

## COMPARISON OF DIFFERENT METHODS FOR $^{210}\text{Pb}$ DETERMINATION IN ENVIRONMENTAL SAMPLES

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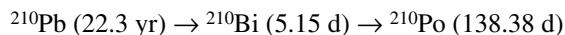
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**ABSTRACT.** Liquid scintillation counting (LSC), gamma spectrometry, and total beta counting are methods for determining  $^{210}\text{Pb}$  concentration in environmental samples. In this research, we investigated a fast, simple method to determine  $^{210}\text{Pb}$  by LSC in environmental samples; the method is capable of estimating concentrations higher than 20 mBq/L for liquid samples. Environmental samples were analyzed by the proposed methodology, and results were compared with other methods on the basis of accuracy, lower limit of detection, time consumption, and sample type.

### INTRODUCTION

$^{210}\text{Pb}$  is one of the most radiotoxic products of the uranium decay chain, presenting a rather long half-life ( $T_{1/2} = 22.3$  yr). When absorbed into the human body,  $^{210}\text{Pb}$  concentrates in bone tissue with a very long biological half-life. Because of its metabolic and dosimetric characteristics,  $^{210}\text{Pb}$  is an important isotope from the point of view of radiation protection. The value of its ingestion dose conversion factor is the highest among the naturally occurring radionuclides (IAEA 1996). Determining  $^{210}\text{Pb}$  concentration in environmental samples on a routine basis is thus one of the most important subjects when monitoring nuclear installations such as those involved in uranium mining and milling. Moreover, tap water regulations also include natural radioactivity; thus, determining the  $^{210}\text{Pb}$  content in aqueous samples (e.g tap and mineral water) has gained importance.  $^{210}\text{Pb}$  determination is also very important for studying sediment chronology in surface water. Methods for determining radionuclides for monitoring purposes usually require low detection limits, and depending on the situation, quicker methods are necessary to help in the decision process.

$^{210}\text{Pb}$ , part of the primordial  $^{238}\text{U}$  decay chain, decays by  $\beta$  emission ( $E_{\beta\text{max}} = 17$  keV [85%] and  $E_{\beta\text{max}} = 61$  keV [15%] followed by  $\gamma$ -radiation [ $E_{\gamma} = 46$  keV (5%)]. The immediate  $^{210}\text{Pb}$  decay product  $^{210}\text{Bi}$  is also a beta emitter with a much higher energy of beta radiation ( $E_{\beta\text{max}} = 1160$  keV [100%]) than its parents. The resulting product  $^{210}\text{Po}$  is an alpha emitter ( $E_{\alpha} = 5503$  keV [100%]), which results from  $^{210}\text{Pb}$  according to the following process:



$^{210}\text{Pb}$  can be determined in environmental samples by a set of methods. Using low-energy gamma spectrometry,  $^{210}\text{Pb}$  can be directly determined by its 46-keV gamma ray. The main advantage of gamma spectrometry is that no radiochemical separation is required prior to the measurement, making it a direct and nondestructive technique. However, the interference of the Compton effect causes high background counting rates in the low-energy gamma spectrum region and the limit of detection (LD) is relatively higher. Moreover, depending on the composition and density of the sample, sample self-absorption of the low gamma energy may require self-absorption corrections, increasing the measurement uncertainties. As a result of the high LD value and measurement uncertainties, gamma spectrometry is generally used solely for  $^{210}\text{Pb}$  determination in soil and sediment samples (San Miguel et al. 2005).

$^{210}\text{Pb}$  concentration can be determined indirectly by measuring its decay product  $^{210}\text{Po}$  by alpha spectrometry with surface barrier detectors. The method is very sensitive but cannot be applied for

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quick analysis due to the long time (>6 months) needed to establish the equilibrium between  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ .

Another way to determine  $^{210}\text{Pb}$  is by measuring its product  $^{210}\text{Bi}$  by gross beta counting in a small proportional counter. The method is based on the chemical separation and concentration of radium and lead in sulfate form. The first step is the precipitation of radium and lead as  $\text{Ba}(\text{Ra},\text{Pb})\text{SO}_4$ . The precipitate is then dissolved with nitrilo-triacetic acid (NTA) and followed by Ra coprecipitation as  $\text{Ba}(\text{Ra})\text{SO}_4$ . Lead remains in the NTA solution, and by adding sodium sulfide, lead is precipitated as  $\text{PbS}$ , which is again dissolved with nitric acid. Subsequently, lead is precipitated as lead chromate and stored for 10 d to allow the ingrowth of  $^{210}\text{Bi}$  activity. The precipitate is then measured for its beta counting rate. The method is very sensitive, with a typical LD value of 3 mBq/L for 400 min of counting time (Godoy et al. 1994).

Liquid scintillation counting (LSC) systems have been used for measuring  $^{210}\text{Pb}$  in environmental samples. Most reported methods are based on the traditional coprecipitation with  $\text{Ba}(\text{Ra},\text{Pb})\text{SO}_4$ . Once lead is separated from radium by EDTA, it is precipitated as  $\text{PbSO}_4$  and purified by dissolution, reprecipitation, and washing. After this process, the precipitate is suspended in a scintillation gel and readied for measurement. The LD value for this method is  $\sim 5$  mBq/L when analyzing 2 L of water (Kim et al. 2001; Wallner 2002).

The aims of this study are to investigate an alternative method for  $^{210}\text{Pb}$  determination in environmental samples by LSC; to compare the capabilities of 3 different methods, LSC, gamma spectrometry, and total beta counting in a proportional counter; and to establish the limits of the application for the purpose of environmental monitoring.

## EXPERIMENTAL

The first step was to choose a suitable cocktail for the  $^{210}\text{Pb}$  determination. Three cocktails were available and compared: i) Instagel<sup>®</sup>, a classical cocktail, nonbiodegradable, with high efficiency and low background; ii) Ultima Gold<sup>™</sup> AB (Packard), which is biodegradable, with excellent sample holding capacity for strong mineral acid and high quench resistance; and iii) OptiPhase HiSafe 3 (Wallac), a biodegradable cocktail that combines good counting efficiency with a very high level of sample acceptance.

Comparison of the 3 cocktails was performed by taking glass vials containing 5 mL of 0.5M HCl spiked with a standard solution of  $^{210}\text{Pb}$  (Amersham). Fifteen mL of the different cocktails were added to the vial solutions and the samples were counted in a LSC (Tri-Carb 3170 TR/SL, Packard). The highest efficiency was obtained for the Instagel cocktail. The efficiency values were  $28.8 \pm 0.5\%$  for Ultima Gold,  $34.3 \pm 0.6\%$  for OptiPhase HiSafe 3, and  $45.1 \pm 0.7\%$  for Instagel. The response curves are shown in Figure 1. Although the Instagel cocktail showed the highest counting efficiency, the environmentally friendly characteristics of OptiPhase HiSafe 3 make this cocktail more suitable for determining lead concentration.

The proposed radiochemical methodology uses the extraction chromatographic technique to preconcentrate and separate lead from the sample. According to the literature, an anionic exchanger in 1.5M HCl could separate Pb from the matrix sample; however, Bi would also be concentrated on the column. After concentration on the loaded column, Pb could be separated from Bi by elution with 0.05M HCl or 0.5M HCl (Figgins 1961; Gibson 1961; Bhatki 1977). Another method using an anionic exchanger proposes 0.5M HBr as the percolation solution to separate Pb from the sample and 1M  $\text{HNO}_3$  as the Pb elution solution to separate Pb from Bi (Godoy 1983).

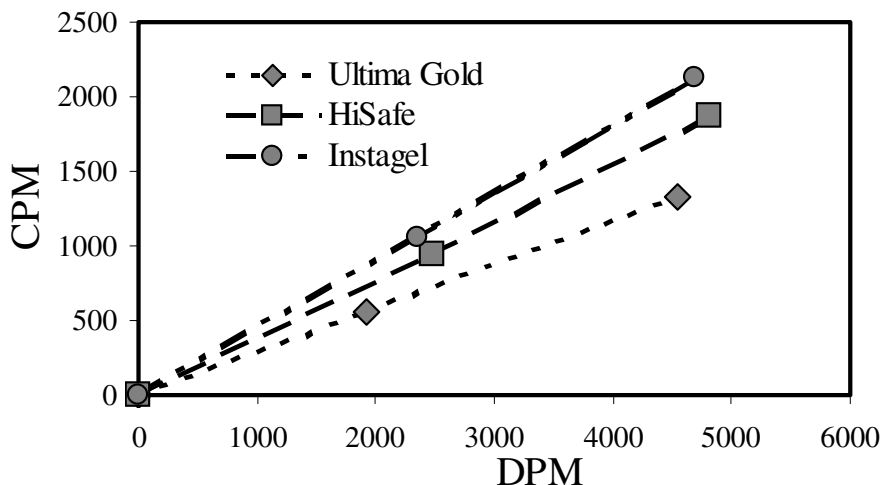


Figure 1 LSC response curves for 3 different cocktails spiked with a standard solution of <sup>210</sup>Pb

Taking the literature into consideration, tests were performed using 41 Bq of <sup>210</sup>Pb in equilibrium with <sup>210</sup>Bi standard solutions in 100 mL of percolation solution (1.5M HCl or 0.5M HBr), 1 g of an ion exchanger (Dowex 1×8, 50–100 mesh, loaded column), and 60 mL of an elution solution (0.05M HCl, 0.5M HCl, or 1M HNO<sub>3</sub>). The elution solutions were dried, dissolved in 5 mL of 0.5M HCl, and transferred to glass vials. Next, 15 mL of OptiPhase cocktail was added to the solutions and the samples were counted in the LSC for 100 min. About 6 hr elapsed from the beginning of chemical separation until the start of LSC measurement.

The best result was obtained by the HBr/HNO<sub>3</sub> method (see #4 in Table 1), with a chemical recovery of 98%, whereas only ~40% recovery was obtained by the method using 1.5M HCl as the percolation solution (Table 1).

Table 1 Comparison of the yields reached for the investigated separation methodologies using an ionic exchanger.

Method	Percolation solution	Elution solution	Overall efficiency (%)	Chemical recovery (%)
1	1.5M HCl	0.05M HCl	11.7 ± 0.3	34.1 ± 0.9
2	1.5M HCl	0.5M HCl	10.4 ± 0.3	30.3 ± 0.9
3	1.5M HCl	1M HNO <sub>3</sub>	13.8 ± 0.3	40.2 ± 0.9
4	0.5M HBr	1M HNO <sub>3</sub>	33.5 ± 0.5	97.7 ± 1.4

No <sup>210</sup>Bi was eluted together with <sup>210</sup>Pb, since its ingrowth curve follows the expected secular equilibrium curve. However, the mixture of eluent solution (1M HNO<sub>3</sub>) and scintillation cocktails resulted in color formation due to the dissociation of nitric acid and release of NO<sub>2</sub>; thus, the aqueous medium was changed from nitric to hydrochloric acid for LSC counting.

To test the acid capacity of the OptiPhase cocktail, the background and the counter efficiency were measured for a hydrochloric concentration ranging from 0.02–0.5 N. The limit of detection was calculated by the Currie (1968) formula. The results showed no significant differences concerning the acidic concentration range. The background counting was around 3.94 cpm, resulting in an LLD of 45 mBq for 100 min of counting time. The proposed <sup>210</sup>Pb LSC method is presented in Figure 2.

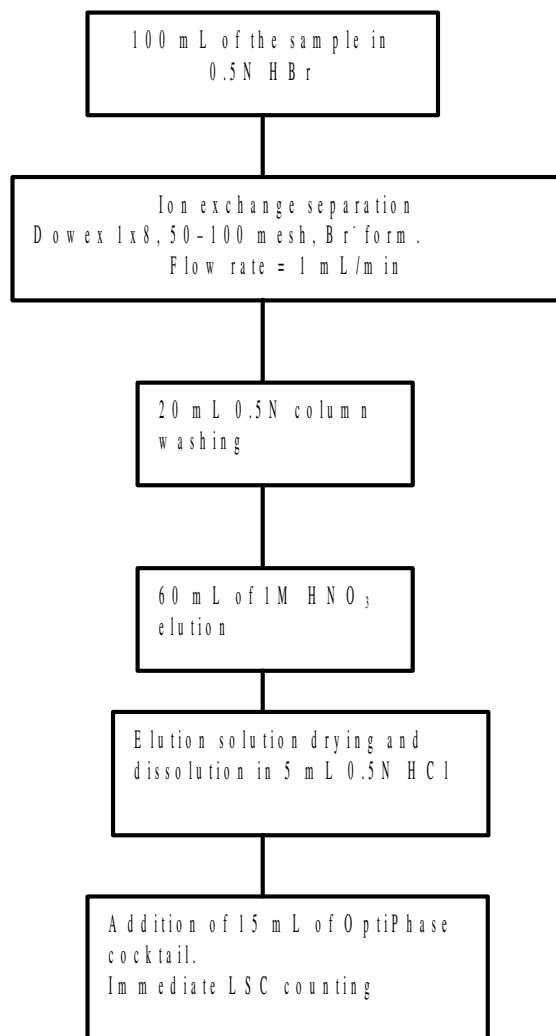


Figure 2 Proposed methodology

To compare the  $^{210}\text{Pb}$  determination methods, 2 available reference samples were analyzed by 3 methods: via the  $^{210}\text{Bi}$  daughter by total beta counting, the LSC method proposed, and gamma spectrometry.

The concentration of radionuclides in the nonresidual fraction of sediments and soils is a current method applied for estimating radiological impact of nuclear and radioactive installations. The non-residual fraction is obtained by leaching the solid sample at low pH value (Godoy 1998). To test the LSC applicability for  $^{210}\text{Pb}$  determination in the nonresidual fraction, 5 g of the reference material soil (IAEA 326) was leached overnight with 0.5M HBr. In order to avoid the Fe(III) adsorption, 1 g of hydroxylamine was added before the ion-exchange separation. After the ion-exchange separation (Figure 2),  $^{210}\text{Pb}$  was determined by LSC (100 min counting time, Tri-Carb 3170 TR/SL, Packard). For comparison with gross beta counting with a proportional counter (PC), the same ion-exchange separation methodology was applied, but 20 mg of Pb carrier was added before the percolation of

the liquid fraction in the column. After Pb elution by 1M HNO<sub>3</sub> solution, Pb was precipitated as PbCrO<sub>4</sub> (Godoy et al. 1998). After 10 days, the beta counting by gas-flow proportional counter determined the amount of <sup>210</sup>Bi (400 min count time, low-background detector, EG&G Ortec Prof. Berthold LB-750). The <sup>210</sup>Pb concentration values determined by LSC and gross beta counting are similar (Table 2), showing that the proposed LSC methodology can be used instead of determining the <sup>210</sup>Pb in the nonresidual fraction of sediment and soil samples. The limit of detection for the proportional measurement was 8 Bq/kg, while the LD value for LSC was 11 Bq/kg.

Table 2 Comparison between sulfate-proportional counter and the proposed method.

Sample	Method	Chemical separation	Result (Bq/kg or Bq/L)	Time consumed
Soil IAEA 326	Total beta counting, in a proportional counter	Overnight leaching of 5 g of soil, with 0.5M HBr, separation on Dowex 1×8, elution with 1M HNO <sub>3</sub> , and precipitation as PbCrO <sub>4</sub> .	36 ± 2	12 d
Soil IAEA 326	LSC	Overnight leaching of 5 g of soil, with 0.5M HBr, separation with Dowex 1×8, elution with 1M HNO <sub>3</sub> , and counting in LSC.	36 ± 3	24 hr
Water IRD-199	Total beta counting, in a proportional counter	Traditional precipitation of Ba(Ra,Pb)SO <sub>4</sub> , followed by Pb separation and precipitation as PbCrO <sub>4</sub>	0.265 ± 0.005	12 d
Water IRD-199	LSC	Evaporation of the sample, acidification of 100 mL sample to 0.5M HBr, separation with Dowex 1×8, elution with 1M HNO <sub>3</sub> , and counting in LSC.	0.22 ± 0.05	30 hr

The IAEA 326 soil sample was analyzed by gamma spectrometry with a GMX HPGe 25%. <sup>210</sup>Pb was analyzed by its 46-keV photon energy, and due to the very low photon energy, the spectrum peak area is corrected for sample self-absorption by transmission measurements. The obtained value of 50 ± 3 Bq/kg is in good agreement with the recommended value of 52.5 (9% uncertainty). The LD value was 21 Bq/kg for 16 hr of counting time.

The reference water IRD-199 was analyzed by 3 methods: the traditional sulfate-gross beta counting with a proportional counter, the proposed LSC methodology, and by gamma spectrometry. The value of <sup>210</sup>Pb concentration obtained via LSC (0.22 ± 0.05 Bq/L) is close to the recommended value (0.26 ± 0.05 Bq/L) and the LD value of the method was 0.02 Bq/L for 400 min of counting time. The sulfate-proportional counter analysis of the water resulted in an activity concentration of 0.265 ± 0.005 Bq/L, which is very close to the recommended value. The method reached a LD value of 0.01 Bq/L for 400 min of counting time. The <sup>210</sup>Pb concentration estimated by gamma spectrometry was <5 Bq/L, which is the LD value of the method for liquid samples (for 16 hr of counting time).

The LSC system allows the counting of the low-energy <sup>210</sup>Pb beta with a good efficiency, while the proportional counter has a very poor efficiency of detection at such a low energy. In fact, only at higher energy does the proportional provide a good efficiency. The value of efficiency of the Berthold proportional counter is 30% for the <sup>210</sup>Bi beta energy. Therefore, measurement by LSC can be immediately performed after Pb separation, without waiting for <sup>210</sup>Bi ingrowth. On the other hand, <sup>210</sup>Bi activity grows quickly in the sample counting: 10 hr after Bi-Pb separation its activity reaches 5.4% of the Pb activity. Hence, in order to avoid an increased measurement uncertainty it is advisable to perform the LSC measurement very soon after Bi-Pb separation. Nevertheless, if a result

needs to be confirmed or if there is a measurement problem, the sample can be counted again after the establishment of Bi-Pb equilibrium.

## CONCLUSION

For measuring  $^{210}\text{Pb}$  in environmental samples, a rather quick and quantitative method was developed. The proposed LSC methodology is a useful method for  $^{210}\text{Pb}$  determination in the nonresidual fraction of soils and sediments and in water samples. The comparison of gamma spectrometry, gross beta counting, and LSC for  $^{210}\text{Pb}$  determination showed that for solid environmental samples, gamma spectrometry, a nondestructive method, is an easier and faster method. The low-background proportional counter has a higher sensibility and reaches a lower limit of detection than the proposed LSC method. The capacity of directly measuring  $^{210}\text{Pb}$ , without needing to wait for the 10-d ingrowth period to establish  $^{210}\text{Pb}$  and  $^{210}\text{Bi}$  equilibrium, is the main advantage of the presented LSC method over the proportional counter one. LSC is a fast method that can help when a quick decision is needed. However, the chemical yield is not quantified and investigation of spiking with stable Pb, followed by determination with methods as atomic emission or ICPOES should be investigated.

## ACKNOWLEDGMENTS

We are very grateful to the staff of Metrology of Radionuclides/IRD/CNEN for supplying the radionuclide standard used in this research.

## REFERENCES

- Bhatki KS. 1977. The radiochemistry of bismuth. National Research Council Report, NAS-NS-3057. Washington D.C.: National Academy of Sciences. 151 p.
- Currie LA. 1968. Limits for qualitative detection and quantitative determination. Application to radiochemistry. *Analytical Chemistry* 40(3):586–93.
- Figgins PE. 1961. The radiochemistry of polonium. National Research Council Report, NAS-NS-3037. Washington D.C.: National Academy of Sciences. 74 p.
- Gibson WM. 1961. The radiochemistry of lead. National Research Council Report, NAS-NS-3040. Washington D.C.: National Academy of Sciences. 160 p.
- Godoy JM. 1983. Entwicklung einer Analysenmethode für die Bestimmung von  $^{238}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{228}\text{Th}$ ,  $^{228}\text{Ra}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  und  $^{210}\text{Po}$  und ihre Anwendung auf Umwelt Proben [PhD dissertation]. Karlsruhe, Germany: KFK. In German.
- Godoy JM, Lauria DC, Godoy MLDP, Cunha RP. 1994. Development of a sequential method for the determination of  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{228}\text{Th}$ ,  $^{228}\text{Ra}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$  in environmental samples. *Journal of Radioanalytical and Nuclear Chemistry* 182(1):165–9.
- Godoy JM, Moreira I, Wanderley C, Simões Filho FF, Mozeto. 1998. An alternative method for determination of excess  $^{210}\text{Pb}$  in sediments. *Radiation Protection Dosimetry* 75(1–4):111–5.
- IAEA [International Atomic Energy Agency]. 1996. International basic safety standards for protection against ionization radiation and for the safety of radiation sources. Safety series No. 115. Vienna: International Atomic Energy Agency.
- Kim Y-J, Kim C-K, Lee J-I. 2001. Simultaneous determination of  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  in groundwater and soil samples by using the liquid scintillation counter-suspension gel method. *Applied Radiation and Isotopes* 54(2):275–81.
- San Miguel EG, Pérez-Moreno JP, Bolívar JP, Aguado JL, García-Tenorio R. 2005. Efficiency calibration for  $^{210}\text{Pb}$  gamma-spectrometric determinations in sediment samples. In: McLaughlin JP, Simopoulos ES, Steinhäusler F, editors. *The Natural Radiation Environment VII*. Radioactivity in the Environment Series, Volume 7. Amsterdam: Elsevier. p 166–74.
- Wallner G. 2002. Determination of  $^{228}\text{Ra}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$  in drinking water using liquid scintillation counting. In: Möbius S, Noakes, JE, Schönhofer F, editors. *LSC 2001, Advances in Liquid Scintillation Spectrometry*. Tucson: Radiocarbon. p 269–74.