

MEASUREMENT OF ^{210}Po AND ^{210}Pb IN GROUNDWATER USING AN ALPHA LIQUID SCINTILLATION COUNTER

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ABSTRACT. Measurement of ^{210}Po and ^{210}Pb in natural waters is important because of their potential carcinogenic risks. The ^{210}Po and ^{210}Pb contents in groundwater and bottled drinking water samples were determined using photon/electron-rejecting alpha liquid scintillation (PERALS[®], Oak Ridge Detector Laboratory, USA) spectrometry. ^{210}Po was extracted via an organic liquid scintillator from the aqueous samples and measured quantitatively by counting the 5.305-MeV alpha particles with a PERALS spectrometer. The concentration ranges of ^{210}Po and ^{210}Pb in groundwater samples were found to be 1.42–12.77 and 1.26–7.81 mBq/L, respectively, from several areas in Saudi Arabia. The concentration of ^{210}Po and ^{210}Pb in bottled drinking water was estimated to be 1.31–2.88 and 1.22–2.53 mBq/L, respectively. ^{210}Pb activity was calculated from the content of ^{210}Po in the samples produced after allowing for a sufficient decay period and using the decay-growth equation. The method was evaluated against the ultra low-level liquid scintillation counting (LSC) technique (Quantulus[™]) and the traditional radiochemical technique. The lower limit of detection of the method based on 180 min of counting and a 0.5-L sample volume is 0.57 mBq/L for ^{210}Po . The results were compared with those obtained from conventional radiochemical separation following the α -spectrometric technique.

INTRODUCTION

^{210}Pb and ^{210}Po are progenies of the ^{238}U series. ^{210}Pb is one of the most radiotoxic daughters of ^{226}Ra . ^{210}Pb ($T_{1/2} = 22.3$ yr) decays by β^- emission to ^{210}Bi ($T_{1/2} = 5.0$ d), which again undergoes decay by β^- emission to ^{210}Po ($T_{1/2} = 138.4$ d). ^{210}Po decays by alpha emission to form the stable lead isotope ^{206}Pb . ^{210}Po poses potential risks to humans for internal radiation exposure by ingestion and inhalation, and ^{210}Po and ^{210}Pb have carcinogenic effects with respect to lung cancer (Zapeczka and Szabo 1987; UNSCEAR 1988; USGS 1998; EPA 2000). When ^{210}Pb is absorbed into the human body, it concentrates in bone tissue and is eliminated very slowly (Flynn 1968; UNSCEAR 1988; Jia et al. 2000). ^{210}Pb and ^{210}Po are of particular environmental concern because of their long half-lives and their possible risk in significantly increasing the internal radiation dose to individuals and whole population groups (UNSCEAR 1988; Kuo et al. 1997; Khater 2002).

^{210}Po , as an alpha emitter, can be measured quantitatively by alpha spectrometry and liquid scintillation counting (LSC) (Shannon et al. 1970; Schery 1980; Hamilton and Smith 1986; Jia et al. 2000; Guogang et al. 2001). ^{210}Pb can be measured by 3 principal radioanalytical methods: low-energy γ -spectrometry, α -spectrometry, and LSC. Low-energy γ -spectrometry can be applied to measure a 46.5-keV photon emitted with a probability of 4% from ^{210}Pb (Yener and Uysal 1996), but this method requires a large sample volume because of the relatively low efficiency and the difficulty of matrix absorption correction (Gogrewa et al. 1996; Tanner et al. 2000). ^{210}Pb can be detected and determined via its β^- -active daughter nuclide ^{210}Bi , or its α -active granddaughter ^{210}Po (Takayuki et al. 1994; Kitzberger et al. 2001; Skwarzec et al. 2003). This method involves the complexity of wet chemistry for the separation of ^{210}Pb from other interfering elements. ^{210}Pb concentration can be inferred from measurement of the α -ray of ^{210}Po after the growth of ^{210}Po from ^{210}Pb (Kim et al. 2001; Guogang et al. 2001). This method involves 2 measurements of ^{210}Po but in only 1 aliquot of the sample. In this case, after the first measurement of ^{210}Po , the resulting solution will be stored until ^{210}Po has grown enough from the decay of ^{210}Pb to make the second measurement, assuming that Po has generated only from Pb decay. Use of LSC after chemical separation of lead is also done;

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^{210}Bi , a decay product of ^{210}Pb , is extracted with the lipophilic scintillator POLEXTM (ETRAC, USA) and then measured (McDowell et al. 1975, 1992; Yener and Uysal 1996; Guogang et al. 2000). ^{210}Bi can also be extracted by 4,4'(5')-bis(*t*-butyl-cyclohexano)-18-crown-6 in isodecanol.

Some efforts have been carried out to quantify ^{210}Po and ^{210}Pb in aqueous samples by different radiochemical techniques, and accuracy problems were also encountered when analyzing ^{210}Po and ^{210}Pb using the conventional techniques. The previous analytical procedures for measuring ^{210}Po and ^{210}Pb were subject to interference from other radionuclides, and difficult sample preparations using alpha spectrometry have been largely applied for the measurement of ^{210}Po , where ^{210}Po was deposited onto a silver planchet from the acid solution containing polonium and the planchet was counted using the spectrometer (Hamilton and Smith 1986; García-Orellana and García-León 2002). The present method involves the solvent extraction system, in which the sample is measured by extracting the nuclide of interest into the organic phase of an immiscible cocktail. The principal reagents used in the extractive method are tertiary amines (Case and McDowell 1982; Cadieux 1990; McDowell 1992). On the basis of these tertiary amines, the extractive cocktail POLEX has been developed for measuring Po in aqueous samples. The cocktail is an organic fluid containing selective chemical extractants for radionuclides combined with a scintillator fluor and energy transfer agents that emit light flashes upon excitation by radioactivity. The electronic device, coupled with a photomultiplier tube, detects light flashes emitted by an extractive scintillator. The light flashes emitted from either alpha or beta/gamma events can be sorted electronically according to their unique pulse shapes. McDowell (1992) used the PERALS[®] (Oak Ridge Detector Laboratory, USA) alpha spectrometer to perform Po measurement using only 1 mL of POLEX for each aqueous sample.

In this work, ^{210}Po and ^{210}Pb in groundwater samples and bottled drinking water samples were determined by i) an extractive LSC method using the specific-nuclide extractant POLEX (Case and McDowell 1982; McDowell 1992); ii) α -spectrometric method; and iii) LSC.

MATERIALS AND METHODS

Materials

Analytical-grade reagents and high-purity deionized water (Milli-Q reagent water system, Millipore, USA) were used throughout this work. A POLEX extractive scintillator was used to extract ^{210}Po from the water and for preparation of the counting samples.

A stock solution of 100.8 mBq/mL of ^{209}Po tracer was prepared by diluting accurately measured amounts of standard solution of ^{209}Po (NIST, USA) with 0.2M HCl; 200 μL of this standard solution was added to the water samples for the recovery study. The accuracy and precision of the method were evaluated using the standard reference materials (NIST, SRM 4326).

All reagents used in the preparation of sample solutions were of analytical grade (Merck, Germany). Pure dry argon was used for bubbling through analytical-grade toluene and for sparging the counting sample (organic phase). The recovery of ^{210}Po in the water samples analyzed was 98% using the ^{209}Po standard reference material.

The activity values of ^{210}Po were measured by a PERALS spectrometer (ORDELA model 8400AB-HV). The counting efficiency of the system was ~99.7% with a background of 0.000033 s^{-1} in the energy region of interest. The software used for spectral analysis was Canberra Genie 2000TM.

Principle of Solvent Extraction

In the PERALS spectrometry system, the extraction of ^{210}Po from the aqueous solution involves the principle of solvent extraction. A solvent extraction system is composed of an organic extractant phase and an aqueous phase. The organic phase consists of one or more extraction reagents dissolved in an organic diluent. These 2 phases are immiscible, but under proper conditions phase transfer of one or more metallic species can occur across the organic/aqueous interface. In some solvent extraction procedures, more than 1 extraction step is required for the quantitative removal of a solute from its original solvent. The solute is more soluble in 1 component of the solvent pair, but in this method 1 extraction is enough. Solvent extraction is greatly influenced by the chemical form (ionic or molecular) of the solute to be extracted, because different forms of the solute can have different solubilities in the solvents.

In an organic/aqueous solvent system, the distribution of a metal, M , between the 2 phases at equilibrium is described by a distribution coefficient, D_M , where:

$$D_M = \frac{(\text{Concentration } M)_{org}}{(\text{Concentration } M)_{aq}} \cdot \frac{V_{org}}{V_{aq}}$$

This is true at any phase ratio, $\frac{V_{org}}{V_{aq}}$. However, it should be noted here that D_M is a concentration ratio, and the amount of metal recovered depends also on the phase ratio. If we call the fraction of the metal recovered the recovery factor, F_R , the relationship:

$$F_R = D_M \left(\frac{V_{org}}{V_{aq}} \right)$$

describes the total organic/aqueous metal ratio.

Thus, if D_M is 1000 and $\frac{V_{org}}{V_{aq}} = 1/10$, then F_R is $= \frac{1000 \times 1}{10} = 100$, and the percent recovery $= \frac{100 \times 100}{(100 + 1)} = 99.0\%$ for the phase ratio 1:10. This calculation indicates the amount of metal extracted into the organic phase.

Chemical Processing of ^{210}Po for α -Spectrometric Measurements

The most widely used technique is the spontaneous deposition of Po on a silver disc from weakly acidic solutions (Flynn 1968; Hamilton and Smith 1986; Cothorn and Rebers 1990; Guogang et al. 2001). This method is subject to interference from oxidants, organic materials, and elements that also deposit on the silver plate. These interferences can be removed by precipitation as well as by concentrating ^{210}Po before plating. Flynn (1968) reported a method for the deposition of ^{210}Po in the presence of large quantities of foreign ions. Plating was carried out by suspending a silver disk in HCl solution adjusted to pH 2.0 and containing some hydroxylamine hydrochloride, sodium citrate, and bismuth. No separation of the interfering ions was required and essentially quantitative recoveries were obtained at 80–90 °C from a standard ^{210}Po solution. However, this method also required some refinements while measurements were made for a trace level of Po in groundwater.

Based on the above method, 0.5 L of filtered water in a 1-L beaker was heated with a hot plate to reduce the volume to 100 mL, and 10 mL of 20% hydroxylamine hydrochloride, 4 mL of 25% sodium citrate, and 20 mg of bismuth were added. The solution was adjusted to pH 1.5 and heated to 80–90 °C. A Perspex holder with a silver disk was placed on the bottom of the beaker, and the sil-

ver disk was immersed in the solution. The solution was stirred with a glass plate using a mechanism connected to a motor. Deposition was carried out at 80 and 90 °C, respectively, varying the time of deposition. Results show that 3 hr were necessary for a quantitative deposition of Po at the above temperatures using this device (Figure 1).

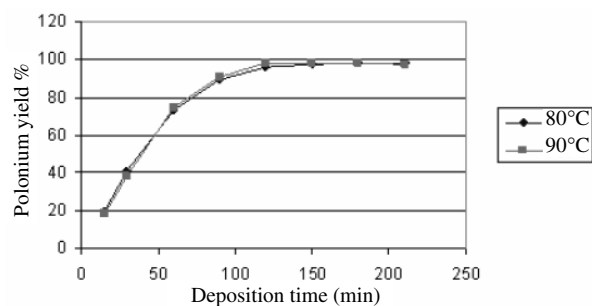


Figure 1 Polonium yields as a function of temperature and time

Chemical Processing of ^{210}Po for the PERALS Technique

The groundwater under investigation contains trace levels of ^{210}Po . Thus, the preliminary requirement was to preconcentrate the water sample and measure the activity of ^{210}Po under the present system. About 0.5 L of filtered water sample was evaporated with a hot plate to 20 mL, and then 3 to 5 mL of concentrated phosphoric acid was added and evaporated to remove other acids; 200 μL of ^{209}Po tracer (9.2945 pCi/mL) was added to study the yield of ^{210}Po in the present system. The phosphoric acid solution was transferred to an equilibration vessel using a small amount of water, and additional water was added to produce a volume twice that of the phosphoric acid solution. The vessel was filled to 20 mL with 1:1 phosphoric acid. One mL of 0.1M HCl was added to the solution and mixed well; 1.3 mL of POLEX extractive scintillator was added, equilibrated for 30 min, and then allowed to rest for phase separation. When the organic and aqueous phases were clearly separated, 1.0 mL of the organic phase was drawn with a pasteur pipette in an appropriate counting tube, sparged with saturated argon, passed through toluene to trap oxygen, and counted in the PERALS spectrometer for 180 min. The organic phase containing ^{210}Po should be visibly clear and as colorless as possible. The objective is to get a maximum amount of light per alpha event into the phototube. Any color in the scintillator will decrease its efficiency and shift the alpha energy spectrum to lower apparent energies (left on the MCA scale) and will degrade both the energy and pulse-shape resolution. All the organic extractive scintillator samples to be counted were sparged with a toluene-saturated, oxygen-free argon gas in order to rid from the organic phase free any dissolved oxygen—because the oxygen dissolved in the sample impairs both energy and pulse-shape resolution. The equilibrium curve is shown in Figure 2 with an equilibration time of 30 min, as the Po transfer from the aqueous phase to organic phase is relatively slow.

Chemical Processing of ^{210}Pb

^{210}Pb concentration can be inferred from the measurement of the α -ray of ^{210}Po after the growth of ^{210}Po from ^{210}Pb (Guogang et al. 2001; Kim et al. 2001). Therefore, lead has to be separated from Po and interfering elements. This method is very sensitive; however, it requires more than 6 months' establishment time for the growth of ^{210}Po from ^{210}Pb (Figure 3).

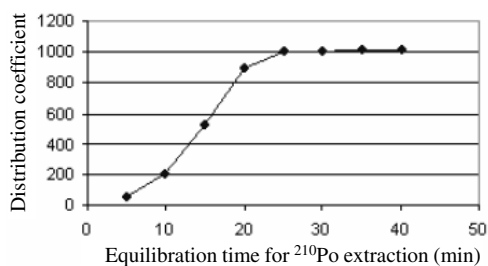


Figure 2 Equilibrium curve for Po extraction from 7.5M phosphoric acid and 0.01M HCl using a POLEX extractive scintillator as a function of equilibration time.

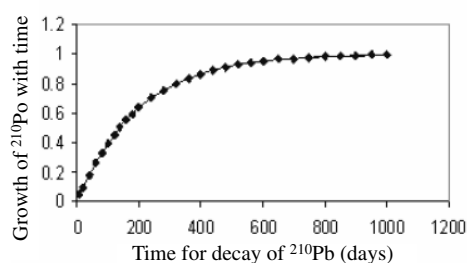


Figure 3 Theoretical ingrowth curve of ^{210}Po from ^{210}Pb decay.

The procedure adopted in this method for separation of lead is based on the conventional BaSO_4 precipitation method used for LSC (Kim et al. 2001; Guogang et al. 2001).

Groundwater collected from the field wells was acidified with hydrochloric acid, and 1 mL of barium carrier solution (25 mg/mL) and lead carrier solution (25 mg/mL) were added and the mixture stirred. After adding 2 mL of 9M sulfuric acid and 2.5 g of ammonium sulfate to the sample (0.5 L), barium (radium) and lead were coprecipitated into $\text{Ba}(\text{Pb})\text{SO}_4$, which was separated by centrifuge and dissolved in 10 mL of hot 0.1M EDTA (pH 9.0) solution and 3 mL of ammonia water. When 5 mL of 10% ammonium sulfate solution was added to the solution and the pH adjusted to 4.2–4.5 with acetic acid, radium and barium were coprecipitated to form BaSO_4 , leaving ^{210}Pb in the solution. After boiling for 2 min, the BaSO_4 precipitate was separated by centrifuge and discarded. The supernatant containing ^{210}Pb was filled up to 100 mL with deionized water and 7 mL of H_2SO_4 (9M) and 2 g of ammonium sulfate was added to coprecipitate PbSO_4 . After centrifuging, the supernatant was discarded, and the precipitate was washed with deionized water and preserved with 2 mL of deionized water for over 6 months to allow for the growth of ^{210}Po . The extractive process for measuring ^{210}Po follows the same procedure of radiochemical treatment as applied for Po measurement. In this work, the analysis of ^{210}Pb in groundwater samples was carried out after separation of ^{210}Pb from ^{226}Ra and after other interfering elements adopting the conventional isolation of the $\text{Ba}(\text{Ra})\text{SO}_4$ precipitate. The recovery of ^{210}Po was evaluated using a ^{209}Po tracer in the water samples and measuring the counts in the peak area of the 4.866-keV alpha energy of ^{209}Po . However, corrections for the growth of ^{210}Po from ^{210}Pb and for the decay of ^{210}Po have to be applied with the resulting calculations and error propagation (see Figure 4, below).

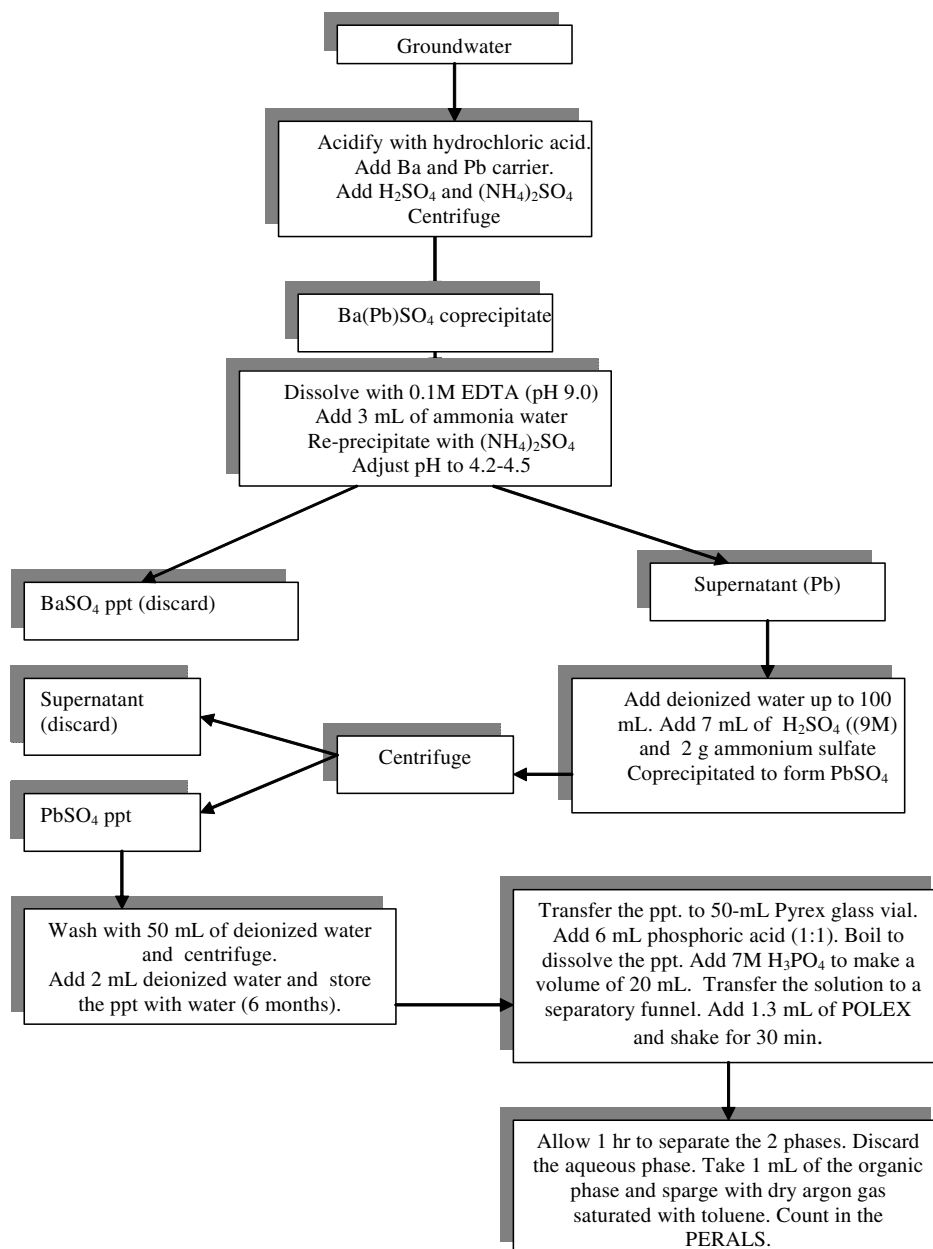


Figure 4 The chemical separation and counting procedures for ²¹⁰Pb in water samples

Sample Measurement

In the organic phase, Po was extracted from the aqueous media in the counting vial (1 mL of the organic phase was measured with a micropipette) and sparged with dry argon gas saturated with toluene. The objective of the sparging was to drive out the dissolved oxygen remaining with the extractant, as it quenches the scintillation pulses from the organic phase. The samples were measured by

using the respective 4.866- and 5.305-MeV alpha peaks of ^{209}Po and ^{210}Po (Figure 5). The samples were counted for 180 min to get adequate counts above the background for ^{210}Po , and the concentration was calculated from the peak area of ^{210}Po in the spectrum region. The chemical yield of ^{210}Po was determined by the material balance technique, using ^{209}Po as a radiotracer for high precision. For calculating ^{210}Pb concentrations, ^{210}Pb was separated from the water samples and then aged 6 months to allow ^{210}Po to decay from ^{210}Pb . The sample was then treated the same way as for the measurement of ^{210}Po . The uncertainties given with the final results are standard deviations resulting from propagation of all random uncertainties incurred anywhere in the entire measurement process. The lower limit of detection (LLD) of the PERALS spectrometry system was 0.57 mBq/L based on a 180-min counting time and 0.5-L sample size. The detector efficiency was ~99.7%.

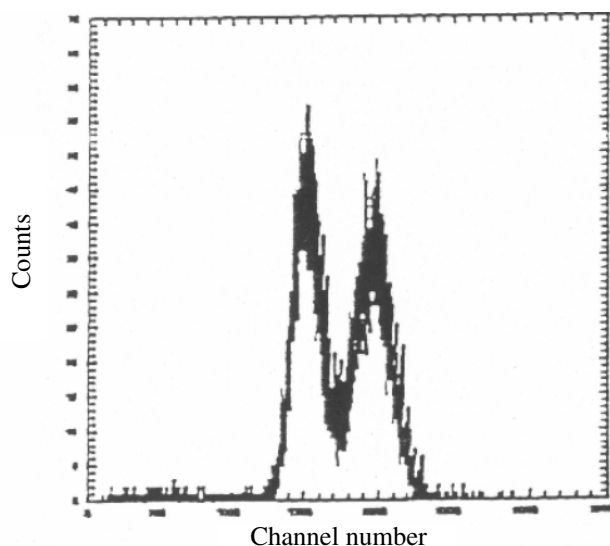


Figure 5 Alpha spectrum of ^{209}Po and ^{210}Po by the PERALS technique for groundwater samples. Units on the x axis are from 0 to 3500 in increments of 500. Units on the y axis are from 0 to 70 in increments of 5.

The following activity calculation was applied:

$$A = \frac{C_{Tot} - C_{BG}}{eff \times T_s} \times \frac{1000}{V}$$

where A = activity (mBq/L) of the sample; C_{Tot} = total counts; C_{BG} = background counts; eff = efficiency of the detector; T_s = counting time in seconds; and V = volume (L) of the sample. The accuracy and precision of the radiochemical methods were evaluated using NIST (National Institute of Standard and Technology) reference materials and estimated at <7%.

The lower limit of detection (LLD) of the α -spectrometry system was 0.77 mBq/L based on an 18-hr counting time and 0.5-L sample size. The chemical yield of spontaneous Po deposition on the silver disk was $83 \pm 8\%$. The detector efficiency of the α -spectrometry system was 20%.

Lower Limit of Detection (LLD)

The LLD of the PERALS method was evaluated using the following equation:

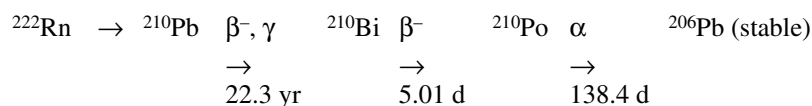
$$LLD(Bq/L) = 3 \frac{\sqrt{B}}{(t\varepsilon RV)}$$

where V is the volume (L) of sample; t is the sample measurement time (s) (which is the same as for the background); ε is the efficiency; and B is the background counts using a radiochemical blank. The LLD value obtained with $t = 10,800$ s was 0.57 mBq/L for 0.5 L of water sample.

RESULTS AND DISCUSSION

The ^{210}Po and ^{210}Pb measured in 60 groundwater samples and 24 bottled drinking water samples are presented in Tables 1 and 2. The comparative values of ^{210}Po measured in the groundwater and drinking water samples using the PERALS method, α -spectrometric method, and LSC are given in Table 1. The bottled drinking waters were collected from local markets. The maximum concentration of ^{210}Po in groundwater samples was 12.77 mBq/L. About 50% of the samples analyzed contained ^{210}Po concentrations of 5.0–12.77 mBq/L. The maximum mean concentration of ^{210}Po recorded in the study was 11.88 ± 0.31 mBq/L. None of the samples exceeded 0.2 Bq/L. Three of the total samples were found to contain Po and Pb beyond detectable concentrations. This level of ^{210}Po in the groundwater is in agreement with results published by Katzlberger et al. (2001). The maximum mean level of concentration of ^{210}Po in the bottled drinking water samples (2.81 ± 0.15 mBq/L) is similar to the results obtained by Skwarzec et al. (2003). The Po isotopes are among the most radiotoxic nuclides; therefore, their concentration in drinking water is very important from a radiological point of view. Moreover, ^{210}Po is the main source from the alpha emitters of the internal dose received by humans (UNSCEAR 1988). The concentration levels of ^{210}Pb in the groundwater samples ranged from 1.26–7.81 mBq/L, which corresponds to <0.1 Bq/L of ^{210}Pb . The maximum concentration of ^{210}Pb was 7.81 ± 0.26 mBq/L. The results are comparable with the findings in the literature (Katzlberger et al. 2001; Kralik et al. 2003). The concentration of ^{210}Pb in the bottled drinking waters ranged from 1.22–2.53 mBq/L, with a mean concentration of 2.42 ± 0.11 mBq/L. The levels of ^{210}Po and ^{210}Pb in the drinking water are permissible for drinking as per the Guidelines for Drinking-water Quality (WHO 1993, 1998), where the acceptable limits are 0.2 Bq/L and 0.1 Bq/L for ^{210}Po and ^{210}Pb , respectively. Katzlberger et al. (2001) found an elevated level of ^{210}Pb in some natural water samples, but there is no substantial explanation as to the water chemistry and the presence of elevated levels of ^{210}Po and ^{210}Pb in groundwater (USGS 1998; Harada et al. 1989). ^{210}Po and ^{210}Pb are derived from the ^{238}U decay series, the same decay series that produces ^{226}Ra . The aquifer materials might carry ^{226}Ra , with ^{210}Po and ^{210}Pb as decay products, and ^{226}Ra remains dissolved in the aquifer water system. Consequently, the daughter products (^{210}Po and ^{210}Pb) of ^{226}Ra are found in water (Cothorn and Rebers 1990; USGS 1998).

^{210}Pb was determined via ingrowth of ^{210}Po . After the separation of ^{210}Pb from the water sample, ^{210}Po ingrew again in the aqueous solution when sufficient time was allowed for the decay of ^{210}Pb . Therefore, ^{210}Pb could be determined by an extraction of ^{210}Po from the solution after a standing time of about 6 months or more. The ^{210}Po is produced from the ^{238}U decay series according to the following sequence of radioactive transformations:



The ^{210}Pb activity can be calculated according to the progenitor/progeny disequilibrium relationship for the boundary condition, with the activity of the progeny at zero time after the separation, i.e.:

$$A_{210\text{Pb}}(t_0) = \frac{A_{210\text{Po}}(t_1)}{(e^{-\lambda_{210\text{Pb}}t_1} - e^{-\lambda_{210\text{Po}}t_1})} \times \frac{\lambda_{210\text{Po}} - \lambda_{210\text{Pb}}}{\lambda_{210\text{Po}}}$$

where t_0 and t_1 refer to the time of the separation of Pb and extraction of Po from the water sample, respectively.

^{210}Pb is present in all systems in minor quantities. Soluble ^{210}Pb does not support its daughter ^{210}Po , so the aqueous Po is derived from Pb adsorbed or precipitated on aquifer materials (King et al. 1982; USGS 1998). The amount of ^{210}Pb present in the water samples is of interest because it decays into the alpha-emitting ^{210}Po . Figure 3 is a plot of the ingrowth of ^{210}Po over a period of 6 months. After 30 d, ^{210}Bi is in secular equilibrium with ^{210}Pb , and as the time passes the growth of ^{210}Po increases with the decay of ^{210}Bi , as its half-life is only 5.0 d. After 6 months, the growth of ^{210}Po is sufficient (~58.8% of ^{210}Pb activity) to measure its activity. Because of its relatively short half-life (138.4 d), decay correction of the ^{210}Po activity is necessary to obtain the ^{210}Po activity in the sample at the time of sampling. Consequently, for the present purposes, it is also necessary for decay correction to measure the activity of ^{210}Pb in the sample at the time of sampling.

The activity concentrations are shown in Tables 1 and 2 and have been corrected for the decay of ^{210}Po to correspond to the sampling time. Uncertainties were calculated according to the law of error propagation. Typical uncertainties of ^{210}Po and ^{210}Pb analysis are 7–8%. The final results of the concentrations of ^{210}Po and ^{210}Pb obtained in the water samples were compared with the reference values. A ^{209}Po tracer was used for the determination of chemical recovery. The detector efficiency of the PERALS system was nearly 99.7%.

Table 1 ^{210}Po activity in the groundwater and drinking water samples measured by different techniques. Quoted uncertainties are 1 σ . For Location 1 to Location 8, samples were collected from each location from different wells. For instance, samples from Location 2 were collected from 8 different wells in Location 2 at the same sampling time. For bottled drinking water, samples were collected from 2 wells (different production lines).

Water samples (locations and identification)	Nr of samples	^{210}Po activity range (mBq/L) via the 3 techniques	^{210}Po activity range (mBq/L) via PERALS method (mean value)	^{210}Po activity range (mBq/L) via α -spectrum method (mean value)	^{210}Po activity range (mBq/L) via LSC method (mean value)
Location-1	8	4.18–6.51	5.88 \pm 0.28	5.54 \pm 0.29	5.12 \pm 0.28
Location-2	8	1.42–2.38	1.64 \pm 0.09	2.12 \pm 0.08	1.98 \pm 0.05
Location-3	7	5.46–7.11	6.77 \pm 0.22	6.15 \pm 0.23	5.86 \pm 0.21
Location-4	7	3.25–4.33	3.67 \pm 0.19	3.51 \pm 0.21	3.86 \pm 0.18
Location-5	8	9.14–12.77	10.34 \pm 0.31	11.26 \pm 0.29	11.88 \pm 0.31
Location-6	7	4.18–5.52	4.86 \pm 0.11	5.24 \pm 0.12	4.46 \pm 0.12
Location-7	8	4.79–6.61	5.78 \pm 0.28	6.15 \pm 0.31	5.27 \pm 0.22
Location-8	7	3.43–4.57	3.81 \pm 0.17	4.36 \pm 0.15	3.74 \pm 0.16
Drinking water-1	2	1.31–1.79	1.43 \pm 0.08	1.68 \pm 0.06	1.52 \pm 0.05
Drinking water-2	2	2.25–2.78	2.67 \pm 0.14	2.29 \pm 0.14	2.51 \pm 0.15
Drinking water-3	2	<LLD	<LLD	<LLD	<LLD
Drinking water-4	2	<LLD	<LLD	<LLD	<LLD
Drinking water-5	2	1.62–2.26	1.71 \pm 0.11	1.92 \pm 0.12	2.11 \pm 0.11
Drinking water-6	2	2.42–2.88	2.74 \pm 0.09	2.51 \pm 0.09	2.81 \pm 0.10
Drinking water-7	2	1.81–2.47	2.37 \pm 0.10	2.11 \pm 0.11	2.23 \pm 0.10

Table 1 ^{210}Po activity in the groundwater and drinking water samples measured by different techniques. Quoted uncertainties are 1σ . For Location 1 to Location 8, samples were collected from each location from different wells. For instance, samples from Location 2 were collected from 8 different wells in Location 2 at the same sampling time. For bottled drinking water, samples were collected from 2 wells (different production lines). (*Continued*)

Water samples (locations and identification)	Nr of samples	^{210}Po activity range (mBq/L) via the 3 techniques	^{210}Po activity range (mBq/L) via PERALS method (mean value)	^{210}Po activity range (mBq/L) via α -spectrum method (mean value)	^{210}Po activity range (mBq/L) via LSC method (mean value)
Drinking water-8	2	<LLD	<LLD	<LLD	<LLD
Drinking water-9	2	1.41–2.26	1.59 ± 0.12	2.15 ± 0.12	1.77 ± 0.11
Drinking water-10	2	1.51–2.26	1.66 ± 0.11	1.81 ± 0.11	1.98 ± 0.10
Drinking water-11	2	1.88–2.37	2.24 ± 0.08	2.11 ± 0.09	2.32 ± 0.07
Drinking water-12	2	2.34–2.87	2.51 ± 0.07	2.76 ± 0.08	2.41 ± 0.07

Table 2 ^{210}Pb activity in the water samples measured by PERALS spectrometry and LSC. Quoted uncertainties are 1σ .

Water samples (locations and identifications)	Nr of samples	^{210}Pb activity range (mBq/L) via the 2 techniques	^{210}Pb activity (mBq/L) via PERALS method (mean value)	^{210}Pb activity (mBq/L) via LSC (mean value)
Location-1	8	3.27–5.18	4.82 ± 0.29	4.43 ± 0.27
Location-2	8	1.26–2.83	2.32 ± 0.08	1.83 ± 0.07
Location-3	7	5.17–7.81	6.15 ± 0.18	6.72 ± 0.16
Location-4	7	2.28–3.25	2.79 ± 0.16	3.11 ± 0.14
Location-5	8	3.41–5.32	4.36 ± 0.24	4.88 ± 0.23
Location-6	7	3.31–4.19	3.63 ± 0.11	3.97 ± 0.12
Location-7	8	4.35–6.17	5.17 ± 0.17	5.83 ± 0.15
Location-8	7	3.15–4.88	4.56 ± 0.18	4.14 ± 0.17
Drinking water-1	2	1.26–1.53	1.44 ± 0.06	1.31 ± 0.06
Drinking water-2	2	2.14–2.53	2.29 ± 0.11	2.42 ± 0.11
Drinking water-3	2	<LLD	<LLD	<LLD
Drinking water-4	2	<LLD	<LLD	<LLD
Drinking water-5	2	1.67–2.14	1.71 ± 0.07	1.92 ± 0.07
Drinking water-6	2	1.43–2.11	1.89 ± 0.09	1.65 ± 0.11
Drinking water-7	2	1.27–1.74	1.63 ± 0.09	1.41 ± 0.08
Drinking water-8	2	<LLD	<LLD	<LLD
Drinking water-9	2	1.65–1.96	1.76 ± 0.09	1.88 ± 0.09
Drinking water-10	2	1.43–1.78	1.58 ± 0.09	1.69 ± 0.07
Drinking water-11	2	1.22–1.38	1.27 ± 0.05	1.32 ± 0.05
Drinking water-12	2	1.48–1.72	1.53 ± 0.07	1.68 ± 0.07

Table 3 Recovery of ^{210}Po using standard reference materials (mBq/L).

Sample code	^{209}Po concentration reference value (mBq/L)	^{209}Po experimental value (mBq/L)	Error (%)	Chemical yield (%)
NIST SRM 4326 ^{209}Po	20.16	19.78 ± 1.2	–1.9	98.1%

Comparison of the Results of PERALS with Alpha Spectrometry and LSC Methods

The groundwater and drinking water samples were analyzed for ^{210}Po using the techniques of PERALS, alpha spectrometry, and LSC. The concentration of ^{210}Pb was measured using the equations of decay of ^{210}Pb and growth of ^{210}Po . Results of 60 groundwater and 24 mineral water samples using the above-mentioned methods are given in Tables 1 and 2. The 3 methods give similar results with uncertainties within 7–8%.

LSC analysis was carried out by directly mixing ~8 mL of the filtered water samples with 12 mL of the commercial cocktail Optiphase HiSafe3 (PerkinElmer, USA) in counting vials. Samples were counted by a Wallac Quantulus 1220TM ultra low-level LS counter with alpha/beta discrimination mode. The detection efficiency of LSC is evaluated by measuring solutions traced with ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ with activity concentrations and standards similar in composition to the samples; the efficiency was ~100%. The minimum detectable activity (MDA) was evaluated using the following equation:

$$\text{MDA (Bq/kg)} = L_d (\epsilon TV)^{-1}$$

where L_d (counts) = $2.71 + 4.65(BT)^{-0.5}$; T is the counting time (s), B is the background count rate (s^{-1}), ϵ is the detection efficiency, and V is the sample volume (L).

The LLD for gross α was 3.78 pCi/L for 500 min of counting time, 8 mL of sample size, and 12 mL of cocktail, 100% E. For gross β , the LLD was 12.9 pCi for 500 min of counting time, 8 mL of sample size, and 12 mL of cocktail, 100% E.

The LSC spectra of the ^{210}Pb and ^{210}Po of the groundwater samples are given in Figure 6.

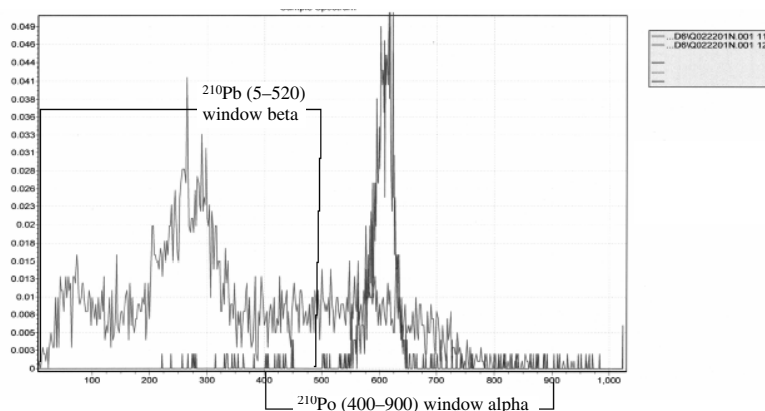


Figure 6 LSC spectra of ^{210}Pb and ^{210}Po for the groundwater samples

The concentrations of ^{210}Po in water samples analyzed by PERALS spectrometry are similar to those analyzed by alpha spectrometry and LSC (Tables 1 and 2). As per the WHO guidelines for drinking water quality and the Canadian guidelines for drinking water quality-supporting document, the maximum acceptable concentrations of ^{210}Po and ^{210}Pb are 0.1 and 0.2 Bq/L, respectively, while the maximum mean concentration values of ^{210}Po and ^{210}Pb in the analyzed drinking waters are 2.71 ± 0.15 and 2.36 ± 0.11 mBq/L, respectively. The values are below the above-mentioned limits. The maximum mean concentration values of ^{210}Po and ^{210}Pb in the groundwater samples are 6.11 ± 0.31 and 5.73 ± 0.27 mBq/L, respectively, which are less than the permissible limits cited in the

drinking water guidelines of WHO and the Canadian guidelines for drinking water. Therefore, the groundwaters in those regions can be taken directly without making any purification for reduction of the Po and Pb levels.

CONCLUSION

This preliminary study indicates the presence of ^{210}Pb and ^{210}Po in the groundwater in a region of Saudi Arabia. The levels of radioactivity of ^{210}Po and ^{210}Pb in the groundwater samples range from 1.42–12.77 and 1.26–7.81 mBq/L, respectively. The concentration levels are relatively small compared with the level of activity ranges 4.4–27.7 mBq/L and 2.7–322.3 mBq/L given by Katzlberger et al. (2001). The concentrations of ^{210}Po and ^{210}Pb in the bottled drinking water determined by the 3 techniques vary between 1.31–2.88 and 1.22–2.53 mBq/L, respectively. The concentration levels of ^{210}Po and ^{210}Pb in the groundwater and bottled drinking water analyzed in this study are low compared with the maximum acceptable limits mentioned in the WHO Guidelines for Drinking-water Quality (WHO 2004), where the limits are 0.1 Bq/L and 0.2 Bq/L for ^{210}Po and ^{210}Pb , respectively. The concentration levels of ^{210}Po and ^{210}Pb in the bottled drinking water are less than the activity level measured in the groundwater samples.

This paper focuses on providing basic contrasts among the 3 techniques in use in determining the concentrations of ^{210}Po and ^{210}Pb in water samples. No comparison of the analyses' costs using the various methods was attempted. The PERALS analysis is a technique that provides high precision, as is reflected by the scintillation peak at full half maximum (FWHM) of ~250 keV and the accurate determination in the aqueous solution. The method is relatively faster than the α -spectrometry method since there are fewer radiochemical manipulations.

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