

# A method for simultaneous determination of $^{210}\text{Pb}$ and $^{212}\text{Pb}$ in drinking water samples

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## Abstract

A sensitive and accurate method for determination of  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  in drinking water samples was developed. In the method Pb was pre-concentrated as hydroxides, separated from alkaline earth elements as PbS precipitate, purified by an anion exchange resin chromatography column, precipitated as  $\text{PbSO}_4$  for source preparation and counted by a low background  $\beta$ -counter. The procedure was checked with a reference material supplied by the IAEA, and the obtained data were in good agreement with the recommended values, showing the recommended procedure can provide reliable results. The minimum detectable activity of the method was  $0.039 \text{ mBq L}^{-1}$  for  $^{210}\text{Pb}$  and  $0.033 \text{ mBq L}^{-1}$  for  $^{212}\text{Pb}$  if a 48 liter of water sample was analyzed. Seventeen drinking water samples were analyzed with a Pb recovery of  $88.8 \pm 5.5\%$ , and the typical activity concentration was in the range of  $0.191\text{-}15.1 \text{ mBq L}^{-1}$  for  $^{210}\text{Pb}$  and of  $1.12\text{-}5.77 \text{ mBq L}^{-1}$  for  $^{212}\text{Pb}$ .

## 1. Introduction

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 ( $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,

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$^{222}\text{Rn}$ ,  $^{210}\text{Pb}$ ,  $^{210}\text{Po}$ ), exist ubiquitously in drinking water, and often contribute significantly to internal dose to the population. Although gross  $\alpha$  and  $\beta$  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 concentration measured, due to the fact that the dose coefficients are only related to the specific radionuclides.

Among the concerned radionuclides, lead isotopes are not only biologically but also radiologically harmful. There are 4 radioactive lead isotopes in nature, *i.e.*  $\beta$ - and  $\gamma$ -emitting  $^{210}\text{Pb}$  ( $T_{1/2}$ : 22.23 yr) and  $^{214}\text{Pb}$  ( $T_{1/2}$ : 26.8 min) in the uranium series,  $\beta$ - and  $\gamma$ -emitting  $^{212}\text{Pb}$  ( $T_{1/2}$ : 10.64 h) in the thorium series, and  $\beta$ - and  $\gamma$ -emitting  $^{211}\text{Pb}$  ( $T_{1/2}$ : 36.1 min) in the actinium series. Due to its chemical behaviors, lead is rather insoluble in natural water and is usually readily adsorbed onto solid particles, and the contents of lead isotopes in water are relatively low. Among the four lead isotopes,  $^{214}\text{Pb}$  and  $^{211}\text{Pb}$ , possessing very short half-lives, low contents and/or poor abundance, are not measurable in the effective time of sample preparation and separation, but  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  are. Especially,  $^{210}\text{Pb}$  together with its granddaughter  $^{210}\text{Po}$  ( $T_{1/2}$ : 138.4 d) can be of great concern from the standpoints of radiation protection due to their radiotoxicity, as they can accumulate in sources of food, for instance, in particular forms of marine life, reindeer and caribou, and contribute to about nearly half of the dose from total internal irradiation by ingested natural radionuclides [1–5]. Therefore, the routine monitoring of the  $^{210}\text{Pb}$  concentration is very important.

For the purpose of studies on the accumulation and migration rate, cycling process in environmental media, bioavailability of the specific contaminant, survey of contamination level in environment and impact assessment, the monitoring of  $^{210}\text{Pb}$  in biological and environmental materials often requires methods that should be sensitive, reliable and applicable to samples of considerable chemical complexity. There are five main kinds of method for the measurement of  $^{210}\text{Pb}$ : (1) direct counting of the low-energy (46.5 keV)  $\gamma$ -ray of  $^{210}\text{Pb}$  using  $\gamma$ -spectrometry equipped with Ge(Li) detector [6, 7]; (2) separation of  $^{210}\text{Po}$ , being an indirect decay product of  $^{210}\text{Pb}$ , and counting of its  $\alpha$  activity by  $\alpha$ -spectrometry [8, 9]; (3) co-precipitation of  $^{210}\text{Pb}$  with Ba as a sulphate, dissolving the sulphate in EDTA, mixing the obtained solution with the scintillation cocktail and measuring by liquid scintillation counting [10, 11]; (4) separation of  $^{210}\text{Bi}$ , the direct progeny of  $^{210}\text{Pb}$ , and counting of its  $\beta$  activity [12], and (5) separation of Pb and counting of the  $\beta$  activity of the in-growing  $^{210}\text{Bi}$  [13–16]. In the literatures [14, 15], the advantages and disadvantages of these methods have been discussed in detail.

It is concluded that the Pb separation method is one of the most practical, sensitive and less time-consuming methods.

In contrast with  $^{210}\text{Pb}$ ,  $^{212}\text{Pb}$ , being a decay progeny of thoron ( $^{220}\text{Rn}$ ), owing to its short half-life the methodology studies on  $^{212}\text{Pb}$  determination in water samples are scarce [17].

Based on the Pb separation procedures [14, 15], more experiments were made on herein, seeking for further developing and improving the  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  separation conditions in water sample. The quality control tests and real sample analyses showed that the developed method for  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  determination in big quantity of water samples is a very sensitive and accurate technique, and can serve as a very useful tool for  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  studies in the fields of health physics, geochronology and environmental science.

## 2. Experimental

### 2.1 Apparatus and reagents

$^{210}\text{Bi}$  for  $^{210}\text{Pb}$  determination and  $^{212}\text{Pb}$ - $^{212}\text{Bi}$  for  $^{212}\text{Pb}$  determination were measured using a 10-channel low-level  $\beta$ -counter (Berthold LB770, Germany). The counting efficiency of the instrument for the  $^{210}\text{Pb}$  measurement was calibrated with a  $\text{PbSO}_4$  precipitate source obtained from a standard  $^{210}\text{Pb}$  solution and that for the  $^{212}\text{Pb}$  measurement was done with a  $\text{PbSO}_4$  precipitate source separated from a standard  $^{232}\text{U}$  solution that is old enough and has reached radioactive equilibrium between  $^{232}\text{U}$  and its progeny  $^{212}\text{Pb}$ . The obtained counting efficiencies were 48.16% for  $^{210}\text{Bi}$  and 88.36% for  $^{212}\text{Pb}$ - $^{212}\text{Bi}$ , respectively. The reagent background was of  $\leq 0.0053$  cps.

The  $^{232}\text{U}$  and  $^{210}\text{Pb}$  standard solutions for instrument calibration, the reference material (IAEA-315) for quality control and the BIO-RAD-AG 1-X4 resin (100–200 mesh) for Pb separation were supplied by Amersham (UK), the IAEA and the Bio-Rad Laboratories (Canada), respectively.  $\text{Pb}(\text{NO}_3)_2$  was used to prepare the carrier solution for Pb separation and all other reagents were analytical grade.

### 2.2 Column preparation

The anion-exchange resin, BIO-RAD-AG 1-X4 (100–200 mesh), was sequentially treated with 6 NaOH, 6 M HCl and distilled water to remove any fine particles as well as other unexpected components. Twelve grams of the resin

were then loaded in an ion-exchange column with dimensions of 13 mm internal diameter and of 250 mm length. Before use, the column was conditioned with 20 mL of 1.5 M HCl.

### 2.3 Preliminary tests

Preliminary tests for determination of  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  in water samples were primarily based on the procedure reported in the literatures [14, 18], in which Pb separation was conducted by coprecipitation with lead and/or iron hydroxide, absorption with a BIO-RAD-AG 1-X4 anion-exchange resin column, purification with  $\text{Na}_2\text{S}$  to precipitate Pb as PbS in 6 M ammonium acetate and source preparation as  $\text{PbSO}_4$ .

#### 2.3.1 Eliminating the interference of alkaline earth elements

Lead forms two series of compound, the stable plumbous salts in which it is bivalent and forms the  $\text{Pb}^{2+}$  in many ways resembling the  $\text{Ba}^{2+}$ , and the less stable covalent plumbic compounds resembling the stannic compound, in which it is quadrivalent. The plumbic compounds are either insoluble or hydrolyzed by water to lead dioxide  $\text{PbO}_2$ . The fate and mobility of lead in environmental water are governed by its chemical and biological behaviors. Due to formation of many precipitates, such as  $\text{PbO}$ ,  $\text{PbO}_2$ ,  $\text{PbS}$ ,  $\text{PbCO}_3$ ,  $\text{PbSO}_4$ , lead halides etc., the concentration of dissolved Pb in environmental waters including drinking water is generally low and variable, depending on formation of soluble complexes. Therefore, for accurate determination of  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  in environmental water a big sampling volume up to 20–100 L is needed.

When the procedure mentioned above was used to treat such a big volume of water sample, in many cases a big quantity of precipitate was obtained in the process of Pb pre-concentration. It was found that the major part of the precipitate is formed by carbonates, due to the fact that (1) the environmental or mineral water samples often contain a certain amount of  $\text{HCO}_3^-$  (30–1343  $\text{mg L}^{-1}$ ), and (2) many transitional ( $K_{\text{spMnCO}_3} = 1.8 \times 10^{-11}$ ,  $K_{\text{spFeCO}_3} = 3.5 \times 10^{-11}$ ,  $K_{\text{spPbCO}_3} = 3.3 \times 10^{-14}$ ,  $K_{\text{spAg}_2\text{CO}_3} = 8.1 \times 10^{-12}$ ,  $K_{\text{spHgCO}_3} = 8.9 \times 10^{-17}$ ) and alkaline earth metals etc. ( $K_{\text{spMgCO}_3} = 1 \times 10^{-5}$ ,  $K_{\text{spCaCO}_3} = 4.8 \times 10^{-9}$ ,  $K_{\text{spSrCO}_3} = 1.1 \times 10^{-10}$ ,  $K_{\text{spBaCO}_3} = 5.1 \times 10^{-9}$ ) can precipitate with  $\text{CO}_3^{2-}$  at the basic condition. Although the carbonates can be destroyed by addition of HCl or  $\text{HNO}_3$  during heating, a big quantity of cations, especially  $\text{Ca}^{2+}$ , are left in the solution, which interfere the  $\text{Pb}^{2+}$  adsorption on the resin exchange column

and deteriorate the effective separation from uranium, radium etc. in the next step.

In order to solve this problem, Jia and Torri [15] have tried to separate Pb as  $\text{PbSO}_4$  precipitate first and this way is working well for 0.5 g of soil or sediment, but it seems not very effective when a big quantity of Ca present in the sample solution, as a big quantity of  $\text{PbSO}_4$  as well as  $\text{CaSO}_4$  is obtained and the latter is not easily soluble in 10–20 mL of 6 M  $\text{NH}_4\text{Ac}$ . A big volume of 6 M  $\text{NH}_4\text{Ac}$  (100–300 mL) could dissolve  $\text{CaSO}_4$  completely, but low Pb recovery was observed due to the increasing solubility of  $\text{PbSO}_4$ .

The second test was to reverse the original analytical procedure of resin exchange separation and PbS purification, *i.e.* after Pb coprecipitation and dissolution, PbS precipitation was made first with addition of 20–30 g of  $\text{NH}_4\text{Ac}$  and 8 mL of 0.5 M  $\text{Na}_2\text{S}$  at pH 6–7. In this case, all the alkaline earth elements remain in solution and are eliminated by centrifugation, and the obtained black PbS and FeS etc. are dissolved by HCl for further purification by resin exchange column. This modification is very successful and with advantages of (1) high Pb recovery and short analytical time, (2) eliminating the most of silicon gel before resin separation and preventing from column blocking, and (3) improving the decontamination effects from main  $\alpha$ - and/or  $\beta$ -emitters, such as uranium, thorium, radium and their other progenies.

### 2.3.2 The mechanism of the $^{210}\text{Pb}$ and $^{212}\text{Pb}$ measurements

As mentioned above, due to their short half-lives and/or low abundance, unsupported  $^{214}\text{Pb}$  and  $^{211}\text{Pb}$  in water sample are not detectable after chemical separation. The unsupported  $^{212}\text{Pb}$  in water is difficult to be directly detected by  $\gamma$ -spectrometry due to its low activity concentration in most of the samples and there is few report concerning the determination of  $^{212}\text{Pb}$  in water samples by chemical separation methods. On the contrary, there are a number of reports about the determination of  $^{210}\text{Pb}$  in water samples by physical and chemical methods [7, 14]. Pb-210 through its daughter  $^{210}\text{Bi}$  can be determined with ease by the most routinely used instrument – low background  $\beta$ -counter. As reported in the reference [14], more accurate  $^{210}\text{Pb}$  concentration can be obtained when  $^{210}\text{Pb}$  and  $^{210}\text{Bi}$  have reached the secular equilibrium about 30 days after the Pb source preparation.

During experiments for determination of  $^{210}\text{Pb}$  in water, it was observed that  $^{212}\text{Pb}$  through both  $^{212}\text{Pb}$  and  $^{212}\text{Bi}$  can be determined simultaneously with  $^{210}\text{Pb}$  using low-background  $\beta$ -counter after pre-concentration

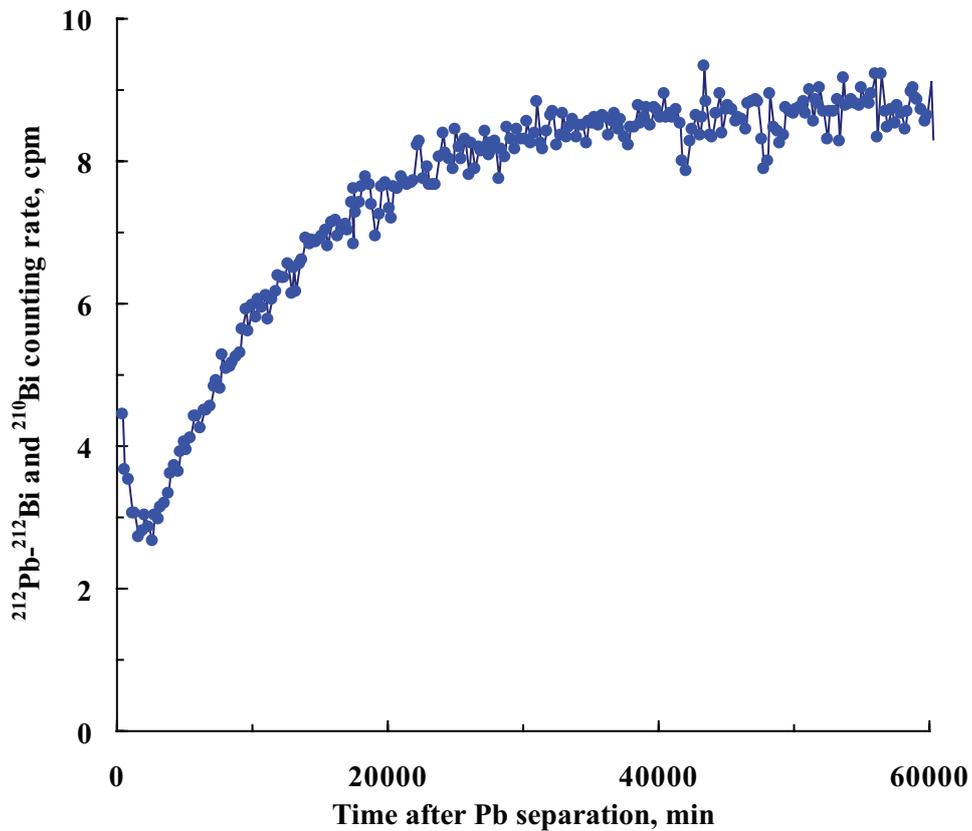


Figure 1: The  $^{212}\text{Pb}$ - $^{212}\text{Bi}$  decay and  $^{210}\text{Bi}$  ingrowth curve of a Pb source obtained from a potable water sample collected in Italy.

and separation. Figure 1 is a typical one, which shows the  $\beta$  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 is found that the figure can be very well resolved into two fractions. The first fraction, located in the counting time of 0–2 days, is dominated by the  $^{212}\text{Pb}$ - $^{212}\text{Bi}$  decay, as shown in fig. 2; while second fraction, located in the time after 2 day counting, is characterized by  $^{210}\text{Bi}$  ingrowth from  $^{210}\text{Pb}$  (fig. 3). Therefore, after deducting the count contribution of the instrumental and reagent backgrounds and the contribution of  $^{210}\text{Bi}$  ingrowth, the first fraction can be used to calculate the  $^{212}\text{Pb}$  activity concentration in water through extrapolation to the Pb separation time, and from the second fraction, the  $^{210}\text{Pb}$  activity concentration can be calculated.

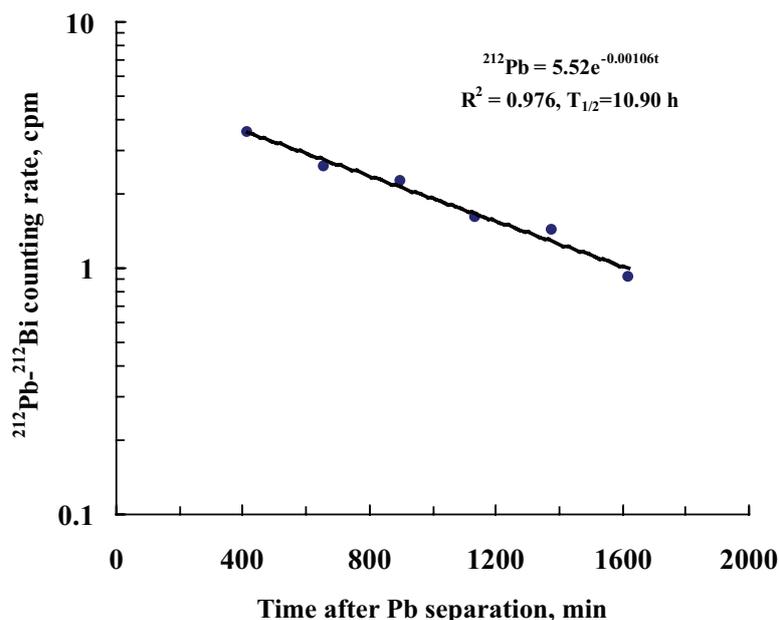


Figure 2: The  $^{212}\text{Pb}$ - $^{212}\text{Bi}$  decay curve of a Pb source obtained from a potable water sample collected in Italy (same water as shown in fig. 1).

## 2.4 Recommended procedure

### 2.4.1 Pre-concentration of Pb from water samples

Thirty to fifty mL of concentrated HCl, 40 mg of  $\text{Fe}^{3+}$  ( $40 \text{ mg Fe}^{3+} \text{ mL}^{-1}$ ) carrier, 25 mg of  $\text{Pb}^{2+}$  ( $25 \text{ mg Pb}^{2+} \text{ mL}^{-1}$ ) carrier are added to 20-50 L of water sample. After 30 min stirring for isotopic exchange between carriers and analytes, the solution is adjusted to pH 9-10 with concentrated ammonia solution to precipitate iron and lead as hydroxides and carbonates, and mixed well. After the precipitate settled down, the supernatant is carefully siphoned off and the precipitate slurry is centrifuged at 4000 rpm. The supernatant is discarded and the precipitate is dissolved with 30-40 mL of concentrated HCl. The solution is then transferred to a beaker and heated to boil for digestion with 2 mL of 30%  $\text{H}_2\text{O}_2$ .

### 2.4.2 Separation of Pb from alkaline earth elements as PbS

The obtained solution (about 150 mL) is neutralized to pH 1.0-1.5 with ammonia solution, and 20-30 g of  $\text{NH}_4\text{Ac}$  are added and dissolved by heating.

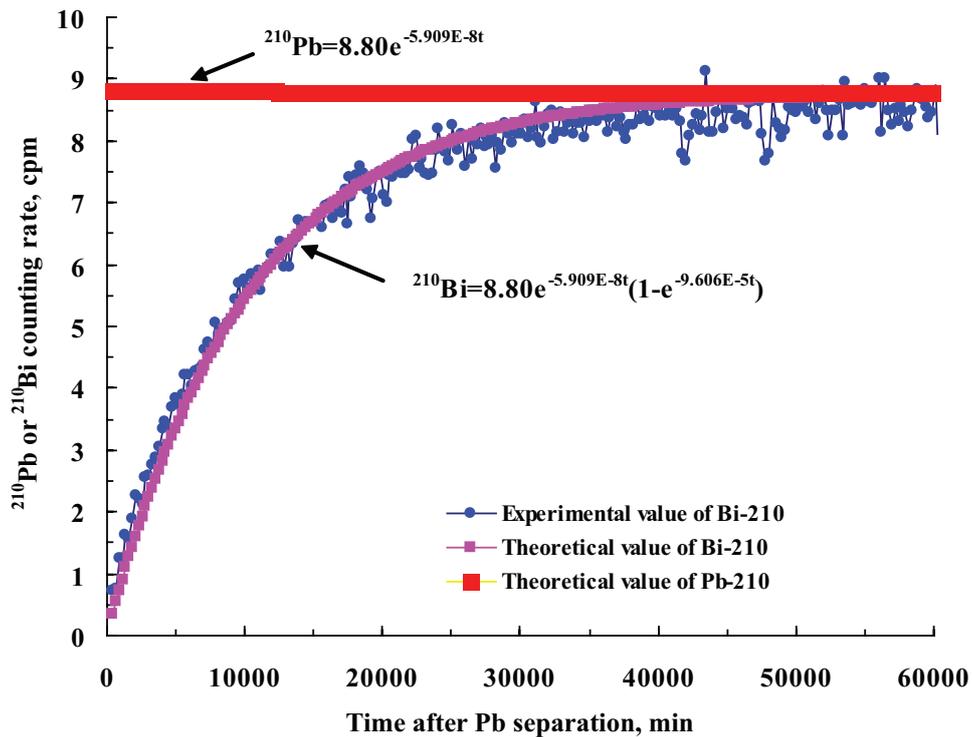


Figure 3: The  $^{210}\text{Pb}$  decay and  $^{210}\text{Bi}$  ingrowth curves (after subtracting the  $^{212}\text{Pb}$  contribution) of a Pb source obtained from a potable water sample collected in Italy (same water as shown in fig. 1).

Eight mL of 0.5 M  $\text{Na}_2\text{S}$  is added, and in this case  $\text{PbS}$  is precipitated while most of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  will remain in the solution. After centrifugation, the supernatant is discarded and the black precipitate is collected. Dissolving the precipitate with 4 mL of concentrated  $\text{HCl}$  and 26 mL of water, digestion is made by adding 2 mL of 30%  $\text{H}_2\text{O}_2$ , then the solution is filtered through a Millipore filter paper (pore size: 0.1  $\mu\text{m}$ ).

#### 2.4.3 Purification of Pb with anion-exchange resin column

The obtained solution in an acidity of 1.5 M  $\text{HCl}$  is passed through a pre-conditioned anion-exchange resin column at room temperature and a free flow rate. After washing with 40 mL of 1.5 M  $\text{HCl}$ , Pb is eluted with 60 mL of distilled water at free flow rate, and the separation time of the pair  $^{210}\text{Pb}/^{210}\text{Bi}$  and  $^{212}\text{Pb}$  is recorded.

#### 2.4.4 Source preparation, measurement and activity concentration calculation

Three mL of concentrated  $\text{H}_2\text{SO}_4$  are added to the collected eluant, which is then evaporated until fuming to destroy the organic matters by oxidation with 1 mL of 30%  $\text{H}_2\text{O}_2$ . Both the precipitate and the solution are centrifuged. The supernatant is discarded and the precipitate is filtered on a weighed filter paper with a diameter of 24 mm (Whatman 42). The sample is dried at  $110^\circ\text{C}$  until constant weight (about 1 h) and weighed again to calculate the Pb chemical yield.

Pb-212 is measured immediately after the chemical separation.  $^{210}\text{Pb}$  is determined by measuring the ingrowth activity of its progeny  $^{210}\text{Bi}$  ( $T_{1/2}$ : 120 h) by a low background  $\beta$ -counter some time after the separation (about one month being suitable). The  $^{210}\text{Pb}$  activity concentration in the water sample ( $C_{Pb-210}$ ,  $\text{Bq L}^{-1}$ ) can be calculated according to eq. (1):

$$C_{Pb-210} = A_{Bi-210}/(1 - e^{-\lambda_{Bi-210}t})\eta Y \nu, \quad (1)$$

where,  $A_{Bi-210}$ , the net count rate of  $^{210}\text{Bi}$  (cps);  $\lambda_{Bi}$ , the  $^{210}\text{Bi}$  decay constant ( $\text{min}^{-1}$ );  $t$ , the  $^{210}\text{Bi}$  ingrowth time after  $^{210}\text{Pb}$  separation (min);  $\eta$ , the detection efficiency for  $^{210}\text{Bi}$ ;  $Y$ , the chemical yield and;  $\nu$ , the sampling volume (L).

The  $^{212}\text{Pb}$  activity concentration in the water sample ( $C_{Pb-212}$ ,  $\text{Bq L}^{-1}$ ) can be calculated by eq. (2):

$$C_{Pb-212} = A_{Pb-Bi-212}/e^{-\lambda_{Pb-212}t}\eta Y \nu, \quad (2)$$

where,  $A_{Pb-Bi-212}$ , the net count rate subtracting the contribution of the blank and  $^{210}\text{Bi}$  (cps);  $\lambda_{Pb-212}$ , the  $^{212}\text{Pb}$  decay constant ( $\text{min}^{-1}$ );  $t$ , the time from  $^{212}\text{Pb}$  separation to counting (min);  $\eta$ , the detection efficiency for  $^{212}\text{Pb}$  ( $^{212}\text{Bi}$ ).

#### 2.5 Detection limits

Taking into account the  $3\sigma$  of the blank count rates ( $0.364 \pm 0.016$  cpm), the counting efficiencies of the instrument for  $^{210}\text{Pb} + ^{210}\text{Bi}$  (48.16%) and for  $^{212}\text{Pb} + ^{212}\text{Bi}$  (88.36%), the radiochemical yields ( $88.8 \pm 5.5\%$ ), the ingrowth or decay factor ( $^{210}\text{Pb}$ : 100%;  $^{212}\text{Pb}$ : 63.8%) and the sampling quantity (48 L), the detection limit, or more precisely, the minimum detectable activity (MDA) of the method for water sample are  $0.039 \text{ mBq L}^{-1}$  for  $^{210}\text{Pb}$  and  $0.033 \text{ mBq L}^{-1}$  for  $^{212}\text{Pb}$ .

Table 1: The  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  activity concentration ( $\text{Bq kg}^{-1}$ ), corrected to the date of 1st Jan. 1993, in the IAEA-315 Marine Sediment\*.

Sample No.	Sample weight, g	Pb yield, %	$^{210}\text{Pb}$ , $\text{Bq kg}^{-1}$	$^{212}\text{Pb}$ , $\text{Bq kg}^{-1}$	$^{212}\text{Pb}/^{210}\text{Pb}$
IAEA-315-1	2.2724	93.3	$27.5 \pm 1.2$	$20.8 \pm 1.6$	0.756
IAEA-315-2	2.0251	99.1	$31.5 \pm 1.4$	$26.1 \pm 1.8$	0.829
IAEA-315-3	2.3418	92.2	$31.3 \pm 1.4$	$22.9 \pm 1.5$	0.732
IAEA-315-4	2.0241	93.1	$30.4 \pm 1.4$	$24.2 \pm 1.6$	0.796
IAEA-315-5	2.2622	92.0	$33.0 \pm 1.5$	$29.5 \pm 1.8$	0.894
IAEA-315-6	1.5548	94.4	$31.0 \pm 1.4$	$25.6 \pm 1.9$	0.826
Mean $\pm$ 1SD		$94.0 \pm 2.6$	$30.8 \pm 1.8$	$24.9 \pm 3.0$	$0.806 \pm 0.057$
Range	1.5548-2.3418	92.2-99.1	27.5-33.0	20.8-29.5	0.732-0.894

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

### 3. Results and discussion

The results were given in tables 1-2, and the reported uncertainty of the obtained activity concentration of radionuclides for individual analysis of a sample was 1 standard deviation (SD), which was estimated from the uncertainties associated with the instrument calibration, the addition of the carrier to the sample and the counting statistics of the sample and the blank etc.

#### 3.1 Quality control

The step of Pb separation from alkaline earth elements as PbS precipitate in the method could also be used to simplify the procedure for  $^{210}\text{Pb}$  determination in soil if the reliable results could be confirmed. For the purpose of quality control, reference material IAEA-315 Marine Sediment supplied by the IAEA was analyzed to check the recommended procedure. The reference material of about 2 g was leached based on the procedure given in the literature [15], and the obtained leachate was analyzed following the 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  $^{210}\text{Pb}$  activity concentration. Due to the presence of unsupported  $^{210}\text{Pb}$  in the IAEA-315, the fraction of unsupported  $^{210}\text{Pb}$  had to be corrected to the reference date.

Table 2: The  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  activity concentration (in  $\text{mBq L}^{-1}$ ) in drinking water samples collected in Italy.

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

The obtained  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  activity concentration in the IAEA-315 is shown in table 1. The mean  $^{210}\text{Pb}$  concentration in the IAEA-315 was found to be  $30.8 \pm 1.8 \text{ Bq kg}^{-1}$  (decay correction to the date of 1st Jan. 1993). It was observed that the relative standard deviation obtained from a set of six analyses of the IAEA-315 is  $\pm 5.9\%$  for  $^{210}\text{Pb}$ . Since all being less than  $\pm 10\%$  the precision for the analyses is well acceptable as far as such a low activity is concerned. The relative bias obtained from the analyses is  $+2.3\%$  for  $^{210}\text{Pb}$ , showing that the mean activity concentration of  $^{210}\text{Pb}$  is in good agreement with the recommended value of  $30.1 \text{ Bq kg}^{-1}$  (the 95% confidence interval:  $26.0\text{--}33.7 \text{ Bq kg}^{-1}$ ).

The mean  $^{212}\text{Pb}$  concentration in the IAEA-315 was found to be  $24.9 \pm 3.0 \text{ Bq kg}^{-1}$ . Although the IAEA did not issue any recommended value for  $^{212}\text{Pb}$ , the reliability of the  $^{212}\text{Pb}$  activity concentration may be judged from the recommended value for  $^{228}\text{Th}$  that is in secular equilibrium with its predecessors  $^{228}\text{Ra}$  and  $^{232}\text{Th}$ . In fact, the  $^{212}\text{Pb}$  activity in the IAEA-315 sample is nearly in equilibrium with  $^{228}\text{Th}$ , as (1) the half-lives of its decay products are short, and (2)  $^{220}\text{Rn}$  escaped from the sealed container is negligible ( $\leq 2\%$ ). In this case, the obtained relative standard deviation and the relative bias of  $^{212}\text{Pb}$  are  $\pm 12\%$  and  $-7.8\%$  respectively. The obtained deviation and bias for  $^{212}\text{Pb}$  are bigger than those for  $^{210}\text{Pb}$ , mainly due to multi-corrections for the instrument background, reagent background, as well as interference of the  $^{210}\text{Bi}$  ingrowth from  $^{210}\text{Pb}$ . But the data of  $^{212}\text{Pb}$  can still be considered as acceptable and in good agreement with the recommended value [ $27.0$  ( $24.0\text{--}28.9$ )  $\text{Bq kg}^{-1}$ ] for  $^{228}\text{Th}$ .

### 3.2 Concentration of $^{210}\text{Pb}$ and $^{212}\text{Pb}$ in drinking water

For the purpose of application of the established method, seventeen brands of drinking water samples were collected and analyzed. As shown in table 2, the typical activity concentration in the analyzed drinking water samples is in the range of  $0.191\text{--}15.1 \text{ mBq L}^{-1}$  for  $^{210}\text{Pb}$  and of  $1.12\text{--}5.77 \text{ mBq L}^{-1}$  for  $^{212}\text{Pb}$ . The calculated activity ratio for  $^{212}\text{Pb}/^{210}\text{Pb}$  is in the range of  $0.289\text{--}16.9$  and with an average value of  $2.58 \pm 4.08$ . In fact, the concentrations of uranium isotopes, radium isotopes and  $^{210}\text{Po}$  in the same water samples have also been determined and the relevant data have been reported elsewhere [19]. If compared with the activity concentration of uranium isotopes, radium isotopes and  $^{210}\text{Po}$  [19], it is shown that: (1) the  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  activity concentration in nearly all water samples is much lower than that of uranium isotopes, but more or less in the same levels as  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{210}\text{Po}$ , and (2) the activity disequilibria are always observable for the pair of

$^{210}\text{Pb}/^{226}\text{Ra}$ , and of  $^{212}\text{Pb}/^{228}\text{Ra}$  in the water samples, in spite of  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  being the most important progenies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , respectively.

The statistic correlation analyses between the concerned components have been made. It was shown that: (1) no correlations between  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  and between  $^{212}\text{Pb}$  and  $^{228}\text{Ra}$  concentration in the drinking water samples were observed, even if each pair of them belongs to the same decay series and with the same chemical valences of 2+; (2) the carbonate presenting in the water samples is one of the most important complexation agent, but no statistic correlations were observable for the pair of neither  $^{210}\text{Pb}/\text{HCO}_3^-$  nor  $^{212}\text{Pb}/\text{HCO}_3^-$ , showing that the effect of  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  on the  $^{210}\text{Pb}$  and  $^{212}\text{Pb}$  dissolution is poor [2] and the behaviors of lead isotopes seems different from radium in water containing  $\text{HCO}_3^-$ ; and (3) a positive correlation between  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  was found in the drinking water samples with a correlation equation of  $[^{210}\text{Po}] = 0.721[^{210}\text{Pb}] + 1.65$  ( $R^2 = 0.4254$ ,  $n = 17$ ,  $P < 0.05$ ).

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