Method validation of a procedure for determination of ^{210}Po in water using DDTC solvent extraction and Sr resin

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For the determination of ^{210}Po in water samples, two alternative procedures (a) DDTC solvent extraction and (b) extraction chromatography using Sr Resin were selected and then validated in terms of trueness, repeatability and reproducibility with a tap water spiked with a known amount of ^{210}Po. In this work the optimization conditions for the auto-deposition of Po for source preparation were also studied.

Introduction

Polonium-210 is a naturally occurring alpha-emitter and exists in the environment as a decay product within the ^{238}U decay chain. ^{210}Po is considered to be one of the most toxic naturally occurring environmental radionuclides,[1] due to its wide distribution and potential for human radiation exposure through ingestion and inhalation.[2,3] In addition, for many sample types (for example, soils and sediments) determination of ^{210}Po is commonly used as a means of determining its progenitor ^{210}Po.

The results of a recent proficiency test organized by the IAEA demonstrated that a number of laboratories are experiencing difficulty in obtaining reliable results for ^{210}Po determination in water samples.[4] This is most likely due in part to the limited number of methods available for its determination. The most commonly used is alpha-spectrometry.[5] In addition, there is a general lack of suitable, recently characterized reference materials for use in quality control.

As a part of its activities to support its Member State laboratories, the IAEA is developing recommended procedures for the determination of selected radionuclides in environmental samples. In the case of ^{210}Po, this started with the collection and review of about 130 papers from the scientific literature.[5] Based on this review, two candidate methods for determination of ^{210}Po in water samples were selected for testing, refinement and validation. The results of this work are the subject of this paper.

For the determination of a low level activity concentration of ^{210}Po in a water sample, it is necessary to handle a large volume of sample. As a simple process the direct evaporation of the water samples has been used for reducing to a small volume of the sample.[6,7] However, this method is very time consuming for a large amount of a sample (>1 L). Therefore, coprecipitation with iron hydroxide[8,9] or MnO_2[10–12] have commonly been used to preconcentrate Po from water samples. When iron hydroxide is used for preconcentration, it is necessary to remove Fe from the sample solution using a solvent extraction step with an extractant such as di-isopropyl ether,[8] because bulk iron may interfere with the purification of Po using solvent extraction or extraction chromatography as well as in the auto-deposition of Po. In the case when MnO_2 is used, manganese can be removed easily from Po by several alternative chemical separation procedures. Therefore, in this work MnO_2 coprecipitation was selected as the method for preconcentration.

Two Po separation procedures, based on DDTC solvent extraction (DDTC-SE)[12] and extraction chromatography using Sr Resin (Sr-EC),[13] were selected for testing. Reports in the literature indicate that both methods have been successfully used for the determination of ^{210}Po in a variety of sample matrices.[7,14–16] The validation of both methods was carried out in terms of trueness, repeatability and reproducibility with tap water spiked with known amount of ^{210}Po. This paper also describes the optimized conditions for auto-deposition of Po.

Experimental

Materials

All the reagents were of an analytical grade (Merck, Germany). Deionized water (18 MΩ·cm^{-1}) was prepared by a Milli-Q Plus system (Millipore, MA, USA) and was used for all dilutions. ^{209}Po and ^{210}Po standard solutions were purchased from NIST (SRM 4326, NIST, USA) and Deutscher Kalibrierdienst (DKD-K-36901), respectively. Sr Resin was purchased from Eichrom, Inc. (Darien, IL, USA). Silver discs (17 mm, 0.3 mm thickness) were stamped from a fine grade (>99.9%) silver plate. ^{210}Po was measured by alpha-spectrometry (Ortec Octete alpha-spectrometry system, USA).

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Table 1. Semi-quantitative analytical result of elements in the tap water of IAEA's laboratories, Seibersdorf, Austria by ICP-MS

Element	Concentration, ppb
Ca	$93.1 \cdot 10^3$
Mg	$26.0 \cdot 10^3$
Na	$9.51 \cdot 10^3$
K	$7.04 \cdot 10^3$
Al	2.80
As	0.59
Ba	54.4
Br	103
Cr	15.5
Cu	5.16
Mn	1.20
Pb	0.15
Se	2.01
Si	$1.08 \cdot 10^3$
Sr	493
U	11.3
Zn	56.4

Sample preparation

Tap water collected at the IAEA's laboratories, Seibersdorf, Austria was used for preparation of test water samples. Some elements in the tap water were determined by ICP-MS (Elan 6000 Perkin-Elmer SCIEX instrument, equipped with a Scott-type spray chamber, a cross-flow nebulizer and a Gilson Minipuls 3 peristaltic pump) in the totalquant mode to screen the elemental composition. Therefore, the accuracy of the totalquant measurements in ICP-MS was not better than 20–30%. The semi-quantitative results of the tap water sample are given in Table 1.

Upon collection, the tap water sample was acidified with concentrated HCl (10 mL/500 mL sample) and spiked with a known activity of ^{210}Po. An aliquot of 500 mL of the water sample was taken in a beaker and about 30 mBq of ^{209}Po tracer was added. The sample was stirred for 1 hour to ensure tracer equilibration. Then, 5 mL of 0.2M $KMnO_4$ and 5 mL of 0.3M $MnCl_2$ were added, and the solution was adjusted to pH 9 with 25% NH_4OH. This solution was stirred for 1 hour and kept overnight to allow the precipitate to settle. The supernatant was decanted carefully so as not to disturb the precipitate and the rest was centrifuged.

For solvent extraction, the precipitate was dissolved with 10 mL of 1% H_2O_2 in 5M HCl. For Sr-EC, the precipitate was dissolved with 10 mL of 1% H_2O_2 in 2M HCl. The sample solutions were heated on a hot plate at 80~90 °C for 30 minutes to decompose hydrogen peroxide, and then Po was separated either by DDTC solvent extraction or by Sr-EC.

Separation of Po

DDTC-SE: The sample solution obtained from the sample preparation process was transferred into a separation funnel and the beaker was washed with 3×5 mL of 5M HCl to give a total of approximately 20 mL. A small amount of ascorbic acid was added to the solution to reduce Fe^{3+} to Fe^{2+}. Po was extracted with 10 mL of 0.1% diethylammonium diethyldithiocarbamate (DDTC) in CH_3CCl_3 for 5 minutes with a shaker (250 rpm), followed by two further extractions with 5 mL of 0.1% DDTC in CH_3CCl_3. If the organic phase was colored, Po was extracted with further aliquots until the color disappeared. The organic phase was combined and gently evaporated to dryness on a hot plate at less than 100 °C. The aqueous phase can be reserved for Pb, Ra, Th and U analyses.[12] For decomposing a small portion of organic material, the Po fraction was evaporated to dryness with 1 mL of 65% HNO_3 and a few drops of 30% H_2O_2, and then twice evaporated to dryness with 1 mL of 32% HCl and 1 mL 65% HNO_3. Finally, the residue was gently evaporated to dryness with 1 mL 32% HCl at 90 °C.

Sr-EC: 3 g of Sr Resin (100–150 μm) was soaked in distilled water for 1~2 hours, then filled into a glass chromatographic column (inner diameter 10 mm), activated with 100 mL of 1M HNO_3 and preconditioned with 100 mL of 2M HCl. The sample solution obtained from the sample preparation process was passed through the column preconditioned in advance and the beaker was washed with 3×2 mL of 2M HCl. The column was then washed with 80 mL of 2M HCl. Po and Pb were sequentially eluted through the column with 60 mL of 6M HNO_3 and 60 mL of 6M HCl, respectively. A small portion of organic material remaining in the Po fraction was treated in the same way as that used in the DDTC-SE. The column with Sr Resin was four times reused for analysis of subsequent samples after the regeneration. The used Sr Resin was regenerated by washing it with 50 mL of deionized water, 10 mL of EDTA (pH adjusted to 7 with NH_3) and 50 mL of deionized water.

Source preparation and measurement

The residue obtained from the separation process was dissolved in 10 mL of 0.5M HCl. The beaker was further rinsed with 2×2.5 mL of 0.5M HCl. A small amount of ascorbic acid (~50 mg) was added to the solution to reduce Fe^{3+} to Fe^{2+}. The pH of the solution was adjusted to pH 1–2 with 6M NaOH and transferred to a Teflon deposition cell. Polonium was spontaneously deposited on a silver disc (active area: 133 mm^2) at 90 °C for 90 minutes with mechanical stirring. After completion of the deposition, the silver disc was removed, rinsed with distilled water and dried in an electric oven. Polonium was measured by α-spectrometry.

*Repeatability, reproducibility and linearity test
of DDTC-SE and Sr-EC methods*

Unfortunately, no matrix reference materials are available for ^{210}Po in water. Consequently, the repeatability and reproducibility of the two separation procedures of ^{210}Po were tested by 10 replicate analyses of two tap water samples spiked with 1.53 Bq·L^{-1} and 13.0 mBq·L^{-1} of ^{210}Po standard, respectively. The concentration of ^{210}Po in the tap water sample was measured separately and added to the spike value to give the actual concentration in the spiked test water sample. The concentration of ^{210}Po from the tap water sample was in every case less than 6% of the spike. The repeatability limit and the reproducibility limit were calculated in accordance with ISO 5725-4.[17]

The relative bias of the two separation procedures was calculated by the following formula:

$$\delta(\%) = \frac{C - X_i}{C} \times 100$$

where C is the theoretical concentration of ^{210}Po in the tap water sample spiked with a certified standard of ^{210}Po, X_i is the measurement result of ^{210}Po in the tap water sample.

For the linearity test, tap water samples spiked with ^{210}Po in the range of 0.01 Bq·L^{-1} to 1.6 Bq·L^{-1} were analyzed by two separation procedures, respectively. A blank was prepared for a set of samples in the same way as the sample.

Test for optimization condition of auto deposition

In auto deposition of Po on a silver disc, the deposition yield of Po depends on several parameters such as pH, solution volume, deposition time, temperature, mechanical stirring and interfering elements existing in the solution.[18] To find optimized conditions for auto deposition of Po, the deposition yield of Po was examined with a known activity of ^{209}Po tracer while varying pH, deposition time, sample volume and temperature with or without stirring. The auto deposition of Po was three times replicated in each condition.

Results and discussion

*Repeatability, reproducibility and linearity test
of DDTC-SE and Sr-EC methods*

Two sets (each set consisted of ten samples) of tap water samples with 1.53 Bq·L^{-1} and 13 mBq·L^{-1} of ^{210}Po were analyzed by DDTC-SE and Sr-EC, respectively. The results are summarized in Table 2. The mean values obtained from both methods are in a good agreement with each other. The relative repeatability and reproducibility limits for both methods were in the range of 10–12%. The relative bias of both methods ranged from 4% to 8.5%, as shown in Fig. 1. The chemical recovery for the DDTC-SE ranged from 54–97% with an average value of 82%. The recovery for Sr-EC with fresh resin ranged widely from 20 to 94% (Fig. 2). The low chemical recovery observed in some cases for the Sr-EC method was probably caused by non-decomposed organic material in the deposition solution. The recovery gradually decreased with reuse of Sr Resin column and dropped suddenly in the fourth reused column (Fig. 3). The results of the linearity test are depicted in Fig. 4. The results showed a good linearity in the tested concentration range for both separation methods.

Measurement of blank

One blank was prepared for each set of samples to correct the contribution of blank to the sample, because the ^{210}Po in the blank is mostly due to chemical reagents used during the separation procedure and influenced by the environment of laboratory where the separation of Po is carried out. The control chart of the count rates of blank samples in DDTC-SE and Sr-EC is given Fig. 5. The count rates of the blanks for the DDTC-SE ranged from 0.0001 to 0.002 cps with an average of 0.0005 cps, while the count rates of the blanks in Sr-EC was in the range of 0.00009 to 0.004 cps with an average of 0.0009 cps. The latter was about two times higher than the former. The elevated count rate in the blank in the Sr-EC may be attributed to the memory effect of Po on the column due to the reuse of Sr Resin. It is desirable to take care of the memory effect of Po in the reused Sr Resin column when in particular ultra low level samples are analyzed. As the count rate of the blank can change with experimental conditions, the detection limit should be estimated based on the count rate of the blank. Assuming that the counting efficiency is 25%; the counting time is 250,000 seconds, the chemical recovery is 80% and the sample volume is 500 mL, the minimum detectable activity (MDA) in DDTC-SE and Sr-EC ranged from 2.2 mBq·L^{-1} to 3 mBq·L^{-1}, depending on the experimental environment.

Table 2. Results of repeatability and reproducibility tests

Validation parameter	Method	
	DDTC-SE	Sr-EC
Repeatability		
Mean ($\overline{X}_r$) in repeatability test, Bq·L^{-1}	1.55	1.58
Repeatability standard deviation (S_r), Bq·L^{-1}	0.06	0.05
Repeatability limit (r_L), Bq·L^{-1}	0.17	0.14
Reproducibility		
Mean ($\overline{X}_L$) in reproducibility test, mBq·L^{-1}	12.7	13.1
Reproducibility standard deviation (S_L), mBq·L^{-1}	0.46	0.57
Reproducibility limit (R_L), mBq·L^{-1}	1.29	1.60
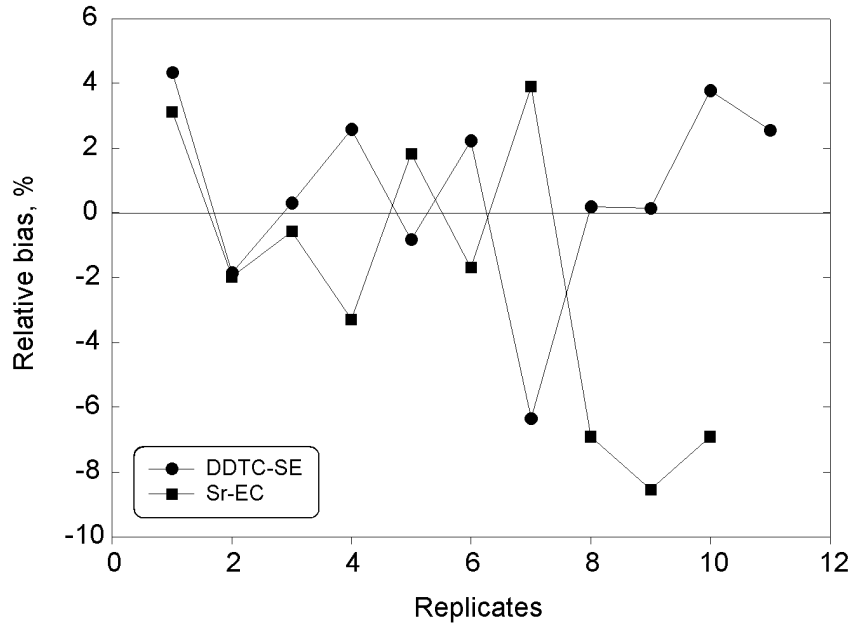
Fig. 1. Relative biases of determination results for ^{210}Po in spiked water samples using DDTC-SE and Sr-EC
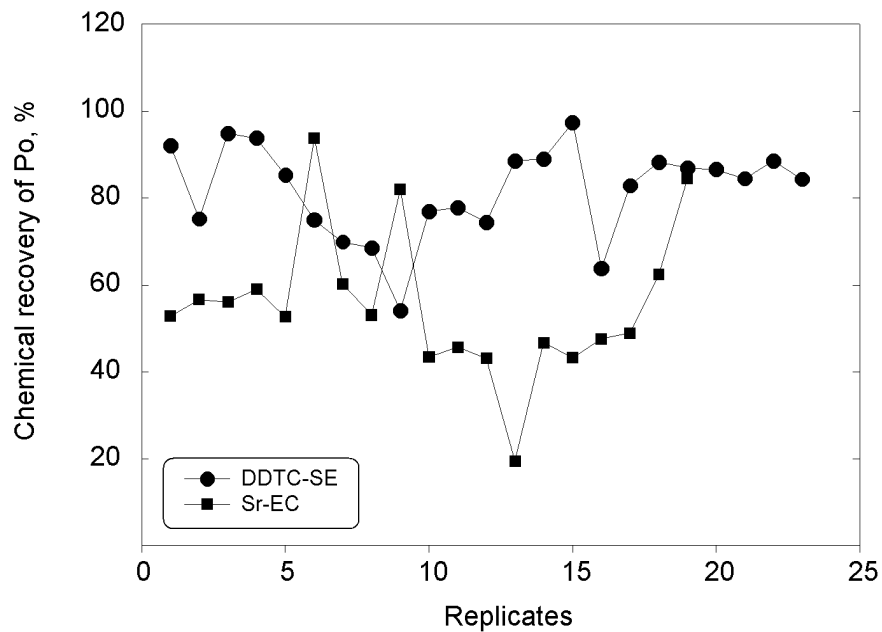
Fig. 2. Chemical recoveries for Po using DDTC-SE and Sr-EC (for fresh resin)
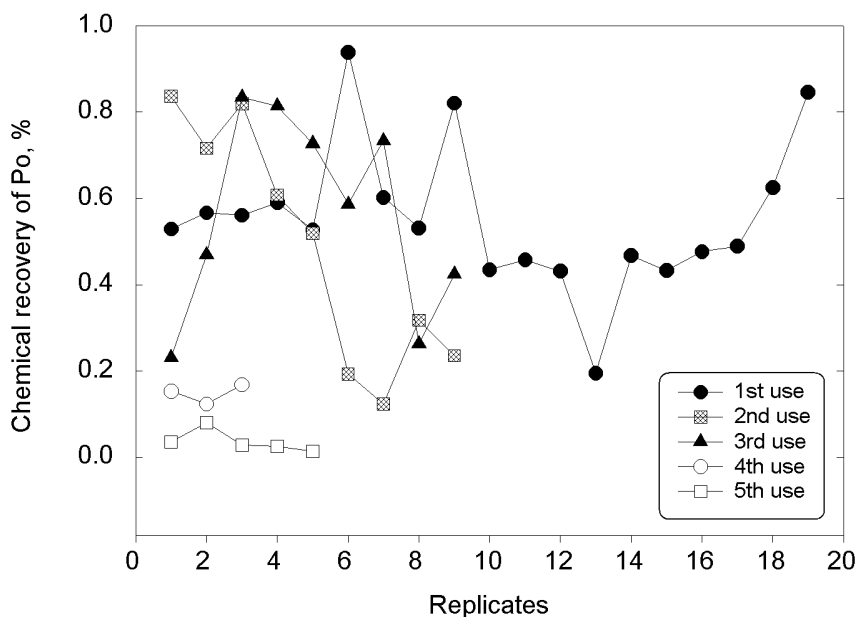
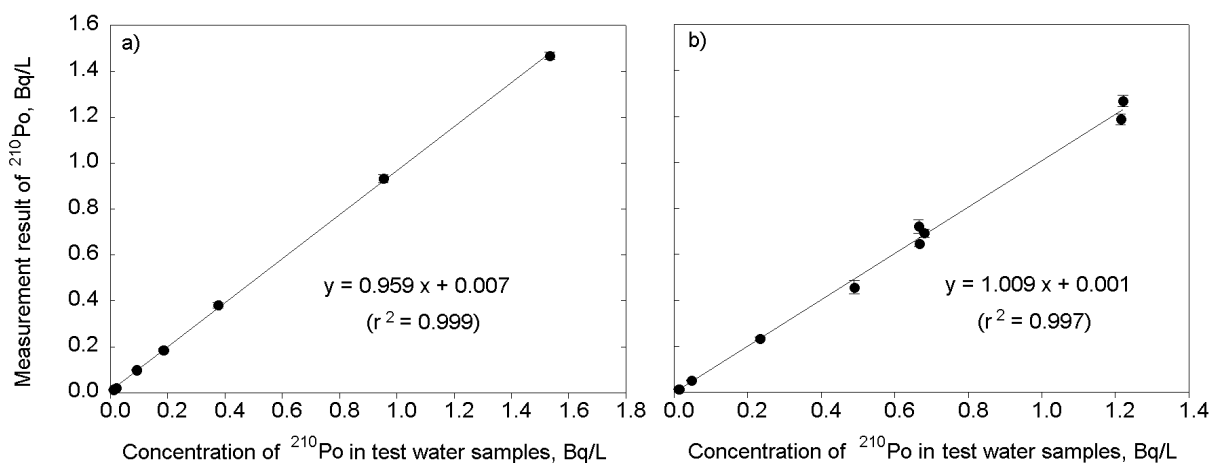*Fig. 3.* Variation of chemical recovery for Po using Sr-EC with reuse of Sr Resin

Fig. 4. Linearity test for (a) DDTC-SE, (b) Sr-EC

Optimized auto deposition condition of Po

As a part of the review of the scientific literature, data were collected on the reported Po deposition conditions.[5] These data are summarized in Table 3. It is apparent that the Po deposition conditions used in laboratories are still variable. The majority of the reported deposition times were 2 hours or longer, and it is likely that the laboratories could save time in this step by optimization of the conditions used.

0.5M HCl was used as a deposition solution in 80% of the literature searched. Some authors reported the pH of the deposition solution, and in about 60% of these cases a pH of 2 was used. The solution volumes and temperatures used were quite variable.

In general, the time required for deposition may be minimized by minimizing the solution volume, maximizing the solution temperature, and agitating by stirring, or by spinning the disc.[18] In the present work an optimized deposition condition for Po on a silver disc (active area: 133 mm^2) was examined in the pH range from 1 to 5 and in the temperatures between 30 and 90 °C, while varying the volume of the deposition solution from 5 to 35 mL.
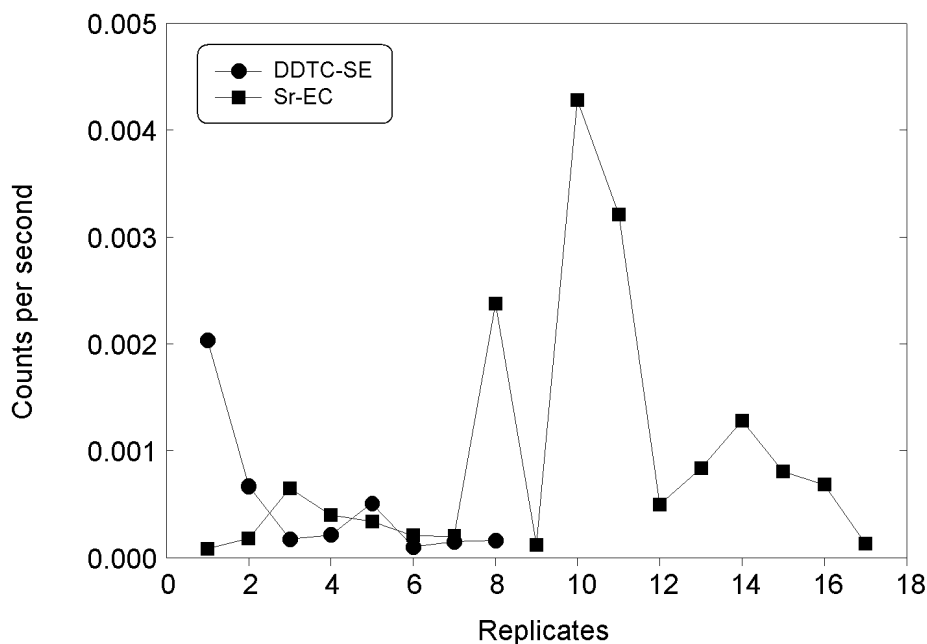
Fig. 5. Control chart of the count rates in blank samples for DDTC-SE and Sr-EC

Table 3. Summary of deposition conditions reported in the literature

Parameter	Deposition condition	Percentage, %	Reference
Deposition time, hours	1–2	27	53
	2–3	32	
	>3	41	
Molality of HCl, M	0.1	7	43
	0.5	79	
	1	9	
	2	5	
pH of deposition solution, mL	1	18	17
	1.5	23	
	2	59	
Volume of deposition solution, mL	10	10	30
	20	27	
	30	3	
	40	10	
	50	24	
	80	3	
	100	20	
	150	3	
Temperature, ºC	<70	12	67
	70–80	19	
	80–90	63	
	90–95	6	

Figure 6 shows the means and standard deviations of two replicate measurements of the yield of Po for a number of pH values of the deposition solution. Based on these data, the optimized conditions for Po deposition appear to be in the range around pH 0–1. It was found that Po can be deposited even at a pH between 0 and −1. Nevertheless, the resolution (FWHM: 0.0319 MeV) of the alpha source prepared in the deposition solution at pH −1 was worse than for that at pH 0 (FWHM: 0.0236 MeV) due to corrosion of the surface of the silver disc (Fig. 7). Conversely, if the deposition solution is pH 3 or higher, the polonium is easily adsorbed onto the surface of the beaker, resulting in a reduced recovery (Fig. 6).
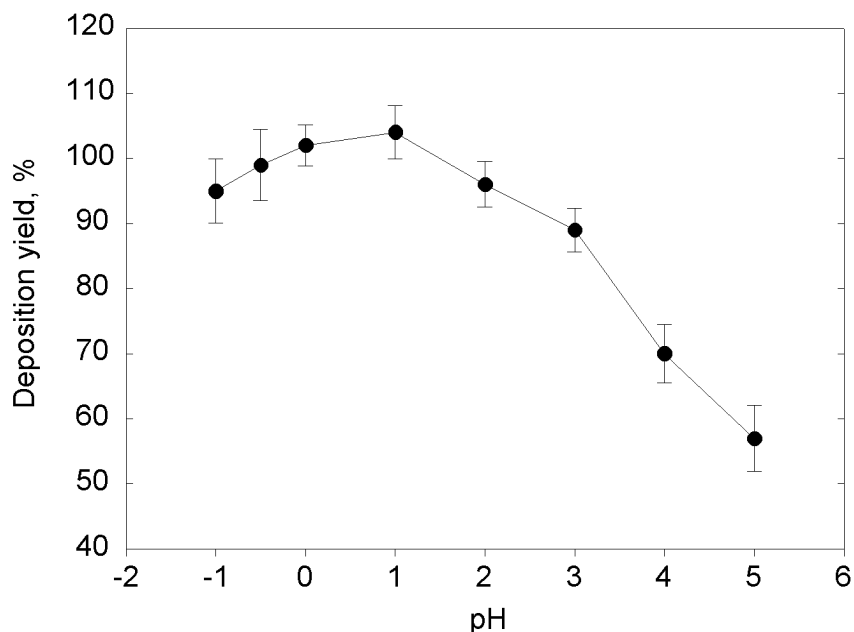
Fig. 6. Variation of the deposition yield (mean ± standard deviation of 2 replicates) with pH under the conditions: 15 mL of deposition solution, 90 °C and 90 minutes deposition time
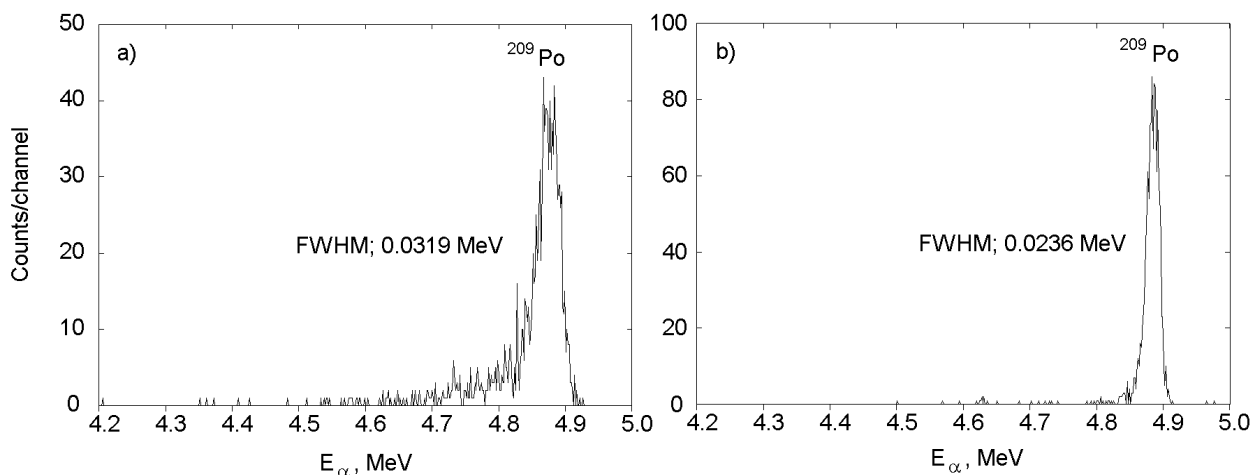

Fig. 7. Resolution of alpha-spectra of ^{209}Po sources prepared at (a) pH –1 and (b) pH 0

Another factor affecting the deposition yield of Po is the organic material in the deposition solution. The solution obtained from the separation procedure of Po using DDTC-SE or Sr-EC was generally evaporated to dryness before the preparation of the source. Sometimes, a small portion of DDTC or crown ether partially extracted from Sr Resin would remain in the residue after evaporation to dryness. It is important to completely decompose any such organic materials before the source preparation, as they can significantly affect the deposition yield of Po. A small portion of DDTC was easily decomposed with a few mL of 65%

nitric acid. On the other hand, it was relatively difficult to decompose a small portion of crown ether extracted from the Sr Resin with only nitric acid.

The deposition yield of Po increased with extending the deposition time from 30 to 90 minutes and was almost uniform between 90 minutes and 180 minutes. About 95% of the polonium was deposited onto the silver plate over 1.5 hours.

Decreasing the volume of the Po deposition solution resulted in an increase in the deposition yield. The maximum deposition yields were obtained with a volume of 5 mL. However, 5 mL of the deposition

solution was too small to quantitatively transfer Po into the beaker to the deposition apparatus. For this reason, 15 mL of deposition solution was used in this work. The deposition yield increased with the temperature of the deposition solution. With mechanical stirring with a glass rod for 1.5 hour, the recovery of ^{209}Po was nearly 100% at 90 °C. An improvement in the deposition at higher temperatures with rotation has been explained by the removal of ozone, which is coated onto the surface of the silver disc as silver oxide or peroxide, formed from the dissolved oxygen in the solution.[19]

In summary, the Po deposition conditions found to be optimal in this study (using a silver disc of active area: 133 mm^2) were 15 mL of deposition solution, pH 0–1, 90 °C and 90 minutes of deposition time with stirring. It should be added that optimal conditions may vary somewhat with different experimental setups used in different laboratories (e.g., shape and size of the deposition apparatus, size of silver disc, method and speed of stirring), however, the conditions given here should be a reasonable starting point.

Conclusions

Two procedures for ^{210}Po analysis in water, DDTC-SE and Sr-EC were selected as potential recommended procedures. Both methods showed good repeatability and reproducibility with 4% of relative repeatability and reproducibility standard deviations. The relative bias of both methods ranged from 4% to 8.5%. The chemical recovery of Po obtained in these trials was higher for DDTC-SE than that for Sr-EC.

Even though Sr Resin can be reused, the analysis cost of DDTC-SE is lower than that of Sr-EC, because of the high cost of the Sr Resin. In addition, the analysis time is less for the DDTC-SE than that required for the Sr-EC. However, in the case that ^{210}Pb and ^{210}Po are to be simultaneously determined Sr-EC would be faster than the DDTC-SE, because in the DDTC-SE ^{210}Pb should be purified using an anion-exchange chromatography after the extraction with DDTC. The results of the validation for both methods showed that either method can be used for the determination of ^{210}Po in water samples, and selected properly according to the purpose of analysis and available facilities.

The deposition conditions for Po found to be optimal in this study were 15 mL of deposition solution, pH 0–1, 90 °C and 90 minutes of deposition time with stirring.

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