Improvements on the method for determining of 210Pb and 210Po in lead

Improvements on the method for determining of ^{210}Pb and ^{210}Po in lead

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Abstract

An improved method is proposed to determine the content of ^{210}Pb in lead using ^{210}Po measured by alpha-ray spectrometry. This improved method, which is based on radiochemical separation by DDTC-toluene extraction, employs EDTA and citrate as masking reagents for the lead ions. To selectively extract polonium from an alkaline solution, the pH dependency was examined using a liquid scintillation counting method. And pH 9 was chosen as an extraction condition. Then ^{210}Po was electrodeposited on a stainless steel disk, and the chemical recovery was followed by ^{209}Po tracer. The effectiveness of the new method was validated by the agreement with the analytical results from five samples as determined by gamma-ray spectrometry.

Keywords: ^{210}Pb; ^{210}Po; ^{209}Po; DDTC extraction; EDTA masking; Electrodeposition ; Alpha-spectrometry; Eco-friendly

1. Introduction

For low-level radioactivity measurements, lead materials are commonly used to shield detectors from environmental gamma and cosmic rays. However, lead generally contains ^{210}Pb ($T_{1/2}$=22.3 y) and its progeny nuclides (Table 1), ^{210}Bi ($T_{1/2}$=5.01 d) and ^{210}Po ($T_{1/2}$=138.4 d). When lead with a high content of ^{210}Pb is used as a shielding material for a gamma-ray detector, the background spectrum exhibits bremsstrahlung in the energy region below 500 keV mainly due to beta-rays from ^{210}Bi and lead X-rays. To measure low-level radioactivity with a Ge detector, for example, lead material with low ^{210}Pb content is necessary.

Several studies have reported the ^{210}Pb concentration in lead materials. We measured the ^{210}Pb concentration in 14 lead materials, and found a concentration range of 0.06-11 Bq/g.[1] Additionally, Weller et al., De Boeck et al. and Inoue et al. have reported the radioactivity of ^{210}Pb in lead.[2-4] Several methods have been adopted to measure ^{210}Pb according to the type of radiation: gamma-rays (46 keV) from ^{210}Pb,[2,4] beta-rays (1.162 MeV) from ^{210}Bi, [1,5] and alpha-rays (5.304 MeV) from ^{210}Po.[3,5]

Table 1

From the viewpoints of simplicity, determination limits, accuracy, and availability of reference materials, each method has merits and demerits. Although gamma-ray spectrometry does not require chemical separation before a measurement, a significant sample amount, at least 100-300 g, is required. Additionally, reference materials for gamma-ray measurements are difficult to obtain, and if a lead reference is unavailable,

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then self-absorption compensation must be calculated because the energy of the emitted gamma-rays from ^{210}Pb is low. In contrast, the ^{210}Pb concentration can be evaluated with as little as a 10 g sample using beta-rays to measure ^{210}Bi, but chemical separation is required. This method poses several problems such as producing significant amounts of toxic lead solution, and an appropriate tracer for chemical recovery correction of ^{210}Bi is not produced. Hence, measuring ^{210}Po by alpha-spectrometry after chemical isolation is attractive because of its high sensitivity due to the low background of an alpha-ray spectrometer. Several researchers have reported methods to separate polonium from lead, bismuth or iron in an acid solution.[6,7,9] The DDTC (diethyldithiocarbamate) extraction method is also applicable to ^{210}Po extraction as a simple method.

The DDTC extraction method is rapid, convenient, and economical. DDTC is a common chelating agent used to form numerous metal ions. [8] Typically, DDTC extraction is performed using carbon tetrachloride, but carbon tetrachloride has a high biological toxicity and is a causative agent of ozone depletion and global warming [WHO: Environmental Health Criteria No.208 (1999)].[10] Therefore we considered to substitute toluene for carbon tetrachloride as a extraction solvent. Although toluene is a little more water-soluble than carbon tetrachloride, it has a low toxicity and is usable as a scintillator.

The stability of the complex varies with pH when employing a chelating reagent like DDTC. With an improvement in this study we tried

to extract polonium from an alkaline solution, because DDTC readily decomposes in an acid solution. This new method has not apparently been used before for separation of polonium from lead. Similarly, a study of separation performance to be influenced by the coexistence ion and/or a study of pH dependency on the presence of a masking reagent has not yet been conducted. In addition, the volatility of the polonium organic complex while heating has been reported by Mabuch.[15-17] Hence, we examined the volatilization loss of a polonium DDTC complex, followed by increasing the temperature.

For alpha-ray spectrometry, plating of ^{210}Po is necessary, and two methods are used: spontaneous deposition and electrodeposition. Silver plating is generally used in spontaneous deposition.[3,5,6,9,14] However, this method has several drawbacks: it is time-consuming, the temperature of the electrolytic solution must be controlled, and the deposition yield is unstable. We initially tried direct polonium deposition from a 0.5 M HNO$_3$ solution of lead containing ascorbic acid onto a silver disk without chemical separation. As a result the chemical recovery was only about 50%. In contrast, the electrodeposition method enforces to deposit the metal ion from solution onto a stainless plate. By this method an improvement of deposition yield is expected. Therefore, we also examined electrodeposition methods[11-13] in terms of the current applied to as well as duration of electrolysis.

2 Experimental

2.1 Samples

^{210}Po samples (A, B, and C) were produced within the last ten years. Sample D was more than a decade old, whereas E, which was used as a roofing tile on Kanazawa Castle, was at least a century old. Among these samples and sample F, which had a high concentration of ^{210}Pb, concentration analyses of ^{210}Po and ^{210}Bi with DDTC were performed. Additionally, the concentrations of ^{210}Pb in samples (A, B, C, D, and E) were determined by gamma-ray spectrometry.

Lead (0.1-1.0 g) was rinsed with 10 mL 2 M HNO$_3$, rinsed with water, dried, and weighed precisely. It was then transferred to a 100 mL conical beaker, dissolved in 20 mL of 2 M HNO$_3$ on a hot plate, and if the residue of lead remained then HNO$_3$ (65%) was added. The lead solution was transferred to a measuring flask and diluted 10-20 mg/mL with water.

2.2 Reagents

^{209}Po tracer solution: A 5 M HNO$_3$ solution with approximately 37 kBq of ^{209}Po (ORNL, USA) was diluted stepwise with 3 M HCl to prepare a stock solution of 30.6 mBq/mL ^{209}Po. The concentration of ^{209}Po in the stock solution was calibrated by a ^{241}Am standard solution (LMRI, France). Bismuth carrier solution (1 µg/mL): Bismuth metal was dissolved in 2 M HNO$_3$, which was subsequently diluted stepwise with 0.1 M HNO$_3$ to 1 µg/mL. Scintillators: PPO (4 g) and POPOP (0.1 g) were dissolved in

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1 L of toluene. Diethyldithiocarbamate (DDTC) solution (1% aqueous solution), EDTANa$_2$ -2H$_2$O solution (10% aqueous solution), ammonium citrate solution (1% aqueous solution) and all reagents were analytical or extra pure grade. Deionized water was prepared by Milli-Q system and was used for all dilutions.

2.3 Chemical separation of polonium

The lead sample solution (1 mL) was placed in a 15 mL centrifuge tube. ^{209}Po tracer solution (30.6 mBq) and bismuth carrier (1μg) were added and thoroughly mixed. Then 2 mL (50 mg equivalent) of EDTA-2Na (10%) solution and 1 mL (10 mg equivalent) of ammonium citrate (1%) solution were added. Then the pH was adjusted to an alkaline solution (pH 9) using ammonia water (28%). Lead and metal ions formed EDTA and citric complexes, which were dissolved in water so that they were masked from extraction, respectively. Then 0.1 mL DDTC (1%) solution and 4 mL toluene were added to the centrifugation tube. After shaking for 1 min, polonium and bismuth were extracted into the organic solvent. The mixture was allowed to stand 1 min. Then the aqueous and the organic layer were rapidly separated. Layer separation was ensured with 5 min centrifugation at 2000 rpm.

At this point, Pb^{2+}, Fe^{3+}, UO_2^{2+}, Th^{4+}, and Ra^{2+} remained in the aqueous phase as the EDTA or citrate complex. The organic phase was transferred to a 20 mL beaker with a pipette. New toluene (1 mL) was

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added to the aqueous phase, and it was washed by shaking. Then the toluene was combined with the extracted organic solvent, and evaporated at 70 ± 10 °C on a hot plate. Continuously the organic substance was decomposed at 120 ± 10 °C by adding 1 mL HNO_3 (65%) and several drops of H_2O_2 (30%) to the beaker.

2.4 Plating (Electrodeposition)

Electrodeposition was achieved using a conventional cell consisting of a Teflon cylinder (20 mm ID, 80 mm tall), platinum anode, and stainless steel disk cathode (24 mm diameter and 0.3 mm thick). This cell is the same as the one used in plutonium or uranium analysis. The distance between the anode and the cathode was 5 mm. An electrolytic solution was prepared by dissolving the extracted substance with 3 mL 0.5 M HCl. The electrolytic solution was then transferred to the electrolysis cell, and 1 mL saturated ascorbic acid was added. The inside of the beaker was washed with 1 mL water, and then the water added to the cell. Electrolysis lasted for 2 h at 0.2 A. After 2 h, 1 mL ammonia water (28%) was added to the cell to terminate electrodeposition. The sample disk was washed with water and acetone. Because polonium is volatile, the sample disk was dried at room temperature without additional heat.

In this experiment, an electrolytic solution (0.5 M HCl) containing ^{209}Po tracer (30.6 mBq) was prepared and ascorbic acid was added. Electrodeposition was carried out with the current ranging from 0.1 A to

0.2 A and a duration of 10-120 min.

2.5 Measurements

Alpha-spectrometry was carried out using a silicon surface barrier detector (450 mm^2) connected to an EG&G ORTE SOLOST alpha-spectrometer. The distance between source and detector was 5 mm. The efficiency of alpha-spectrometer was a solid angle of 25% (of 4π).

In this study, each half-life of ^{209}Po and ^{210}Po was sufficiently long so that the effect of the decay on the analytical results was insignificant, and was therefore ignored. Blanks and standards were measured to verify the performance of all aspects of the procedures and instrumentation.

Liquid scintillation counting was carried out using a 25 mL vial. Total alpha and beta-ray counts were measured by Aloka LB-Ⅱ low background liquid scintillation counter on P-channel (100-2000 keV).

2.6 Examination of DDTC extraction

To examine the pH dependency of the polonium extraction, radioactivity of organic phase (toluene scintillator) was measured with a liquid scintillation counter. A lead sample F (36 mg) with high ^{210}Po content was used for this experiment. Each aliquot of the aqueous solution of the lead sample was placed into a 25 mL vial with EDTA, citrate, and DDTC. The volume of the aqueous solution was adjusted to 10 mL with water, and ammonia water (28%) was used to adjust the pH from 6.5 to

12.5 while monitoring with a pH meter. Metal ions in this sample solution did not form a hydroxide precipitate in the examined pH range in the presence of EDTA and citrate. Next, 10 mL toluene scintillator was added to the vial, and then the vial was capped. After shaking for 1 min, [210]Bi and [210]Po were extracted to the scintillator. The radioactivity of the vial was measured for 300 min (60 min x 5 times) using a liquid scintillation counter.

Mixing was again performed after the vial stood for nine days, and the newly generated [210]Bi and [210]Po were extracted from the aqueous layer. The change in the count rate was observed. This showed an obvious change in pH, so the organic layer was transferred to another vial, a new scintillator was added, and then the radioactivity was measured.

2.7 Examination of evaporation loss

After extraction of [210]Po to toluene from the lead sample B solution, the organic solution was divided into eight 20 mL beakers. Each organic solution evaporated at 70 ± 10 °C on a hot plate. Then the temperature of the hot plate was increased stepwise to 120 ± 10 °C and 135 ± 5 °C. After heating, the organic residue was decomposed with nitric acid and hydrogen peroxide. Then 30.6 mBq of [209]Po tracer was added to each beaker and digested with 3 mL 0.5 M HCl. After adding 1 mL of saturated ascorbic acid solution, electrodeposition was carried out, and the activities of [210]Po and [209]Po were measured by alpha-spectrometer. The

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volatilization loss of ^{210}Po activity was evaluated after correcting for electrodeposition loss by ^{209}Po recovery.

3. Results and discussion

3.1 DDTC solvent extraction

To extract low concentrations of ^{210}Po from a solution with a high concentration of lead ions, the pH dependency of the masking effects of EDTA and citrate were examined. Figure 1 shows the extraction results. The count rate is calculated from the gross counts of ^{210}Po alpha-rays and ^{210}Bi beta-rays by scintillation counting. The count rate of ^{210}Po and ^{210}Bi extracted at pH 6-10 remained nearly constant, and nuclides were quantitatively extracted. However, the count rate at pH 6-7 declined slightly during the measurement. We initially speculated that this decline was due to a quenching effect. Thus, re-extraction was attempted after nine days. Although both the original and re-extracted samples exhibited similar count rates in the pH region of 8-10, the decline in the counting rate was more pronounced in the acidic region of pH 6-7; nevertheless total activity in a vial was not changed.

Fig. 1

Hence, to examine the cause of this phenomenon, the organic phase was transferred to another scintillation vial, and the variation in the radioactivity was observed. Figure 2 shows the results. At pH 8-10, the count rate decreased with a half-life of five days beginning on the tenth measurement day, but the count rate remained constant at pH 6-7 or above

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pH 11, and the counting rates at all levels of pH eventually reached a steady value. This suggests that ^{210}Bi radioactivity influences the variation of the counting rate. The remaining radioactivity was then counted as ^{210}Po alpha-rays, which was confirmed by the half-life and scintillation spectrum. Thus, polonium was quantitatively extracted throughout the examined pH regions from 6.5 to 12, and the polonium complex is highly stable in organic solvent.

On the other hand, bismuth at pH 8-10 formed a stable complex that is extracted by the organic layer, although this complex appeared unstable at other pH levels. In particular, it is believed that the DDTC-Bi complex forms in an acidic state; however, this may be due to the influence of DDTC ligand decomposition by acid. In addition, in an alkaline state, formation of another chemical species such as hydroxide may affect extraction. Thus, the optimal condition is pH 9 to extract ^{210}Bi and ^{210}Po in an alkaline environment considering the quantitative extraction and stability of DDTC. Adjusting the pH 9 by ammonia water (28%) is easy due to the buffering action of citrate ammonium. In an actual extractive separation, pH control was carried out by turning red of phenolphthalein at pH 8.3-10.

Fig. 2

3.2 Extraction solvent

Table 2 compares the analytical results of using toluene and carbon tetrachloride as extraction solvents. Although the sample mass varied from

18 to 110 mg, separation of the organic (toluene) and aqueous phases went smoothly; we did not encounter problems such as reduction of the organic phase volume due to dissolution or emulsion formation. In addition, the coefficient of variation concerning the analytical results was <5 %. The experimental error should be <5 %, and if radioactivity counting error is taken into consideration, we believe that a single analysis can provide sufficient evaluation.

Table 2

3.3 Evaporation of polonium (DDTC complex salt)

Table 3 shows the results along with Mabuchi's experimental result. According to Mabuchi, volatilization losses appeared when the DDTC-Po complex was heated above 100 °C for 15-30 min. However, in our study the DDTC-Po complex did not volatilize even at 135 ± 5 °C for 100 min. This difference is probably due to the small amount of ammonium salt dissolved in toluene. Although volatilization did not occur, for safety reasons, evaporation should be carried out at 80 °C to decrease the risk of fire by igniting toluene.

Table 3

3.4 Plating (Electrodeposition)

Figure 3 shows the time variation of the electrodeposition yield. Increasing the current from 0.1 A to 0.2 A realized an increased deposition in a shorter time. And electrodeposition was completed in 2 h at room temperature. In conclusion, 0.2 A for 2 h at room temperature provides

satisfactory deposition results. A special mixing apparatus and a heat controlling device are unnecessary.

In this method most of coexisting elements (except bismuth) are removed by DDTC solvent extraction. Although bismuth is deposited, only the ^{210}Po alpha-rays are detected on the sample disk, and the ^{210}Bi beta-rays do not influence the measurement. Figure 4 shows the measured alpha-spectrum, and interference nuclide peaks are not observed.

The deposition yield in a tracer experiment indicates at least 90% polonium deposition. However, chemical recovery of actual samples fluctuated between 64-99% (see Tables 2 and 4). Although the cause of fluctuation is unclear, it is likely due to electrodeposition, rather than extraction, because the DDTC solvent gave a quantitative extract and the DDTC-Po complex did not suffer from evaporation loss.

3.5 Measurement and analytical precision

In the electrodeposition method discussed above, ^{210}Bi was simultaneously extracted with ^{210}Po, and both nuclides were deposited on a stainless steel disk. Because ^{210}Pb and ^{210}Po are at radioactive equilibrium within the sample, the measured radioactivity of ^{210}Po, ^{210}Bi, and ^{210}Pb is identical before chemical separation. The measured radioactivity of the sample on the disk is obviously from ^{210}Po and ^{210}Bi. Because ^{210}Bi is always decaying to ^{210}Po, this decay must be reflected in

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the analytical results in accordance with the duration of decay.

As the radioactivity of each nuclide (A_0) is in radioactive equilibrium immediately after extraction separation, on t days after extraction separation the radioactivity of ^{210}Po in the measurement sample varies in accordance with eq. 1:

$$A_{Po} = \frac{\lambda_{Po}}{\lambda_{Po} - \lambda_{Bi}} A_{0Bi}\left(e^{-\lambda_{Bi}t} - e^{-\lambda_{Po}t}\right) + A_{0Po}e^{-\lambda_{Po}t} \quad \text{- - (1)}$$

where λ_{Bi} and λ_{Po} are the decay constants of ^{210}Bi and ^{210}Po, respectively. At the time of extraction, the separated activity of ^{210}Bi (A_{0Bi}) is equal to that of ^{210}Po (A_{0Po}). When ^{210}Po radioactivity is calculated as a function of $t \leq 7$, the decrease in ^{210}Po is $< 1\%$. Therefore, in experiments lasting less than a week a decay correction is unnecessary.

Given that lead is a decay product of uranium or thorium, the lead content of long half-life radioactive elements from the uranium and thorium series is another problem. However, in gamma-ray background spectra produced using lead shields, the existence of uranium or thorium peaks has not been reported.[1,4] In addition, as reported previously,[1] the activity concentrations of ^{238}U, ^{232}Th, and ^{226}Ra in lead are $< 0.2/1.0/2.0$ mBq/g, respectively, which is 1/1000 or less radioactivity compared to ^{210}Pb. According to the above observations, it is reasonable to ignore other radioactivity sources except for ^{210}Pb sources when inspecting lead objects. In addition, α-ray spectrum and radioactive decay of the sample showed perfect a separation of polonium from lead.

Table 4 shows the results of lead sample ^{210}Po analysis using this improved method as well as the gamma-ray spectrometry results of the lead samples. Chemical recovery, reproducibility, and precision using this method are satisfactory: evaluated samples had counting errors < 5% and average chemical recovery > 75%.

The MDA (minimum detectable activity) of ^{210}Po in lead was 3 mBq/g with a sample size of 0.01 g lead and with a measurement time of 80,000 sec. The total analysis time was 6 h, which included the time from the sample dissolution to the electrodeposition. Incidentally, when ^{210}Pb has a low concentration, the sample weight must be increased; this is achieved by increasing the proportion of EDTA and extending measurement time.

4. Conclusion

An improved method was established for the determination of ^{210}Pb in lead shield, based on the ^{210}Po measurement. A simple, rapid and eco-friendly radiochemical procedure was accomplished for the isolation of ^{210}Po.

This method realized a scale down of sample size from 100 g to 0.01 g comparing γ-ray spectrometry with alpha-spectrometry. There is a good agreement between the analytical results obtained by two methods. And furthermore the new method shows a very good reproducibility.

It was confirmed that the polonium DDTC complex was selectively

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extracted (using EDTA and citrate as masking reagents) into the toluene from an alkaline solution (pH 9), leaving lead. Employing toluene as the extract solvent instead of carbon tetrachloride will contribute to the safety of human and natural environment.

Chemical recovery was improved to 75% (average) up from 50% of spontaneous deposition method. Electrodeposition was a more effective method than spontaneous deposition. The deposition conditions for polonium found to be optimal in this study were 5 mL of 0.5 M HCl solution, 0.2 A (64 mA/cm^2), room temperature and 120 minutes of deposition time.

Hence, this quantitative method is quick, accurate, safe, eco-friendly and economical, and is applicable to analyze environmental samples such as water, sediment, bio-materials as well as a variety of electronic components that may contain ^{210}Pb (^{210}Bi and ^{210}Po).

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Fig. 1　　Variation of the gross counts for extracted ^{210}Po(α) and ^{210}Bi(β)

　　with pH

Fig. 2　　Time variation of the gross counts for nuclides in the organic

　　　　layer after DDTC extraction with pH

Fig. 3　Deposition yield of polonium as a function of time with different

　　　　electrolysis current

Fig. 4　Example of an alpha-ray spectrum of ^{209}Po and ^{210}Po by DDTC

　　　　extraction from lead

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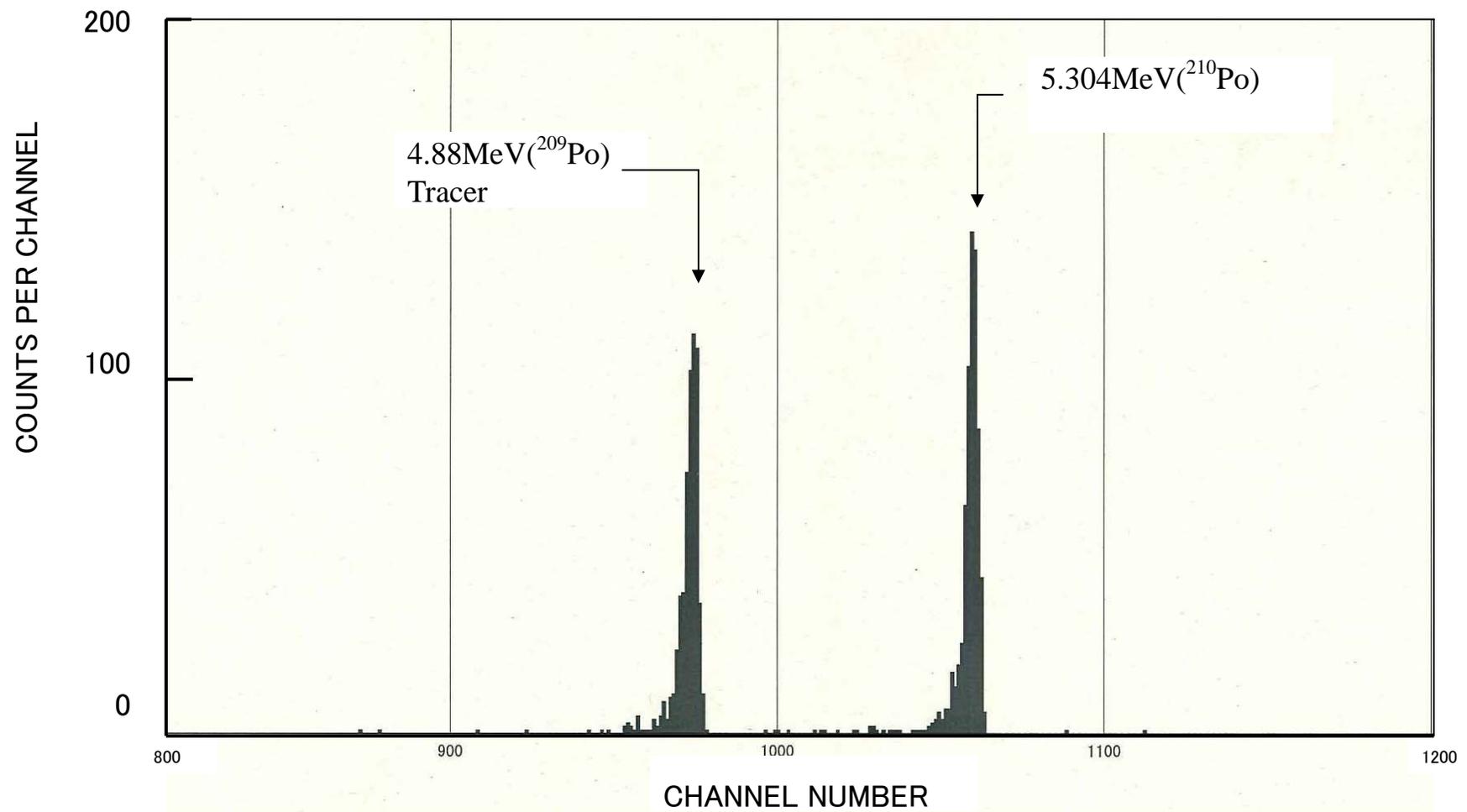
Fig. 4   Example of an alpha-ray spectrum of ^{209}Po and ^{210}Po by DDTC extraction from lead
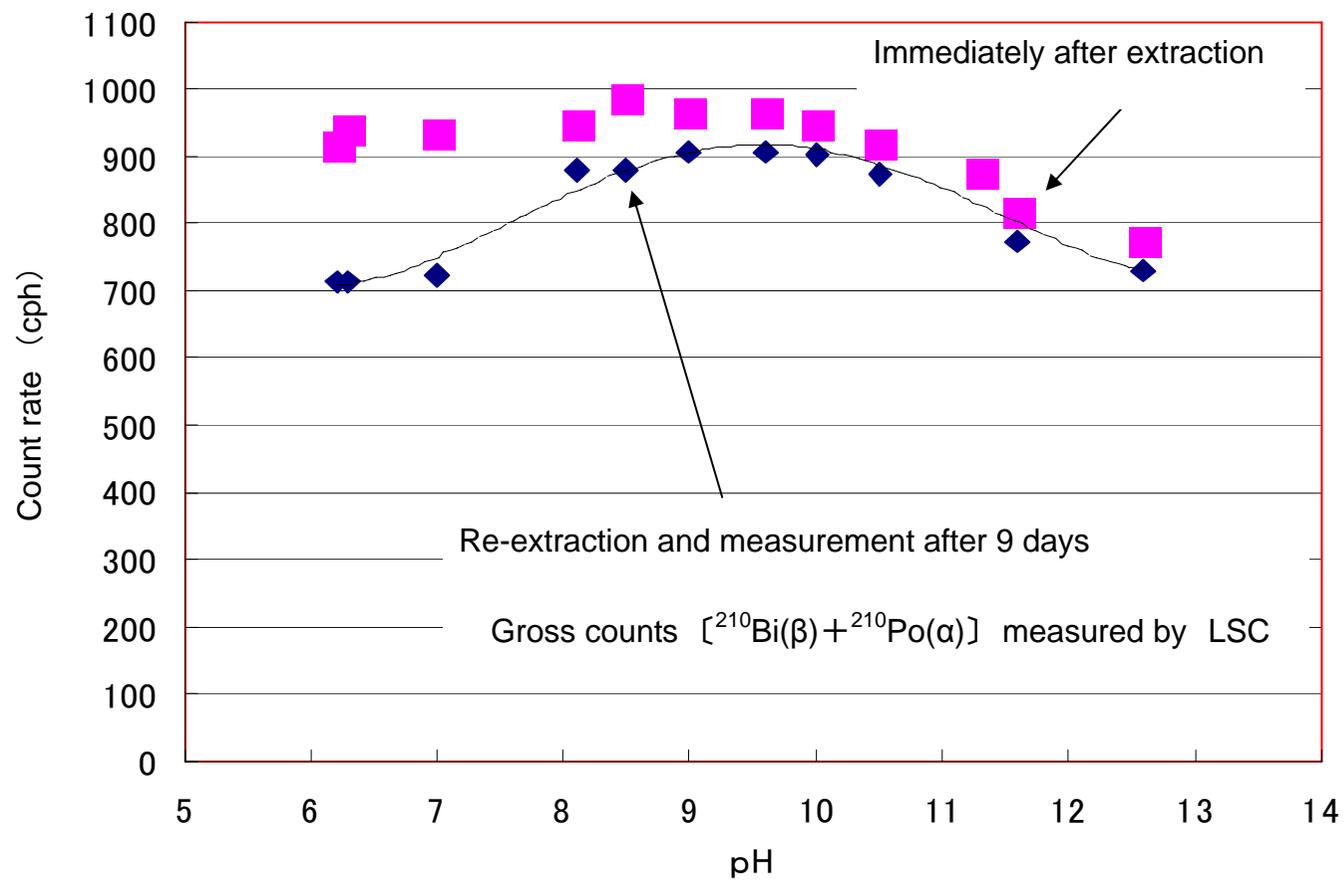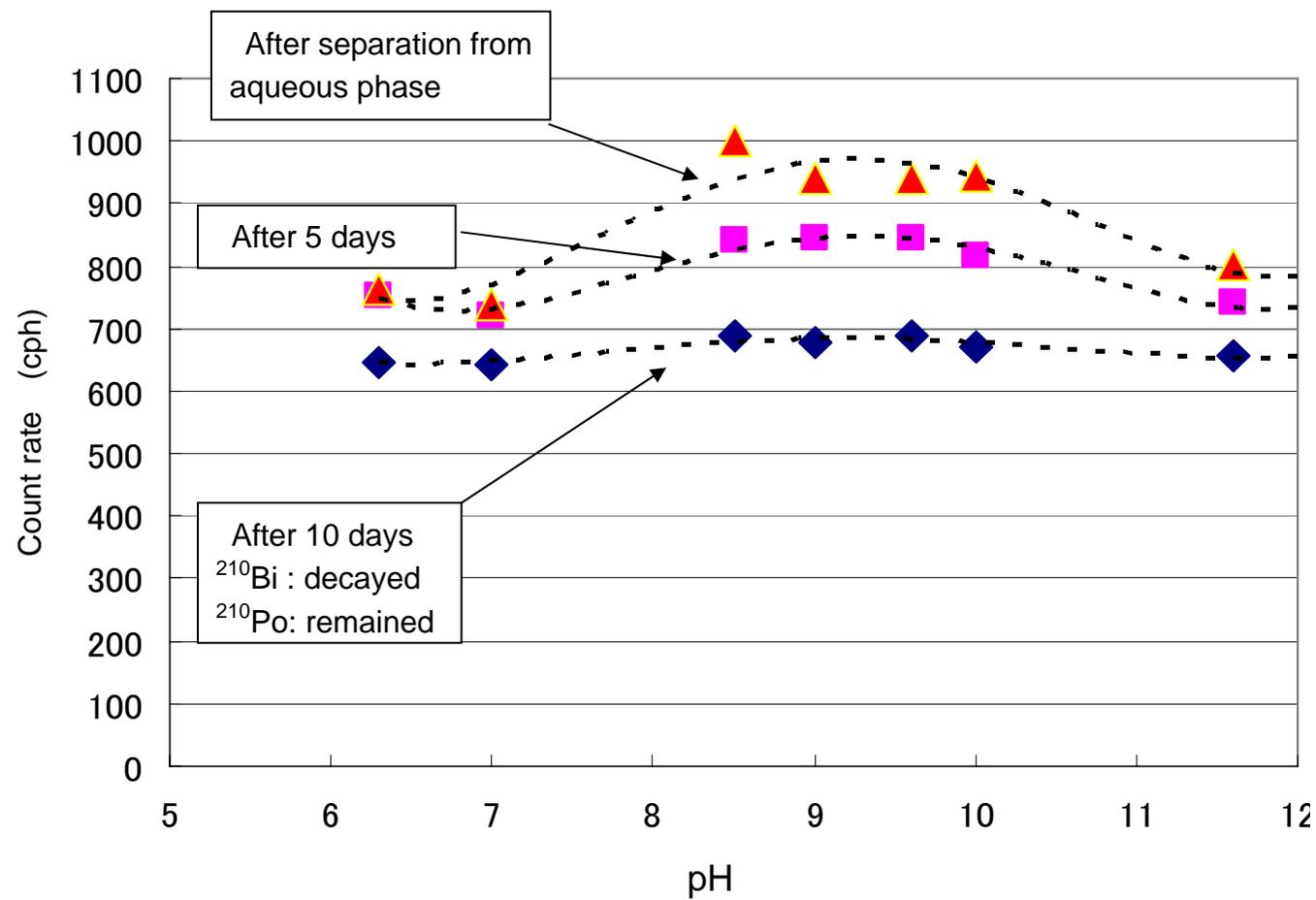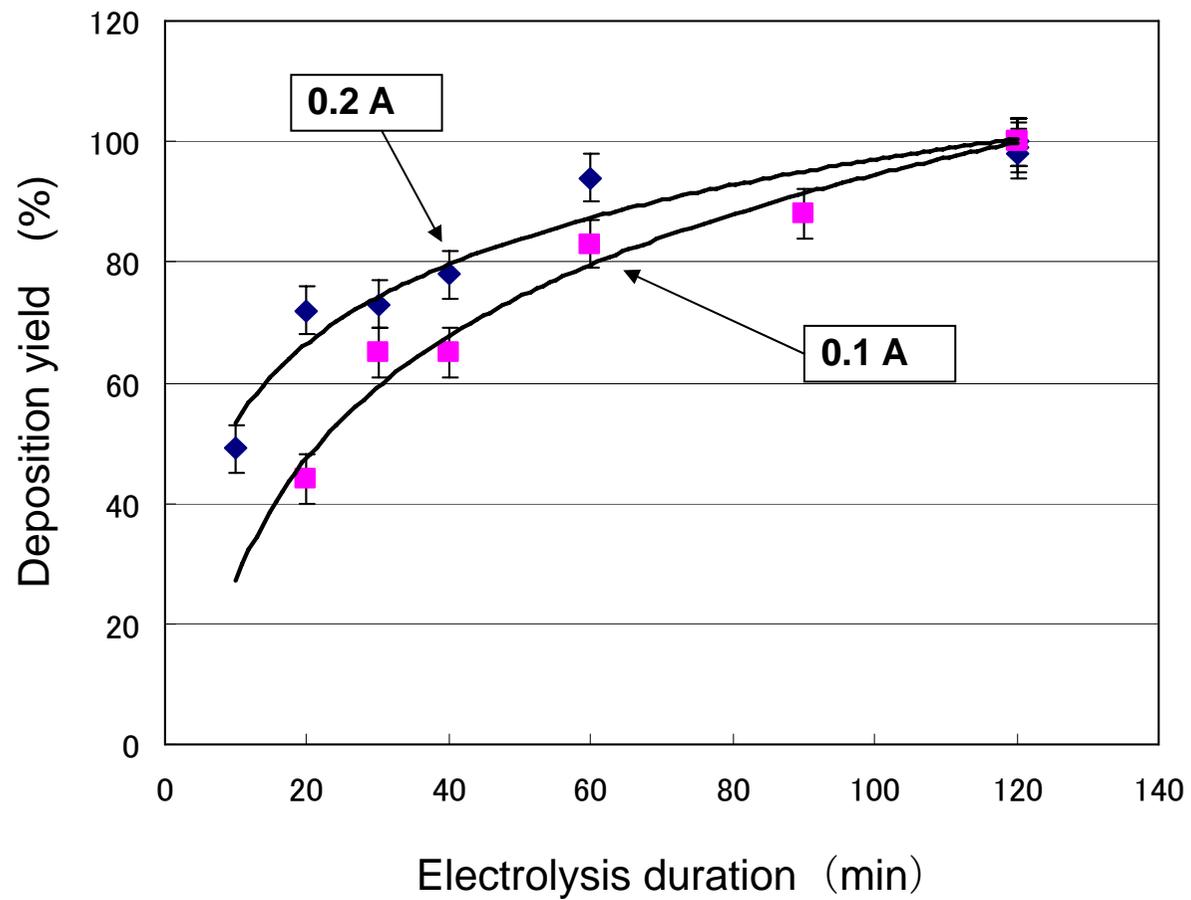
Table 1 Characteristics of ^{210}Pb and its progeny nuclides (^{210}Bi and ^{210}Po)

Nuclide	Decay	Energy (keV)		Half-life	Chemical form in acid solution
^{210}Pb	β_1^-	17	84 %	22.3 y	Pb^{2+}
	β_2^-	63	16 %		
	γ	46.5	4.3 %		
	IC		~80 %		
^{210}Bi	β^-	1162	100 %	5.01 d	Bi^{3+}
^{210}Po	α	5304	100 %	138.4 d	Po^{4+} [$PoCl_2^{2+}$, $Po(OH)_2^{2+}$]

Table 2　Comparison of two extraction solvents (toluene and carbon tetrachloride)

Sample number	Sample weight (mg)	Extraction solvent	Chemical recovery (%)	^{210}Pb(^{210}Po) concentration[*1] Bq/g	Average ^{210}Pb concentration[*2] Bq/g	Coefficient of variation
Pb-F-1	18.2	carbon tetrachloride	92	4.65 ± 0.25	4.60 ± 0.30	6.5%
Pb-F-2	18.2	carbon tetrachloride	92	4.28 ± 0.23		
Pb-F-3	18.2	carbon tetrachloride	81	4.87 ± 0.42		
Pb-F-4	18.2	toluene	100	4.57 ± 0.20	4.57 ± 0.23	5.0%
Pb-F-5	18.2	toluene	81	4.48 ± 0.21		
Pb-F-6	18.2	toluene	99	4.17 ± 0.11		
Pb-F-7	36.5	toluene	66	4.73 ± 0.25		
Pb-F-8	36.5	toluene	68	4.64 ± 0.16		
Pb-F-9	116	toluene	78	4.82 ± 0.24		
Pb-F-10	18.2	toluene	85 [*3]	4.74 ± 0.13	4.74 ± 0.13	-

*1: One sigma counting error

*2: One standard deviation

*3: Corrected recovery: electrodeposition only

Table 3 Temperature and time dependent volatilization loss of DDTC-Po complex

Study	Temperature (°C)	Heating time (min)	Radioactivity (mBq/sample)	Remaining radioactivity ratio (%)
Current study	70±10	0	102 ± 5	(base)
	70±10	30	104 ± 5	100
	70±10	90	109 ± 5	100
Mabuchi	100	15	-	99
	105	30	-	99.2
	105	30	-	92.6
Current study	120±10	30	109 ± 5	100
	120±10	60	101 ± 5	100
	120±10	120	106 ± 5	100
Mabuchi	110	30	-	86.6
	120	30	-	89.1
Current study	135±5	30	100 ± 5	100
	135±5	100	108 ± 5	100
Mabuchi	130	30	-	74.6
	150	15	-	79

Temperature: Range of thermo-regulator on the hot plate. Sample temperature confirmed by a radio-thermometer
Heating time: Time after toluene evaporated

Mabuchi[16,17] :   DDTC-Po salt extracted with carbon tetrachloride and heated 15 min

Table 4　Results of lead sample analysis

Sample	Sample weight (mg)	Chemical recovery (%)	Alpha-ray SP ^{210}Po Bq/g-lead	Average ^{210}Pb(^{210}Po) Bq/g-lead	Gamma-ray SP ^{210}Pb Bq/g-lead	Remarks
A	16.1	73	1.93±0.13			
	16.1	82	2.17±0.13	2.02±0.13	1.85±0.07	－
	16.1	65	1.98±0.13			
B	9.2	68	3. 09±0.23			
	9.2	72	3. 32±0.19			－
	18.4	80	3.00±0.11	3.13±0.12	3.13±0.13	
	18.4	80	3.20±0.17			
	18.4	64	3.14±0.19			
	46.0	83	3.05±0.15			
C	20.5	75	1.35±0.08			
	20.5	66	1.43±0.10	1.41±0.04	1.41±0.06	－
	20.5	64	1.44±0.10			
D	31.8	64	0.28±0.03			Old lead
	31.8	79	0.31±0.01	0.30±0.02	0.32±0.08	
	31.8	78	0.32±0.01			
E (Kanazawa castle lead tile)	110	68	0.0035±0.0010	0.0035±0.0010	0.005±0.002	Very old lead
				0.004±0.001		Previously measured by M. Uesugi et al.[1]

Sample:　Samples A－D are from commercially available lead; D is old lead; E is very old lead (100+ years)

Counting time:　Samples A-D counted for 80,000 sec; E counted for 230,000 (α-ray), and counted for 400,000 sec (γ-ray)

For γ-ray spectrometry, sample weight was ~300 g.