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Determination of ^{210}Pb and ^{212}Pb in water and their radiological impact to the public *via* drinking water

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Abstract A sensitive and accurate method for determining ultra low-level ^{210}Pb and ^{212}Pb in water samples through double measurements was developed. Pb was pre-concentrated as hydroxides, separated from alkaline earth elements as PbS precipitate, purified by an anion exchange resin chromatography column, precipitated as $PbSO_4$ for source preparation and counted by a low background β-counter. The procedure was checked with IAEA reference materials, and the results agreed well with the recommended values. The minimum detectable activity was 0.062 mBq·L^{-1} for ^{210}Pb and 0.053 mBq·L^{-1} for ^{212}Pb with a 48 L water sample. Seventeen drinking water samples were analyzed, with a Pb recovery of 88.8±5.5%, and the typical activity concentrations were 0.191−15.1 mBq·L^{-1} for ^{210}Pb and of 1.12−5.77 mBq·L^{-1} for ^{212}Pb. The estimated committed effective doses to adult members of the public in Italy due to intake of ^{210}Pb and ^{212}Pb in drinking water were 0.096−7.59 μSv·a^{-1} and 0.005−0.025 μSv·a^{-1}, respectively.

Key words ^{210}Pb, ^{212}Pb, Dose evaluation, Drinking water

1 Introduction

The general public are exposed to radiations from naturally occurring radioactive elements in the earth's crust and from cosmic radiation of extraterrestrial origin. It is reported that natural sources contribute more than 98% of the global human radiation dose, excluding medical exposures[1]. The global average dose from natural sources is about 2.4 mSv/a. About one-third of this dose is due to external radiation (terrestrial plus cosmic), and remaining two-thirds are due to inhalation and ingestion of radionuclides in air, water and food.

There is an elevated concern about the radiological characteristics and impact of drinking water. In fact, the naturally occurring radionuclides, such as those in the uranium series and the thorium series (^{238}U, ^{234}U, ^{226}Ra, ^{228}Ra, ^{228}Th, ^{222}Rn, ^{210}Pb, ^{210}Po), exist ubiquitously in drinking water, and often contribute significantly to internal dose to the population. Although gross α and β activity measurements can serve as a screening tool for authority to control drinking water quality, for dose estimation it is necessary that the specific radionuclide in drinking water should be identified and their individual activity concentrations measured, due to the fact that the dose coefficients are only related to the specific radionuclides.

Among the concerned radionuclides, there are four lead radioisotopes in nature, i.e. β- and γ-emitting ^{210}Pb ($T_{1/2}$= 22.23 a) and ^{214}Pb ($T_{1/2}$=26.8 min) in the uranium series, β- and γ-emitting ^{212}Pb ($T_{1/2}$= 10.64 h) in the thorium series, and β- and γ-emitting ^{211}Pb ($T_{1/2}$=36.1 min) in the actinium series. Due to their chemical behaviors, lead compounds are rather insoluble in natural water and are usually adsorbed onto solid particles, hence the relatively low contents of lead isotopes in water. Among the four lead radioisotopes, ^{214}Pb and ^{211}Pb, of very short half-lives and low contents or poor abundance, are not measurable in an effective time of sample preparation and separation, but ^{210}Pb and ^{212}Pb are measurable. Especially, ^{210}Pb with its daughter ^{210}Po ($T_{1/2}$=138.4 d) are of great concern from the standpoints of radiation protection due to their radiotoxicity, as they can accumulate in sources of food and drinking waters and contribute to nearly half of the dose from total internal

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irradiation by ingested natural radionuclides[2-6]. Therefore, routine monitoring of the ^{210}Pb concentrations in water is important.

For studies on the contamination level, accumulation and migration rate, cycling process, and bioavailability of specific contaminant in environmental media, and on the radiation impact assessment, monitoring ^{210}Pb in biological and environmental materials often requires methods that are sensitive, reliable and applicable to samples of considerable chemical complexity. There are five methods for determination of ^{210}Pb: (1) direct counting of the low-energy (46.5 keV) γ-ray of ^{210}Pb using γ-spectrometry with a low energy HPGe-detector[7,8]; (2) separation of ^{210}Po, which is an indirect decay product of ^{210}Pb, and counting of its α activity by α-spectrometry[9,10]; (3) co-precipitation of ^{210}Pb with Ba or Pb as a sulphate or sulfide, dissolving the sulphate in EDTA or dissolving the sulfide in HCl, mixing the obtained solution with scintillation cocktail and measuring by liquid scintillation counting[11–13]; (4) separation of ^{210}Bi, the direct progeny of ^{210}Pb, and counting of its β activity[14]; and (5) separation of Pb and counting of the β activity of the in-growing ^{210}Bi[15–18]. We have discussed the advantages and disadvantages of these methods in detail[16,17], and concluded that Pb separation is a practical, sensitive and fast method.

In contrast to ^{210}Pb analysis, methodology studies on determination of ^{212}Pb in water samples are scarce[19,20]. In fact, γ-spectrometry is preferably used to measure ^{212}Pb in water samples, but its minimum detection activity (MDA: ~ 0.1 Bq·L^{-1}) is too high to determine the ^{212}Pb contents in most water samples, especially the environmental waters; while β-counter can be used to accurately determine ^{212}Pb in water, but radiochemical concentration and separation of ^{212}Pb from water is needed.

Based on ^{210}Pb determination procedures for environmental samples, more experiments were made on herein[16,17], aimed at developing a sensitive and accurate technique for determining ^{210}Pb and ^{212}Pb in water samples through double measurements, and at applying the technique for ^{210}Pb and ^{212}Pb studies in health physics, geochronology and environmental science.

2 Experimental

2.1 Apparatus

Bismuth-210 for ^{210}Pb determination and ^{212}Pb-^{212}Bi for ^{212}Pb determination were measured using a 10-channel low-level β-counter (Berthold LB770, Germany). The counting efficiency for ^{210}Pb measurement was calibrated by $PbSO_4$ precipitate source obtained from a standard ^{210}Pb solution, and that for ^{212}Pb measurement was done by $PbSO_4$ precipitate source separated from a standard ^{232}U solution, which was old enough to reach radioactive equilibrium between ^{232}U and its progeny ^{212}Pb. The counting efficiencies of 48.2% for ^{210}Bi and 88.4% for ^{212}Pb-^{212}Bi were obtained, and the background was ≤ 0.0061 cps.

2.2 Reference materials and reagents

The ^{232}U and ^{210}Pb standard solutions for instrument calibration, the reference materials (IAEA-315 and IAEA-434) for quality control and the BIO-RAD-AG 1-X4 resin (100-200 mesh) for Pb separation were supplied by Amersham (UK), IAEA and the Bio-Rad Laboratories (Canada), respectively. $Pb(NO_3)_2$ was used to prepare the carrier solution for Pb separation, and all other reagents were of analytical grade.

2.3 Column preparation

The anion-exchange resin, BIO-RAD-AG 1-X4 (100–200 mesh), was sequentially treated with 6 mol·L^{-1} NaOH, 6 mol·L^{-1} HCl and distilled water to remove any fine particles and unexpected components. Twelve grams of the resin were loaded in an ion-exchange column (Φ13 mm×250 mm). Before use, the column was conditioned with 20 mL HCl (1.5 mol·L^{-1}).

2.4 Sampling

In this work, drinking water was defined as water that can be used for drinking, including bottled mineral water, tap water, well water and lake water etc. Seventeen drinking water brands were sampled, most of which were popularly consumed in Italy. Due to great variability of the ^{210}Pb and ^{212}Pb concentrations in environmental water samples and the short half-life of ^{212}Pb, a big volume of water (20–50 L) for each

brand was taken and the relevant analysis was done as immediately as possible after sampling (within 24 h). Therefore, the reported results of ^{210}Pb and ^{212}Pb corresponded to the date of sample analyses.

2.5 Preliminary tests

Preliminary tests for determining ^{210}Pb and ^{212}Pb in water samples were based on the procedure in Refs.[16,21], in which Pb separation was conducted by co-precipitation with lead and/or iron hydroxide, absorption with a BIO-RAD-AG 1-X4 anion-exchange resin column, purification by precipitation Pb as PbS in 6 mol·L^{-1} ammonium acetate and source preparation as $PbSO_4$.

2.5.1 Eliminating the interferences

Lead forms two series of compound, the stable plumbous salts in which it is bivalent and forms the Pb^{2+} (resembling the Ba^{2+} in many ways), and the less stable covalent plumbic compounds resembling the stannic compound, in witch it is quadrivalent. The plumbic compounds are either insoluble or hydrolysed by water to PbO_2. The fate and mobility of lead in environmental water are governed by its chemical and biological behaviours. Due to formation of many precipitates, such as PbO, PbO_2, PbS, $PbCO_3$, $PbSO_4$, lead halides etc, the concentrations of dissolved Pb in environmental waters including drinking water are generally low and variable, depending on formation of soluble complexes. Therefore, for accurate determination of ^{210}Pb and ^{212}Pb in environmental waters, big sampling volumes of 20–50 L are needed.

When the procedure mentioned above was used to treat the big-volume water samples, in many cases a big quantity of precipitate was obtained in the process of Pb pre-concentration. It was found that the precipitate is mainly carbonates, due to the fact that (1) the environmental or mineral water samples often contain a certain amount of HCO_3^- (30–1343 mg·L^{-1}), and (2) many transitional and alkaline earth metals can precipitate with CO_3^{2-} in basic conditions. Although the carbonates can be destroyed by adding HCl or HNO_3 while heating, a big quantity of cations, especially Ca^{2+}, are left in the solution, interfering the Pb^{2+} adsorption on the resin exchange column and deteriorate effective separation from uranium and radium in the next step.

We tried to separate Pb as $PbSO_4$ precipitate. While this way worked well for 1.0 g soil or sediment[17], it did not seem very effective when a big quantity of Ca present in the sample solution, as a big quantity of $PbSO_4$ and $CaSO_4$ was obtained, and the latter is not easily soluble in 10–20 mL of 6 mol·L^{-1} NH_4Ac. A big volume of 6 mol·L^{-1} NH_4Ac (100–300 mL) could dissolve $CaSO_4$ completely, but low Pb recovery was observed due to the increasing solubility of $PbSO_4$.

Therefore, we tried to reverse the original analytical procedure of resin exchange separation and PbS purification. After Pb co-precipitation and dissolution, PbS precipitation was made first by adding 20–30 g NH_4Ac and 8 mL of 0.5 mol·L^{-1} Na_2S at pH 6–7. In this case, all the alkaline earth elements remain in solution and were eliminated by centrifugation. The obtained black PbS and FeS were then dissolved by HCl for further purification by anion resin exchange column. This modification proved successfully in the high Pb recovery and short analytical time, in the effective elimination of silicon gel before resin separation and prevention from column blocking, and in the improved decontamination effects from main α- and/or β-emitters, such as uranium, thorium, radium and other progenies.

2.5.2 The measurement principle

As mentioned above, due to their short half-lives and low abundance, ^{214}Pb and ^{211}Pb in water sample are not detectable after chemical separation. It is difficult to detect ^{212}Pb in water directly by using γ-spectrometry with an MDA of ~ 0.1 Bq·L^{-1} due to its low activity concentration in most of the water samples, and there is few reports concerning the determination of ^{212}Pb in water samples by chemical separation methods[20]. On the contrary, a number of authors reported their determination of ^{210}Pb in water samples by physical and chemical methods[8,16]. ^{210}Pb through its daughter ^{210}Bi can be determined with ease by the routinely used instrument — low background β-counter. As mentioned in Ref.[16], more accurate ^{210}Pb concentration can be obtained when ^{210}Pb and ^{210}Bi have reached the secular equilibrium about 30 days after the Pb source preparation.

In experiments for determining ^{210}Pb in water, ^{212}Pb through both ^{212}Pb and ^{212}Bi could be determined simultaneously with ^{210}Bi, the daughter of ^{210}Pb, using low-background β-counter after pre-concentration and separation. As a typical result, Fig.1a shows the β counting rate as a function of time after the Pb source preparation from a mineral water sample based on the recommended procedure. After careful treatment of the data, it was found that the figure can be well resolved into two fractions. The first fraction, located in the counting time of 0–2 days, is dominated by the ^{212}Pb-^{212}Bi decay, as shown in the insert of Fig.1a, while second fraction, located in the time after 2 day counting, is characterized by ^{210}Bi ingrowth from ^{210}Pb (Fig.1b). Therefore, after deducting the count contribution of the instrumental and reagent backgrounds and the contribution of ^{210}Bi in-growth, the first fraction can be used to calculate the ^{212}Pb activity concentration in water through extrapolation to the Pb separation time, and from the second fraction, the ^{210}Pb activity concentration can be calculated.

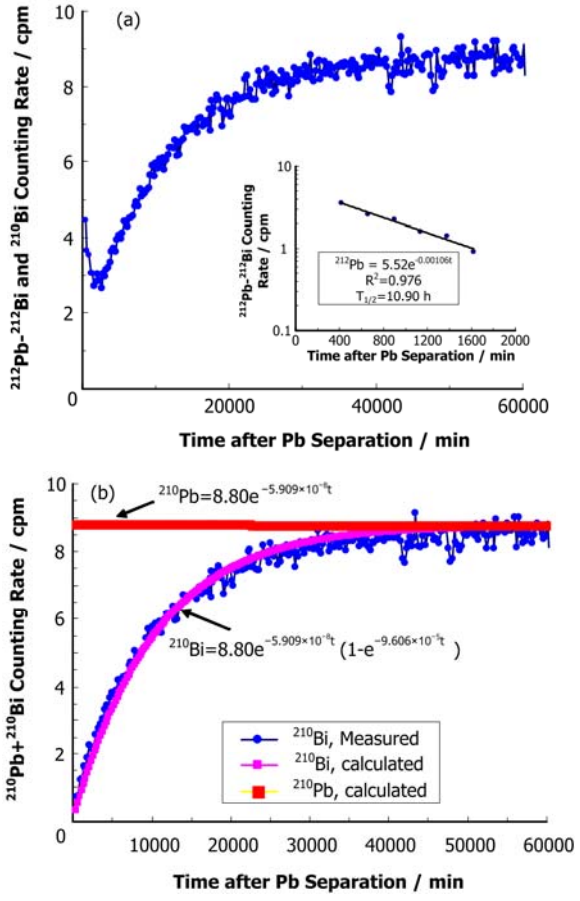

Fig.1 The ^{212}Pb-^{212}Bi decay and ^{210}Bi in-growth curve of a Pb source obtained from a potable water sample collected in Italy.

As shown in Fig.2, the finding was confirmed by analysis of a water sample characterized with very low ^{210}Pb activity (0.24 cpm). Therefore, simultaneous determination of ^{210}Pb and ^{212}Pb in water samples is achievable based on the principle of double measurements using a low background β-counter. The detailed procedure for Pb pre-concentration and separation and equations to calculate the ^{210}Pb and ^{212}Pb activity concentrations are given in Section 2.6.

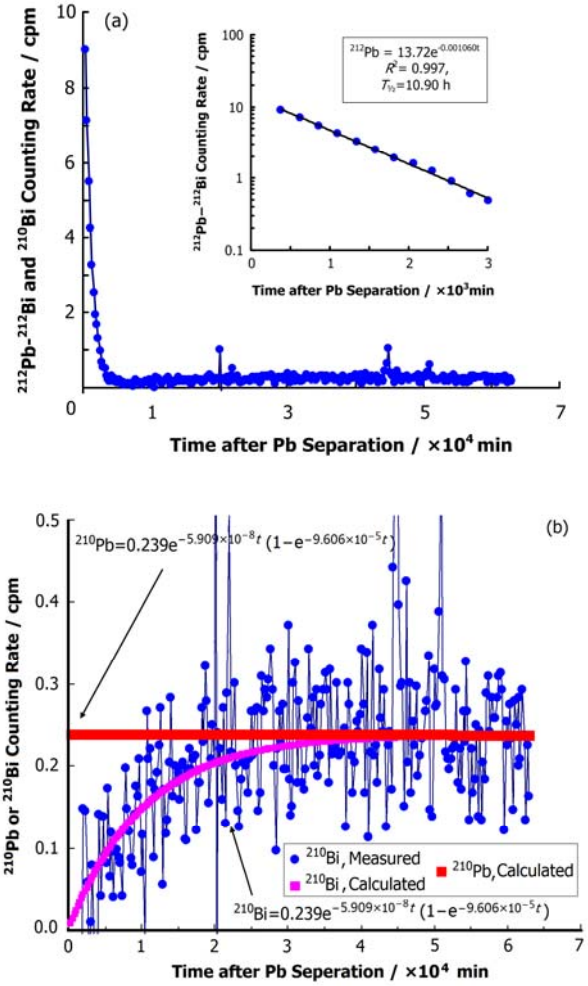

Fig.2 The ^{212}Pb-^{212}Bi decay and ^{210}Bi in-growth curve of a Pb source obtained from a tap water sample collected in Italy.

2.5.3 Detection efficiency of the instrument

A standard solution of ^{210}Pb was used to calibrate efficiency of the low background β-counter for determination of ^{210}Pb. The 1 mL ^{210}Pb standard solution (12.7 Bq·mL^{-1}), 0.8 mL Pb^{2+} carrier (25 mg Pb^{2+}·mL^{-1}) and 20 mL 2 M HNO_3 were added in a beaker, which was then heated to reach the isotopic equilibrium. After cooling to room temperature, $PbSO_4$ precipitation and source preparation were done

following the procedure given in Section 2.6.4. About one month after the source preparation, the ^{210}Pb activity was determined by measuring the in-growth activity of its progeny ^{210}Bi. The counting time was flexible to ensure the relative counting statistic error of ≤2%. The detection efficiency for ^{210}Pb was obtained as ratio of the detected activity of ^{210}Pb+^{210}Bi to the given value of ^{210}Pb.

A standard solution of ^{232}U was used to calibrate the efficiency of the instrument for determination of ^{212}Pb. The age of the solution was long enough to achieve the secular equilibrium with its progenies (^{228}Ra, ^{228}Ac, ^{228}Th, ^{224}Ra, ^{220}Rn, ^{216}Po and ^{212}Pb). A beaker was added with 0.607 Bq (0.0571 Bq·mL^{-1}) of ^{232}U or ^{212}Pb standard solution, 1 mL Fe^{3+} carrier (40 mg Fe^{3+} per mL), 0.8 mL Pb^{2+} carrier (25 mg Pb^{2+} per mL) and 20 mL 2 mol·L^{-1} HNO_3. It was heated to reach isotopic equilibrium. After cooling to room temperature, ^{212}Pb separation and source preparation were done following the procedure given in Section 2.6.1–2.6.4. The activity of ^{212}Pb-^{212}Bi was immediately determined after reaching their radioactive equilibrium. The counting time was flexible to ensure the relative counting statistic error of ≤2%. The detection efficiency for ^{212}Pb was obtained as ratio of the detected activity rate of ^{212}Pb+^{212}Bi to the given standard value of ^{232}U or ^{212}Pb.

2.6 Recommended procedure

2.6.1 Pre-concentration of Pb from water samples

Concentrated HCl of 30–50 mL, 1 mL Fe^{3+}carrier (40 mg Fe^{3+} per mL) and 1 mL Pb^{2+} carrier (25 mg Pb^{2+} per mL) were added to a water sample of 20–50 L. After 30 min stirring for isotopic exchange between carriers and analytes, the solution was adjusted to pH 9–10 with concentrated ammonia solution to precipitate iron and lead as hydroxides and carbonates, and well mixed. After the precipitate settled down, the supernatant was carefully siphoned off and the precipitate slurry was centrifuged at 4000 rpm. The supernatant was discarded and the precipitate was dissolved with 30–40 mL concentrated HCl. The solution was then transferred to a beaker and heated to boil for digestion with 2 mL of 30% H_2O_2.

2.6.2 Separation of Pb from alkaline earth elements

The obtained solution (about 150 mL) was neutralized to pH 1.0–1.5 with ammonia solution, and 20–30 g NH_4Ac was added and dissolved by heating, then 8 mL 0.5 mol·L^{-1} Na_2S were added. In this case, PbS was precipitated while most of Ca^{2+} and Mg^{2+} would remain in the solution. After centrifugation, the supernatant was discarded and the black precipitate was collected. Dissolving the precipitate with 4 mL concentrated HCl and 26 mL water, digestion was made by adding 2 mL 30% H_2O_2. The solution was filtered using a Millipore filter paper (pore size: 0.1 μm).

2.6.3 Purification of Pb

The obtained solution in an acidity of 1.5 mol·L^{-1} HCl was passed through a pre-conditioned anion-exchange resin column at room temperature and a free flow rate. After washing with 40 mL 1.5 mol·L^{-1} HCl, Pb was eluted with 60 mL distilled water at free flow rate, and the separation time (t_0, min) of the pair ^{210}Pb/^{210}Bi and ^{212}Pb was recorded.

2.6.4 Source preparation, measurement and calculation

The collected eluant was added with 3 mL concentrated H_2SO_4, and was evaporated until fuming to destroy the organic matters by oxidation with 1 mL 30% H_2O_2. Both the precipitate and solution were centrifuged. The supernatant was discarded and the precipitate was filtered on a weighed filter paper of *Φ*24 mm (Whatman 42). The sample was dried at 110°C until constant weight (about 1 h) and weighed again to calculate the Pb chemical yield. ^{212}Pb was measured immediately by a low background β-counter after the chemical separation. The time interval between the separation time of ^{212}Pb (t_0) and the start of the ^{212}Pb measurement was recorded as t_1 (min), and the counting time of ^{212}Pb as t_2 (min). ^{210}Pb was determined by measuring the in-growth activity of its progeny ^{210}Bi ($T_{1/2}$=120 h) about one month after the separation. The time interval between the separation time of ^{210}Pb (t_0, min) and the start of the ^{210}Bi measurement was recorded as t_3. The ^{210}Pb activity concentration in the water sample ($C_{\text{Pb-210}}$, Bq·L^{-1}) can be calculated by

$$C_{\text{Pb-210}}=A_{\text{Bi-210}}/[(1-e^{-\lambda_{\text{Bi-210}}t_3})\eta_1 Yv] \quad (1)$$

where $A_{\text{Bi-210}}$ is the net count rate of ^{210}Bi (cps), $\lambda_{\text{Bi-210}}$=9.604×10^{-5} min^{-1} is the decay constant of ^{210}Bi,

η_1 is detection efficiency for ^{210}Bi, Y is the chemical yield, and v is the sampling volume (L). The ^{212}Pb concentration in the water sample ($C_{\text{Pb-212}}$, Bq·L^{-1}) can be calculated by:

$$C_{\text{Pb-212}}=A_{\text{Pb-Bi-212}}\lambda_{\text{Pb-212}}t_2/[(1-e^{-\lambda_{\text{Pb-212}}t_2})e^{-\lambda_{\text{Pb-212}}t_1}\eta_2 Yv] \quad (2)$$

where, $A_{\text{Pb-Bi-212}}$ is the net count rate subtracting the contribution of the blank and ^{210}Bi (cps), $\lambda_{\text{Pb-212}}$= 1.086×10^{-3} min^{-1} is decay constant of ^{212}Pb, and η_2 is the detection efficiency for ^{212}Pb(^{212}Bi).

As ^{212}Bi is of $T_{1/2}$=60.54 min, but 4−5 h are needed from Pb separation and source preparation to ^{212}Pb measurement, by the time of measurement ^{212}Pb-^{212}Bi will have reached the radioactivity equilibrium. Therefore, in Eq.(2) the radioactivity equilibrium correction of ^{212}Pb-^{212}Bi is neglected. In order to reduce affection of the growing count contribution of ^{210}Bi, the counting time of ^{212}Pb/^{212}Bi can be 30−60 min as far as the counting statistic error concerns, and in this case the decay correction of ^{212}Pb during the ^{212}Pb measurement can be negligible. Therefore, Eq.(2) can be simplified as:

$$C_{\text{Pb-212}}=A_{\text{Pb-Bi-212}}/[e^{-\lambda_{\text{Pb-212}}t_1}\eta_2 Yv] \quad (3)$$

2.7 The minimum detectable activity

Considering the blank count rates (0.364±0.016 cpm), counting time (1440 min or 60 min), counting efficiencies of the instrument for ^{210}Pb+^{210}Bi (48.2%) and for ^{212}Pb+^{212}Bi (88.4%), the radiochemical yields (88.8±5.5%), the in-growth or decay factor (^{210}Pb: 100%, ^{212}Pb: 63.8%) and the sampling quantity (48 L), the minimum detectable activity (MDA) of the method for water sample are 0.062 mBq·L^{-1} for ^{210}Pb and 0.053 mBq·L^{-1} for ^{212}Pb[22].

3 Results and discussion

Uncertainties of the activity concentrations were estimated using all the uncertainties associated with the instrument calibration, the carrier addition to the sample, the counting statistics of the sample and the blank sources, etc.

3.1 Quality control

In general, the following approaches can be used to review the quality of a radioanalytical method: (1) to analyze the certified reference materials or similar matrices and to compare the obtained results with the recommended values, (2) to participate the comparison activities between different international laboratories, and (3) to analyze the spiked samples. Due to the fact that large amounts of water as the reference material for ^{210}Pb and ^{212}Pb analysis were not available, instead, we used reference material IAEA-315 marine sediment. The reference material of about 2 g was leached based on the procedure in Ref.[17]. The obtained leachates were analyzed following the recommended procedure for water samples. The precision was evaluated by the relative standard deviation obtained from a set of six analyses. The accuracy was assessed by the term of relative bias, which reflects the difference between the experimental mean and recommended value of the ^{210}Pb activity concentration. Due to the presence of unsupported ^{210}Pb in the IAEA-315, the fraction of unsupported ^{210}Pb should be corrected to the reference date.

The ^{210}Pb and ^{212}Pb activity concentrations in IAEA-315 are shown in Table 1. The mean ^{210}Pb concentration in IAEA-315 was found to be 30.8±5.9% Bq·kg^{-1} (decay correction to 1st Jan. 1993) from six analyses, and the <10% precision of analyses is well acceptable as far as such a low activity is concerned. The relative bias obtained from the analyses is +2.3% for ^{210}Pb, showing that the mean activity concentrations of ^{210}Pb are in good agreement with the recommended value of 30.1 Bq·kg^{-1} (the 95% confidence interval: 26.0−33.7 Bq·kg^{-1}). The mean ^{212}Pb concentration in IAEA-315 was found to be 26.5±3.2 Bq·kg^{-1}. Although IAEA did not issue any recommended value for ^{212}Pb, the reliability of the ^{212}Pb activity concentration may be judged from the recommended value for ^{228}Th that is in secular equilibrium with its predecessors ^{228}Ra and ^{232}Th (27.0 Bq·kg^{-1}). In fact, the ^{212}Pb activity in the IAEA-315 sample is also in equilibrium with ^{228}Th, as its decay products are of short half-lives, and ^{220}Rn escaped from the sealed container is negligible (≤2%).[23] In this case, the obtained relative standard deviation and the relative bias of ^{212}Pb are ±12% and −1.8%, respectively. The deviation for ^{212}Pb is bigger than that for ^{210}Pb, mainly due to multi-corrections for its decay,

the instrument background, reagent background, and interference of the ^{210}Bi in-growth from ^{210}Pb. However, the data of ^{212}Pb can still be considered as well acceptable and in good agreement with the recommended value [27.0 (24.0−28.9) Bq·kg^{-1}] for ^{228}Th. Experiments showed that determination of ^{212}Pb in closed (unsealed) soil sample can well predict the concentrations of ^{228}Ra and ^{232}Th. Although the residence time of ^{220}Rn and its progenies in the closed samples are not well known, ^{220}Rn escaping seems negligible, too.

Table 1 The ^{210}Pb and ^{212}Pb concentrations (in Bq·kg^{-1}), corrected to the date of 1st Jan. 1993, in the IAEA-315 marine sediment*

Sample No.	Sample weight / g	Pb yield / %	^{210}Pb	^{212}Pb	^{212}Pb/^{210}Pb
1	2.2724	93.3	27.5 ±1.2	22.2 ±1.7	0.808
2	2.0251	99.1	31.5 ±1.4	27.8 ±2.0	0.883
3	2.3418	92.2	31.3 ±1.4	24.4 ±1.6	0.781
4	2.0241	93.1	30.4 ±1.4	25.8 ±1.8	0.850
5	2.2622	92.0	33.0 ±1.5	31.5 ±1.9	0.954
6	1.5548	94.4	31.0 ±1.4	27.3 ±2.0	0.882
Mean±*SD*		94.0 ±2.6	30.8 ±1.8	26.5 ±3.2	0.860 ±0.062
(Range)		(92.0–99.1)	(27.5–33.0)	(22.2–31.5)	(0.808–0.9541)

* The recommended value (95% confidence interval) of ^{210}Pb and ^{228}Th are 30.1 (26.0−33.7) and 27.0 (24.0−28.9) Bq·kg^{-1}, respectively.

The method was also used to participate the inter-laboratory measurement of ^{210}Pb concentration in IAEA-434 phosphogypsum (IAEA-CU-2008-4) organized by IAEA. The ^{210}Pb concentration we obtained was 680±28 Bq·kg^{-1}, while the certified value is 680±58 Bq·kg^{-1}.

3.2 Concentrations of ^{210}Pb and ^{212}Pb in drinking water

The ^{210}Pb and ^{212}Pb are intermediate members of the ^{238}U and ^{232}Th decay series, arising from ^{226}Ra through ^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po, and from ^{228}Ra through ^{228}Ac, ^{228}Th, ^{224}Ra, ^{220}Rn and ^{216}Po. Measurements of ^{210}Pb and ^{212}Pb in water, soil, sediment, sand, rock and biological samples are important for studies in health physics, environmental science and geology, as they are not only radiologically toxic but also biologically harmful, and can be tracers for a number of processes of their geochemical cycling, ecological migration, biological uptake rate and availability in the atmosphere, hydrosphere and biosphere.

As shown in Table 2, typical activity concentrations in the drinking water samples are of 0.191−15.1 mBq·L^{-1} for ^{210}Pb and 1.12−5.77 mBq·L^{-1} for ^{212}Pb. The activity ratio for ^{212}Pb/^{210}Pb is 0.289−16, averaged at 2.58±4.08. Concentrations of uranium, thorium and radium isotopes, and ^{210}Po, in the same water samples were also determined (Table 3). Comparisons of the activity concentrations of ^{210}Po[24], and uranium, thorium and radium isotopes showed that the ^{210}Pb and ^{212}Pb activity concentrations in almost all water samples were much lower than that of uranium isotopes, but much higher than that of thorium isotopes, and more or less in the same levels as ^{226}Ra, ^{228}Ra and ^{210}Po. And the activity disequilibria could be observed for the pair of ^{210}Pb/^{226}Ra and ^{212}Pb/^{228}Ra in the water samples, though ^{210}Pb and ^{212}Pb are the most important progenies of ^{226}Ra and ^{228}Ra, respectively.

Statistic correlation analyses between the components were made. No correlations of ^{210}Pb/^{226}Ra and ^{212}Pb/^{228}Ra concentrations in the drinking water samples were observed, even though each pair belongs to the same decay series and with the same oxidation state of 2+. The carbonate presenting in the water samples is an important complexion agent, but no statistic correlations were observed for the pair of neither ^{210}Pb/HCO_3^- nor ^{212}Pb/HCO_3^-, indicating little effect of HCO_3^- or CO_3^{2-} on the ^{210}Pb and ^{212}Pb dissolution and behaviors of the lead isotopes seem different from radium in water containing HCO_3^-. A correlation between ^{210}Po and ^{210}Pb was found in the drinking water samples. The correlation equation reads [^{210}Po]=0.721[^{210}Pb]+1.65 (R^2=0.4254, n=17, P<0.05). This is because ^{210}Pb and ^{210}Po have similar chemical behaviors of valent 2+ and 4+ in water, and ^{210}Po is the granddaughter of ^{210}Pb.

Table 2 The ^{210}Pb and ^{212}Pb concentrations (in mBq·L^{-1}) in some Italian drinking water samples

Sample code and name (origin)		Water volume / L	Pb yield /%	^{210}Pb	^{212}Pb	^{212}Pb/^{210}Pb
1	Blues Aura (Umbria)	45.95	90.5	0.327±0.018	1.17±0.07	3.57
2	Egeria (Roma)	28.2	83.6	10.2±0.4	3.22±0.18	0.317
3	Guizza (Pescara)	38.0	93.9	3.62±0.15	1.12±0.08	0.308
4	Panna (Firenze)	28.0	92.6	5.11±0.21	1.77±0.11	0.346
5	Rocchetta (Perugia)	36.9	88.1	1.78±0.08	2.82±0.15	1.58
6	Lete (Caserta)	28.8	94.4	3.26±0.14	1.67±0.11	0.512
7	Vitasnella (Brescia)	27.8	91.0	8.65±0.36	3.17±0.18	0.367
8	Sangemini (Terni)	28.0	94.4	1.80±0.08	3.14±0.17	1.74
9	Brioblu Rocceetta (Perugia)	39.0	85.2	1.44±0.06	2.79±0.15	1.94
10	Vera (Padova)	38.4	89.9	6.66±0.28	1.93±0.11	0.289
11	San Benedetto (Vinece)	41.9	86.0	3.69±0.15	1.63±0.10	0.442
12	Lieve (Perugia)	46.0	89.7	0.806±0.036	4.03±0.20	5.01
13	Ferrarelle (Caserta)	27.8	93.1	4.27±0.18	3.26±0.18	0.764
14	Uliveto (Pisa)	40.0	85.4	0.458±0.024	2.48±0.14	5.41
15	Capannelle (Roma)	29.2	72.0	15.1±0.6	5.77±0.30	0.383
16	CSM tap water (Roma)	48.0	89.7	0.191±0.12	3.22±0.19	16.9
17	Magliana tap water (Roma)	37.5	89.9	0.562±0.028	2.27±0.13	4.05
Mean±*SD*			88.8 ± 5.5	3.99±4.11	2.67±1.15	2.58±4.08
(Range)			(72.0–94.4)	(0.2–15.1)	(1.12–5.77)	(0.29–16.9)

Table 3 The radioisotope concentrations (in mBq·L^{-1}) in drinking water samples collected in Italy*

Samples	^{238}U	^{234}U	^{235}U	^{232}Th	^{230}Th	^{228}Th	^{226}Ra	^{228}Ra	^{224}Ra	^{210}Po
1	16.8±0.9	17.1±0.9	0.86±0.17	0.0011±0.0002	0.0021±0.0003	0.100±0.004	4.76±0.23	1.50±0.18	0.64±0.24	0.40±0.04
2	59.8±2.4	84.4±3.3	3.31±0.33	0.0019±0.0004	0.0053±0.0007	0.927±0.057	3.56±0.25	10.2±0.9	2.17±0.36	11.3±0.5
3	6.14±0.29	6.43±0.30	0.29±0.05	0.0010±0.0003	0.0006±0.0004	0.0048±0.0014	1.19±0.10	1.23±0.24	1.12±0.23	0.50±0.04
4	7.21±0.38	13.2±0.6	0.35±0.08	0.0012±0.0003	0.0033±0.0006	0.0674±0.0032	2.49±0.17	1.95±0.27	0.35±0.16	3.39±0.20
5	2.33±0.15	3.37±0.19	0.16±0.04	0.0019±0.0013	0.0075±0.0023	0.0830±0.0067	2.72±0.20	1.18±0.21	0.73±0.21	1.01±0.06
6	20.5±1.2	23.3±1.3	0.98±0.21	0.0007±0.0002	0.0026±0.0003	0.176±0.006	3.07±0.21	2.92±0.38	0.90±0.24	1.37±0.11
7	78.5±4.2	71.4±3.8	4.10±0.54	0.0008±0.0002	0.0015±0.0004	0.166±0.006	26.6±1.2	5.01±0.41	0.93±0.16	7.37±0.45
8	14.2±0.7	13.4±0.7	0.42±0.11	0.0008±0.0003	0.0033±0.0007	0.0653±0.0037	8.74±0.47	3.47±0.33	0.64±0.19	1.29±0.10
9	1.39±0.20	2.09±0.23	0.08±0.05	0.0008±0.0004	0.0008±0.0007	0.0449±0.0033	1.61±0.11	0.74±0.22	0.53±0.26	5.93±0.36
10	12.0±0.8	15.3±1.0	0.99±0.21	0.0007±0.0002	≤ 0.0008	0.0068±0.0008	0.50±0.06	0.55±0.11	0.46±0.17	1.48±0.09
11	12.4±0.7	21.6±1.0	0.68±0.14	0.0014±0.0004	≤ 0.0008	0.325±0.013	0.52±0.06	0.10±0.14	<MDA	2.71±0.19
12	2.91±0.18	5.02±0.24	0.20±0.05	0.0013±0.0002	0.0014±0.0003	0.0307±0.0016	2.95±0.20	2.54±0.27	1.11±0.28	0.32±0.03
13	16.0±0.8	20.7±1.0	1.22±0.18	0.0018±0.0003	0.0017±0.0005	1.32±0.05	60.8±2.3	25.7±1.9	3.17±0.45	10.7±0.6
14	4.13±0.23	8.29±0.37	0.27±0.05	0.0027±0.0014	0.0036±0.0032	0.897±0.031	14.4±0.7	6.19±0.63	1.34±0.35	0.61±0.06
15	103±3	135±4	3.48±0.41	0.0019±0.0004	0.0023±0.0006	0.219±0.008	1.11±0.22	4.95±0.86	1.01±0.44	6.55±0.36
16	0.206±0.064	0.249±0.066	<MDA	0.0011±0.0003	0.0010±0.0005	0.0649±0.0030	10.8±0.6	11.8±1.1	7.97±1.12	0.13±0.01
17	7.22±0.36	7.55±0.37	0.51±0.10	0.0013±0.0004	0.0012±0.0007	0.0014±0.0010	4.97±0.28	1.53±0.25	1.53±0.61	0.15±0.01
Mean±*SD*	21.4 ±29.7	26.4±36.3	1.12±1.30	0.0013±0.0006	0.0023±0.0019	0.265±0.393	8.87±14.9	4.80±6.32	1.45±1.84	3.25±3.72
(Range)	(0.206–103)	(0.249–135)	(<MDA–4.1)	(0.0007–0.0027)	(0.0008–0.0075)	(0.0014–1.32)	(0.50–60.8)	(0.10–25.7)	(MDA–7.97)	(0.13–11.3)

* Refer to Table 2 for name (origin) of the drinking water samples.

3.3 Committed effective dose for adult public members due to intake of ^{210}Pb and ^{212}Pb in drinking water

The risk evaluation of lead for the general public involves radiological and biological toxicities. In this paper, only the radiological toxicity is evaluated. Assuming an annual water consumption of 730 L·a^{-1}, as is specified in Guidelines for Drinking-Water Quality[25,26]. Based on the ^{210}Pb and ^{212}Pb activity concentration in each water sample in Table 2, the annual intake rate, and the dose coefficients of 0.69 μSv/Bq for ^{210}Pb and 0.006 μSv/Bq for ^{212}Pb per unit intake recommended by the International Commission on Radiological Protection[27], the annual committed effective doses to the adult public members for each type of water intake were shown in Table 4. The doses are 0.096−7.59 μSv·a^{-1}, averaged at 2.13±2.08 μSv·a^{-1}, from ^{210}Pb intake, and 0.005−0.025 μSv·a^{-1}, averaged at 0.012±0.005 μSv·a^{-1}, from ^{212}Pb in the analyzed drinking waters. The major dose contribution of lead is from ^{210}Pb, and the dose fraction from ^{212}Pb is only about 0.56%, which seems less significant.

Table 4 Committed effective doses (in μSv·a^{-1}) to adults of the public in Italy from intake of ^{210}Pb and ^{212}Pb in drinking water.

Samples	^{210}Pb	^{212}Pb	^{210}Pb+^{212}Pb	^{212}Pb/^{210}Pb
1	0.165	0.0051	0.170	0.0310
2	5.12	0.0141	5.14	0.0028
3	1.82	0.0049	1.83	0.0027
4	2.57	0.0077	2.58	0.0030
5	0.895	0.0123	0.907	0.0138
6	1.64	0.0073	1.65	0.0044
7	4.36	0.0139	4.37	0.0032
8	0.908	0.0138	0.922	0.0151
9	0.724	0.0122	0.736	0.0169
10	3.35	0.0084	3.36	0.0025
11	1.86	0.0072	1.87	0.0038
12	0.406	0.0177	0.42	0.0435
13	2.15	0.0143	2.16	0.0066
14	0.231	0.0109	0.242	0.0471
15	7.59	0.0253	7.62	0.0033
16	0.096	0.0141	0.110	0.1469
17	0.283	0.0100	0.293	0.0352
Mean±*SD*	2.13±2.08	0.0121±0.0049	2.14±2.08	0.0219±0.0366
(Range)	(0.1–7.6)	(0.005–0.025)	(0.1–7.6)	(0.0025–0.147)

*Refer to Table 2 for name (origin) of the drinking water samples.

As far as all the measured radioisotopes are concerned[24,28], the total doses for all the drinking water samples are 2.81−38.5 μSv·a^{-1}, averaged at 10.9±10.6 μSv·a^{-1}[3], being well below the reference level of the committed effective dose (100 μSv·a^{-1}) recommended by the WHO for drinking water. As shown in Table 5, the dose contribution fractions from ^{210}Pb and ^{212}Pb are 1.25%−55.7%, averaged at 21.2±15.9%. Therefore, the two lead isotopes, mainly ^{210}Pb, play an important role in the internal exposure due to drinking water intake.

Table 5 The dose contribution fractions from the most important radioisotopes of uranium, thorium, radium, polonium and lead.

Samples	U	Th	Ra	Po	Pb
1	34.2	0.17	50.5	10.1	4.88
2	19.5	0.19	22.7	37.8	19.6
3	12.2	0.01	25.2	12.2	50.4
4	9.25	0.05	19.4	38.1	33.1
5	6.36	0.18	37.1	27.7	28.4
6	23.5	0.15	32.7	18.3	25.2
7	21.9	0.04	33.2	26.8	18.1
8	14.6	0.06	54.1	17.2	14.0
9	1.81	0.04	10.7	76.5	10.8
10	16.1	0.01	6.64	21.5	55.7
11	21.3	0.31	2.87	42.0	33.1
12	9.63	0.08	66.1	9.70	14.5
13	3.40	0.18	66.3	24.3	5.62
14	5.93	0.65	82.3	7.20	3.25
15	34.0	0.05	11.3	23.5	31.1
16	0.18	0.04	97.2	1.25	1.25
17	18.7	0.02	66.2	4.63	10.4
Mean±*SD*	14.9±10.3	0.13±0.16	40.3±28.1	23.5±18.2	21.2±15.9
(Range)	(0.2–34.2)	(0.01–0.65)	(2.8–97.2)	(1.3–76.5)	(1.3–55.7)

* Refer to Table 2 for name (origin) of the drinking water samples.

4 Conclusion

The method is devoted for determination of ultra low-level ^{210}Pb and ^{212}Pb concentrations in water samples through double measurements. Accuracy of the method was checked with IAEA reference materials, and the result agreed well with the recommended values. The minimum detectable activity is 0.062 and 0.053 mBq·L^{-1} for ^{210}Pb and ^{212}Pb, respectively, with a 48 L water sample. Seventeen drinking water samples were analyzed, with an average Pb recovery of 88.8±5.5%, and the typical activity concentrations are 0.191−15.1 and 1.12−5.77 mBq·L^{-1} for ^{210}Pb and ^{212}Pb, respectively. The committed effective doses to adult members of the

public in Italy due to drinking water intake are estimated at 0.096−7.59 and 0.005−0.025 μSv·a^{-1} for^{210}Pb and ^{212}Pb, respectively, hence a more important dose contributor of ^{210}Pb than ^{212}Pb. The dose contribution fractions from ^{210}Pb and ^{212}Pb together are 21.2±15.9% taking into account all the measured radioisotopes. The method is a sensitive and accurate, being a useful technique for ^{210}Pb and ^{212}Pb studies in health physics, geochronology and environmental sciences.

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