Time-Efficient Method for the Determination of 210Pb, 210Bi, and 210Po Activities in Seawater Using Liquid Scintillation Spectrometry

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A novel method has been developed for determining the natural decay series radionuclides (NDS), ^{210}Pb, ^{210}Bi, and ^{210}Po, in seawater by way of state-of-the-art liquid scintillation spectrometry. For ^{210}Pb analysis, the method makes use of a ^{212}Pb yield tracer, prepared by ion exchange separation from aged Th(NO$_3$)$_4$. ^{210}Bi recovery is determined using ^{207}Bi as the yield tracer, and ^{210}Po is determined using the conventional ^{208}Po yield tracer. The limits of detection for this method are 0.32, 0.34, and 0.004 mBq l^{-1} for ^{210}Pb, ^{210}Bi, and ^{210}Po, respectively. The analysis can be completed within 10 days, as compared with up to one year for traditional methods. Results are presented for a preliminary study of ^{210}Pb, ^{210}Bi, and ^{210}Po in the dissolved and particle-bound phases of Irish Sea water.

The world's ocean system is the ultimate sink for the majority of contaminants released into the environment. In particular, the surface oceans and the near-shore environment are of major importance in this context, because they are the zones of contaminant input to the marine environment and have high levels of geochemical and biological activity. Within these areas, most particle reactive species are removed from the dissolved phase by sorption onto particles, with subsequent removal to the sediment through particle settling. Characterizing these sorption and settling rates is fundamentally important for developing an understanding of the biogeochemical cycling of contaminant metals; however, direct quantification of these processes is extremely difficult. Natural decay series (NDS) radionuclides, especially those in the ^{238}U decay chain (Figure 1), have been employed widely as tracers of the rates of such marine processes by exploiting situations of radioactive disequilibrium resulting from geochemical differences between parent and daughter nuclides in the decay chain. Frequently, NDS radionuclides have also been employed as proxies for particle reactive pollutant metals, nutrients, and organic carbon to determine rates of scavenging and particle removal.[1−6]
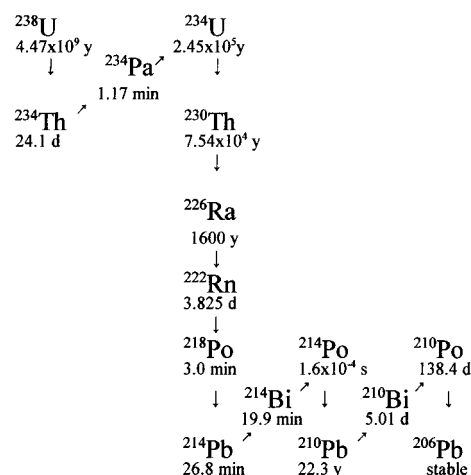

Figure 1. ^{238}U natural decay series.

The radionuclide pairs, ^{210}Po/^{210}Pb and ^{210}Pb/^{226}Ra, have been successfully employed in the study of a wide range of marine processes including (i) Pb residence times in the Atlantic and Pacific Oceans,[7] (ii) relative removal rates of Po and Pb by plankton[8,9] and organic detritus,[10,11] (iii) prediction of the mixing and cycling behavior of particle reactive pollutants, such as Pu and Am,[12] and (iv) biological productivity and boundary scavenging.[6]

There are many methods for the determination of ^{210}Po and ^{210}Pb in aquatic matrixes, but all of them are based on the same basic procedure, varying mainly in the method employed for preconcentration.[13−19] After preconcentration, the sample is dis-

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solved in a suitable solution, from which Po can be spontaneously deposited onto silver foils[20] and the activity determined by α spectrometry. In sediments, [210]Po and ^{210}Pb are often found in equilibrium, and the activity of ^{210}Pb can be estimated from that of its [210]Po granddaughter.[21] However, in the upper water column, equilibrium is rarely achieved and separate determinations of ^{210}Pb and [210]Po are required. To achieve this, [210]Po is initially removed for analysis, after which the sample is respiked with the Po yield tracer and stored for at least 6 months to allow [210]Po to grow in from [210]Pb. Po is then replated from the solution, and the activity of ^{210}Pb is calculated from the [210]Po ingrowth. The obvious disadvantage of this method is that it typically takes upward of 6 months to determine both the ^{210}Pb and [210]Po activities. Other problems that can arise are (i) incomplete initial plating of Po, leading to a systematic underestimation of the ^{210}Pb activity and (ii) partial [210]Bi plating onto the silver foil,[22] resulting in an error in the [210]Po determination as a result of its in-growth from [210]Bi. Furthermore, [210]Bi determinations are not possible using these methods. The ability to measure [210]Bi (half-life = 5 d), which is also a particle reactive species, is potentially very important, because it would allow processes occurring on a time scale of days to be investigated, for example, primary production blooms.

Church and co-workers[23] recognized the potential for a more time efficient procedure and developed a method that allows determination of ^{210}Pb, [210]Bi, and [210]Po within one month of sampling; however, this method remains subject to the problems of attempting specific plating, that is, silver foils may remove Bi from solution and any unplated Po may plate onto the nickel foils.[24] The analytical protocol presented here was designed to advance that described by Church and co-workers and to enable ^{210}Pb, [210]Bi, and [210]Po to be measured within ~10 days.

EXPERIMENTAL SECTION

Instrumentation. Three instruments were used in the procedures described below. Liquid scintillation spectrometry (LSS) was carried out using a Packard Tri-Carb 3170 TR/SL (Packard Instrument Co., Downers Grove, Chicago, IL).[25]

All scintillation counting was carried out using 20-mL low-potassium, borosilicate glass vials and an Ultima Gold-LLT liquid scintillation cocktail (Packard Instrument Co., Downers Grove, Chicago, IL).

γ spectrometric determination of the [207]Bi yield tracer activity was carried out using a Canberra Industries 35% relative efficiency,
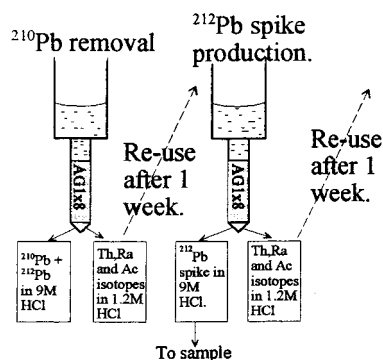
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Figure 2. [212]Pb purification scheme.

N-type high-purity germanium (HPGe) γ photon detector with a thin beryllium window. α spectrometric analysis of [210]Po utilized a Canberra Industries quad-α spectrometer, model 7404, with four 450-mm² passivated implanted planar silicon (PIPS) detectors.

Yield Tracers. [207]Bi ($t_{1/2}$ = 33.4 years) was purchased from Los Alamos National Laboratory, Los Alamos, NM. [208]Po ($t_{1/2}$ = 2.898 y) was purchased from Amersham International plc, U.K. [212]Pb ($t_{1/2}$ = 10.6 h) was prepared from thorium nitrate as described below.

Sill and Willis[26] presented a method for the purification of [212]Pb as a tracer for Pb studies, but despite its potential, no use has been made of [212]Pb in marine tracer studies because of its short half-life. Typically, stable Pb is employed as the yield tracer, with analysis either by precipitation and gravimetric analysis as $Pb(SO)_4$,[27] $Pb(CrO)_4$,[15] or Pb oxalate[28] or by atomic absorption spectrometry (AAS).[14] [212]Pb has the advantage over stable Pb of being rapidly analyzed by γ spectrometry, and it is not subject to variations in the chemical purity of the precipitated lead salt. Sill and Willis[26] used a dithiocarbamate extraction from $Th(NO_3)_4$ solution to purify [212]Pb, but this method requires the use of perchloric acid. For safety reasons, an ion exchange procedure based on data from Saito[29] was adopted. The $Th(NO_3)_4$ used in this study was manufactured more than 30 years ago; therefore, the entire [232]Th decay series is in radioactive equilibrium. Approximately 1.2 g of $Th(NO_3)_4$ was used to obtain a purified solution containing ~2000 Bq of [212]Pb; however, because the $Th(NO_3)_4$ also initially contained [230]Th, which is part of the [238]U decay series (Figure 1), ^{210}Pb was also present as a result of ingrowth. It was, therefore, necessary to perform a two-step purification (Figure 2), whereby the Pb was separated from the $Th(NO_3)_4$ solution and discarded. [212]Pb was then allowed to grow in over at least one week and was then separated whenever required. Under these conditions, ^{210}Pb in-growth will be negligible. If insufficient time has elapsed since the manufacture of the $Th(NO_3)_4$ for [228]Ra ($t_{1/2}$ = 5.75 years) to reach equilibrium with [232]Th, the [228]Th will be partially unsupported, and therefore, the activity will vary according to the Bateman equations.

If the [228]Ra is in equilibrium with the [232]Th, the fraction containing Th, Ra, and Ac, eluted before the [212]Pb, can be repeatedly reused as a virtually inexhaustible source of [212]Pb, with

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the generation of no radioactive waste and with an ingrowth time of one week producing sufficient ^{212}Pb for use as a yield tracer. To determine the count rate of the ^{212}Pb after purification by anion exchange, a 1-mL aliquot was removed from the 30-mL fraction that contains the ^{212}Pb and was analyzed for 1 h by HPGe γ spectrometry. It is not necessary to determine the absolute activity of the ^{212}Pb yield tracer, since the procedure for determining Pb recovery from the water samples is simply based upon relative count rates between the 1-mL subsample and the Pb fraction recovered at the end of the analysis, that is, the ratio of ^{212}Pb counts determined in the 1-mL subsample divided by the ^{212}Pb counts measured in the Pb fraction recovered at the end of the analysis will give a measure of recovery, once radioactive decay and the differing volumes of ^{212}Pb spike (1 mL and 29 mL) have been taken into account.

Sample Preconcentration. A 20-L seawater sample was filtered, using a small compressor, through a 22-cm Whatman cellulose nitrate filter (0.22 μm) held in a filtering mount that was designed and built in-house. The seawater was then acidified with 50 mL of 12 M HCl and spiked with 0.01 Bq of ^{208}Po, 1 Bq of ^{207}Bi, and ~2 kBq of the ^{212}Pb tracer as described above, together with 200 mg of Fe^{3+} carrier (as $FeCl_3$). The sample was shaken vigorously and left overnight to allow isotopic equilibrium to be established between the yield tracers and the radionuclides of interest. The following morning, 65 mL of 18 M NH_4OH was added to precipitate Fe^{3+} as $Fe(OH)_3$, and air was bubbled through the sample for 20 min to ensure thorough scavenging by the $Fe(OH)_3$ precipitate, which was then separated by filtration through a Whatman cellulose nitrate filter (0.22 μm). The precipitate was purified by dissolving in 2 M HCl, followed by reprecipitation of the $Fe(OH)_3$ with 18 M NH_4OH. The sample was then centrifuged for 5 min, and the supernatant was discarded. The precipitate was then washed three times with 30 mL of reverse-osmosis water.

The $Fe(OH)_3$ precipitate was then dissolved in 20 mL of 9 M HCl, 20 mL of 15 M HNO_3 was added, and the solution was heated under reflux for 1 h to ensure that the sample was fully oxidized before removal of the Fe^{3+} carrier by solvent extraction using diisopropyl ether (DIPE). Complete sample oxidation is important, because Kimura and Ishimori[30] have shown that during DIPE extraction, Po can also be removed from the aqueous phase if it is in the reduced form. Following Fe removal, the sample was heated gently to near dryness, and the residue was dissolved in 2 mL of 2 M HCl. This process was repeated twice to ensure the sample was totally dissolved in 2 M HCl, with no residual nitrate ions present.

For analysis of particulate material, the 0.22 μm cellulose nitrate filters were spiked with ^{212}Pb, ^{207}Bi, and ^{208}Po, placed in Teflon beakers, and digested on a hotplate using 40 mL of 15 M HNO_3 and 12 M HCl before the addition of 20 mL of 26 M HF. Once all HF was evaporated, the residue was dissolved in 9 M HCl, and 50 mg of Fe^{3+} carrier are added. Fe^{3+} was precipitated as $Fe(OH)_3$ by the addition of 18 M NH_4OH. The precipitate was centrifuged and washed with reverse osmosis water as in the aqueous phase analysis. The $Fe(OH)_3$ precipitate was then dissolved in 2 M HCl.

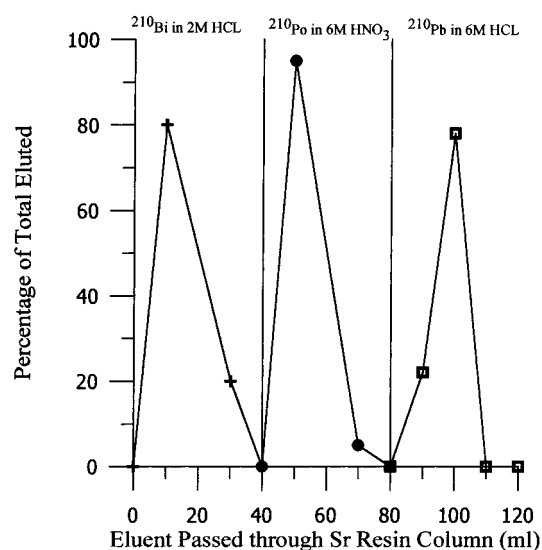(30) Kimura, K.; Ishimori, T. *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva* **1956**, *28*, 151.

Figure 3. Sr resin elution diagram for ^{210}Pb, ^{210}Bi, and ^{210}Po.

Separation of Pb, Bi, and Po. A prepacked column of Eichrom Sr resin (100−150 μm particle diameter) was conditioned sequentially with 50 mL of reverse osmosis water, 50 mL of 6 M HNO_3, 25 mL of 6 M HCl, and 25 mL of 2 M HCl. The sample, in solution in 2 M HCl, was then loaded onto the column, and two 20-mL aliquots of 2 M HCl were passed through to elute Bi and Fe. Two 20-mL aliquots of 6 M HNO_3 were used to elute Po, and then two 15-mL aliquots of 6 M HCl were used to elute Pb. This procedure was adapted from that of Vadja et al.,[28] who used 3 g columns of Sr resin and larger volumes of acid. The prepacked columns used in the present procedure provide comparable resolution of ^{210}Pb, ^{210}Bi, and ^{210}Po and have the advantages that (i) they are convenient; (ii) they give highly reproducible separations; (iii) less Sr resin is required; (iv) less acid is required to elute the nuclides; (v) preparation is simpler, because a standard column size is maintained throughout; and (vi) elution is faster.

The optimum volumes of acids noted above were determined by performing a series of elution experiments as follows. A known activity of ^{210}Pb solution in equilibrium with ^{210}Bi and ^{210}Po was freeze-dried, and the residue was dissolved in 3 mL of 2 M HCl. The solution was passed through a preconditioned Sr resin column, and the nuclides eluted sequentially using 2 M HCl, 6 M HNO_3, and 6 M HCl for Bi, Po, and Pb, respectively. The eluate was collected in a series of 10- and 20-mL fractions, which were heated to near dryness after which the residual solutions were transferred quantitatively to 20-mL scintillation vials and carefully taken to dryness. Each residue was redissolved in 1 mL of 0.1 M HCl, 5 g UG-LLT cocktail was added, and the sample was shaken vigorously. Individual samples were then counted by liquid scintillation spectrometry for 60 min in the normal count mode (NCM). The percentage recovery of each nuclide in each aliquot was determined by relating the count rate in each fraction eluted to the count rate derived for an aliquot of each yield tracer equivalent to that added to the Sr resin column (Figure 3).

Purification of Bi Fraction. Initially, analysis of the Bi fraction was undertaken without further purification; however, interferences from other nuclides of both anthropogenic and natural series origins that are present in the seawater were observed, and

Table 1. LSS Counting Efficiencies, Background Count Rates, and Figures of Merit for ^{210}Pb and ^{210}Bi When Counted at a Range of Delay before Burst (DBB) Settings

| count mode	^{210}Pb efficiency (%) (0−40 keV)	background (cpm) (0−40 keV)	E^2/B	^{210}Bi efficiency (%) (15−2000 keV)	background (cpm) (15−2000 keV)	E^2/B
NCM	96.8 ± 2.8	9.11	1030 ± 30	92.7 ± 0.3	6.02	1430 ± 20
LLCM DBB @ 800 ns	93.7 ± 2.8	3.76	2330 ± 80	90.2 ± 0.3	3.95	2060 ± 40
LLCM DBB @ 700 ns	93.1 ± 2.8	3.50	2480 ± 90	89.9 ± 0.3	3.77	2140 ± 50
LLCM DBB @ 600 ns	91.9 ± 2.8	3.35	2520 ± 90	88.8 ± 0.3	3.65	2160 ± 50
LLCM DBB @ 500 ns	90.4 ± 2.8	3.31	2470 ± 90	87.3 ± 0.3	3.61	2110 ± 50
LLCM DBB @ 400 ns	87.9 ± 2.8	3.23	2390 ± 90	84.6 ± 0.3	3.45	2080 ± 50
LLCM DBB @ 300 ns	83.3 ± 2.8	2.91	2380 ± 90	78.8 ± 0.3	2.92	2130 ± 50
LLCM DBB @ 200 ns	76.1 ± 2.8	2.57	2250 ± 80	68.2 ± 0.3	2.37	1960 ± 50
LLCM DBB @ 100 ns	61.3 ± 2.8	2.25	1670 ± 60	52.5 ± 0.3	1.73	1600 ± 50
LLCM DBB @ 75 ns	54.2 ± 2.8	2.10	1400 ± 60	31.3 ± 0.3	0.98	1000 ± 40
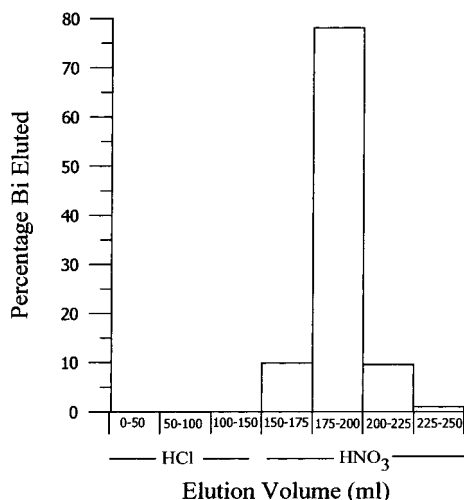
Figure 4. Bi elution on Eichrom AG1 × 8 anion-exchange resin.

the method was modified as follows: Bi was separated from interfering nuclides by anion exchange on a 4 cm³ column of Eichrom AG 1 × 8 resin for which the elution behavior is well-documented.[29,31]

The Bi fraction, in 2 M HCl, was taken to near dryness and redissolved in 0.5 M HCl. The drying and redissolution steps were repeated twice to ensure that the samples were always at a constant molarity (0.5 M). The column was preconditioned with 40 mL of 0.5 M HNO$_3$ followed by 40 mL of 0.5 M HCl. The sample was loaded onto the column and any residual Fe, together with U and Th, were eluted using three 50-mL aliquots of 0.5 M HCl. The Bi was subsequently eluted with four 25-mL aliquots of 0.5 M HNO$_3$ (Figure 4).

Preparation of the Counting Sources. The Bi fraction, contained in ~100 mL of 0.5 M HNO$_3$, was reduced in volume, transferred to a 20-mL scintillation vial, and carefully taken to dryness. The residue was redissolved in 1 mL of 0.1 M HCl, 5 g of scintillation cocktail was added, and the sample was shaken vigorously.

The Po fraction, in 6 M HNO$_3$, was heated until almost dry, taken up in 50 mL of reverse osmosis water, and then 5 mL of 0.3 M NH$_2$OH·HCl was added. ^{208}Po and ^{210}Po were spontaneously deposited onto copper foils at 95 °C over a period of 3 h.[22] The plating solution was maintained at a constant volume by adding

reverse osmosis water of the same temperature. After plating, the foil was dried and analyzed by α spectrometry.

The Pb fraction was dried down as quickly as possible to a small volume and was transferred to a 20-mL scintillation vial. The sample was taken to dryness, and the residue was dissolved in 1 mL of 0.1 M HCl. The sample was analyzed by γ spectrometry, and the yield was determined from the ratio of counts in the γ spectrum of the 1 mL subsample of spike (removed immediately after ^{212}Pb separation from Th(NO$_3$)$_4$) to those in the sample spectrum after correcting for radioactive decay. A 5-g sample of scintillation cocktail was subsequently added to the vial, which was stored for at least 10 days to allow the ^{212}Pb yield tracer to decay, after which the ^{210}Pb activity was determined by LSS. The times of all elutions were noted so that the amount of in-growth of ^{210}Bi from ^{210}Pb could be determined.

Liquid Scintillation Counting Efficiencies. The delay before burst settings were chosen by counting purified aliquots of ^{210}Pb and ^{210}Bi at a range of DBB settings. ^{210}Pb and ^{210}Bi were purified on a 2-mL prepacked column of Sr resin, and the eluted fractions were prepared for LSS in the same manner as the samples. This ensured that the degree of quenching and the counting geometry were the same for the spikes and the samples. The activity of the ^{210}Pb spike is known, and this allowed the calculation of any ^{210}Bi which had ingrown and was an interference within the ^{210}Pb counting window of 0−40 keV. Background vials containing 1 mL of 0.1 M HCl and 5 g of UG-LLT cocktail were also counted at the same range of DBB settings. The optimum DBB setting was a compromise between low backgrounds (on a low DBB setting) and a high counting efficiency (on a high DBB setting). To find the best signal-to-noise ratio, the E^2/B (counting efficiency^2/background) factor was calculated for each DBB setting. The highest E^2/B for both ^{210}Pb and ^{210}Bi (Table 1) was at a DBB setting of 600 ns.

Liquid Scintillation Counting Procedures. (i) Bismuth. To dark-adapt the sample, the vial containing the purified Bi fraction was placed in the liquid scintillation spectrometer for at least 1 h prior to counting. The sample was counted together with (i) background vials containing 1 mL of 0.1 M HCl and 5 g of UG-LLT, and (ii) "spiked" samples consisting of the ^{207}Bi yield tracer taken to dryness and redissolved in 1 mL of 0.1 M HCl. This allowed any changes in the activity of the spike to be monitored. The samples were counted for 3 × 200 min, with the LLCM activated and with the DBB set to 600 ns. In addition to reducing background, the LLCM also reduces the interference from ^{207}Bi.

(31) Kraus, K. A.; Nelson, F. *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva*, **1956**, *7*, 113.
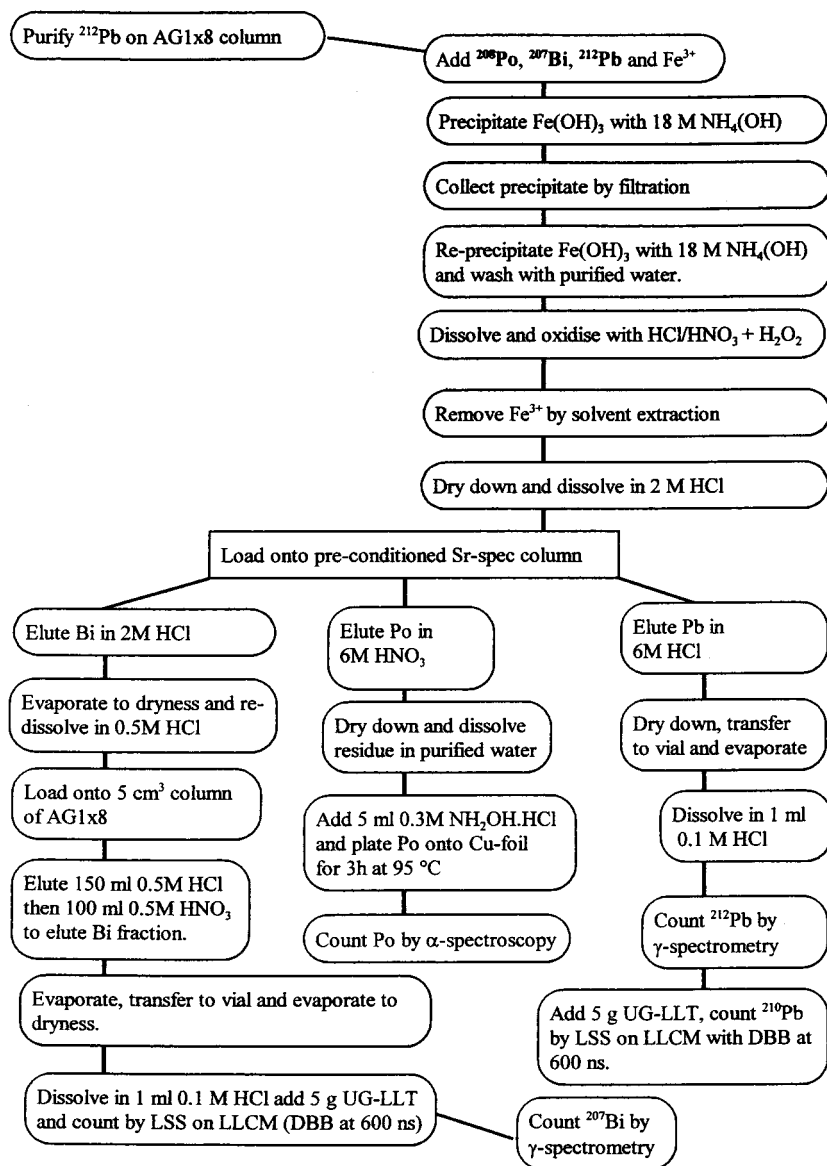
Purify ^{212}Pb on AG1x8 column

Add ^{208}Po, ^{207}Bi, ^{212}Pb and Fe^{3+}

Precipitate Fe(OH)$_3$ with 18 M NH$_4$(OH)

Collect precipitate by filtration

Re-precipitate Fe(OH)$_3$ with 18 M NH$_4$(OH) and wash with purified water.

Dissolve and oxidise with HCl/HNO$_3$ + H$_2$O$_2$

Remove Fe^{3+} by solvent extraction

Dry down and dissolve in 2 M HCl

Load onto pre-conditioned Sr-spec column

Elute Bi in 2M HCl

Evaporate to dryness and re-dissolve in 0.5M HCl

Load onto 5 cm^3 column of AG1x8

Elute 150 ml 0.5M HCl then 100 ml 0.5M HNO$_3$ to elute Bi fraction.

Evaporate, transfer to vial and evaporate to dryness.

Dissolve in 1 ml 0.1 M HCl add 5 g UG-LLT and count by LSS on LLCM (DBB at 600 ns)

Elute Po in 6M HNO$_3$

Dry down and dissolve residue in purified water

Add 5 ml 0.3M NH$_2$OH.HCl and plate Po onto Cu-foil for 3h at 95 °C

Count Po by α-spectroscopy

Elute Pb in 6M HCl

Dry down, transfer to vial and evaporate

Dissolve in 1 ml 0.1 M HCl

Count ^{212}Pb by γ-spectrometry

Add 5 g UG-LLT, count ^{210}Pb by LSS on LLCM with DBB at 600 ns.

Count ^{207}Bi by γ-spectrometry

Figure 5. Schematic representation of the proposed method.

This is due to a proportion of the ^{207}Bi γ photons interacting with the quasiactive BGO guard, producing pulses with a long decay constant that are coincident with the short decay constant pulses brought about by the interaction of the β^+ particles and the Ultima Gold LLT cocktail in the vial. The resulting co-incident pulse is likely to be rejected. The ^{210}Bi counting efficiency is also reduced, but this effect is less significant.

Counting windows were set at 0−2000 keV and 15−2000 keV. A 69.2 ± 0.9% portion of the ^{207}Bi counts were found in the first 15 keV, and 30.9 ± 1.1% were found in the 15−2000 keV window. Once the sample had been counted by LSS, the vial was counted for 10 h using the HPGe γ photon detector to determine the ^{207}Bi yield. Although the LS spectra of ^{210}Bi and ^{207}Bi overlap, ^{210}Bi determination can still be achieved through knowledge of relative counting efficiencies by γ spectroscopy and LSS. Subtraction of the ^{207}Bi count rate from the total count rate provides the ^{210}Bi count rate. The ^{210}Bi specific activity can be derived from the chemical yield of the ^{207}Bi tracer and the known counting efficiency of ^{210}Bi as follows:

Table 2. Reagent Blank Activities (mBq L^{-1}) for ^{210}Pb, ^{210}Bi, and ^{210}Po

	dissolved	particulate
^{210}Pb	0.013	0.04
^{210}Bi	0.06	0.023
^{210}Po	0.021	0.013

γ_C = count rate obtained by γ spectroscopy of ^{207}Bi in the spike.

γ_S = count rate obtained by γ spectroscopy of ^{207}Bi in the sample.

LSS$_C$ = liquid scintillation spectrometry count rate (cpm) of the ^{207}Bi in the spike, in a 15−2000 keV counting window.

LSS$_S$ = liquid scintillation spectrometry count rate (cpm) of the sample in a 15−2000 keV counting window. It should be noted that this is a composite spectrum of ^{210}Bi and ^{207}Bi.

A 30.9 ± 1.1% portion of the ^{207}Bi counts, determined in a 0−2000 keV counting window, were found in the 15−2000 keV counting window, but the counting efficiency of ^{210}Bi in a 15−2000 keV counting window was 88.8 ± 0.3%.

Table 3. Initial Data for ^{210}Pb, ^{210}Bi, and ^{210}Po in the Dissolved and Particulate Phases of Surface Seawater Samples[a]

sample code	^{210}Pb (mBq/L) dissolved	1 σ error (mBq/L)	^{210}Pb (mBq/L) particulate	1 σ error (mBq/L)	^{210}Bi (mBq/L) dissolved	1 σ error (mBq/L)	^{210}Bi (mBq/L) particulate	1 σ error (mBq/L)	^{210}Po (mBq/L) dissolved	1 σ error (mBq/L)	^{210}Po (mBq/L) particulate	1 σ error (mBq/L)
31.5.00	1.43	0.07	ND[b]		d		ND		0.144	0.011	ND	
19.6.00	1.78	0.14	ND		d		ND		0.064	0.007	ND	
07.8.00	0.53	0.059	0.86	0.075	d		d		0.073	0.007	0.54	0.030
29.8.00	0.42	0.041	SL[c]	SL	d		d		0.121	0.013	0.41	0.026
11.9.00	0.64	0.067	0.3	0.038	0.09	0.02	0.87	0.079	0.102	0.015	0.51	0.038

[a] Collected May−Sept 2000 1.5 miles west of St. Bees Head in the northeast Irish Sea [b] Not determined. [c] Sample Lost. [d] Interference present.

The fractional recovery of Bi is calculated via the respective γ spectrometry count rates in the 569 keV ^{207}Bi photopeak using the following equation:

$$\text{fractional recovery of Bi } (R) = \frac{\gamma_S}{\gamma_C}$$

Although other photopeaks were measured, only the peak at 569 keV was used because (i) it has a high γ intensity (98%) and (ii) there are no other peaks occurring at this energy, and hence, the measurement is free from interferences. Peaks with a high γ intensity occur at ~74 and 85 keV, but these suffer from interferences from the Pb X-rays that occur in the background.

The LSS count rate from ^{207}Bi only is given by

$$\text{LSS}_S \text{ for } {}^{207}\text{Bi} = R \times \text{LSS}_C$$

Therefore, the counts resulting from ^{210}Bi only are

$$\text{LSS}_S \text{ for } {}^{210}\text{Bi} = \text{Total LSS}_s - \text{LSS}_s \text{ for } {}^{207}\text{Bi}$$

and the activity of ^{210}Bi in the sample is

$$\text{activity of } {}^{210}\text{Bi (Bq L}^{-1}) =$$

$$\frac{\text{LSS}_S \text{ for } {}^{210}\text{Bi}}{0.888 \times \text{sample vol } (L) \times R \times 60}$$

The activity thus calculated is decay-corrected back to the time of separation from ^{210}Pb.

(ii) Lead. A 1-h count by HPGe γ spectrometry allows the chemical yield of the ^{212}Pb tracer to be determined from the count rate in the 238 keV photopeak. The recovery of ^{212}Pb is calculated by decay-correcting the count rate obtained for both the 1-mL spike of ^{212}Pb and the sample (containing ^{212}Pb yield tracer) back to the time of purification. The ^{212}Pb spike contained 1 mL of the 30 mL eluted and the sample contained the remaining 29 mL. The recovery of Pb can be calculated with an error of <4%. The determination of ^{210}Pb was again carried out by counting the sample for 3 × 200 min on the liquid scintillation spectrometer. Background samples made at the same time as the final dissolution in 0.1 M HCl were also included.

A flow diagram for the full method is presented in Figure 5.

Quenching. The degree of quenching in the sample will affect the counting efficiency of the nuclide of interest, and maintaining a constant level of quenching of the Bi and Pb fractions is essential for an accurate determination of ^{210}Bi and ^{210}Pb. The samples must be free from any color and must contain no quenching agents in addition to those that are present in the background samples. When the vials are being taken to dryness on a hotplate, the temperature should be sufficiently high to evaporate the acids, but care should be taken to prevent the residue from baking onto the vial. If the samples are not totally dried, then any residual acid will increase the level of quenching. If any residue remains undissolved in the 0.1 M HCl, the contents of the vial are repeatedly oxidized with 12 M HCl, 18 M HNO$_3$, and 35% H$_2$O$_2$ until the sample is totally colorless and fully dissolved in 0.1 M HCl.

Detection Limits. It is important to establish the lower limit of detection (LLD). This has been described by Currie[32] and later authors[33,34] as

$$\text{LLD (Bq L}^{-1}) = \frac{4.66\sqrt{B}}{EVT60}$$

where B is the mean background expressed in counts, E is the fractional counting efficiency, V is the sample volume (L), T is the count time (minutes), and 60 is the Bq-to-dpm conversion factor.

The background values in the Pb and Bi counting windows for a DBB of 600 ns are presented in Table 1. The sample volume was 20 L and the counting efficiencies were 91.9, 88.8, and 20.0% for ^{210}Pb, ^{210}Bi, and ^{210}Po, respectively. This produced MDAs of 0.32, 0.34, and 0.004 mBq L^{-1} for ^{210}Pb, ^{210}Bi, and ^{210}Po, respectively.

Blanks. Blank samples were run to check the purity of each fraction and to determine any background levels of ^{210}Pb, ^{210}Bi, and ^{210}Po that may be introduced from the reagents. This was achieved by following the analytical protocol as described above but with 20 L of reverse-osmosis water replacing the seawater sample (Table 2).

Initial Results. Seawater samples were collected ~2.5 km west of St. Bees Head in the Irish Sea during the period from

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(33) Passo, C. J., Jr; Roberts, D. J. In *Advances in Liquid Scintillation Spectrometry 1994*; Cook, G. T., Harkness, D. D., MacKenzie, A. B., Miller, B. F., Scott, E. M., Eds.; Radiocarbon, Tuscon, AZ, 1996; pp 67−75.
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May to September 2000 and analyzed using the method detailed above. The results are presented in Table 3.

DISCUSSION AND CONCLUSIONS

Rapid processing of samples is required (i) to minimize the time from sampling to chemical purification in order to limit ^{210}Bi ingrowth from ^{210}Pb and (ii) because of the short half-life of the ^{212}Pb tracer; however, the advantages of this method are obvious. First, the time from sampling to final results can be as little as 10 days, as compared with up to one year with the traditional method. Second, there is no error in the ^{210}Po determination introduced by co-deposited ^{210}Bi decaying to produce ^{210}Po, because ^{210}Po and ^{210}Bi are chemically separated by the Eichrom Sr resin column. Third, the method also introduces the possibility of routine ^{210}Bi determination, together with ^{210}Po/^{210}Pb analysis, and offers the

opportunity to examine the geochemical cycling of the ^{210}Pb/^{210}Bi/^{210}Po system in the marine environment.

The dissolved ^{210}Pb values measured during this study are in the range of $0.42-1.78$ mBq L^{-1}, an order of magnitude similar to previously reported results for the Irish Sea[12] and other research.[11,13] The ^{210}Po/^{210}Pb ratios for the summed dissolved and particulate phases are between 0.44 and 0.65, which is similar to ratios observed in the Pacific and Indian Oceans[35,36] and in the nearshore environment.[37]

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