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SEQUENTIAL AND RAPID DETERMINATION OF Po-210, Bi-210 AND Pb-210 IN NATURAL WATERS

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Summary—A sequential and rapid separation method for the determination of radon daughter nuclides, Pb-210, Bi-210 and Po-210 has been developed for application to natural waters. Rapid separation is attained by the use of the same hydrochloric acid solution. After isolation of the three radionuclides from the sample by co-precipitation with added Fe^{3+}, polonium isotopes are first spontaneously deposited onto a silver disc from a 0.5*N* hydrochloric acid solution. Next, bismuth isotopes are electrodeposited onto a platinum net cathode coupled with a platinum coil anode at 1.2 V. Finally, lead isotopes are electrodeposited onto a platinum net cathode at 1.8 V from the remaining solution by adding hydroxylamine hydrochloride as an anodic depolarizer. This method can be applied to meteorological precipitation samples where these three nuclides are separated within 10 hr after the sampling with chemical yields of more than 80% for Po-210 and Bi-210 and more than 70% for Pb-210. This method is applicable to other environmental water samples.

A pair of two radon daughters, Pb-210 (half-life 22.3 years) and Po-210 (138 days) have been used to determine the mean atmospheric residence times of aerosols since 1960s.[1–3] The pair has also been used as a tracer of removal processes of heavy metals from sea-water.[4,5] A shorter half-life nuclide of 5.01 days, Bi-210 inbetween Pb-210 and Po-210 in the decay series is useful if it is precisely measured. Fry and Menon[6] first measured Bi-210 and Pb-210 in meteorological precipitations. A large difference between the residence times of atmospheric aerosols estimated from Bi-210/Pb-210 and Po-210/Pb-210 has been reported.[7–9] We have not yet determined a radioactive disequilibrium between Pb-210 and Bi-210 in sea-water.

Because of the short half-life of Bi-210, it is necessary to separate it from Pb-210 within a short time and then the method should not be tedious. The analyses of those three radionuclides were carried out with an ion exchange method,[7,10,11] a co-precipitation method[7,8] and a solvent extraction method.[12] Applying these to a sea-water sample of a few tens of liters for the precise determination of Bi-210, takes more than 2 days after sampling. Consequently, such a determination would have a relatively large error because of the long period of separation of Bi from Pb after sampling. In our previous paper,[13] we succeeded in separating Bi-210 onto a platinum net cathode from a dilute hydrochloric acid solution medium by applying a controlled potential electrolysis method.[14,15] This method, however, is somewhat complicated, because it is necessary to add nitric and perchloric acids and evaporate it to nearly dryness to decompose the reducing agent and to change the medium to a fluoroborate solution for electrodepositing lead onto an anode as PbO_2 and for the separation of U, Th, Pa, *etc.* by the INS method.[16] We have examined and developed a method of sequential separation of three radionuclides by only changing the applied voltage stepwise for the electrodepositions in the hydrochloric acid media.

EXPERIMENTAL

Carrier and spike solution

The following solutions were prepared. All reagents used were of the analytical grade made by Wako Pure Chemical Industries Ltd.

Pb^{2+} solution: 3.202 g of lead nitrate [$Pb(NO_3)_2$)], dried at 110°C was dissolved in 1 l. of 1*N* nitric acid solution. The final concentration was 2.003 mg Pb^{2+}/ml.

Bi^{3+} solution: about 4.6 g of bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$] was dissolved in 1 l. of 1*N*

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nitric acid solution. The concentration was determined to be 1.990 mg Bi^{3+}/ml by the gravimetric method precipitating BiOCl.

Fe^{3+} solution: 24 g iron chloride ($FeCl_3 \cdot 6H_2O$) was dissolved in 300 ml of 10*N* hydrochloric acid solution and purified by extracting into an equivalent volume of diisopropylether. Then the extracted Fe^{3+} was returned to deionized water. After adding 5 ml concentrated nitric acid, the two phase mixture was heated on a hot plate to volatilize the remaining diisopropylether. This solution was diluted to 500 ml with deionized water. The final concentration was 10 mg Fe^{3+}/ml.

Po-208 solution: about 2.5 dpm/ml of Po-208 in 1*N* nitric acid solution was prepared. The radioactivity was calibrated with a standard reference material, 'Climax Mill Tailings', supplied from the U.S. Environmental Protection Agency.

Apparatus

Platinum electrodes: a cylindrical platinum net cathode (55 mesh, 45 mm in height, 35 mm in diameter) and a spiral platinum wire anode (150 mm in length, 1 mm in diameter) were used.

A dual DC power supply: Model 327B, Showa Electronics Co., Ltd with a digital panel meter was used to control the applied potential at the electrodeposition.

An alpha counter: silicon surface barrier detector (Ortec BR-23-450-100, Ortec BA-025-45-100) connected to a 4096-channel pulse height analyzer (Northern Model IT-5400) or a 1024-channel pulse height analyzer (Tracor Northern Model TN-1705) were used, of which counting efficiency was about 30%.

A beta counter: a 2π gas flow GM counter (Aloka Model LBC-451) was used under an atmosphere of Q gas flowing, which had background activity of about 0.6 cpm and counting efficiency of about 35%. The counting efficiencies corrected the self-absorption by the beta activity sources and were used for the calculation of activities for each sample.

Recommended procedure

An outline of the analytical procedure developed is shown in Fig. 1 and described below.

Pretreatment

The sample collected, preferably more than 3 l. for a rain-water sample or 100 l. for a sea-water sample, was immediately acidified with 10 ml concentrated nitric acid per 1 l. of sample volume, and vigorously stirred after adding Pb^{2+} and Bi^{3+} carriers each 5 ml (10 mg), an Fe^{3+} scavenger (100 mg for a rain sample or 1 g for a sea-water sample), and 5 ml of Po-208 tracer solution. After letting it stand for 3 hr, the solution was neutralized with a 1:1 ammonium hydroxide solution until the pH was 8–9 by checking with a pH test paper, and the Fe^{3+} precipitate formed. After vigorous stirring, the solution was left standing until the supernatant became clear. Then the solution volume was reduced by decantation, and the precipitation collected by centrifugation. In a preliminary experiment using 200 l. of seawater and standing for 3 hr after forming the Fe^{3+} precipitation, the recoveries at the collection by centrifugation were about 70% of Fe, Pb and Bi added. In the case of analyzing a meteorological precipitation sample, which has a relatively small volume, the solution should be transferred to a glass beaker, heated on a hot plate and stood. The precipitate collected was dissolved with 30 ml of 1:1 nitric acid and the solution filtered using a filter paper (Advantec 5B, 125 mm in diameter) to remove the residue. The residue was washed with a small amount of concentrated nitric acid and deionized water.

Purification and determination of polonium-210

The Fe^{3+} hydroxide precipitate was again made with ammonium hydroxide solution and dissolved with 10 ml of 5*N* hydrochloride acid after collecting by centrifugation. The solution was transferred to a 100 ml Teflon beaker with the washing solution and diluted to 100 ml with deionized water. For the sea-water samples, large quantities of Fe^{3+} added were removed by the diisopropylether extraction method. After adding 50 mg of L-ascorbic acid, a silver disc (25 mm in diameter) coated with Teflon paste on the other side was floated, and the solution kept at 80°C for 2–3 hr on a hot plate. Polonium is spontaneously plated onto the silver disc. After washing the silver disc with deionized water, the alpha activities of Po-208 and Po-210 were counted by an alpha spectrometer.

Purification and detection of bismuth-210

The solution, after removal of polonium, was transferred to a 100 ml glass beaker with deionized water, and added to 1.2 g hydroxylamine hydrochloride and 1 ml concentrated nitric acid. Bismuth was electrodeposited onto a platinum net cathode at 1.2 V for 30–45 min from the

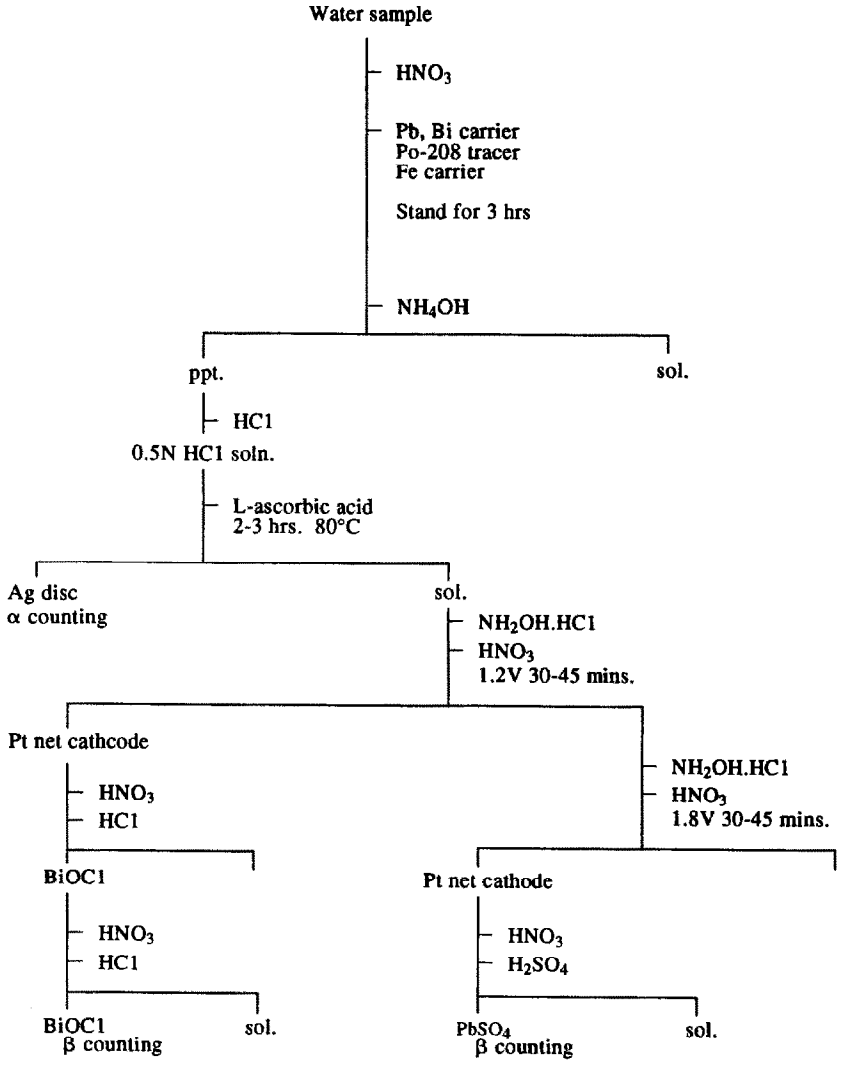

Fig. 1. Recommended analytical procedure for Pb-210, Bi-210 and Po-210 in water samples.

solution stirring with a magnetic stirrer. The bismuth deposited was dissolved into a glass beaker with a few ml of concentrated nitric acid and a small amount of deionized water. The solution was evaporated to dryness on a hot plate, and the residue dissolved with 2 ml concentrated nitric acid and diluted to 30 ml with deionized water. Ammonium hydroxide (1:2) was slowly added to the boiling solution until it became opalescent, then 5 ml of 0.2*N* hydrochloric acid was added in order to precipitate bismuth oxychloride (BiOCl). The precipitate was collected on a preweighed membrane filter (German Supor-450, 0.45 μm pore size, 25 mm in diameter) washing with a small amount of hot deionized water and ethanol. The filter was dried at 60°C, and weighed to determine the chemical yield of Bi-210. The beta activity was immediately counted by a 2π gas flow GM counter.

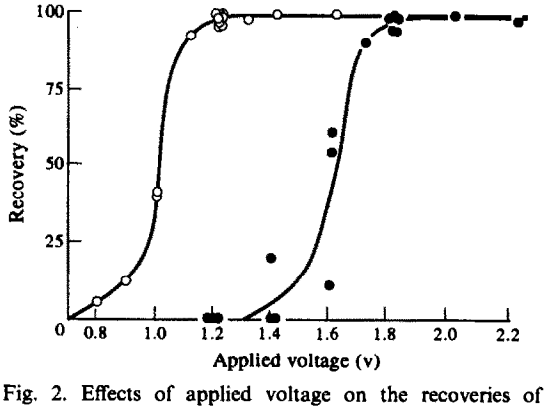

Fig. 2. Effects of applied voltage on the recoveries of bismuth (○) and lead (●) at the electrodeposition.

On a research vessel having no chemical balance, the chemical yield can be determined by the atomic absorption spectrometric

analysis of bismuth after counting the beta activities.

Purification and determination of lead-210

Ten grammes of hydroxylamine hydrochloride and 1 ml concentrated nitric acid were added to the remaining solution. Lead in the solution was electrodeposited onto a platinum net cathode at 1.8 V for 30–45 min. The lead deposited was dissolved into a glass beaker with a few ml of concentrated nitric acid and a small amount of deionized water. After evaporating it to dryness, the residue was dissolved with 2 ml concentrated nitric acid and the solution diluted to 30 ml with deionized water. Two milliliters of concentrate sulfuric acid was added to this solution to produce lead sulfate ($PbSO_4$). The lead sulfate precipitate was collected on a preweighed membrane filter (German Supor-450, 0.45 μm pore size, 25 mm in diameter), dried and weighed to determine the recovery of lead. If only Pb-210 was counted immediately after isolation, the counting efficiency was much lower. The determination of levels in meteorological precipitation and sea-water samples is not possible. Therefore, its beta activity was counted after one month when a secular equilibrium between Pb-210 and Bi-210 was attained (>98%).

Correction for the bismuth-210 activity

Bi-210 formed from Pb-210 after the sampling and decayed after the separation was corrected as follows. The mid-times of the sampling and the electrodeposition were used as the times of the sampling and the separation of Bi-210 from Pb-210. The chemical yield of Bi-210 was determined by the gravimetric method of BiOCl.

$$Y = \frac{W \times (209.0/260.4)}{9.950} \times 100, \qquad (1)$$

where Y is the chemical yield of Bi-210 (%), and W is the weight of BiOCl precipitation. The chemical yield was also obtained by the atomic absorption method after the beta counting. There was no significant difference between the two methods.

$$A_2 = \frac{\text{apparent counting rate}}{Y \times E/10000} \cdot \frac{\lambda_{Bi} t_3}{1 - \exp(-\lambda_{Bi} t_3)}, \qquad (2)$$

where A_2 is the activity of Bi-210 at the beginning of counting (dpm), E is the counting efficiency of corrected the self-absorption by the beta activity sources (%), t_3 is the counting time (min) and λ_{Bi} is the decay constant of Bi-210 (9.61×10^{-1} min^{-1}).

$$A_1 = A_2 \exp(\lambda_{Bi} t_2), \qquad (3)$$

where A_1 is the activity of Bi-210 at the time of the separation of Bi from Pb (dpm) and t_2 is the period between the separation and the beginning of counting (min).

$$A_1 = A_{Pb} \frac{\lambda_{Bi}}{\lambda_{Bi} - \lambda_{Pb}} \{\exp(-\lambda_{Pb} t_1) - \exp(-\lambda_{Bi} t_1)\} + A_0 \exp(-\lambda_{Bi} t_1), \qquad (4)$$

where A_0 is the activity of Bi-210 at the sampling (dpm), A_{Pb} is the activity of Pb-210 (dpm), t_1 is the period between the times of the sampling and the separation of Bi from Pb, and λ_{Pb} is the decay constant of Pb-210 (5.91×10^{-8} min^{-1}). In this equation the loss due to the radioactivity decay of long-lived Pb-210 can be neglected and then we get

$$A_0 = A_1 \exp(\lambda_{Bi} t_1) - A_{Pb}\{\exp(\lambda_{Bi} t_1) - 1\}. \qquad (5)$$

RESULTS AND DISCUSSION

Determination of applied voltage at the electrodeposition of bismuth

The effect of applied voltage at the electrodeposition on the recoveries of bismuth was examined with 100 ml of 0.5N hydrochloric acid solution each containing 10 mg of Bi and Pb and 20 mg of Fe^{3+}. To the solution of 50 mg and L-ascorbic acid, 1.2 g of hydroxylamine hydrochloride and 1 ml of nitric acid were added. The electrodeposition procedures were run for 30 min at various voltages. The amounts of bismuth and lead electrodeposited onto a platinum net cathode were measured by the flame atomic absorption method (Hitachi, polarized zeeman atomic absorption spectrophotomer Z-8000). The recovery against the voltage is plotted in Fig. 2. The electrolysis of bismuth started at an applied voltage of more than 0.8 V and attained nearly a quantitative recovery at 1.2 V. The average recovery of bismuth at 1.2 V was 98.1 ± 1.6% ($N = 16$). The level of contamination of lead was only 0.9 ± 0.2% ($N = 16$) at 1.2 V. This small contamination may be due to insufficient washing of the electrode after the electrodeposition, which can be eliminated by making the bismuth oxychloride precipitate (see Fig. 4). Narita *et al.* (1989)[13] have reported that

Table 1. Pb-210, Bi-210 and Po-210 in a standard solution* (in dpm/g)

No.	Pb-210	Bi-210	Po-210
1	238 ± 5	240 ± 5	235 ± 6
2	237 ± 4	244 ± 5	244 ± 5
3	245 ± 4	241 ± 5	236 ± 6
Mean†	240 ± 3	242 ± 2	238 ± 4

*The certified radioactivity of Pb-210; 240.4 ± 3.5 dpm/g. Errors attached are the 1σ values of counting statistics.
†90% confidence level.

the optimum applied voltage for bismuth is 1.4 V, which is higher than 1.2 V in this study. This may be due to the difference in the cell resistance: Narita *et al.* (1989)[13] used a graphite rod anode.

Determination of applied voltage at the electrodeposition of lead

The optimum condition for the electrodeposition of lead from the solution after the separation of bismuth was examined using 100 ml of 0.5*N* hydrochloric acid solution containing 10 mg Pb and 20 mg Fe^{3+} added 50 mg of L-ascorbic acid. Lead was electrolyzed at the applied voltage above 1.4 V and recovered almost quantitatively at 1.8 V (Fig. 2). The average recovery of lead at 1.8 V was 95.5 ± 1.6% ($N = 4$). However, for a voltage higher than 1.6 V, chlorine gas was generated from the anode. In order to avoid the generation of chlorine gas, 10 g of hydroxylamine hydrochloride was used as an anode depolarizer. Although 1.2 g of hydroxylamine hydrochloride was already added as an anodic depolarizer, 10 g was required for the lead electrodeposition because of the consumption of it during the electrodeposition of bismuth and a rapid consumption rate due to the higher supplied voltage during the electrodeposition of lead. In this study we decided to add 10 g of hydroxylamine hydrochloride and 1 ml of nitric acid to the solution after bismuth was separated and to carry out the electrolysis at 1.8 V.

Analysis of a standard equilibrium solution of Pb-*210*, Bi-*210 and* Po-*210*

A standard solution assumed to be in a secular equilibrium for Pb-210, Bi-210 and Po-210 was analyzed by the method proposed and described above. This solution was calibrated with the standard reference material, 'Climax Mill Tailings' supplied from the U.S. Environmental Protection Agency. The results given in Table 1 show no significant difference between the activities of the three nuclides and agree well with the calibrated value within 1σ values of counting statistics.

Analysis of Pb-*210*, Bi-*210 and* Po-*210 in natural samples*

This method for the determination of Pb-210, Bi-210 and Po-210 was applied to meteorological precipitation samples and sea-water samples. The results obtained are listed in Tables 2 and 3. Polonium was not analyzed in the sea-water samples.

The precipitation samples were collected using a box type collector, which was 60 cm high and whose upper open side was 90 × 90 cm in area, on the roof (10 m above) of the building for experiments at the Hakodate Campus of Hokkaido University in January 1990. In order to prevent a resuspension of the ambient accumulation snow and soil dust, the collector was set up on a stand 1 m high, and a polyethylene bag covered with the collector was replaced

Table 2. Pb-210, Bi-210 and Po-210 in meteoric precipitations in Hakodate*

Date	Sample volume (*ml*)	Pb-210 concentration (*dpm/l.*)	Bi-210/Pb-210	Po-210/Pb-210
12/1/90	6550	12.0 ± 0.2	0.368 ± 0.015	0.0366 ± 0.0015
13/1/90	3330	41.6 ± 0.5	0.445 ± 0.025	0.0433 ± 0.0016
14/1/90	7200	38.0 ± 0.6	0.515 ± 0.022	0.0391 ± 0.0017
15/1/90	2880	52.4 ± 0.6	0.358 ± 0.016	0.0279 ± 0.0009
17/1/90	1870	38.0 ± 0.6	0.327 ± 0.022	0.0200 ± 0.0009
18/1/90	6550	27.8 ± 0.4	0.418 ± 0.015	0.0358 ± 0.0013
20/1/90	2840	17.4 ± 0.2	0.484 ± 0.018	0.0400 ± 0.0017
22/1/90	6450	26.7 ± 0.4	0.457 ± 0.019	0.0753 ± 0.0028
24/1/90	4070	21.3 ± 0.4	0.407 ± 0.017	0.1283 ± 0.0034
25/1/90	6820	28.6 ± 0.4	0.380 ± 0.016	0.0832 ± 0.0031
26/1/90	4440	18.3 ± 0.4	0.353 ± 0.017	0.0503 ± 0.0027
27/1/90	667	34.4 ± 0.8	0.453 ± 0.019	0.0477 ± 0.0024
29/1/90	2600	27.5 ± 0.5	0.463 ± 0.017	0.0423 ± 0.0018

*All samples were snow collected at the Hakodate Campus of Hokkaido University (41° 48′ N, 140° 44′ E). Errors attached are the 1σ values of counting statistics.

Table 3. Pb-210 and Bi-210 in sea-water (in dpm/100 l.)

Depth (*m*)	Sample volume (*l.*)	Pb-210	Bi-210
0	200	3.84 ± 0.18	4.09 ± 0.23
0	200	3.59 ± 0.18	3.64 ± 0.26
40	165	4.15 ± 0.19	4.02 ± 0.23
60	175	4.40 ± 0.24	4.19 ± 0.28
90	175	4.15 ± 0.21	4.14 ± 0.31

The samples were collected at 42° 11′ N, 140° 35′ E in Funka Bay, 14 February 1991. Errors attached are the 1σ values of counting statistics.

every 24 hr. Over 18 months, 196 samples were collected. These three nuclides were separated within 10 hr of sampling. Consequently, the mean counting error of the ratio of Bi-210 to Pb-210 could be held to 4.4%. Table 2 shows the data on January 1990. The ratios of Bi-210 to Pb-210 and Po-210 to Pb-210 ranged from 0.327 to 0.515 and from 0.0200 to 0.1283, respectively. The implication of these results will be discussed elsewhere. As shown in Fig. 3, we obtained sufficiently high chemical yields for both nuclides through the whole analytical procedure proposed here. The decay of the Bi-210 fraction is shown in Fig. 4. There was no significant difference between the determination at 10 days

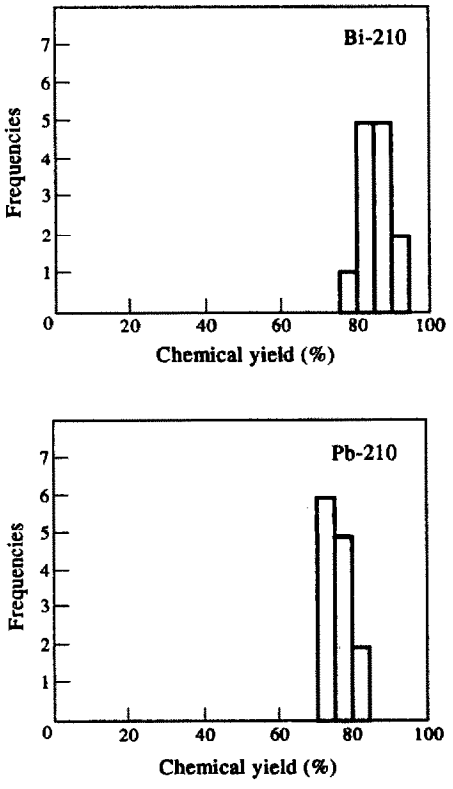

Fig. 3. Histogram of the chemical yields of Bi-210 (top) and Pb-210 (bottom) in precipitation samples ($N = 13$) through the whole analytical procedure.

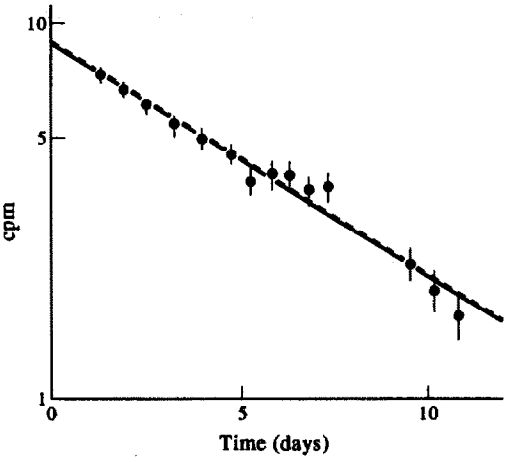

Fig. 4. Change in radioactivities of the Bi-210 fraction with time (days). A solid line was obtained by the least squares method. A dashed line refers to the theoretical decay. Error bars are the 1σ values of counting statistics.

after the isolation from Pb-210 fraction, which had 5% of counting error, and the theoretical decay, indicating the contamination of Pb-210 fraction was less than 1%. The experimentally determined half-life obtained from the slope of the best fit regression line was 4.95 ± 0.65 days, which agrees with the half-life of 5.01 days of Bi-210.

The sea-water samples were collected from the center of the Funka Bay (42° 11′ N, 140° 35′ E) in February 1991. For the surface water, duplicate analyses were done. The sample volumes were each about 200 l. Two nuclides were separated with average chemical yields of more than 65% for Bi-210 and more than 60% for Pb-210. No significant difference was found between the radioactivities of Pb-210 and Bi-210, even though the separation of Bi-210 from Pb-210 was completed within 30 hr after the sampling.

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