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Radiochemical determination of lead-210 in environmental water samples using Cerenkov counting

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A relatively simple method has been developed for the determination of ^{210}Pb via its β-emitting daughter, ^{210}Bi. Lead-210 was separated from interfering elements as lead sulphate. The precipitate was dissolved in an alkaline solution of EDTA and the Cerenkov signal produced by the build-up of ^{210}Bi was counted 30 days after storage using tritium channel of a liquid scintillation counter. Cerenkov counting efficiency was found to be approximately 20%. A lower limit of detection of 5.1 mBq/l (based on 3σ of the background with 500 minute counting time) was achieved. Chemical recoveries in the range of 70–100% were determined gravimetrically. Interference associated with currently used methods is avoided. Data from both spiked samples and natural samples are presented.

Introduction

Lead-210 ($T_{1/2} = 21$ y) is one of the most toxic naturally occurring radionuclides present in drinking water. It is also considered to be an important radionuclide in dating the upper layers of sediments, ice and peat deposits of the past 150 years[1] and as a tracer for some environmental studies.[2] Therefore, a reliable and easy method for ^{210}Pb determination is required. Lead-210 can be determined indirectly by measuring the activity of one of its daughters [^{210}Po ($T_{1/2} = 138$ d) and ^{210}Bi ($T_{1/2} = 5.1$ d)] after sufficient ingrowth.[1,3] These indirect measurements are sensitive enough to detect low levels of ^{210}Pb. Measurement of ^{210}Bi can either be performed using a proportional counter or a liquid scintillation counter after its separation from ^{210}Pb. Alpha-spectroscopy has been used for the measurement of ^{210}Po after its separation on a silver disc by self deposition, secular equilibrium between ^{210}Pb and ^{210}Po being assumed.[1] Problems associated with α-spectroscopy are self-absorption and low counting efficiency (long counting time). Liquid scintillation counting methods offer high counting efficiency, ease of sample preparation and a large number of samples can be processed but the method suffers from high background. Lead-210 has been determined directly, after its separation as $PbSO_4$ from the sample, using liquid scintillation technique. Interference from the build-up of ^{210}Bi being one of the problems.[4,5] Gamma-spectrometry can be also used for ^{210}Pb determination by measuring its γ peak at 46.5 keV.[6] In most of the methods mentioned above, except γ-spectrometry, ^{210}Pb and ^{210}Bi should be separated from each other to avoid interference.

In previous work,[7–10] Cerenkov counting has proved to be an efficient method for determination of some naturally occurring radionuclides, viz. ^{226}Ra, ^{222}Rn, ^{238}U, ^{234}Th and ^{228}Th. In the present work, a relatively simple method for determination of ^{210}Pb is described. Cerenkov signal produced by ^{210}Bi in secular equilibrium with ^{210}Pb is used for the determination of the latter. Lead is separated and purified as lead sulphate from the sample which is then dissolved in 12 ml of an alkaline EDTA solution and counted after one month using the tritium channel of a liquid scintillation counter. There is no need to separate ^{210}Bi from lead, as there is no interference. In addition, any liquid scintillation counter with a tritium channel can be used. Unlike liquid scintillation, the Cerenkov process is unaffected by chemical quenching and has a lower background count rate.

Experimental

Materials and equipment

The radioactive standard solution, ^{210}Pb, was supplied by Damri, France. The carrier solutions and other reagents utilized were of A. R. grade materials and the water was distilled. All counting operations were carried out using a Packard Liquid Scintillation Analyzer 1500 CA.

Sample preparation for counting

The following separation procedure is a modified form of that used by To:[3]

(1) One milliliter of lead carrier (30 mg/ml, nitrate solution) and 1 ml of barium carrier (5 mg/ml, chloride solution) was added per 1 l water sample which is then heated to 80 °C.

(2) 30 ml of 1 mol · l^{-1} H_2SO_4 was added to the sample while being stirred. The sample was heated for a further 30 minutes and left aside for 4 hours. The supernatant was discarded and the $PbSO_4$–$BaSO_4$ precipitate was washed twice with 0.1 mol · l^{-1} H_2SO_4 and dissolved with 2 ml of alkaline solution of EDTA (0.25 mol · l^{-1}), 8 ml of distilled water was added and the sample was heated to assist dissolution.

(3) While the sample being stirred, acetic acid was added dropwise until barium(radium) sulphate precipitate appears at pH 4. The sample was then digested for 5 minutes.

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(4) To the supernatant which contains the Pb–EDTA complex, more acetic acid was added to lower the pH to 1 where $PbSO_4$ was reprecipitated.

(5) The precipitate was washed twice with 0.1 mol · l^{-1} H_2SO_4 and dried for recovery determination gravimetrically. The precipitate was then dissolved in 12 ml of EDTA solution and counted one month later in a plastic counting vial using the tritium channel of a liquid scintillation counter. Lead-210 activity was determined from the following expression:

$$^{210}Pb = C/E \cdot Y \cdot V \text{ (Bq/l)}$$

where C – Cerenkov count rate of ^{210}Bi corrected for background at equilibrium with ^{210}Pb, counts/s,
E – Cerenkov counting efficiency of ^{210}Bi,
Y – lead chemical recovery,
V – sample volume, l.

Results and discussion

Cerenkov radiation produced by ^{210}Bi is measured in order to determine ^{210}Pb. After chemical isolation of a lead sample, the produced Cerenkov signal is due to ^{210}Bi; the ^{210}Pb β-emitting daughter which grows in the counting vial and reaches secular equilibrium after one month Fig. 1. Lead-210 does not produce Cerenkov radiation because it has a maximum energy of 63 keV which is below the Cerenkov threshold (265 keV).

The radiochemical separation procedure used here has been chosen for two reasons. Firstly, it has been widely used for separation of radium prior to its determination, therefore, ^{226}Ra can be determined from the same sample using Cerenkov counting.[10] Secondly, the counting solution does not contain any color quenchers.

In order to determine the counting efficiency for ^{210}Bi, standard solution of ^{210}Pb was used. Aliquots of ^{210}Pb EDTA solution (12 ml) were prepared and counted in plastic and glass vials one month after storage. The measured Cerenkov counting efficiency for ^{210}Bi, in full

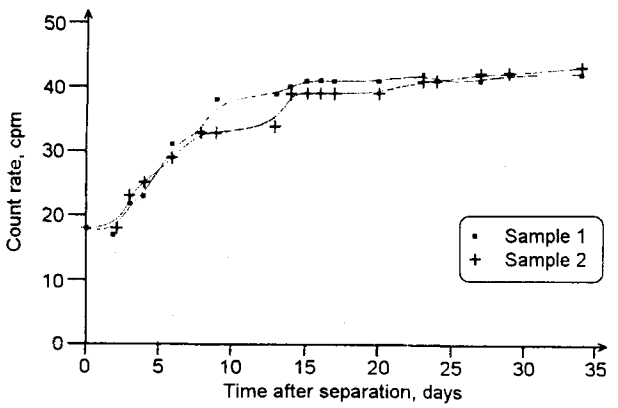

Fig. 1. Ingrowth of ^{210}Bi Cerenkov signal

Table 1. Spiked water samples results

^{210}Pb activity added, Bq/l	Chemical recovery, %	^{210}Pb activity found, Bq/l	Accuracy, %
1.79	91	1.57	12.46
1.79	100	1.73	7.28
1.79	82	1.71	7.12
1.79	100	1.72	7.19
1.79	100	1.99	1.13

Accuracy, % = $100(X_i-X_t)/X_t$, where X_i and X_t are measured and known activities, respectively.

Table 2. Some natural samples results

Location	Type of water	^{210}Pb, mBq/l	
		Proposed method	To's method
Qutina	Lake	269.4	271.5
Homs	River	353.7	340.6
Hamma	River	110.3	120.0
Tel Salhab	River	470	501.9

secular equilibrium with ^{210}Pb, was 18.26% and 19.77% for glass and plastic vials, respectively. This difference in the counting efficiency is due to the fact that a plastic vial is more transparent to Cerenkov radiation than a glass vial. Several factors affecting Cerenkov counting efficiency have been studied. Cerenkov counting efficiency was increased by a factor of 10% when the amount of lead carrier was increased from 8 to 60 mg per sample and this is due to the increase in the refractive index. Other factors such as sample counting volume and EDTA concentration have been studied and found to have little effects.

Separation using the $PbSO_4$ precipitate is a good method since high chemical recovery can be achieved and monitored gravimetrically. In addition, the precipitate is easily recrystallized to allow a quick separation from other elements, but not from other lead isotopes. ^{212}Pb ($T_{1/2}$ = = 10.6 hour) and ^{214}Pb ($T_{1/2}$ = 26.8 min) and their daughters ^{214}Bi and ^{214}Bi are β-emitters and produce Cerenkov radiation in aqueous solutions. However, there is no Cerenkov signal produced by these isotopes after 3 days because their short half-lives. In addition, there is no need to separate ^{210}Bi from ^{210}Pb since ^{210}Pb does not produce Cerenkov radiation.

Using 15 ml of 0.25 mol · l^{-1} EDTA solution, the limit of detection (LLD) obtained (based on three times of the standard deviation of the background measurement in the tritium channel and on a 500 min counting time) was 5.10 mBq/l. This value is lower than those reported using proportional counters[2] and liquid scintillation counters[3,4] and it is suitable for environmental measurements.

Analysis of 10 spiked water samples (1 l) containing equal activities gave mean accuracies of 7.87%. Some of these results are presented in Table 1. While, the mean

precision was determined by analyzing a 5 liter spiked sample five times and found to be 4.09%.

A gravimetric method has been used for determination of lead recovery which is a widely used method. High recoveries in the range of 70% to 100% with a mean value of 86.7% were observed since effectively only two separation steps are involved. In addition, only one chemical recovery (for Pb) is required, while using other methods based on Bi measurement, two chemical recoveries (for Pb and Bi) are required.

The application of the proposed method for the determination of ^{210}Pb in some natural waters is demonstrated by the results in Table 2, where they are compared with those determined using the method by TO.[3]

Conclusion

Lead-210 can be determined via its β-emitting daughter, ^{210}Bi using Cerenkov counting. The method is simple and there is no need to separate ^{210}Bi from ^{210}Pb as required using other currently used methods. The LLD value obtained allow the proposed method to be used for natural water samples including drinking water. The method can be used for any type of sample which ultimately can be obtained in aqueous form. As in the case of most methods based on ^{210}Bi (or ^{210}Pb) measurements, a disadvantage is the delay time (about one month) required to establish secular equilibrium.

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