

Determination of ^{210}Pb and ^{210}Po in Environmental Samples by Alpha Ray Spectrometry Using an Extraction Chromatographic Resin

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A determination method using an extraction chromatographic resin (EiChroM Sr.SpecTM) has been developed for ^{210}Pb and ^{210}Po in environmental samples by alpha ray spectrometry. ^{210}Pb and ^{210}Po were coprecipitated simultaneously on CuS at pH 4.0 - 5.5. These nuclides were then adsorbed on a Sr.SpecTM resin column (0.79×4.0 cm) in 4 M HCl. The ^{210}Pb and ^{210}Po on the resin were eluted with 8 M HCl and 6 M HNO₃, respectively. ^{210}Po was determined by alpha-ray spectrometry after plating on a stainless-steel disk. ^{210}Pb was determined as ^{210}Po produced from ^{210}Pb decay. The method was applied to soil (IAEA-326) and sediments (NIST-4354, IAEA-135, IAEA-368) standard reference materials, and the results agreed with their recommended values. The chemical yield of Po ranged from 56 to 99% and the yield of Pb was 95%. The detection limits of ^{210}Pb and ^{210}Po were 0.6 mBq/sample at a counting time of 70000 s.

Keywords Polonium-210, lead-210, alpha ray spectrometry, extraction chromatography, standard reference material

^{210}Po ($t_{1/2}=138.38$ d) occurs naturally *via* ^{210}Pb ($t_{1/2}=22.3$ y) and ^{210}Bi ($t_{1/2}=5.15$ d) in the ^{238}U decay chain. The contribution of ^{210}Pb , ^{210}Bi and ^{210}Po to the internal radiation dose to human has been estimated to be around 8%.¹ Various analytical methods have been applied to the separation and determination of ^{210}Po .^{2,3}

Recently, a crown ether loaded extraction chromatographic resin (EiChroM Sr.SpecTM) was applied to the selective separation of Pb and Po in several samples. Vajda *et al.* determined the distribution coefficients of Bi, Pb and Po on Sr.SpecTM in 0.5 - 8 M HCl, and developed a large-column method for the separation of ^{210}Pb and ^{210}Po in standard samples.⁴ The resin was applied to the separation of Pb (^{210}Pb) for measurements by thermal ionization mass spectrometry⁵, graphite furnace atomic absorption spectrometry⁶ and liquid scintillation counting.⁷ However, the distribution coefficients for Fe and Cu on the resin in a HNO₃ and HCl solution are not available in the literature.

In this study, the weight distribution coefficients of Fe, Cu, Pb, Bi and Po on the resin in HCl and HNO₃ solutions were determined using a batch equilibrium method, after which the elution behavior of Po and several elements from the resin column was examined. Subsequently, the coprecipitation behavior of Pb and Po on CuS was examined. The plating condition was investigated for counting samples in the alpha ray spectrometry of Po. Moreover, the loss of Po in ashing samples was examined because of its volatility. From a series of investigations, it was found that Pb and Po were effectively isolated from interference elements

using a Sr.SpecTM resin short column (2 ml).

Finally, a combination of coprecipitation and Sr.SpecTM resin separation was developed for the determination of ^{210}Pb and ^{210}Po in several standard materials (sediments, soils) and biological samples (shellfish, seaweed) by alpha ray spectrometry.

Experimental

Alpha ray measurements

An EG & G ORTEC Model 576A alpha ray spectrometer with a Canberra [passivated ion-implanted planar silicon (PIPS) detector having 450 mm² of an active area] was used for alpha ray measurements. The counting efficiencies, determined by measuring JRIA (Japan Radioisotope Association) standard uranium sources, were typically 20 - 30% with this arrangement. The energy resolutions, determined with LMRI (Laboratoire de Métrologie des Rayonnements Ionisants, France) standard ^{243}Am sources, were typically 20 - 40 keV full width at the half-maximum peak height (FWHM) at 5.47 MeV.

Tracer

The ^{208}Po tracer solution supplied by AEA Technology, UK was diluted to activity concentration of approximately 60 mBq/ml in 1 M HCl, and stored in a Teflon bottle.

Reagents

All of the reagents used were of analytical grade. Water was purified with an ORGANO PURIC Model-S

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pure-water system. The Cu carrier solution was prepared by dissolution of Cu metal (Kanto Chemicals Co., Inc., purity, 99.99%) to have a final Cu concentration of 10.2 mg/ml in 1 M HNO₃. The Pb carrier solution was prepared by dissolving an aged Pb plate, giving a final Pb concentration of 18.5 mg/ml in 1 M HNO₃.

Apparatus

The concentration of stable elements was determined with SEIKO Instruments SPS-1200AR ICP-AES. Freeze drying for biological samples was carried out with the EYELA Model FDU-830. A Yokogawa electric Inc. PH-81-53J pH meter was used for pH measurements.

Extraction chromatographic resin column

An EiChroM Sr.SpecTM resin prepacked column (particle size; 100 – 150 μm, column size; 0.79 cm i.d.×4.0 cm) was used. The resin, bis-4,4'(5')-*t*-butyl-cyclohexano-18-crown-6, was loaded on an Amberchrom CG-71TM (polymethacrylate). The detailed characteristics of the resin and packed column were proved by Horwitz *et al.*⁸

Plating

A Tokyo photo electric Inc. ANA-2-4 was used as a power supplier and heating apparatus. A SUS-304 stainless-steel polished disk (25 mmφ, 1 mm thick) was used as a cathode. A coiled Pt wire (1 mmφ) was used as an anode. The cell consisted of a Teflon cylinder (25 mmφ×80 mm) with a stainless-steel base. The disk was set as a cathode to the base. The distance between the cathode and the anode was kept at 5 mm. In another experiment, a Ni-polished disk (purity 99.9%, 25 mmφ, 1 mm thick) was used for spontaneous deposition methods. The Ni disk was set to the base. Po was deposited onto Ni disk by only heating.

Determination of the weight distribution coefficient

The weight distribution coefficients [D_w ; (amount of ion per g of dry resin)/(amount of ion per ml of the solution)] were determined by a batch-equilibrium method at room temperature by loading a known amount of metal ion on 0.1 g of the resin. The equilibrium period was 24 h.

Recommended procedures

The recommended chemical procedures consist of 4 steps: (1) decomposition of the sample, (2) coprecipitation with CuS, (3) separation by Sr.SpecTM resin and (4) plating of Po. These procedures are shown below.

Biological samples

A 2–5 g freeze-dried sample was weighed for analysis. An 80 mBq of ²⁰⁸Po tracer, 500 μg of Pb carrier and 10 mg of a Cu carrier were added to the sample. The sample was decomposed with a HNO₃ and H₂O₂ mixture under heating at 120°C. After the sample was

decomposed, the sample solution was converted to the chloride form. The solution was then diluted to 1 M HCl and the insoluble substance was filtered off.

Two milliliters of the saturated ascorbic acid solution was added to the filtrate, and then adjusted to pH 4–5 with 4 M NH₄OH. After 10 ml of 1.3 M ethanthioamide was added to the solution, the solution was heated to 120°C until the CuS precipitate appeared to coagulate. The precipitate was separated by filtration using a cellulose nitrate membrane filter disk. The precipitate was then dissolved with small amounts of 4 M HCl.

The sample solution was loaded on a Sr.SpecTM resin column. Cu and Bi were washed out with 8 ml of 4 M HCl. Subsequently, the column was washed with 20 ml of 8 M HCl to remove Pb. The Pb fraction was stored for 3–6 months to grow ²¹⁰Po from ²¹⁰Pb decay. Then, Fe remaining on the column was washed by 4 ml of 6 M HNO₃. Finally, Po was eluted by 16 ml of 6 M HNO₃.

The Po fraction was evaporated nearly to dryness and the organic compounds in the fraction were decomposed with a few milliliters of HCl and HNO₃. After decomposition, the solution was converted to the chloride form. The solution was diluted with 10 ml of 0.5 M HCl, and 1 ml of a saturated ascorbic acid solution was added to the solution. The solution was transferred into the electric cell. Polonium was plated onto a stainless-steel disk for 2.5 h at a current density of 20 mA/cm². After plating, the disk was rinsed with H₂O and acetone, and dried at room temperature. The activities of ²⁰⁸Po and ²¹⁰Po were determined by alpha ray spectrometry.

Geological samples

A 1–5 g sample was weighed for analysis. An 80 mBq of ²⁰⁸Po tracer, 500 μg of Pb carrier and 10 mg of Cu carrier were added to the sample, which was then decomposed with HNO₃ and HF mixture under heating at 120°C. After the sample was decomposed, the solution was converted to the chloride form. The solution was then diluted to 1 M HCl and the insoluble substance was filtered off. The procedure after that was the same as that for biological samples. Because geological samples usually contain large amounts of Fe, however, repeating coprecipitation was recommended.

²¹⁰Pb determination

The Pb fraction was stored for 3–6 months to grow ²¹⁰Po from ²¹⁰Pb decay in the solution. After the Pb fraction was stored, a ²⁰⁸Po tracer was re-spiked to the Pb fraction to repeat Po separation with the resin column and plating. The stable Pb concentration in the fraction was determined by an ICP-AES for calculation of Pb recovery. The recovery of ²¹⁰Pb was corrected based on the stable Pb content in the sample. The ²¹⁰Pb concentration was calculated from the ²¹⁰Po produced from ²¹⁰Pb decay using Bateman's equation.⁹

Results and Discussion

Weight distribution coefficients and elution behavior

The measured D_w values given in Figs. 1 and 2. The D_w values are plotted against the concentration of HCl and HNO₃, respectively. As can be seen in Figs. 1 and 2, the D_w value of Pb(II) decreases along with an increase in the HCl molarity, but Pb(II) is strongly adsorbed in the HNO₃ solution, because of a strong affinity of 18-crown-6 derivatives for the Pb(II) ion.¹⁰

Fe(III) and Po(IV) show a similar behavior. Both were strongly adsorbed on the resin in a HCl solution,

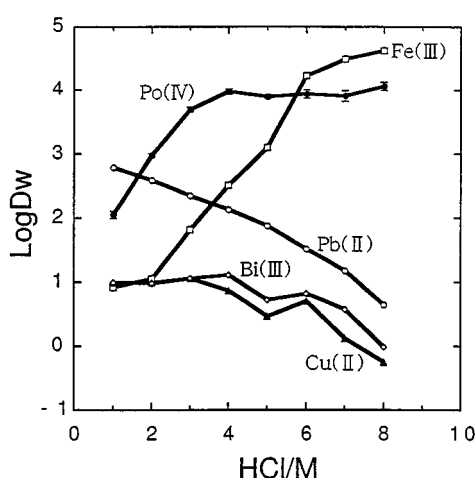


Fig. 1 Weight distribution coefficients of Fe(III), Cu(II), Pb(II), Bi(III) and Po(IV) between the extraction chromatographic resin and HCl solution as a function of molarity. Resin, Eichrom Sr.SpecTM; Particle size, 100 - 150 μ m; [Fe]=225 μ M; [Cu]=216 μ M; [Pb]=63.5 μ M; [Bi]=61.2 μ M; activity of ²⁰⁸Po=0.6 Bq.

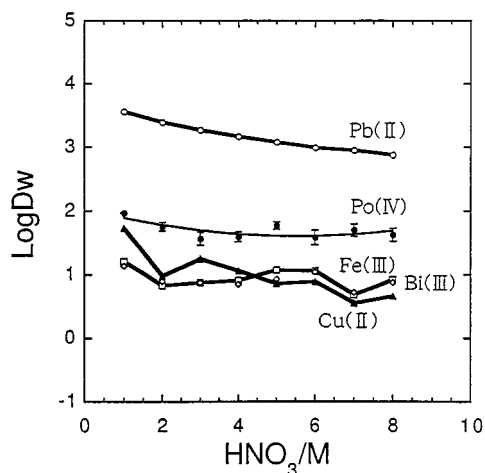


Fig. 2 Weight distribution coefficients of Fe(III), Cu(II), Pb(II), Bi(III) and Po(IV) between the extraction chromatographic resin and HNO₃ solution as a function of molarity. Resin, Eichrom Sr.SpecTM; particle size, 100 - 150 μ m; [Fe]=225 μ M; [Cu]=216 μ M; [Pb]=63.5 μ M; [Bi]=61.2 μ M; activity of ²⁰⁸Po=0.6 Bq.

and were weakly adsorbed on the resin in a HNO₃ solution. Watari *et al.* have discussed the strong affinity of the Fe(III) ion to Amberlite XAD-7TM in a HCl solution, and inferred a hydrophobic interaction between the FeCl₄⁻ complex and the XAD-7TM resin.¹¹ Honjo described that chloride complexes of Fe(III), Au(III), Sb(III) and Ga(III) were extracted with crown ethers.¹⁰ It is considered that these interactions can be related to the strong affinity of the Fe(III) ion to Sr.SpecTM resin. It can be presumed that the adsorption mechanism of Po(IV) is the same as that of Fe(III) based on the adsorption behavior of Po(IV) and the large stability constant of PoCl₆²⁻ ($\beta_{ML}=10^{14}$).²

The adsorptions of Cu(II) and Bi(III) were weak at any concentration of HCl and HNO₃. These results suggest that these elements could be separated by the Sr.SpecTM resin column.

The elution behaviors of Po, Bi, Cu, Fe and Pb from the Sr.SpecTM resin column are presented in Fig. 3. Under the present condition, Pb and Po were successfully separated from other elements. Furthermore, these elements were recovered quantitatively in this procedure. The recovery of Pb was 101 \pm 3% and that of Po was 95 \pm 2%.

Plating conditions

The effect of the plating conditions on the recovery of Po is shown in Fig. 4. Polonium plated out quantitatively on a stainless-steel disk by electrodeposition with a reductant. The yield was about 70% at 1 h and approached 100% at 2 h. In the spontaneous deposition method, however, the yield increased along with the plating time up to around 4 h; afterward it reached a constant value of 75%. A very low yield was noticed in the electrodeposition procedure without any reductant on a stainless-steel disk.

In this study, therefore, the plating was carried out for 2.5 h at a current density of 20 mA/cm² in 0.5 M HCl

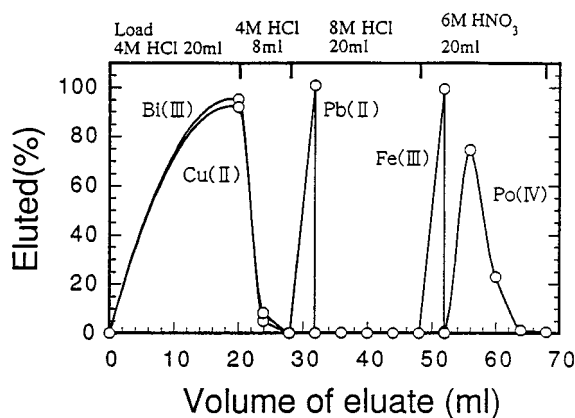


Fig. 3 Elution behaviors of Fe, Cu, Bi, Pb and Po with the extraction chromatographic resin column. Resin, Eichrom Sr.SpecTM; particle size, 100 - 150 μ m; column, 0.79 cm i.d. \times 4.0 cm; amount of Fe=3.6 μ mol; amount of Cu=160 μ mol; amount of Pb=46 μ mol; amount of Bi=98 μ mol; activity of ²⁰⁸Po=0.15 Bq.

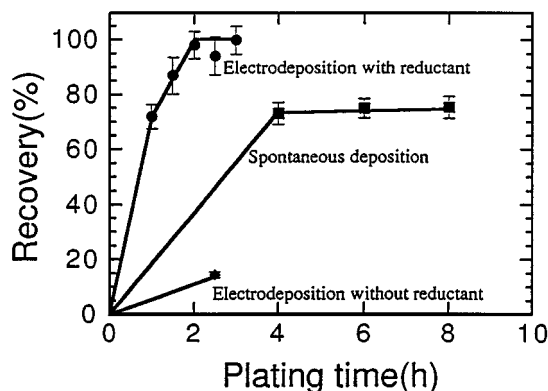


Fig. 4 Effect of the plating conditions on the recoveries of polonium. (●) electrodeposition on SUS-304 disk in 0.5 M HCl with reductant; concentration of ascorbic acid, 60 mM; temperature, 85°C; (◆) electrodeposition on SUS-304 disk in 0.5 M HCl; temperature, 25°C; (■) spontaneous deposition on Ni disk in 0.5 M HCl; concentration of ascorbic acid, 60 mM; temperature, 85°C.

containing ascorbic acid.

Coprecipitation

The coprecipitation behavior with CuS is shown in Fig. 5. Polonium and Bi were coprecipitated with CuS at pH 1 to 5.5. Above pH 4.0, Pb was coprecipitated just as Po and Bi. The contamination of Fe(III) ion was eliminated by the presence of ascorbic acid as a reductant. Furthermore, it was confirmed that U and Th were not coprecipitated. In this study, Pb, Bi and Po were collected simultaneously with CuS at pH 4.0 to 5.5.

Loss of Po in sample preparation by ashing

It has been well known that Po is a volatile element.^{2,3} The effect of the ashing temperature on the loss of Po was examined using freeze-dried viscera of shellfish (*Batillus cornutus*) samples. The samples in porcelain dishes were heated in an electric furnace at 100°C for 12 h, 450°C for 12 h and 600°C for 12 h. Lost(%) of Po was calculated using:

$$\text{lost(\%)} = \frac{C_1 - C_2}{C_1} \times 100,$$

where C_1 and C_2 mean the Po concentration in the freeze-dried sample and the heated samples, respectively. The results are shown in Fig. 6. The loss of Po was observed to increase along with the increase in temperature, and Po was completely lost at 600°C. These findings agreed with those of earlier works, and it is thought that the products of sublimation in air are probably the dioxide.^{3,12} Based on the present results, we selected the freeze-dried methods for the biological sample preparation and heating method at 40°C for 12 h for soil, ore and sediment sample preparation.

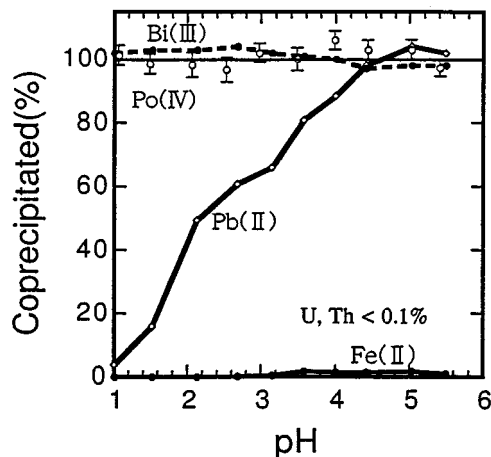


Fig. 5 Effect of pH on the recoveries of Po, Bi, Pb in the CuS coprecipitation procedure. [Pb]=15.0 μM; [Bi]=4.89 μM; [Cu]=1.72 mM; [Fe]=18.0 mM; [Th]=3.64 μM; [U]=4.38 μM; activity of ²⁰⁸Po=0.60 Bq; [CH₃CSNH₂]=133 mM.

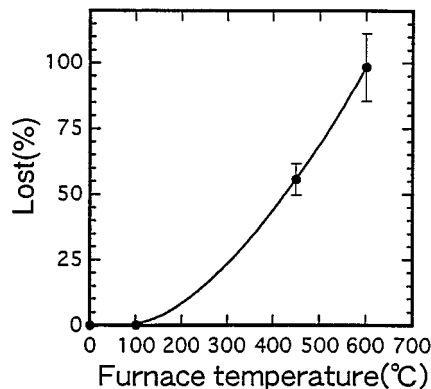


Fig. 6 Effect of the furnace temperature on the losses of polonium.

Applications

Standard reference materials were analyzed in order to examine the reproducibility and accuracy of the present method. The results are given in Table 1. In standard reference material more than two years old, ²¹⁰Po was in secular equilibrium with ²¹⁰Pb, having approximately equal activities. Therefore, the determined values of ²¹⁰Po in the standard reference materials were compared with their recommended value of ²¹⁰Pb.

The mean value of ²¹⁰Po for NIST-4354 is 124 Bq/kg, which is in good agreement with the recommended value (120 Bq/kg).

The mean value for IAEA-135 in this work was 75 Bq/kg, which is 50% higher than the recommended value (average; 49±17 Bq/kg), but is comparable to the value (72 and 68 Bq/kg) reported by Vajda *et al.*⁴

The value for IAEA-326 is in good agreement with the recommended value. The value for IAEA-368 is 31 Bq/kg, which is higher than the recommended value (median; 23.2 Bq/kg), but is in the range of the reported values (10 - 37 Bq/kg).

We also applied the method to biological samples.

Table 1 Analytical results of ^{210}Po in standard reference materials

Sample	Weight/ g	^{210}Po Bq/kg $\pm \sigma^a$	^{208}Po yield, %	Recommended value $^{210}\text{Pb}^d$ Bq/kg
NIST-4354 (Freshwater lake sediment)	0.547 0.548	127 \pm 4.4 121 \pm 4.5 [mean 124 \pm 4.2 ^c]	56 63	120 15 – 80 ^b (average 49 \pm 17)
IAEA-135 (Irish sea sediment)	0.964 0.998	71 \pm 3.9 78 \pm 4.4 [mean 75 \pm 4.9 ^c]	56 65	1.7 – 81 ^b (average 45.6 \pm 17)
IAEA-326 (Kursk black soil)	2.13	51 \pm 1.6	82	10 – 37 ^b (median 23.2)
IAEA-368 (Pacific ocean sediment)	5.51	31 \pm 0.9	91	

a. Propagated counting statistics. b. Reported data range. c. Standard deviation. d. ^{210}Po was in secular equilibrium with ^{210}Pb in standard reference material. Therefore, the determined values of ^{210}Po are compared with their recommended value of ^{210}Pb .

Table 2 Analytical results of ^{210}Pb and ^{210}Po in biological samples

Sample	Tissue of organ	^{210}Pb Bq/kg $\pm \sigma^a$	Pb yield, %	^{210}Po Bq/kg $\pm \sigma^a$	^{208}Po yield, %	$^{210}\text{Po}/^{210}\text{Pb}$
Shellfish (<i>Batillus cornutus</i>)	muscle	1.5 \pm 0.2	95	7.7 \pm 0.2	91	5
Seaweed (<i>Gelidium amansii</i>)	whole body	—	—	9.2 \pm 0.4 10.3 \pm 0.4 9.5 \pm 0.4 9.6 \pm 0.4 [mean 9.7 \pm 0.5 ^b]	99 92 95 94	

a. Propagated counting error. b. Standard deviation.

The results are given in Table 2. ^{210}Po was in secular equilibrium with ^{210}Pb in a seaweed sample, because it was more than two years old. The concentration of ^{210}Pb was lower than that of ^{210}Po , and the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio was 5 in a shellfish sample. According to Yamamoto *et al.*⁹, the ratio of $^{210}\text{Po}/^{210}\text{Pb}$ ranges from 3 to 55 in the muscle of Japanese shellfish. The mean value for a seaweed sample is 9.7 ± 0.5 Bq/kg, which is comparable with the literature value.⁹

The chemical yield of Po ranged from 56 to 99% and that of Pb was 95%. However, the difference in the yield of Po between sediments and biological samples was observed. It is thought that the low chemical yield of Po in sediment is presumably because of the loss of Po by its volatility at the sample decomposition.

In conclusion, the extraction chromatographic resin was useful for Pb and Po separation. The resin shows a high D_w value of Po in a HCl solution, and Po was readily eluted by a HNO₃ solution. The analytical results of the standard reference materials agreed with their recommended values. The chemical yield of Po ranged from 56 to 99% and the yield of Pb was 95%. The detection limits of ^{210}Pb and ^{210}Po were 0.6

mBq/sample based on three-times the counting statistics at a counting time of 70000 s.

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