

Radiochemical Determination of Low-Level Lead-210 in Environmental Water Samples

Dominic To

Radiochemistry Laboratory, Kansas Health and Environmental Laboratory,
Kansas Department of Health and Environment, Topeka, Kansas 66620-0001

INTRODUCTION

Lead-210 is a naturally occurring radionuclide of the uranium-238 series. The existence of lead-210 in environmental water results mainly from the decay of its precursor radon-222. In surface and shallow-well waters, lead-210 concentration is usually low due to the volatility of radon and/or rapid adsorption of the nuclide into sediments. However, in deeper wells, lead-210 concentration may reach as high as 200 pCi/L.¹ The high concentration of lead-210 in deeper wells may be attributed to the presence of high radon-222 activity.

Current National Primary Drinking Water Regulations require that the concentration of soluble β and photon-emitting radionuclides in drinking water not produce a dosage of more than 4 mrem effective dose equivalent (ede) per year.² At such level, the presence of even a minute amount of lead-210 in drinking water is of health and regulatory concern because the lead-210 concentration estimated to correspond to 4 mrem ede per year is 1 pCi/L. In order to determine whether water samples obtained from public water systems are in compliance with the regulations, an analytical method capable of determining lead-210 concentration below 1 pCi/L is necessary.

The lead-210 concentration in water can be measured directly by γ -ray spectrometry or liquid scintillation counting.³ However, these direct counting methods do not achieve the 1 pCi/L sensitivity level due to uncertainties associated with measurement of the low-percent-abundant (4.1%) 46.5-keV photopeak resulting from decay of lead-210 and high backgrounds associated with the conventional liquid scintillation analyzer, respectively. Although lead-210 could also be determined directly by ICP-MS, to measure 1 pCi/L (13 fmol/L) would require another order of magnitude of preconcentration over the method being described to reach a detection limit of 10 ppt.

Alternatively, lead-210 concentration in environmental samples can be determined by measuring the activity of one of the daughters (^{210}Bi or ^{210}Po) of lead-210 after sufficient ingrowth period.⁴⁻⁶ The lead-210 concentration is then extrapolated from the daughter activities. These indirect measurement methods, although sensitive enough to detect a low level of lead-210 in water samples, often involve lengthy and/or laborious steps.

The present paper describes a relatively simple and sensitive method for the determination of low-level lead-210 in environmental water samples. The method involves (i) concentration and separation of lead-210 from other naturally occurring radionuclides that may be present in the sample and (ii) isolation of bismuth-210 in the form of bismuth oxychloride from the sample, after a suitable ingrowth period, for β counting. The procedures for the concentration and separation of lead-210 are modified from those used by Goldin⁷ to determine radium concentration in water.

EXPERIMENTAL SECTION

Apparatus. A Tennelec Model LB5100 low-background α/β counting system equipped with gas-flow detector and anticoincidence guard detector was used to count bismuth oxychloride. The β background of the α/β counting system is less than 1 count/min. A Wallac Model 1409 liquid scintillation multichannel analyzer was used to count lead-210 and bismuth-210. Barium-133 radioactivity was determined by counting the samples with a Princeton Gamma-Tech Ge(Li) detector interfaced to a Nuclear Data 6600 computer-based data acquisition system. Chemical yields of lead carbonate and bismuth oxychloride were determined gravimetrically to 0.1-mg precision.

Reagents and Solvents. Lead-210, radium-226, natural uranium, and barium-133 standards were obtained from the National Institute of Standards and Technology. The concentrations of bismuth and lead carrier solutions were 10 and 20 mg/mL, respectively. Fresh radium-226 solution was prepared by adding a known quantity of radium-226 standard solution to 25 mL of distilled water in a centrifuge tube. Radium-226 was coprecipitated with barium and lead sulfate. Barium sulfate was separated from lead and converted to carbonate as described in the Sample Analysis section. The barium carbonate was dissolved in 1 M nitric acid. The radium-226 concentration was determined by γ counting of the resulting solution. The removal of lead-210 in the freshly prepared radium-226 solution was confirmed by the absence of the 46.5-keV lead-210 photopeak in the γ -ray spectrum. Further verification of lead-210 removal was made by analyzing an aliquot of the fresh radium-226 solution with the liquid scintillation analyzer. OptiPhase HiSafe3 scintillation cocktail (LKB-Wallac Scintillation Product) was used for all liquid scintillation counting. The result indicated the absence of lead-210 in the solution.

Counter Efficiency. The counting efficiency of the low-background counter was determined by counting $^{210}\text{BiOCl}$ at different masses. $^{210}\text{BiOCl}$ was prepared by adding a known quantity of $^{210}\text{Pb}/^{210}\text{Bi}$ equilibrium standard solution to lead carbonate, which was prepared by boiling lead sulfate in a 2 M sodium carbonate solution. A few drops of 6 M HCl, followed by various amounts of bismuth carrier solution, were added to the lead carbonate. The resulting mixture was heated in a hot water bath until a clear solution was obtained. Distilled water was added to the solution to precipitate $^{210}\text{BiOCl}$. $^{210}\text{BiOCl}$ was then filtered, weighed, and counted with the α/β low-background counter. The counting efficiency over a range of $^{210}\text{BiOCl}$ mass was determined after yield and decay correction.

Sample Analysis. Figure 1 shows the procedures for the analysis of lead-210 in 1-L water sample. A known quantity of lead-210 standard solution was added to the sample, followed by methyl orange indicator and 5 mL of 1 M citric acid. The sample was made basic with concentrated ammonium hydroxide solution. Sixty milligrams of lead and 20 mg of barium carriers were added, and the mixture was heated to boiling. Fifty milliliters of 18 N sulfuric acid was added to precipitate lead and barium sulfate, which was collected and washed with 10 mL of concentrated nitric acid and then distilled water. Fifteen milliliters of 0.05 M alkaline EDTA solution was added to dissolve the sulfate and then glacial acetic acid was added to reach a pH of 4.0. After further digestion, the barium sulfate was separated from lead by centrifuging and the supernatant fluid saved. To precipitate lead sulfate, the pH of the supernatant was adjusted to 1.0 with 18 N sulfuric acid and the mixture was digested for ~30 min with occasional stirring. The precipitation of lead sulfate marked the beginning of the bismuth-210 ingrowth period. After digestion, lead sulfate was separated and washed with two 15-mL portions of hot distilled water. Lead carbonate was obtained by heating the lead sulfate in 20 mL of 2 M sodium carbonate solution. After the chemical yield of lead was determined, the

(1) Personal communication. U.S. Environmental Protection Agency. Addendum to Occurrence of Man-Made Radionuclides in Public Drinking Water Supplies. EPA, 1991g, May 20, 1991.

(2) *Fed. Regist.* 1991, 56, (July 18), No. 138.

(3) Blais, J. S.; Marshall, W. D. *Anal. Chem.* 1988, 60, 1851-1855.

(4) Holtzman, R. B. *Health Phys.* 1963, 9, 385.

(5) Petrow, H. G.; Cover, A. *Anal. Chem.* 1965, 37, 1659-1660.

(6) Sill, C. W.; Willis, C. P. *Anal. Chem.* 1965, 37, 1661-1671.

(7) Goldin, A. S. *Anal. Chem.* 1961, 33, 406-409.

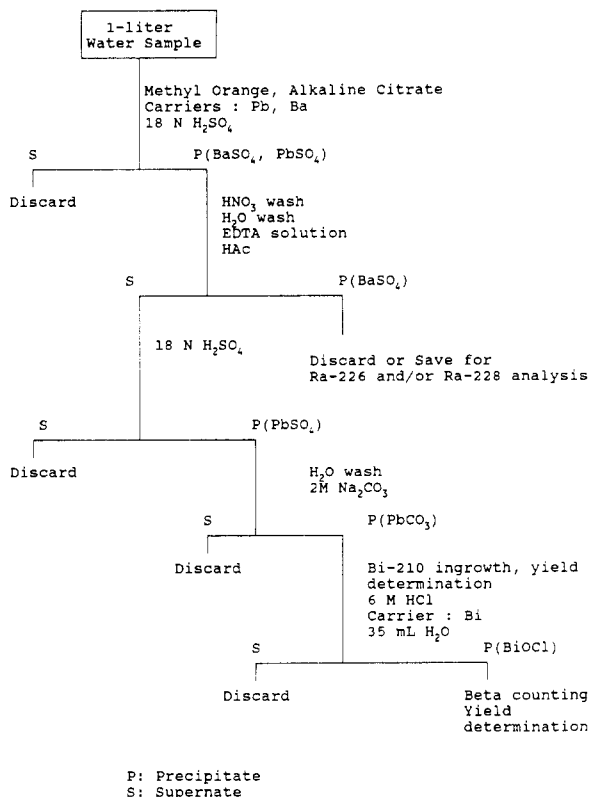


Figure 1. Analysis of lead-210 in environmental water sample.

lead carbonate was stored for sufficient time to allow bismuth-210 to ingrow.

At the end of the ingrowth period, a few drops of 6 M HCl and 5–10 mL of distilled water were added to the lead carbonate. Twenty milligrams of bismuth carrier was added, and the resulting mixture was digested in a hot water bath until a clear solution was obtained. About 35 mL of distilled water was then added to precipitate bismuth oxychloride. If bismuth oxychloride does not form after the solution is digested for 20 min, a few drops of concentrated ammonium hydroxide solution can be added to assist the formation of bismuth oxychloride. The formation of bismuth oxychloride marked the end of bismuth-210 ingrowth and the beginning of bismuth-210 decay. Bismuth oxychloride was separated by centrifuge and washed twice with 20 mL of hot distilled water. The oxychloride was then filtered, dried, weighed, and β counted. The lead-210 concentration was calculated by using the following equation:

$$^{210}\text{Pb (pCi/L)} = C/E(2.22)Y_1Y_2ID$$

where C is the net β count rate of ^{210}Bi ; E is the counting efficiency of $^{210}\text{BiOCl}$; Y_1 and Y_2 are the chemical yields of lead and bismuth, respectively; I is the ingrowth factor [$1.0006(e^{-\lambda_1 t} - e^{-\lambda_2 t})$], λ_1 and λ_2 are decay constants of ^{210}Pb and ^{210}Bi , respectively, and t is the ingrowth period; and D is the decay correction for ^{210}Bi .

Effect of pH on the Formation of Lead Sulfate in Alkaline EDTA Solution. A known amount of lead carrier was mixed with 20 mL of distilled water in a centrifuge tube. To precipitate lead sulfate, 18 N sulfuric acid was added, and after separation, the lead sulfate was dissolved in 0.05 M alkaline EDTA solution. A known quantity of lead-210 standard solution, in equilibrium with its daughters, was added to the EDTA solution from which lead sulfate was reprecipitated by adding various amounts of 18 N sulfuric acid. The pH of the solution was measured and the lead sulfate was filtered, dried, and weighed. The percent recovery of lead was determined gravimetrically.

RESULTS AND DISCUSSION

Environmental water samples often have high contents of sulfate which, if present, may cause premature precipitation of lead and barium carriers when added to these samples.

Table I. Effect of pH on the Recovery of Lead in EDTA Solution

pH of EDTA soln	% recovery ^a of lead as lead sulfate
1.5	84.7 ± 3.4
1.0	96.5 ± 4.4
0.5	96.3 ± 4.0

^a These numbers represent the mean values and standard deviations at the 95% confidence level from three separate determinations.

Table II. Determination of ^{210}Pb in Water Samples

lead-210 concn (pCi/L)		lead-210 concn (pCi/L)	
added	found ^a	added	found ^a
190.0	183.8 ± 7.0	9.6	9.8 ± 1.5
96.0	96.8 ± 4.1	5.8	6.3 ± 1.2
76.8	74.6 ± 3.0	1.0	1.3 ± 0.5
57.6	54.6 ± 3.0	28.0 ^b	25.2 ± 3.0
38.4	37.3 ± 1.9	11.5 ^b	11.2 ± 1.6
19.2	18.4 ± 4.1	5.8 ^b	5.4 ± 1.0
13.4	14.2 ± 2.3		

^a Three separate determinations were performed. ^b These samples were spiked with natural uranium and radium-226.

Quantitative precipitation of lead and barium cannot be ensured if this occurs. To prevent early precipitation of the carriers, a masking agent such as alkaline citrate was mixed with water samples prior to the addition of carriers. Lead and barium would not precipitate until sulfuric acid was added to dissociate the metal-citrate complexes and precipitate lead and barium. After separation from the sample as sulfates, lead and barium were washed with concentrated nitric acid to remove polonium-210. Polonium-210, although primarily an α emitter, may interfere with β counting of bismuth-210 when counted together with the latter, by absorption of the energy of α particles by the counter window. This interference, although it can be corrected empirically, is undesirable for low-level β counting of bismuth-210.

Alkaline EDTA solution was used to complex lead and barium in solution. The influence of pH on the metal-EDTA complex stability provides the basis for the separation of lead-210 in solution from its daughters and other interfering radionuclides. Acetic acid was used to lower the pH of the EDTA solution. Precipitation of lead or barium was not observed until the solution pH reached 4. To ascertain that the precipitate contains only barium and, hence, radium, a known quantity of barium-133 standard solution was added to the water sample, which was analyzed using the procedures described. The barium sulfate residue and the EDTA solution from which the precipitate was separated were analyzed for barium-133 activity using the γ -ray spectrometer. Analysis of the γ -ray spectrum found no barium-133 activity in the EDTA solution, while over 90% of the added barium-133 activity was recovered in the precipitate. This result shows that complete separation of barium from the sample was achieved in EDTA solution by adjusting the pH to 4.

The effect of pH on the stability of the lead-EDTA complex in solution was also studied. Table I shows the percent recovery of lead as sulfate at various pH of the EDTA solution. As described in the Experimental Section, these samples were spiked with a known quantity of standard solution of lead-210 in equilibrium with its daughters bismuth-210 and polonium-210. Lead-210 and its daughters served as tracers to follow the chemical separation of lead in EDTA solution. Lead sulfate was counted with the α/β low-background counter. No net α counts were observed in the α channel, indicating that polonium-210 was separated from lead-210. Lead sulfate was redissolved in alkaline EDTA solution after

Table III. Advantages and Disadvantages of Existing Methods for Measuring Lead-210 in Water Samples

method of analysis	advantage	disadvantage
(I) direct counting	these methods usually require no or little sample preparation or chemical separation	low sensitivity
(1) γ -ray spectrometry; liquid scintillation counting		
(2) ICP-MS		sample preconcentration required
(II) indirect measurement	low detection limit can be achieved with these methods	long waiting period
(1) polonium		laborious procedures (method used for mill effluent with high contents of heavy metals)
(2) Sill and Willis		lengthy steps of sample evaporation-digestion
(3) modified Petrow and Cover		

being α counted. An aliquot of EDTA solution was taken and analyzed with a liquid scintillation analyzer. The activities of lead-210 and bismuth-210 were determined. Only lead-210 activity was found present in the sample. The absence of polonium and bismuth activity in lead sulfate suggests that their EDTA complexes did not precipitate, even at such low pH. The separation of bismuth-210 from lead-210 ensures a pure lead-210 sample for bismuth-210 ingrowth.

Water samples obtained from wells often contain natural uranium and radium as well as lead-210. These naturally occurring isotopes are potential interferences to the separation of lead-210. To test the present method in the analysis of such samples, water samples containing known quantities of lead-210 were spiked with natural uranium standard solution free of lead-210 and freshly prepared radium-226 solution. Freshly prepared radium-226 solution was used in order to eliminate lead-210 that may be otherwise present in the radium-226 standard solution. The amount of lead-210 that ingrows into a prepared radium-226 solution within a 5-day period is $\sim 0.01\%$ of the parent radium-226 activity.⁸ The total radium-226 and uranium added to the sample were 53 and 77.8 pCi/L, respectively. Shown in Table II are experimental results of analyses of 1-L water samples that were spiked with lead-210 and those spiked with lead-210, uranium, and radium-226.

The experimental results agree within experimental error with the known lead-210 concentration. A two-tailed t test was used to test the data in Table II. The calculated t values range from 0.53 to 2.83, which are below the tabulated 10% t value ($P = 0.1$) of 2.92, indicating no apparent bias in the method.

The presence of uranium and radium in the water samples does not appear to affect the results of the analyses. The effectiveness of separation of lead-210 from the uranium and radium isotopes was tested by counting the lead carbonate

with the α/β low-background counter. No α activity was found in the lead carbonate. The presence of other naturally occurring lead isotopes such as ^{214}Pb , ^{212}Pb , and ^{211}Pb will not interfere with the analysis either, since the half-lives of these isotopes are so short that they will decay away during the bismuth-210 ingrowth period.

The overall recoveries of lead and bismuth are 77.1% and 82.0%, respectively, from the sample analyses. The counting efficiency of bismuth-210 is 38% and the average β background of the α/β counter is 1 count/min. Based on these figures, the minimum detection limit of the method is 0.6 pCi/L at the 95% confidence level.

CONCLUSIONS

The study described in this paper demonstrates that lead-210, in an environmental water sample, can be separated from other naturally occurring radionuclides as lead sulfate by varying the pH of the EDTA solution that contains the lead-EDTA complex. After a suitable ingrowth period, bismuth-210 can be isolated as bismuth oxochloride, and the lead-210 concentration can be calculated from the daughter activity.

Summarized in Table III are the advantages and disadvantages of the existing methods for measuring lead-210 in water samples. The method reported here provides several advantages over the existing methods: (1) a higher sensitivity (detection limit less than 1 pCi/L), compared to the direct counting methods, can be achieved as a result of the relatively high chemical yields of lead and bismuth obtainable with the present method. Higher sensitivity also results because of the higher counting efficiency and the lower background of most of the commercially available low-background α/β counters; (2) the need for a long waiting period (polonium method), and the time-consuming evaporation-digestion steps in the modified Petrow and Cover⁹ method are avoided; and (3) the method can be coupled with the method recommended by the United States Environmental Protection Agency for the determination of radium-226 and radium-228 in water.^{10,11}

RECEIVED for review March 10, 1993. Accepted June 17, 1993.

(8) Kirby, H. W. *Anal. Chem.* 1954, 26, 1063-1071.

(9) *Environmental Measurements Laboratory Procedures Manual*, 27th ed.; HASL-300; U.S. Department of Energy, Government Printing Office: Washington, DC, 1992; Vol. 1, pp 4.5.73-80.

(10) Percival, D. R.; Martin, D. B. *Anal. Chem.* 1974, 46, 1742-1749.

(11) Personal communication. Brooks, I. B.; Blanchard, R. L. A *Procedures for the Determination of Radium-228*. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1981.