210}Po, whose half-lives are 5.0 days and 138.4 days, respectively), have been widely used as tracers for environmental processes, which include studies on atmospheric, oceanic and terrestrial systems. Some examples include assessments of material fluxes to the seafloor (chemical scavenging), studies of the mechanism and rates of trace metal supply and removal from the ocean, the quantification of several atmospheric processes, including monitoring of sources and time scales and movement of air masses, determination of residence times, removal rate, washout ratios and deposition velocities of aerosols, and for chemical behavior estimations of analogous species (Baskaran, 2011; Gao et al., 2018; Schwing et al., 2017; Semertzidou et al., 2016; Sert et al., 2016; Thomson and Turekian, 1976; Zaborska et al., 2007; Zhong et al., 2020).

In this work, three techniques used for ^{210}Pb determinations have

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been compared, which were chosen due to their common usage in determinations of ^{210}Pb in environmental materials which typically contain low levels of ^{210}Pb activities. Radiometric measuring methods are based on the decay of ^{210}Pb and daughters, as shown in Fig. 1.

In the case of the gamma-ray spectrometry, a high purity germanium detector was employed (HPGe) (Barba-Lobo et al., 2021b), make it possible to determine ^{210}Pb by using its gamma emission (E_γ = 46.5 keV). Beta counting, through its daughter ^{210}Bi ($E_{\beta,max}$ = 1.2 MeV), ^{210}Pb being previously isolated through solvent extraction, solid-phase extraction membranes, precipitation or ion exchange. ^{210}Bi is measured by liquid scintillation counter (LSC), gas flow proportional counter or Geiger-Müller detector (Arinc et al., 2011; Brown, 2005; Clayton and Bradley, 1995; Marley et al., 1999; Peck and Smith, 2000; Pérez et al., 2003; Stojkovic et al., 2020). Alpha spectrometry is performed through its daughter ^{210}Po, using silicon detector or gas flow proportional counter. ^{210}Po is removed from the samples by solvent extraction (Chen et al., 2001; Clayton and Bradley, 1995), solid-phase extraction disk membrane (Marley et al., 1999) or self-deposition on a silver disk (Hurtado et al., 2003; Zaborska et al., 2007).

This comparison was carried out according to the procedure for validation of analytical methods in terms of their operational characteristics. In this way, several parameters have been evaluated as for example linearity, precision, proportionality, detection limit, as well as time spent, size and type of matrix. The goal of this comparison of techniques to determine ^{210}Pb activity concentrations is to study whether the three techniques provide comparable results, and to find which one is the most appropriate depending on the type of sample, precision required for the results, time and degree of analytical expertise.

2. Materials and methods

2.1. Sampling and pre-treatment

Different types of samples were used in this work: quartz filters from atmospheric aerosols, phosphogypsum (PG), soils and sediments. All samples were collected in a geographical area from the Huelva province.

A large chemical industry complex is in the surrounding of the city of Huelva, which includes, among other factories, an oil refinery and several industries dedicated to the extraction and/or production of several materials, such as copper, iron, phosphate fertilizers, and titanium-dioxide pigments. The wastes produced in the process of production of phosphate fertilizers (phosphogypsum) are stored in stacks comprising an area of 1200 ha.

The types of samples as well as the techniques used to determine ^{210}Pb activity concentrations in them are summarized in Table 1. In this table, the codes and an estimate of the amount of sample necessary (PG (Mas et al., 2006), Filters (Lozano et al., 2011), Soils (UNSCEAR, 2000)) to reach the minimum detectable activities (MDAs) are also shown.

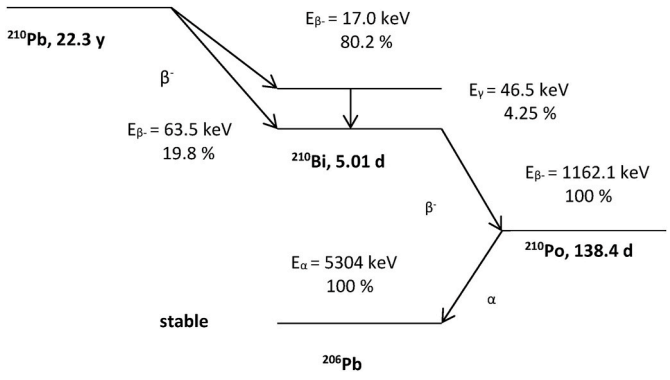

Fig. 1. Radioactive decay of ^{210}Pb (data taken from TOI LUND, 1999).

Table 1
Samples used in this work. An estimation of amount of sample necessary based on previous studies and estimated MDA values are also shown. (*) Estimated activity in Bq L^{-1}.

Sample	Code	Radiometric Technique	*MDA* (mBq)	^{210}Pb (Bq kg^{-1})	Sample size
PGs	F1 – F10	Alpha	1	400–1000	0.3 g
		Cherenkov	30		0.3 g
		Gamma	100		5 mL vial (~6 g)
Filters	E1 – E10	Alpha	1	1000-5000*	1 mL
		Cherenkov	30		2 mL
		Gamma	100		5 mL
Soils	S1 – S4	Alpha	1	20–30	0.5 g
		Cherenkov	30		5 g
		Gamma	100		5 mL vial (~7 g)
Sediments	S5 – S10	Alpha	1	400–1000	0.3 g
		Cherenkov	30		0.3 g
		Gamma	100		5 mL vial (~6 g)

2.1.1. Phosphogypsum samples

PG is a by-product (considered NORM material, Naturally Occurring Radioactive Materials), formed during the production of phosphoric acid through the chemical treatment of phosphate rocks. As it is well-known, the phosphate rock contains high levels of ^{210}Pb (Bolívar et al., 1996). Because of the industrial process, the natural radioactivity associated to the phosphate rock is fractionated and more than 90 % of ^{210}Pb is released in the waste (Bolívar et al., 2009).

Ten PG samples were collected in PG stacks (Fig. 2), at 30 and 60 cm depth in 2002. Then, they were grounded, homogenized and, finally, dried at 60 °C to avoid the loss of the structural water ($CaSO_4{\cdot}2H_2O$). The whole procedure can be found elsewhere (Mas et al., 2006).

2.1.2. Atmospheric filters

Three locations were selected for sampling surface air aerosols: The first one, named “El Arenosillo”, it is located closed to the Doñana Natural Park, and is not influenced by any anthropogenic pollution (Adame et al., 2010). The second station, “La Rábida”, is located closed to the industrial complex of Huelva, and the third, “El Carmen”, is located in Huelva and can be considered as an urban area (Fig. 2). The aerosol samplings were performed in 2005 by using a high volume PM_{10} sampler, this being an Andersen type sampler (flow of 68 m^3 h^{-1} according to US EPA protocols (EPA, 1996)), using rectangular quartz microfiber filters, Schleicher and Schuell QF20 (25.4 cm × 20.3 cm). The sampling time was generally 48 h (corresponding to a volume of 3.3 × 10^3 m^3).

Ten filters were collected for the present work. After sampling, the filters were conditioned by drying them in an oven at 200 °C for 4 h and placed in a dryer for 48 h until constant weight. For radionuclide determinations, the filter was divided into two equal halves and only one of them was measured. This part was digested in strong acids (described in a section below) and dissolved in 20 mL 0.4 M HNO_3 in polyethylene vial. Aliquots from this vial were taken for either radiochemical procedures or for direct measurement by gamma spectrometry (Lozano et al., 2011).

2.1.3. Soil and sediment samples

Soils were collected from the north of Huelva province in 2006, specifically from municipal territories of Aroche and Santa Olalla in the

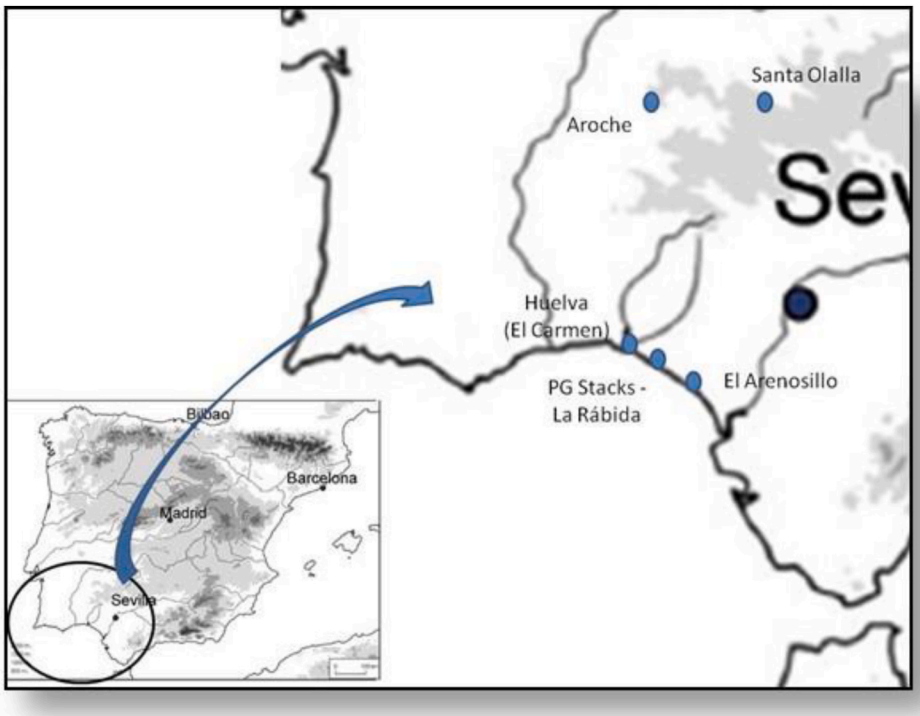

Fig. 2. Location of sampling points.

mountain area. The sampling was made with an Auger sampler. Soil samples were collected at different depths. On the other hand, sediments were collected close to the PG Stacks in 2009 (Fig. 2).

^{210}Pb, ^{210}Bi and ^{210}Po are in secular equilibrium in all samples previously mentioned, since they have been stored for more than 2 years, where the times needed to reach the secular equilibrium between ^{210}Pb and ^{210}Bi and between ^{210}Pb and ^{210}Po are approximately 50 days and 2 years, respectively.

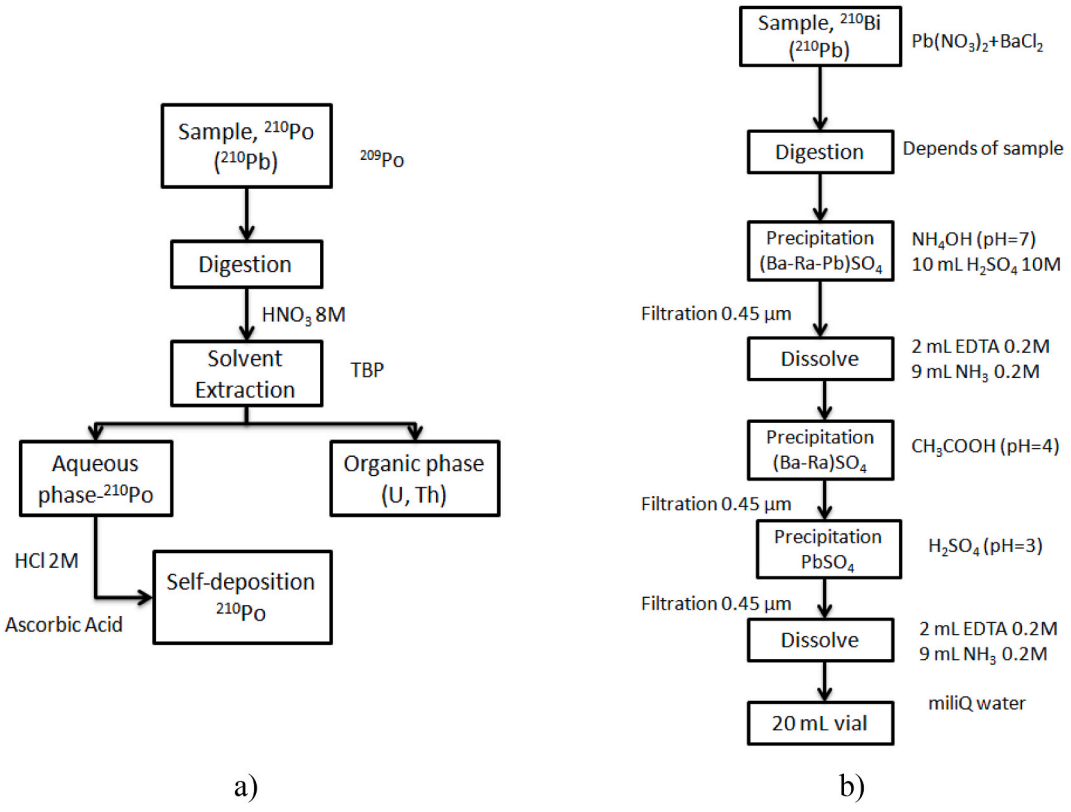

Fig. 3. Scheme of the radiochemical method for determination of ^{210}Pb by alpha-particle spectrometry (a) and by Cherenkov counting (b).

2.2. Digestion

The employed dissolution processes depend on the composition of each type of sample. In order to obtain the recovery yield (chemical or gravimetric), samples are traced at the beginning of dissolution process when alpha spectrometry and Cherenkov counting measurements are required:

Phosphogypsum (PG), which mainly contains $CaSO_4{\cdot}2H_2O$, is digested with 10 mL of aqua regia and evaporated. Then, the sample is treated according to the radiometric method for measuring the ^{210}Po.

Filters, mostly contain quartz and trace metals. They are cut and then, a half is put into a Teflon vessel and digested with strong acid (8 mL of 40 % HF + 3 mL of 65 % HNO_3 + 1 mL of 37 % HCl). After the evaporation, 10 mL of $HClO_4$ are added and the solution is evaporated to dryness. Then, 10 mL of 65 % HNO_3 are added and the solution is evaporated again to dryness. Finally, the dry sample is dissolved in 20 mL of 3 M HNO_3. Aliquots from this dissolution are taken for each of the analysis method.

Soils, with heterogeneous composition (mostly oxides of Si, group I and II, Fe, Al and Ti, and organic material) and *sediments*, containing mostly Si, Na, Mg, Al, K, Ca and Fe, and trace metals as well as V, Cd and Cr, lanthanides and actinides, were digested in the same way as filters.

2.3. Radiometric methods

The scheme for the radiochemical method used to determine ^{210}Pb by alpha-particle spectrometry and by Cherenkov counting is shown in Fig. 3.

2.3.1. ^{210}Pb determination by alpha-particle spectrometry

^{210}Pb is determined by alpha spectrometry through its daughter ^{210}Po. The radiochemical procedure (Fig. 3 a) is mainly based on a solvent extraction with tributyl phosphate (TBP) (Holm and Fukai, 1977). Each sample is spiked with ^{209}Po ($T_{1/2}$ = 115 years), digested depending on the kind of sample (Section 2.2) and evaporated. The ^{209}Po solution is SRM4326 from NIST. Then, the residue is taken up into 20 mL of 8 M HNO_3 and 5 mL of TBP are added in order to extract the aqueous phase in which ^{210}Po is eluted. Then, Po-isotopes are spontaneously deposited in acid solution (20 mL 2 M HCl), onto silver disks (El-Daoushy et al., 1991) adding acid ascorbic and with a gentle agitation during 8 h. The plating of polonium onto silver disks is a very selective process where polonium is successfully discriminated (Hurtado et al., 2003). After deposition, disks were washed with distilled water and counted by alpha spectrometry.

The activity of ^{210}Po was determined using a silicon detector (EG&G Ortec). The alpha-particle spectrometer system was made up of eight chambers, where each one of them was equipped with ion-implanted silicon detectors of 450 mm^2 (passivated implanted planar silicon (PIPS) detectors), being the detection efficiency about 25 % (Hou and Roos, 2007). The typical counting time is 2 days and the recovery yield of the procedure ranged from 60 % to 90 % (Hierro et al., 2012).

The activity concentration of ^{210}Po in the sample is obtained from the spectrum of the sample recorded in the alpha spectrometer through the expression:

$$a_{210Po} = \frac{a_{209Po}\, N_{210Po}\, m_{209Po}}{N_{209Po}\, m}\, e^{\lambda_{210Po}\Delta t} \tag{1}$$

where $N_{209_{Po}}$ and $N_{210_{Po}}$ are the net counts in the region of spectrum corresponding to ^{209}Po and ^{210}Po respectively, $a_{209_{Po}}$ is the activity concentration of ^{209}Po tracer added, m_{209Po} and m are the tracer and sample mass, respectively, λ_{210Po} is ^{210}Po decay constant and Δt is the time elapsed between the Po self-deposition onto the silver disc and the counting start. Besides, it is necessary to clarify that in the case of the uncertainty related to a_{210Po}, $\sigma(a_{210Po})$, the uncertainties of a_{209Po}, N_{209Po} and N_{210Po} were the main contribution sources to $\sigma(a_{210Po})$.

The recovery yield of the procedure, Rq, is determined through the following equation:

$$Rq = \frac{N_{209Po}}{\varepsilon\, P_\alpha\, A_{209Po}\, t} \tag{2}$$

where N_{209Po} are the net counts of tracer, A_{209Po} is the tracer activity added, P_α is the emission probability of an alpha particle (100 % in this case), t is the counting time and ε is the efficiency of detection.

2.3.2. ^{210}Pb determination by Cherenkov counting

The second technique used in this work consists of the measurement of the Cherenkov light produced by ^{210}Bi in aqueous matrix by LSC.

Fig. 3b) shows the scheme of the radiochemical procedure. ^{210}Pb was determined following a selective precipitation method (Kim et al., 2001; Lebecka et al., 1993; Mosqueda et al., 2008; Villa et al., 2007) using carriers of Ba and Pb ($BaCl_2$ and $Pb(NO_3)_2$, respectively) in which chemical Ra separation occurs. The procedure is summarized as follows:

i) Digested and diluted samples are heated at 80 °C and stirred for 5 min in a hotplate magnetic stirrer, and NH_4OH 30 % w/w is added up to pH = 7. The precipitation of lead in sulphate form as Ra-Pb-$BaSO_4$ was obtained by adding 10 mL of 10 M H_2SO_4 (Villa et al., 2005). The precipitate was then isolated by filtration through a 0.45 μm Millipore filter.
ii) The sulphate precipitate is re-dissolved using 2 mL of 0.2 M EDTA and 9 mL of 0.2 M NH_3 (Moreno et al., 2000). Then, 20 mL of distilled water is added.
iii) The solution is heated at 80 °C and glacial acetic acid is added to pH = 4. (Ba–Ra)SO_4 is formed and Pb remains on supernatant.
iv) After filtration, solution is heated and NH_4OH 30 % w/w is added to get pH = 7. $PbSO_4$ is formed by adding 5 mL of 10 M H_2SO_4. The precipitate is filtrated through a 0.45 μm Millipore filter, dried and weighed to calculate gravimetrically the chemical recovery through the following expression:

$$Rq = \frac{Pa_{Pb}\, m_{PbSO_4}}{m_{Pb}\, Pm_{PbSO_4}} \tag{3}$$

where Pa_{Pb} is the Pb atomic weight (207.2 g mol^{-1}), m_{PbSO_4} is the mass of the precipitate obtained, Pm_{PbSO_4} is the molecular weight of lead sulphate (303.3 g mol^{-1}) and m_{Pb} is the weight of lead in 1 mL of carrier added as $Pb(NO_3)_2$.

v) The sulphate precipitate is re-dissolved using 2 mL of 0.2 M EDTA and 9 mL of 0.2 M NH_3, diluted in 50 mL of Milli-Q water, evaporated to 20 mL at 80 °C and transferred into a plastic vial for Cherenkov measurement after 50 days. The final solutions obtained are colourless.

The ^{210}Pb (^{210}Bi) activity concentration, a_{210Bi}, is obtained through the following equation:

$$a_{210Bi} = \frac{R_S - R_b}{\varepsilon\, m\, Rq\, 60}\, e^{\lambda_{210Bi}\Delta t} \tag{4}$$

where R_s and R_b are the counting rate of the sample and background (given in counts per minute), respectively, ε is the counting efficiency, m is the sample mass, Rq is chemical recovery, λ_{210Bi} is ^{210}Bi decay constant and Δt is the time elapsed between the ^{210}Pb separation and the counting start. In the case of the uncertainty related to a_{210Bi}, $\sigma(a_{210Bi})$, the main sources that contributed to $\sigma(a_{210Bi})$ were the uncertainties of R_s, R_b and ε.

Although ^{210}Pb and ^{210}Bi are both beta emitters, only the second one has a maximum β energy (1162 keV) higher than the Cherenkov threshold in pure water (263 keV). Due to the continuous energy distribution of the emitted electrons, the measurement of this beta particle emitter requires chemical separation of the ^{210}Pb and waiting for 50

days to count in order to ensure secular equilibrium between ^{210}Pb and ^{210}Bi. The main advantages of this technique are the simplicity of the chemical method and the speed in the measurements. Moreover, ^{210}Bi is the only radionuclide in the ^{210} Pb day chain to be detected and the attenuation of electrons is less than for alpha particles, especially for high-energy electrons.

The measurements have been carried out by a LSC analyzer, Tri-Carb 3170 TR/SL. This device needs two parameters to be calibrated: background and counting efficiency, which in turn depends on the degree of color quenching. By this method and this device, a minimum detectable activity of 30 mBq and 12 % counting efficiency have been previously obtained (Mosqueda, 2009). On the other hand, since the type of scintillation vial seems to influence the background of the counter (Hurtado et al., 2003; Vaca et al., 1998), plastic vials have been used instead. Furthermore, the LSC system is protected against external radiation with a passive lead shielding which covers the whole counting system. The LSC operates in coincidence mode.

2.3.3. ^{210}Pb determination by gamma-ray spectrometry

As it is well-known gamma spectrometry allows a multi-elemental analysis and samples do not require any isolation treatment before counting. However, samples need to be grinded and homogenized. Then, samples were transferred onto polyethylene vials of 5 mL volume, where they are compacted and finally, they are taken to the detector. Counting times ranged between 24 and 48 h depending on the activity of the samples.

^{210}Pb activity concentration in the sample, a_{210Pb}, is obtained through the following equation:

$$a_{210Pb} = \frac{G - B - F}{\varepsilon\, P_\gamma\, t\, m}\, e^{\lambda_{210Pb}\Delta t} \tag{5}$$

where G is the Gross area of the full-energy peak, and B and F are the Compton continuum and the background due to the environmental conditions in the laboratory, respectively. Based in previous calculus, $F = (7.3 \pm 0.9)\ 10^{-4}$ cps. Then, P_γ is the emission probability (0.0425(4) taken from TOI LUND, 1999), t is the counting time, m is the sample mass, ε is the full-energy peak efficiency, λ_{210Pb} is ^{210} Pb day constant and Δt is the time elapsed between a reference date and the counting start. In the case of the a_{210Pb} uncertainty, $\sigma(a_{210Pb})$, resulted from propagating uncertainties in Eq. (5), the main sources that contributed to $\sigma(a_{210Pb})$ were the uncertainties of G, B, F, ε and P_γ. Consequently, it is expectable that when gamma-ray spectrometry is employed, higher activity concentration uncertainties are obtained, since there are more uncertainty contribution sources. This is very consistent with the results that will be shown in Section 3.3.3.

The efficiency calibration of the detector was accomplished using the following Standard Reference Materials: RGU-1, RGTh-1 from IAEA, as well as KCl which contain 4940 ± 15 Bq kg^{-1}, 3250 ± 45 Bq kg^{-1} and 16740 ± 240 Bq kg^{-1} of ^{238}U, ^{232}Th and ^{40}K, respectively, where all radionuclides are in secular equilibrium in the cases of the ^{238}U- and ^{232}Th-series. See Barba-Lobo et al. (2021b), for further information about the efficiency calibration method. The efficiency calibration of the spectrometer has to consider the influence of self-absorption of the gamma-ray, which in turn depends on the energy considered (46.5 keV), as well as on the composition and the apparent density of the matrix. See Barba-Lobo et al. (2021a), Bonczyk (2018) for further information about self-absorption corrections. Self-absorption corrections for the measurements of ^{210}Pb were carried out based on methods described elsewhere (Appleby et al., 1992; Appleby and Piliposian, 2004).

In Table 2, the mass attenuation coefficients at 46.5 keV for each type of matrix are calculated from the composition of each sample. Since the mass attenuation coefficients, η, are very similar for all samples belonging to each type of the selected matrices (PG, filter, soil, sediment), an unique value of η can be considered for each type of the four sample matrices at 46.5 keV. Thus, attenuation coefficients have been calculated through the Bragg's law (see Barba-Lobo et al., 2021a), since the major elemental compositions of the samples are known by X-Ray Fluorescence provided by the Central Laboratories of the University of Huelva located at the Campus "El Carmen" (see Table A.6 in Supplementary material for further information about the chemical compositions of all samples selected in this work). On the other hand, counting efficiencies for ^{210}Pb in the standard geometry for each type of matrix used in this study are also shown in Table 2.

Table 2
Mass attenuation coefficients, η, and full-energy peak efficiencies, ε, at 46.5 keV for each type of matrix.

Sample	η (cm^2 g^{-1})	ε (%)
PGs	0.56 ± 0.03	38.1 ± 1.7
Filters	0.370 ± 0.015	48.9 ± 1.9
Uncontaminated Soils	0.440 ± 0.018	43 ± 2
Contaminated Sediments	0.49 ± 0.03	44.0 ± 1.8

To determine the ^{210}Pb activity concentration by gamma-ray spectrometry, the samples were measured with a well-type HPGe detector (Canberra) with a full-width at half-maximum (FWHM) of 1.33 keV at 122 keV and 2.04 keV at 1332 keV, and a peak/Compton ratio of 56.2/1. The detector was coupled to a multichannel analyzer and the detector was shielded with 10 cm of lead. In order to avoid interferences of X-rays from the Pb in the shielding, a layer of 2 mm thick of Cu layer is inserted between the Pb shield and the detector (Ramadhan and Abdullah, 2018). The detector is in a room with walls and ceiling made of 75 cm thick concrete at the basement of a four-store building.

The quality assurance of radioanalytical measurements was regularly ensured through participation in intercomparison exercises organized by the International Atomic Energy Agency (IAEA), as well as the periodic measurement of certified reference materials (IAEA-326 soil; NIST-1646a estuarine sediment, etc.).

3. Results and discussion

3.1. Minimum detectable activity

The lower limit of detection (L_D), minimum detectable activity (MDA), for each radiometric method were calculated based on Currie (2004). Thus, MDA is defined by the following equation:

$$MDA = \frac{L_D}{\varepsilon\, Rq\, t\, P} e^{\frac{\Delta t}{T_{1/2}}\, ln2} \tag{6}$$

where ε is the efficiency, Rq is the recovery yield, t is the counting time, P is emission probability, Δt is the elapsed time between a reference date and counting end, $T_{1/2}$ is the radionuclide half-life. In this work, L_D is defined by the Eq. (7):

$$L_D = 2.71 + 3.29\, \sigma_0 \tag{7}$$

where σ_0 is the standard deviation of the net counts due to the background.

The MDA for gamma spectrometry can be estimated considering that P, the probability of emission of ^{210}Pb gamma-ray is 0.0425(4) and Rq is 1. The counting time is about 1.5 days (129600 s) for PG, soil and sediment; and 268852 s for filters. The background has been obtained for each matrix: the blank chosen for solid samples has been a vial containing air, and for dissolved filters, a vial containing 0.4 M HNO_3.

In the case of alpha spectrometry, the emission probability assigned to ^{210}Po is 1, counting time is 2 days, the average efficiency is about 0.25 and the time elapsed between self-deposition (reference date) and counting is 5 days. As blank of filter samples, we have chosen a blank filter for which the complete procedure described above has been applied, whereas as blank for solid samples, a 0.4 M HNO_3 solution has been used and the same radiochemical procedure has been applied.

In the case of determination of ^{210}Pb by Cherenkov counting, the emission probability assigned to ^{210}Bi is 1, counting time is 600 min and the average efficiency is 0.12 (Mosqueda, 2009). The blank of samples has been prepared with 2 mL of 0.2 M EDTA + 9 mL of 0.2 M NH_3 + 1 mL of Pb^{2+} carrier (30 mg/mL), and deionized water to 20 mL.

Table 3 shows the MDA values obtained for each radiometric method for the different kind of samples.

3.2. Activity concentrations of ^{210}Pb

In Table 4, the results obtained for ^{210}Pb determinations in each type of sample by the different methods are shown. From this table, it is possible to observe that the activity concentrations range from 11(6) Bq kg^{-1} to 1343(66) Bq kg^{-1}. The lower activities correspond to uncontaminated soils and filters whereas the upper values correspond to phosphogypsum and contaminated sediments. Activity concentrations obtained through the different methods are in good agreement since all values have not significant differences from each other for 2σ confidence level.

In order to evaluate if there are significant differences between the methods used to determine ^{210}Pb, a linear fit of the results obtained by the different methods has been done. Thus, the results obtained for the linear fits are shown in Table 5. Besides, the comparison has been made for each type of matrix as well as for the whole set of data.

In Fig. 4, the results for the comparison taking into account all samples are shown. As it can be observed, the slopes for the linear fits range from 0.92 to 1.16, whereas the determination coefficient (R^2) varies from 0.903 to 0.998. These values indicate that there is a very good agreement between the three methods to obtain the ^{210}Pb activity concentrations. When the whole set of data is considered, a better fitting (R^2 about 0.990) is obtained compared with the ones resulted from the cases for which the fittings were done for each type of matrix. This fact can be explained because when all data are used to do the linear fit, the calculations are extended to a large range of activity concentration data.

As can be seen from Table 5 and Fig. 4, the results obtained from the fittings for the whole set of data are similar than those obtained when only one type of matrix is considered.

3.3. Statistics

In this paragraph some parameters related to the fits done will be analyzed. The linear fit $y = (a \pm \sigma_a) + (b \pm \sigma_b)\,x$, where a and b are the parameters resulted from the linear fittings and σ_a and σ_b are their uncertainties, respectively.

Table 3
L_D and *MDA* for each type of matrix and for each radiometric method. $B + F$ counts from a blank, ε is the counting efficiency obtained by gamma spectrometry, and *Rq* is the recovery yield for alpha-particle spectrometry and Cherenkov counting.

Method	Sample	$B + F$ (counts)	L_D (counts)	$\varepsilon(Rq)$	*MDA* (mBq)
Gamma spectrometry	Phosphogypsum	672	123	0.38	77
	Soil			0.43	60
	Sediment			0.44	57
	Filter	329	405	0.49	86
Alpha spectrometry	Phosphogypsum	5	70	0.72	0.4
	Soil			0.55	0.6
	Sediment			0.92	0.3
	Filter	207	13	0.60	0.3
Cherenkov counting	Phosphogypsum	768	132	0.72	53
	Soil			0.68	49
	Sediment			0.66	49
	Filter			0.81	43

Table 4
Activity concentrations for ^{210}Pb by alpha and gamma spectrometric techniques, as well as by Cherenkov counting in the different samples.

Sample type	Sample code	Alpha spectrometry	Gamma spectrometry	Cherenkov
PGs	F1	637 ± 37	633 ± 44	641 ± 32
	F2	656 ± 17	646 ± 48	544 ± 23
	F3	617 ± 34	616 ± 41	624 ± 22
	F4	825 ± 10	845 ± 47	759 ± 59
	F5	633 ± 40	680 ± 49	671 ± 51
	F6	537 ± 21	510 ± 23	529 ± 47
	F7	649 ± 14	633 ± 44	623 ± 46
	F8	334 ± 7	343 ± 18	334 ± 29
	F9	309 ± 7	320 ± 12	325 ± 28
	F10	553 ± 11	548 ± 24	544 ± 29
FILTERS	E1	37 ± 2	38 ± 5	32 ± 5
	E2	123 ± 3	125 ± 10	120 ± 6
	E3	31.0 ± 1.0	28 ± 5	22 ± 5
	E4	114 ± 3	148 ± 12	112 ± 6
	E5	73 ± 2	57 ± 6	53 ± 6
	E6	109 ± 17	115 ± 9	101 ± 6
	E7	48.0 ± 1.0	48 ± 5	46 ± 5
	E8	44 ± 2	38 ± 5	35 ± 5
	E9	56 ± 8	57 ± 6	56 ± 5
	E10	43 ± 2	45 ± 6	54 ± 5
SOIL - SEDIMENTS	S1	55 ± 3	49 ± 5	54 ± 17
	S2	21 ± 2	13 ± 5	16 ± 3
	S3	23 ± 4	11 ± 6	23 ± 2
	S4	27 ± 2	26 ± 5	31 ± 6
	S5	166 ± 5	176 ± 15	155 ± 21
	S6	589 ± 23	576 ± 30	550 ± 48
	S7	156 ± 5	154 ± 12	138 ± 22
	S8	1327 ± 25	1343 ± 66	1299 ± 42
	S9	426 ± 7	424 ± 22	434 ± 24
	S10	308 ± 7	308 ± 17	309 ± 27

Table 5
Slope and intercept obtained in the comparison between the three radiometic methods. The comparative has been carried out for all samples as well as for each type of matrix (uncertainties at one sigma level).

Methods	Sample type	Slope (b)	Intercept (a)	R^2
Gamma - Cherenkov	ALL SAMPLES	1.038 ± 0.014	−0.2 ± 1.7	0.990
	PGs	1.10 ± 0.06	−40 ± 30	0.975
	SOIL-SEDIMENTS	1.05 ± 0.02	−6 ± 3	0.997
	FILTERS	1.16 ± 0.09	−3 ± 6	0.942
Alpha - Cherenkov	ALL SAMPLES	1.018 ± 0.006	3.8 ± 0.6	0.989
	PGs	1.16 ± 0.05	−59 ± 24	0.983
	SOIL-SEDIMENTS	1.011 ± 0.011	1.1 ± 1.3	0.996
	FILTERS	0.92 ± 0.10	9 ± 5	0.903
Gamma - Alpha	ALL SAMPLES	1.017 ± 0.013	−2.7 ± 1.7	0.992
	PGs	0.98 ± 0.05	12 ± 22	0.991
	SOIL-SEDIMENTS	1.01 ± 0.02	−6 ± 3	0.998
	FILTERS	1.17 ± 0.11	−9 ± 7	0.927

3.3.1. Linearity

The linearity is based on the relative standard deviation of the slopes, S_b/b (in %), where for a good linearity, S_b/b must be less than or equal to 2 % (see Table A.1 in Supplementary material), we note that in the cases corresponding to all samples, the relationship between the methods was clearly lineal, obtaining a S_b/b value less than 1.4 %.

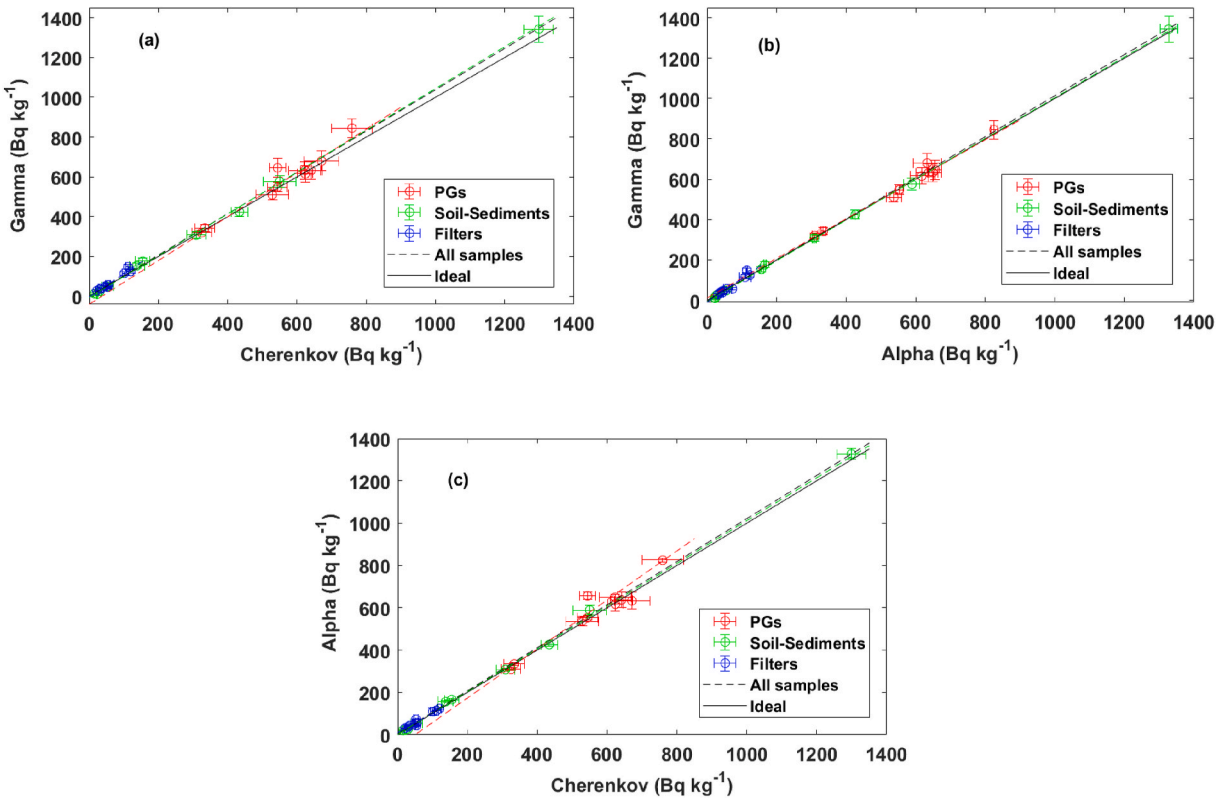

Fig. 4. Comparison of results obtained for different methods: gamma spectrometry vs Cherenkov counting (a), gamma spectrometry vs alpha spectrometry (b) and alpha spectrometry vs Cherenkov counting (c).

3.3.2. *Proportionality*

The proportionality is based on the variance of independent term, S^2_a, (zero being the ideal case) (see Table A.2 in Supplementary material), it is possible to observe that for the cases related to all samples, the results obtained by alpha spectrometry vs Cherenkov counting show the best proportionality, obtaining $S^2_a = 0.36$.

3.3.3. *Precision*

Based on the average relative uncertainty, <*Uncertainty*> (%), of each radiometric method (see Table A.3 in Supplementary material), for the entire range of activities, that is, considering all samples, the most precise method is alpha spectrometry (<*Uncertainty*> = 4.9 %), as found in bibliography (Aqqarwal, 2016). However, the Cherenkov counting and gamma spectrometry show similar accuracies (<*Uncertainty*> = 10 % and 11 %, respectively). These relative uncertainties are very consistent with the sources that contribute to the calculations of the activity concentration uncertainties, which were previously studied in Section 2.3 for each radiometric technique.

3.3.4. *Statistical test for differences between methods*

To study whether each pair of radiometric methods give results that do not differ significantly, it is very useful to analyze the difference, d, between each pair of measurements ("pairwise testing"). The null hypothesis is "there are no significant differences between the values obtained by the two methods", proving that the mean of the differences, $d_{average}$, is not significantly different from zero. The parameter t is obtained by the following equation:

$$t = d_{average}\sqrt{n}/s_d \quad (8)$$

where n is the number of samples analyzed, s_d is the standard deviation of the differences, and t is the t-student value for (n-1) degrees of freedom.

In Table A.4 (in Supplementary material), the results for the comparison of each pair of methods, for 29 degrees of freedom, a confidence interval of $P = 0.95$ and 2-tailed test are summarized.

It is observed that in all cases, the obtained values for t, t_{exp}, were lower than $t_{critical}$ (2.0), so the null hypothesis cannot be rejected. Consequently, the methods do not provide significantly different values for ^{210}Pb activity concentrations.

3.3.5. *F test for comparison of standard deviations*

In this case, it consists of comparing standard deviations or two random errors dataset. In this case, the null hypothesis is that populations are normal and the variances of each population are equal, that is, the variance ratio, F, must be one. Thus, the values for the relations of variances, as well as the critical value of F, $F_{critical}$, for a 2-tailed test, $P = 0.95$ and 29 degrees of freedom are shown in Table A.5 (see Supplementary material).

It is observed that in all cases, the F values were lower than $F_{critical}$ (this being 1.90) and, consequently, the null hypothesis is accepted. Therefore, no relevant differences between the two variances for a significance level of 5 % were found.

4. Conclusions

In the present work, a comparative study on three alternative radiometric methods (alpha spectrometry, gamma spectrometry and liquid scintillation) for determining ^{210}Pb has been carried out. It has been shown that in the results obtained by the three methods, there were no significant differences. It has also shown the linearity of the results in the wide range of activity concentrations used in this work, and that the most precise method was found for the case corresponding to the alpha spectrometry.

The main drawback of ^{210}Pb measurement by alpha spectrometry arises from the need for keeping the samples for 2 years in order to reach ^{210}Pb-^{210}Po secular equilibrium. Typically, ^{210}Pb-^{210}Po are separated

before 2 years, and ^{210}Pb is isolated and stored more than 3 months for the in-growth of ^{210}Po, and the new generated Po is measured. Either way, the time spent to wait is high enough. Moreover, this method has several advantages among which the following stand out: relatively little radiochemistry time and few manipulations are involved. Because of the very low background counts and the high counting efficiency, the detection limits are low, obtaining a good precision. This radiometric technique is appropriate when the results are not quickly required, but a high precision is needed to detect very low activity.

Gamma spectrometry is the easiest and fastest method: The sample can be directly measured. However, the self-absorption and interference from other gamma-X rays have to be considered. The detection limit is higher than alpha spectrometry. This method is preferable when higher sample size is available, it is useful for measuring high levels of ^{210}Pb, and for the cases when high precision is not required as well as the results must be given soon.

For Cherenkov counting, ^{210}Pb needs to be separated from the matrix through a long although simple chemical process. Then, ^{210}Pb separated is stored during 50 days for the in-growth of ^{210}Bi, less time than alpha spectrometry, and there is no interference. However, the detection limit is higher and is not proper in order to measure samples whose activities are relatively small.

CRediT authorship contribution statement

E. Cuesta: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **A. Barba-Lobo:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **R.L. Lozano:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **E.G. San Miguel:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Validation, Writing – original draft, Writing – review & editing. **F. Mosqueda:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **J. P. Bolívar:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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