

DIRECT ^{210}Pb DETERMINATION IN ENVIRONMENTAL SAMPLES BY LIQUID SCINTILLATION COUNTING AND ITS VALIDATION THROUGH γ -RAY SPECTROMETRY

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ABSTRACT. ^{210}Pb is a natural radionuclide belonging to the ^{238}U series and is one of the most important isotopes to be determined in environmental samples because it is considered an excellent tracer of several processes in nature. However, direct determination of this nuclide via traditional radiometric techniques is far from straightforward since ^{210}Pb emits only relatively soft beta particles and a low-energy gamma ray with a low probability of emission. We propose a rigorous method for direct ^{210}Pb determination in sediment samples by LSC. The method includes careful calibration and adaptation of the experimental system based on a low-background spectrometer, Quantulus 1220TM. There are 2 objectives to the calibration: efficiency improvement and optimum alpha/beta separation using a pulse-shape discrimination system (PSA). On one hand, a detailed study of the PSA system is essential because, after the isolation of ^{210}Pb from the environmental matrix, some traces of its alpha-emitting daughter ^{210}Po or other natural alpha emitters might be present during the measurement. Moreover, the appearance of quenching in the sample affects not only counting efficiency but α/β discrimination as well. The quenching effects are also studied in both efficiency considerations and for α/β separation and are included in the calibration. On the other hand, a new approach is proposed based on calculation of an effective radiochemical yield, allowing the determination of ^{210}Pb levels in the analyzed samples without a previous direct determination of the counting efficiency. ^{210}Pb counting efficiency determination is avoided because in most of the available standards, ^{210}Pb is in secular equilibrium with its daughter ^{210}Bi . As the ^{210}Bi low-energy tail overlaps in the ^{210}Pb spectrum, it is difficult to precisely determine the ^{210}Pb efficiency. The optimized method was applied for determining ^{210}Pb concentrations in a set of riverbed sediments affected to a quite variable degree by anthropogenic inputs of this nuclide, which has been validated by comparing those results to the ones obtained by applying γ -ray spectrometry. Although it is a direct, non-destructive technique, precise determination of the activity requires knowing the full energy peak efficiency and self-absorption correction for the low-energy gamma ray emitted. This task was performed using Monte Carlo simulation.

INTRODUCTION

^{210}Pb determination in environmental samples is of crucial importance in radiological impact studies and for dating sediments and other environmental compartments. For this reason, accurate measurement techniques are needed to correctly determine ^{210}Pb in environmental samples. ^{210}Pb can be measured through the determination of ^{210}Po by alpha spectrometry (Moser 1993) or directly by gamma spectrometry (Cannizzaro et al. 1999; San Miguel et al. 2002), measuring the 46.5-keV photon emitted with an intensity of 4.0% during its decay. Cerenkov counting of ^{210}Bi , once secular equilibrium with ^{210}Pb is reached, is another technique used to measure ^{210}Pb . This technique has an easy sample treatment (Hurtado et al. 2003) but has the drawback of lower counting efficiencies than liquid scintillation counting (LSC).

The use of LSC for directly determining ^{210}Pb in environmental samples is a promising alternative method (see Wallner 1997; Blanco et al. 2004). Nevertheless, due to the complexity of the ^{210}Pb decay scheme, which includes low-energy beta particles from ^{210}Pb and high-energy beta particles from ^{210}Bi as well as alpha particles from ^{210}Po , it is still necessary to calibrate the detector for proper ^{210}Pb counting (Villa et al. 2003). Currently, some liquid scintillation counters, such as the Quantulus 1220TM, allow for simultaneous alpha and beta detection and their subsequent separation.

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However, this separation is not 100% efficient and alpha-beta interferences have to be evaluated and minimized.

We developed a quick and easy radiochemical technique to measure ^{210}Pb in sediments by LSC. Furthermore, we combined this procedure with a calibration of the liquid scintillation counter to obtain the most accurate results and a lower limit of detection. It is difficult to precisely determine ^{210}Pb counting efficiency, mainly because ^{210}Pb standards are usually in secular equilibrium with ^{210}Bi and ^{210}Po . Even though alpha-beta discrimination is properly adjusted to separate alpha (^{210}Po) and beta emissions (^{210}Pb - ^{210}Bi), we will not be able to avoid the ^{210}Bi low-energy tail interferences in the ^{210}Pb beta window.

There are different methods to approach this problem. Blanco et al. (2004) studied the interference of the ^{210}Bi tail in the ^{210}Pb window. We studied with success the possibility of using a pure beta emitter (such as ^{99}Tc) instead of ^{210}Pb to obtain the counting efficiency (Villa et al. 2003). The advantage of our method is that there is no need to account for ^{210}Bi interference. Furthermore, it is not necessary to know the ^{210}Pb counting efficiency because the method is based on empirical determination of a parameter where radiochemical yield and counting efficiency are included. To check the accuracy of the technique, we measured ^{210}Pb activity concentration in riverbed sediments using 2 different techniques of measurement, LSC and γ spectrometry using the Monte Carlo simulation for efficiency calculation.

EXPERIMENTAL PROCEDURE

Sampling

A first sampling campaign was carried out in 1999 in an estuary of the Odiel and Tinto rivers (SW Spain). Sediment samples were collected from the same sampling stations located near phosphogypsum piles and phosphoric acid factories. In each sampling station, 5 kg of superficial sediment samples were directly collected from the riverbed with a dredge. Samples were then dried, homogenized, and stored for later treatment.

Radiochemical Procedure

The first treatment step (see Figure 1) consists of a total dissolution of the sample. First, an aliquot of 5 g (dry weight) was taken from each sediment sample, and a carrier (25 mg Ba^{2+} and 30 mg Pb^{2+}) was added. The sediment was ashed at 250 °C for 1 hr and then at 550 °C for 12 hr. Next, ashes were digested with aqua regia (10 mL of concentrated HNO_3 and 35 mL of HCl 35%) while heating for 4 hr. A few milliliters of H_2O_2 were repeatedly added during the digestion. Concentrated HNO_3 was then added and the sample was filtered.

After neutralization, H_2SO_4 was added to the solution to precipitate simultaneously barium (and consequently radium) and lead in the form of BaSO_4 and PbSO_4 . The precipitate was filtered using a Millipore filter (0.45- μm pore diameter), dried, and then redissolved with EDTA and NH_4OH . By adding some drops of glacial acetic acid (CH_3COOH), the pH was lowered to 4.5, at which point only $(\text{Ba-Ra})\text{SO}_4$ precipitates (Lebecka et al. 1993). The solution containing only Pb was filtered again, discarding the precipitate.

Finally, PbSO_4 precipitates adding H_2SO_4 to the solution until $\text{pH} = 3$. The precipitate was recovered in a Millipore filter (0.45- μm pore diameter), dried, and weighed to gravimetrically obtain the radiochemical yield.

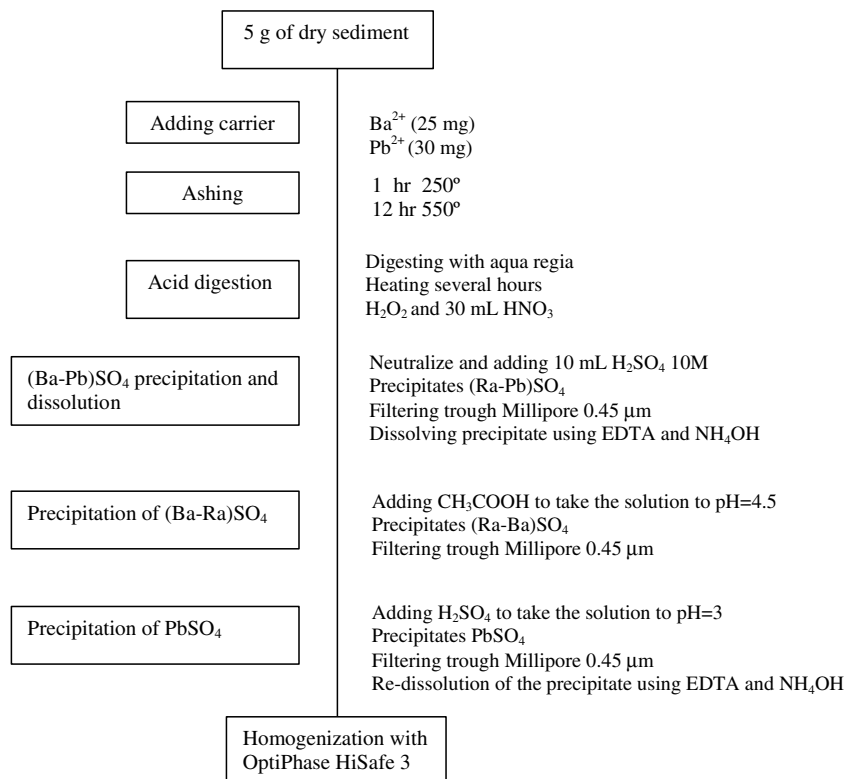


Figure 1 Radiochemical procedure scheme

Finally, PbSO₄ precipitate was dissolved with EDTA in an ammonia medium. The dissolution was evaporated to 9 mL, placed into a 20-mL glass vial, and mixed with 16 mL of OptiPhase HiSafe 3 (PerkinElmer, USA) scintillation cocktail, thus filling the vial. This proportion of sample/cocktail was chosen to make the ratio coincide with the one used for ^{226}Ra measurements, where the vial is filled with cocktail to avoid ^{222}Rn losses.

The radiochemical yields obtained (see Table 3) vary from 20% to 95%, with 60% as the mean value. Using this method, a great part of the ^{210}Pb is recovered in most samples.

LIQUID SCINTILLATION MEASUREMENTS

Detection System

Samples were measured using a Quantulus 1220 low-background scintillation spectrometer equipped with a pulse-shape analyzer (PSA) to achieve separation and simultaneous counting of α and β events. A parameter (PSA threshold level) in the PSA circuit can be adjusted from values 1 to 256 to obtain the best separation between α and β events. To avoid the growth of the ^{210}Pb daughter ^{210}Bi ($T_{1/2} = 5.0$ d) after sample preparation, measurement is done immediately following preparation. In relation to its alpha-emitter daughter, in an immediate measurement ^{210}Po ($T_{1/2} = 138$ d) cannot be detected yet by the spectrometer.

^{210}Bi and ^{210}Po Interferences: Calibration of the Alpha-Beta Discrimination System

Alpha-beta separation using PSA is not perfect. Some beta events will be classified as alpha events (beta interference, τ_β) and alpha events will be classified as beta (alpha interference, τ_α). The net counting rates measured in a chosen window of the alpha spectrum must be corrected by τ_β . Conversely, a similar correction for alpha interference (τ_α) must be made in the beta spectrum. The optimum PSA level is usually set at the PSA threshold level that minimizes the total interference, $\tau = \tau_\alpha + \tau_\beta$ (Villa et al. 2003). However, this is not always the case.

The main problem in evaluating interference is that, generally, interferences are not constant for every radionuclide and depend strongly on the quenching level in the sample; thus, it is necessary to choose appropriate pure alpha and beta emitters and establish the relationship between interference and quenching level to obtain the proper alpha and beta interference. Alpha interference is considered in first approximation, independent from the energy of the emission; however, beta interference is strongly energy dependent (Villa et al. 2003). The suitability of the pure beta emitter for the calibration therefore depends on its energy of emission; the pure beta emitter must be similar in energy to the beta emitter(s) we intend to calibrate.

Given that we consider interference (τ_α) not dependent upon the energy, it is directly evaluated using a ^{239}Pu standard. However, as interference (τ_β) is known to be energy dependent, a more detailed study of beta interference must be done. In this work, we study the unquenched case; previously, we studied (Villa et al. 2003) the alpha and beta interferences that account for the quenching degree.

As pure a beta emitter, we chose ^{40}K . Given that the ^{40}K ($E_{\text{max}} = 1.312 \text{ MeV}$) and ^{210}Bi ($E_{\text{max}} = 1.161 \text{ MeV}$) maximum energy of emission are very close, ^{40}K is considered optimum to calibrate the complete ^{210}Pb - ^{210}Bi spectrum (Villa et al. 2003).

Table 1 presents alpha, beta, and total interferences for ^{40}K in both the ^{210}Pb (1–350 channels) and total ^{210}Pb - ^{210}Bi window (1–1024 channels) in unquenched samples using a 105-PSA threshold level. Our aim is to test if ^{40}K is a good option for ^{210}Pb discrimination from its alpha-emitter daughter ^{210}Po .

Table 1 Alpha, beta, and total interferences for the optimum PSA threshold level 105 using ^{40}K and ^{239}Pu as pure emitters. PSA 105 is chosen to be the optimum PSA level because it minimizes the total interference.

Window	PSA level	β interference (τ_β)		α interference (τ_α)		Total interference (τ)	
		$\pm 1 \sigma$	$\pm 1 \sigma$	$\pm 1 \sigma$	$\pm 1 \sigma$		
^{210}Pb	105	0.00010	0.00025	0.070	0.003	0.070	0.003
^{210}Pb - ^{210}Bi	105	0.032	0.001	0.070	0.003	0.102	0.003

Following the definitions for alpha, beta, and total interference given by Sánchez-Cabeza (1993), 105 is chosen to be the optimum PSA threshold level because the value minimizes the total interference when using ^{40}K and ^{239}Pu as pure emitters ($\tau = 0.102 \pm 0.003$, the corresponding total interference). As we see in Table 1, β interference in the ^{210}Pb - ^{210}Bi window, using the optimum PSA level, is small but not negligible; however, the β interference in the ^{210}Pb window, the window that we use in our measurement, is lower than in the ^{210}Pb - ^{210}Bi window. Thus, using the optimum PSA level 105, the interference is $\tau_\beta = 0.00010 \pm 0.00025$ for the ^{210}Pb window and $\tau_\beta = 0.032 \pm 0.001$ for the ^{210}Pb - ^{210}Bi window. The reason for this behavior is that τ_β increases with increasing beta-energy

emitters (Villa et al. 2003), meaning that in these measurement conditions beta interference in the ^{210}Pb window is negligible.

Figure 2 shows a beta spectrum obtained from a standard sample of ^{210}Pb , which corresponds to ^{210}Pb and $^{210}\text{Bi}/^{210}\text{Po}$ in secular equilibrium.

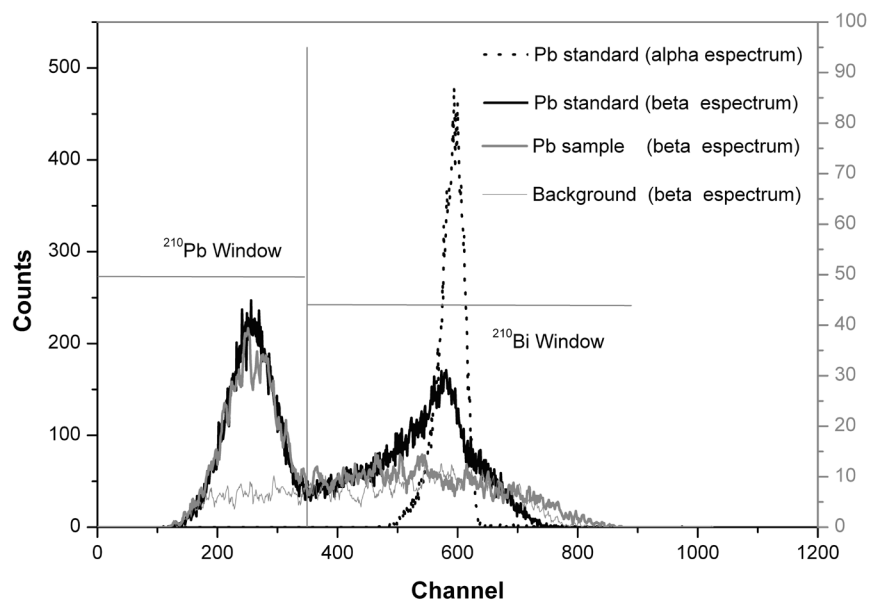


Figure 2 ^{210}Pb - ^{210}Bi - ^{210}Po , beta, and alpha spectra of a standard sample and ^{210}Pb spectrum of a sediment sample measured just after the radiochemical procedure (measured using PSA level 105).

In relation to the alpha interference, one can clearly see that there will not be alpha interference in the ^{210}Pb beta window because the spectra do not overlap. Nevertheless, the alpha spectrum will drift to low-energy channels in quenched samples and overlap the ^{210}Pb spectrum, and in that case, a new calibration should be performed.

To summarize, ^{40}K was chosen as the standard source to minimize total interference in the complete ^{210}Pb - ^{210}Bi window, and the corresponding optimum PSA level was set to 105. Furthermore, for this case beta interference is negligible in the ^{210}Pb window, the window we are setting for the measurements. Alpha interference is also negligible in the ^{210}Pb window, given that the spectra for ^{210}Po and ^{210}Pb in unquenched samples do not overlap.

Finally, we focus on the ^{210}Pb and ^{210}Bi beta spectra in the standard sample, where ^{210}Pb and ^{210}Bi are in secular equilibrium. The ^{210}Bi low-energy tail noticeably overlaps with the ^{210}Pb spectrum. This contribution would overestimate calculation of the ^{210}Pb counting efficiency if any correction is done. Figure 2 also shows the spectrum of a sediment sample measured immediately after the radiochemical procedure; both spectra fit in the ^{210}Pb window.

From Figure 2, we conclude that the ^{210}Pb counting efficiency for an immediate measurement after the radiochemical treatment is not affected by the ^{210}Bi contribution. For this reason, every measurement will occur just after the treatment.

Activity Concentration Determination: Calculating Effective Yield

Using the ^{210}Pb spectrum window (1–350 channels), ^{210}Pb activity concentration (Bq/kg) for an immediate measurement is usually calculated as:

$$A(^{210}\text{Pb}) = \frac{R_{1-350} - R_b}{R_q \cdot \varepsilon \cdot m \cdot 60} \quad (1)$$

where R_{1-350} is the total counting rate (in cpm) in the ^{210}Pb spectrum window, R_b is the background counting rate in the ^{210}Pb spectrum window (in cpm), m is the mass of the aliquot taken for the radiochemical procedure (in kg), ε is the counting efficiency, and R_q is the radiochemical yield.

Given that ^{210}Pb counting efficiency is difficult to determine accurately, we propose using the so-called “effective radiochemical yield” parameter (Y), in which the radiochemical yield and counting efficiency are included. This parameter is defined according to $Y = R_q \times \varepsilon$ and is determined empirically. Using this parameter, we avoid directly calculating the counting efficiency.

We evaluate the effective radiochemical yield from the precipitate of PbSO_4 ; therefore, we must make a calibration curve for stable lead mass versus effective radiochemical yield. When using a gravimetric method to evaluate the radiochemical yield, we have to take into account 2 factors (otherwise the yield will be overestimated or underestimated): 1) dissolution of the PbSO_4 precipitate cannot be 100% effective and some ^{210}Pb might be lost; 2) when measuring the final precipitate, we can be measuring other substances apart from PbSO_4 . Using a calibration curve, effective yield versus the mass of precipitate, we overcome the 2 major disadvantages of using a gravimetric yield method.

Five sediment samples were traced with a known amount of ^{210}Pb and the radiochemical method was applied to those samples. The calibrated solution used to calculate the effective yield was provided by Spanish CIEMAT; the activity concentration is 0.1058 Bq/mg, with an error of 0.37%.

For those samples, the effective radiochemical yield can be calculated as:

$$Y = \frac{R_{1-350} - R_b}{A_c(^{210}\text{Pb}) \cdot 60} \quad (2)$$

where R_{1-350} is the counting rate (cpm) in the ^{210}Pb window of the calibration source beta spectrum, R_b is the background counting rate (cpm) in the same window, and $A_c(^{210}\text{Pb})$ (in Bq) is the activity added to the calibration source. Thus, we represent the mass of the stable lead of the precipitate PbSO_4 , m_{Pb} (in mg), versus the effective radiochemical yield (Y) (see Figure 3 for results). Y can then be evaluated from a linear fitting through the origin:

$$Y = (18.52 \pm 0.03) \cdot m_{\text{Pb}} \quad (3)$$

Finally, the activity concentration, $A(^{210}\text{Pb})$, for an unknown sample is calculated according to the formula:

$$A(^{210}\text{Pb}) = \frac{R_{1-350} - R_b}{Y \cdot m \cdot 60} \quad (4)$$

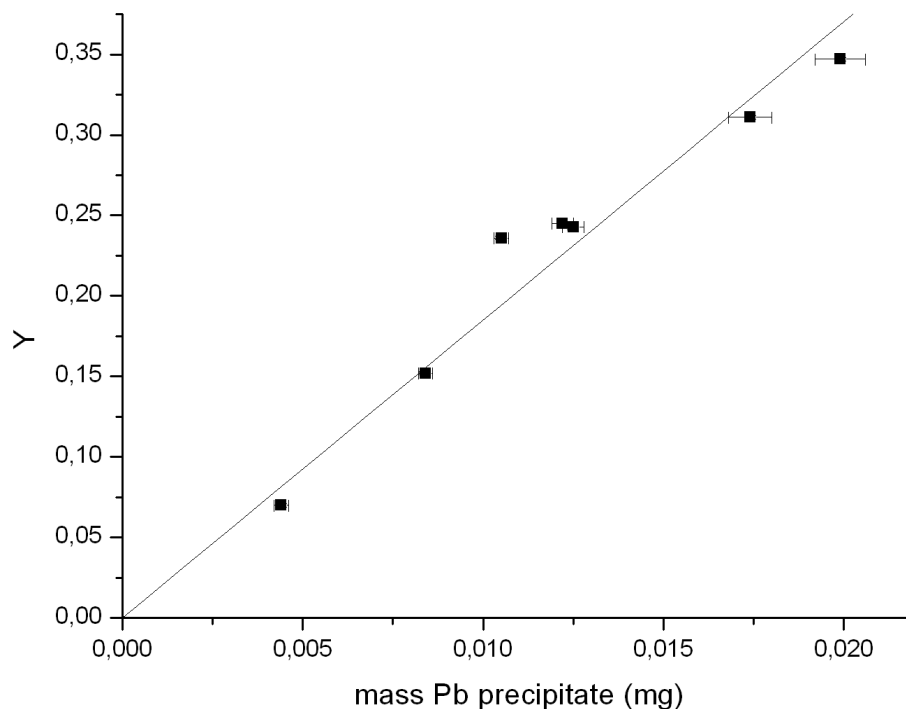


Figure 3 Lead mass in PbSO_4 final precipitate versus effective radiochemical yield. The linear fitting of the points has been included ($1\text{-}\sigma$ error).

Reproducibility of the method was checked by measuring 3 aliquots from 2 different samples, T3 and OT5. T3 was collected in an area strongly affected by natural radionuclide enhancements due to leaching from nearby phosphogypsum piles, while OT5 is a sediment sample collected from the open sea with natural radionuclide levels typical of unperturbed environments (Absi et al. 2004). Results are given in Table 2. A typical standard deviation of 1% was found in both cases—not only for the one affected by phosphogypsum discharges (T3) but also for the unaffected one (OT5), confirming the reproducibility of the method.

Table 2 Specific activity (Bq/kg) obtained for 3 aliquots of 2 different sediment samples from the Tinto-Odiel estuary. The uncertainty of the average is the standard deviation of the result of the 3 aliquots.

Aliquot	A (Bq/kg)	$\pm 1 \sigma$
T3-1	372	24
T3-2	377	16
T3-3	377	16
<i>average</i>	375	3
OT5-1	57	2
OT5-2	56	3
OT5-3	45	3
<i>average</i>	53	6

γ -SPECTROMETRY MEASUREMENTS

Detection System

For the γ -spectrometry determinations, a Canberra n-type Reverse Electrode Germanium (REGe) detector was used. Its relative photo-peak efficiency is 30% at 1332 keV. A lead shield (10-cm-thick regular shield) and an inner copper layer (5 mm) surround the detector to protect it against environmental radiation.

Measurements of sediments were done in a petri dish (44.0 mm radius, 14.5 mm height). Each sample was dried, homogenized, and introduced in a petri dish.

Efficiency Calibration

Counting efficiency for ^{210}Pb was calculated through Monte Carlo simulation using code GEANT4. All Monte Carlo codes generally give computed values that deviate significantly (>10%) from the experimental data due to uncertainties associated with the values of the detector dimensions supplied by the manufacturer. For this reason, a quick procedure for detector geometry optimization was carried out with calibrated point sources. Therefore, Monte Carlo simulation allows us to calculate the efficiency calibration curve for the petri dish counting geometry (Hurtado et al. 2004).

Self-Absorption Corrections

An important disadvantage that has yet to be considered is the high self-absorption of the soft gamma particle emitted, which depends upon the composition and density of the sample. Thus, it would be necessary, before measurement, to spike each sediment sample with a known amount of ^{210}Pb to obtain the appropriate counting efficiency; the drawback is that this destroys the sample. A solution to this problem is to make corrections to the self-absorption, given the composition and density of the sample (San Miguel et al. 2002). Another alternative using γ spectrometry is to use Monte Carlo simulation techniques, such as the ones described here, that calculate directly the sample counting efficiency (in a petri dish), given the composition of the sample (Hurtado et al. 2004). The sample composition was obtained using TTPIXE techniques (Martín et al. 1996). There are 2 methods (below) to calculate sample counting efficiencies, including self-absorption corrections.

Direct Method

Using the optimized detector dimensions, we calculate the efficiency of petri geometry for each sample. This way, we introduce into the Monte Carlo simulation the sample composition (Z_i), its apparent density (η), and its height (L) into the petri dish, thus obtaining the efficiency curve.

Indirect Method

The efficiency for each sample is:

$$\varepsilon = f\varepsilon_0 \quad (5)$$

where f is the self-absorption correction factor and ε_0 is the reference efficiency (i.e. a petri dish with air) calculated using optimized detector dimensions in the Monte Carlo simulation. The correction factor is given by:

$$f = \frac{1 - e^{-\mu\rho L}}{\mu\rho L} \quad (6)$$

where μ is the mass attenuation coefficient (cm²/g) obtained for each sample via Bragg's formula:

$$\mu = \sum w_i \mu_i$$

where the mass fraction of each component i in the sample (w_i) can be obtained since its composition is known by TTPIXE.

A comparison between the direct and indirect methods is shown in Figure 4. We conclude that the indirect method is preferred since it gives equal results to the direct method, is faster, and is more easily implemented.

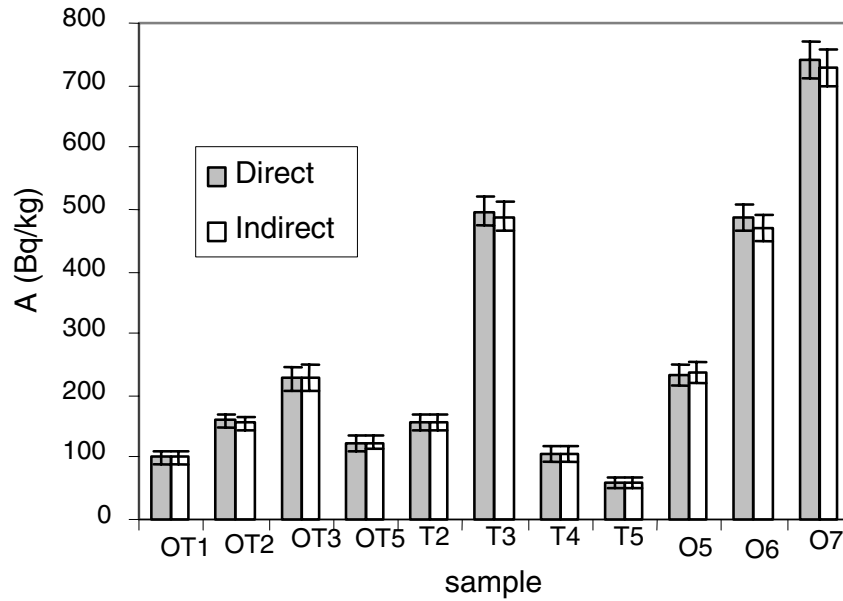


Figure 4 Comparison between direct and indirect method applied to determination of ²¹⁰Pb activity concentration in different samples using γ spectrometry, including self-absorption corrections via Monte Carlo simulation.

RESULTS AND DISCUSSION

In order to corroborate the accuracy of the obtained results, the LSC results were compared with those found by a direct measurement of ²¹⁰Pb via γ spectrometry (results are given in Table 3). One can see that both methods give equal results within the error; furthermore, the method gives also a very good reproducibility. These results guarantee the quality and accuracy of the method set-up.

The limit of detection (L_d ; Currie 1968) indicates the capacity limit for a technique. This expression is thus very useful to compare the measurement limitation of both techniques. The formula given by Currie (1968) is:

$$L_d = \frac{(2.71 + 4.65 \sqrt{R_b \cdot t})}{t} \tag{7}$$

where t is the counting time for the background and sample and R_b is the background counting rate.

Table 3 Specific activity (Bq/kg) of sediment samples collected in 1999 from the Tinto-Odiel estuary, measured by liquid scintillation counting (LSC) and gamma spectrometry. Radiochemical yield and effective efficiency obtained for LSC.

ID	²¹⁰ Pb (LSC)		Radiochemical yield		Effective radiochemical yield		²¹⁰ Pb (γ spectrometry)	
	A (Bq/kg)	$\pm 1 \sigma$	$\pm 1 \sigma$	$\pm 1 \sigma$	$\pm 1 \sigma$	$\pm 1 \sigma$	A (Bq/kg)	$\pm 1 \sigma$
PO5-99	233	24	0.608	0.021	0.338	0.011	233	17
PO7-99	721	72	0.606	0.020	0.337	0.011	741	30
PT2-99	104	11	0.733	0.025	0.407	0.014	105	12
PT4-99	143	15	0.346	0.012	0.192	0.007	157	12
PT5-99	62	7	0.547	0.018	0.304	0.010	59	8
POT1-99	111	11	0.729	0.025	0.405	0.014	101	11
POT2-99	168	17	0.526	0.018	0.292	0.010	160	10
POT3-99	246	25	0.462	0.016	0.257	0.009	227	20
POT4-99	5.4	7.6	0.190	0.007	0.119	0.004	n.d.	
POT5-99	110	11	0.608	0.021	0.338	0.011	123	11

In addition to L_d , it is very common to cite the minimum detectable activity (MDA). The MDA (in Bq) is given by:

$$MDA = \frac{L_d}{Y \cdot 60} \quad (8)$$

The activity, calculated using (Equation 6) with a 1440-min measuring time, is 1150 mBq and 9.5 mBq for γ spectrometry and LSC, respectively.

Although the γ -spectrometry technique has the higher MDA, its main advantage in determining ²¹⁰Pb concentrations in sediment samples is that no radiochemical techniques are needed, making the method direct and non-destructive. However, it would be necessary to know the composition of the sample (i.e. TPIXE), which results in a considerable increase in the sample measurement time.

In relation to LSC counting, our proposed method is accurate with a simple and relatively short radiochemical treatment, and has one of the lowest MDA values. Furthermore, it is convenient for routine determinations since, due to its high efficiency, the measurement counting time is ~600 min to obtain 1% of uncertainty. This counting time is less than what is needed in γ spectrometry to obtain the same uncertainty.

CONCLUSIONS

A method for ²¹⁰Pb measurement in sediments samples via LSC is proposed based on a final precipitation of PbSO₄. The major improvement of this method is the calculation of an effective radiochemical yield using a fitting curve. The accuracy of the gravimetric method to calculate the radiochemical yield is improved in several ways.

We compared the results measuring certain samples by LSC to measurements obtained using γ -spectrometry techniques. We found that the LSC method gives very accurate results compared to the γ -spectrometry method. We also found that LSC is a very effective technique to measure ²¹⁰Pb activity concentrations because it allows for the measurement of recent sediments. Furthermore, LSC is a very accurate and rapid technique with a very acceptable minimum detectable activity.

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