

# A Procedure for the Rapid Determination of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ in Drinking Water by Liquid Scintillation Counting

**IAEA**

International Atomic Energy Agency

A PROCEDURE FOR THE RAPID  
DETERMINATION OF  $^{226}\text{Ra}$  AND  $^{228}\text{Ra}$   
IN DRINKING WATER BY LIQUID  
SCINTILLATION COUNTING

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## FOREWORD

Since 2004, the environment programme of the IAEA has included activities aimed at the development of a set of procedures for the determination of radionuclides in terrestrial environmental samples. Reliable, comparable and 'fit for purpose' results are essential requirements for any decision based on analytical measurements. For the analyst, tested and validated analytical procedures are extremely important tools for the production of such data. For maximum utility, such procedures should be comprehensive, clearly formulated and readily available to both the analyst and the customer.

This publication describes a procedure for the rapid determination of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in drinking water. The determination of radium in drinking water is important for protecting human health, since the consumption of drinking water containing radium may lead to an accumulation in the body, contributing to the radiological dose. The method is based on the separation of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  from interfering elements using  $\text{PbSO}_4$  and  $\text{Ba}(\text{Ra})\text{SO}_4$  coprecipitation steps. The isotopes  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are then determined by liquid scintillation counting. The procedure is expected to be of general use to a wide range of laboratories, including the laboratories of the Analytical Laboratories for the Measurement of Environmental Radioactivity (ALMERA) network, both in emergency situations and for routine environmental monitoring purposes.

The method was established after an extensive review of papers from the scientific literature, and was tested and validated in terms of repeatability and trueness (relative bias) in accordance with International Organization for Standardization guidelines. Reproducibility tests were performed at expert laboratories. The calculation of massic activities, uncertainty budget, decision threshold and detection limit are also described.

The IAEA wishes to thank all the participants for their valuable contributions to develop the procedure and review this publication, especially C.-K. Kim for the design of the method development activity, R. Kleinschmidt and M. Cook (Australia), who assisted in drafting the manuscript and provided validation data, and the four expert laboratories (National Food Chain Safety Office, Hungary; Japan Chemical Analysis Center, Japan; Korea Institute of Nuclear Safety, Republic of Korea; and Jožef Stefan Institute, Slovenia) that contributed to the reproducibility testing. The IAEA officer responsible for this publication was A. Pitois of the IAEA Environment Laboratories.

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## 1. INTRODUCTION

Radium is a radioactive element for which no stable isotope is known. The mass numbers of the known radioisotopes range from 206 to 230. Among them, two radium radioisotopes,  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , are very significant from a radiological protection point of view due to their relatively long half-lives, presence in nature as radionuclides from the uranium and thorium decay series, and high dose conversion factors. The uranium and thorium decay series are shown in Figs. 1–2 in Appendix I. Radium radioisotopes are important because they can be easily incorporated into bones due to having similar properties to other elements from Group II (i.e. calcium) and producing short-lived radionuclides of high massic activity. For the general public, the consumption of food and water containing radium may lead to the accumulation of these radionuclides in the body, contributing to radiological dose.

Radium radioisotopes are often present in industrial waste products, referred to as Naturally Occurring Radioactive Material (NORM). It encompasses substances with enhanced concentrations of natural radionuclides, which occur at production sites and in the environment as a result of industrial or mining activities. Therefore, national and international regulators have shown an increasing interest in regulating radium levels in most industries and consumer products for the protection of human health and environment.

For radiological dose assessment, geochronological studies and environmental monitoring purposes, radium radioisotopes have been measured by several techniques, including gamma-ray spectrometry, alpha spectrometry, mass spectrometry and liquid scintillation counting techniques.

The radium radioisotopes  $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$  and  $^{226}\text{Ra}$  are alpha-particle emitters and can be directly measured by alpha spectrometry. The radium isotope  $^{228}\text{Ra}$ , which is a beta-particle emitter, can indirectly be measured by alpha spectrometry via its progeny  $^{228}\text{Th}$ . However, because of the long half-life of  $^{228}\text{Th}$  ( $T_{1/2} = 1.9$  y), the in-growth period ranges between 3 and 18 months (depending on the  $^{228}\text{Ra}$  activity and required sensitivity), and hence alpha spectrometry is not an adequate measurement method for routine analysis of  $^{228}\text{Ra}$ .

Gamma-ray spectrometry is a useful non-destructive method that permits the simultaneous determination of many radionuclides in a bulk sample [1–2], without the need for complex and time consuming radiochemical separations as undertaken for alpha spectrometry. However, it is limited by the weak emission probabilities of many potentially useful emission lines, the relatively poor efficiency of the High Purity Germanium (HPGe) detectors over a wide range of energy, the difficult task of precisely calibrating the efficiency of the detector, and the need to evaluate self-absorption effects [3].

Mass spectrometric methods have been used for the determination of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , although mass spectrometric determination of  $^{228}\text{Ra}$  has only occasionally been reported due to its short half-life (5.75 y). The main advantages of mass spectrometric methods are high sensitivity and short analysis times, although radiochemical pre-concentration and separation procedures are usually unavoidable. The major problems in mass spectrometric analysis are the formation of isobaric and polyatomic interferences, the formation of multiple charged ions, the abundance sensitivity (or tailing) of neighbouring atoms, matrix effects and mass fractionation during detection [4].

Liquid scintillation counting (LSC) is often used for the determination of radium radioisotopes in environmental samples, especially in liquids [5–6]. Methods using LSC can provide high sample throughput, and acceptable detection limits for several radium radioisotopes [7–10]. Quenching, poor energy resolution and relatively high background, especially in comparison with alpha spectrometry, are however limitations of this technique [11–12].

Gross alpha/beta activity analysis has been widely applied to drinking water [13]. This method is however non radionuclide-specific and faces many sources of interferences leading to a large spread of results (up to two orders of magnitude), as observed in interlaboratory comparisons [14–15].

Taking into account the availability of LSC to simultaneously measure  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  at the same time with acceptable detection limit, this publication introduces a procedure for rapid determination of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in drinking water, to be used for screening of activity levels in emergency situations and for routine environmental monitoring purposes. The procedure was validated in accordance with ISO guidelines.

## 2. SCOPE

This publication describes a method for the rapid determination of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in drinking water using liquid scintillation counting following the chemical separation of radium. The method can be used for the fast detection of contamination of drinking water by radium in emergency situations or for routine environmental monitoring purposes.

The method is suitable for the analysis of 0.5 L of drinking water containing less than 100 mg kg<sup>-1</sup> barium.

## 3. NORMATIVE REFERENCES

The principles of the normative references, which have been applied to this document, can be found in the list below.

- ISO 11929:2010. Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation – Fundamentals and application;
- ISO/TS 21748:2004. Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation;
- ISO/IEC Guide 98-3:2008. Uncertainty of measurement – Part 3: Guide to the expression of uncertainty in measurement;
- ISO 5725-1:1994. Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions;

- ISO 5725-2:1994. Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method;
- ISO 5725-4:1994. Accuracy (trueness and precision) of measurement methods and results – Part 4: Basic methods for the determination of the trueness of a standard measurement method;
- ISO 7870-1:2007. Control charts – Part 1: General guidelines;
- QUAM:2012.P1 EURACHEM/CITAC Guide, 2012. Quantifying Uncertainty in Analytical Measurement.

#### 4. RESPONSIBILITIES

It is the responsibility of the analyst to follow this procedure and to establish appropriate safety and health practices. Compliance with national and/or internal chemical and radiological safety rules is obligatory. Although the method has been carefully tested each laboratory should perform an individual validation procedure.

#### 5. TERMS AND DEFINITIONS, SYMBOLS AND ABBREVIATIONS

In the following,  $u(x)$  indicates the uncertainty in quantity  $x$ :

$A_x$ : Certified massic activity of the analyte on reference date ( $\text{Bq}\cdot\text{kg}^{-1}$ ).

$A_x^t$ : Massic activity of the analyte in the quality control sample on reference date ( $\text{Bq}\cdot\text{kg}^{-1}$ ).

$a_x$ : Massic activity of the specific analyte on the sampling date ( $\text{Bq}\cdot\text{kg}^{-1}$ ).

$C_x$ : Target massic activity of the specific analyte in the quality control sample prepared for the validation of the procedure ( $\text{Bq}\cdot\text{kg}^{-1}$ ).

$m_{s-x}$ : Mass of the certified standard solution taken for the analysis of the specific analyte (kg).

$m_{t-x}$ : Mass of the quality control sample taken for the analysis of the specific analyte (kg).

$m_s$ : Mass of sample (kg).

$n_x^s$ : Net count rates of the specific analyte in the certified standard solution ( $\text{counts}\cdot\text{s}^{-1}$ ).

$n_x^t$ : Net count rates of the specific analyte in the quality control sample ( $\text{counts}\cdot\text{s}^{-1}$ ).

$n_x$ : Net count rates of the specific analyte in the sample ( $\text{counts}\cdot\text{s}^{-1}$ ).

$PI$ : Precision index (%).

$R_{226\text{Ra}}$ : Chemical recovery of  $^{226}\text{Ra}$ .

$R_{228Ra}$ : Chemical recovery of  $^{228}Ra$ .

$R_L$ : Reproducibility limit ( $Bq \cdot kg^{-1}$ ).

$r_L$ : Repeatability limit ( $Bq \cdot kg^{-1}$ ).

$r_{g-x}^s$ : Gross count rates of the specific analyte in the standard solution ( $counts \cdot s^{-1}$ ).

$r_{g-x}^t$ : Gross count rates of the specific analyte in the quality control sample ( $counts \cdot s^{-1}$ ).

$r_{g-x}$ : Gross count rates of the specific analyte in the sample ( $counts \cdot s^{-1}$ ).

$r_{0-x}$ : Gross count rates of the specific analyte in the blank sample ( $counts \cdot s^{-1}$ ).

$S_r$ : Standard deviation of repeatability ( $Bq \cdot kg^{-1}$ ).

$S_R$ : Standard deviation of reproducibility ( $Bq \cdot kg^{-1}$ ).

$T_{s-x}$ : Counting time of the specific analyte in the sample (s).

$t_{0-x}$ : Counting time of the specific analyte in the blank (s).

$t_{s-x}$ : Time interval between the measurement date and the reference date of the specific analyte in the certified standard solution (s).

$t_{t-x}$ : Time interval between the measurement date and the reference date of the specific analyte in the quality control sample (s).

$t_x$ : Time interval between the measurement date and the sampling date (s).

$\varepsilon_x$ : Counting efficiency of the specific analyte.

$\varepsilon_x^c$ : Overall efficiency of the specific analyte in the quality control sample.

$\lambda_x$ : Decay constant of the specific analyte ( $s^{-1}$ ).

$\overline{X}_x$ : Mean of all measured values of the specific analyte in the quality control sample for the validation of the procedure ( $Bq \cdot kg^{-1}$ ).

$x_x^*$ : Decision threshold of the specific analyte ( $Bq \cdot kg^{-1}$ ).

$\xi_x$ : Detection limit of the specific analyte ( $Bq \cdot kg^{-1}$ ).

$\delta$ : Relative bias of the method (%).

$u_{mb}$ : Uncertainty of the analytical balance (kg).

AAS: Atomic Absorption Spectroscopy.

ALMERA: Analytical laboratories for the measurement of environmental radioactivity.

EDTA: Ethylenediaminetetraacetic acid.

FWHM: Full width at half-maximum.

HDPE: High-density polyethylene.

HPGe: High purity germanium

IAEA: International atomic energy agency.

ICP-OES: Inductively coupled plasma optical emission spectroscopy.

ICP-MS: Inductively coupled plasma mass spectrometry.

ISO: International organization for standardization.

LSC: Liquid scintillation counter.

MCA: Multichannel analyser.

MDL: Minimum detectable limit.

NORM: Naturally occurring radioactive material.

PP: Polypropylene.

ROI: Region of interest.

rpm: Revolutions per minute.

## 6. PRINCIPLE

Barium co-precipitation is used as a method of separation for radium due to the very similar chemical properties of barium and radium. The exploitation of the ability of barium to react with an excess of sulphate ions to produce a precipitate allows the quantitative analysis of environmental activity concentrations of radium in water.

The inclusion of a lead carrier allows the removal of  $^{210}\text{Pb}$  from solution, which increases the accuracy of  $^{228}\text{Ra}$  measurement, as  $^{210}\text{Pb}$  can cause spectral interference. The removal of  $^{210}\text{Pb}$  is achieved by lowering the pH of the solution to re-precipitate barium sulphate using acetic acid in which lead sulphate is soluble. This allows  $^{210}\text{Pb}$  to remain in solution and therefore be removed.

The source preparation is achieved by suspending the barium sulphate precipitate in the EDTA solution. Barium sulphate is insoluble in water, alkalis and acids, but EDTA increases the solubility due to the complexation of barium and the speciation effect. The EDTA molecule inhibits barium sulphate nucleation and added heat forces complexation. This enables the use of a naphthalene-based scintillation cocktail to gain better spectral resolution than with the use of a gel-forming cocktail.

The flow chart of the procedure is given in Appendix II.

Massic activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in the sample are calculated from net count rates of the sample, sample amount and the overall efficiency that can be obtained from spiked sample with known activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , and that shows the ability of the method to extract radium (chemical recovery) as well as the ability (counting efficiency) of the instrument to detect it.

## 7. EQUIPMENT AND CHEMICALS

### 7.1. EQUIPMENT

- Standard laboratory equipment;
- Hot plate with magnetic stirrer;
- Centrifuge;
- Analytical balance with accuracy of 0.1 mg;
- Water bath with temperature controller;
- Vortex;
- Low background liquid scintillation counter (LSC);
- Elemental analysis technique for Ba and Ca determination;
- pH meter or pH papers;
- 600 mL glass beaker;
- 50 mL HDPE or PP centrifuge tubes;
- 5 mL and 10 mL Eppendorf pipettes;
- Micropipette for 50  $\mu\text{L}$  volume;
- Transfer pipettes;
- 20 mL low background plastic liquid scintillation vials.

### 7.2. CHEMICALS

- Pb carrier: 2.397 g  $\text{Pb}(\text{NO}_3)_2$ , 0.5 mL 14.4M  $\text{HNO}_3$  made up to 100 mL with de-ionized water;
- Ba carrier: 2.836 g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , 0.5 mL 14.4M  $\text{HNO}_3$  made up to 100 mL with de-ionized water;
- 0.25M EDTA;
- 10M HCl (32%);
- 14.4M  $\text{HNO}_3$  (65%);
- 9M  $\text{HSO}_4$ ;
- 25%  $\text{NH}_3$  solution;
- 96 % glacial acetic acid;
- Analytical grade ammonium sulphate (solid);
- 10% ammonium sulphate solution;
- Scintillation cocktail suitable for alpha/beta separation (Optiphase Hisafe 3)
- $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  certified standard solutions;
- Alpha emitter standard solution ( $^{241}\text{Am}$  or  $^{210}\text{Po}$  or  $^{242}\text{Pu}$ );
- Beta emitter standard solution  $^{90}\text{Sr}/^{90}\text{Y}$ .

## 8. PROCEDURE

Prior to the start of the analysis of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in the water sample, it is recommended to determine the Ca and Ba contents of the sample using an elemental analysis technique (for example, AAS, ICP-OES or ICP-MS). If the Ba concentration is higher than the limit ( $100 \text{ mg}\cdot\text{kg}^{-1}$ ), it is recommended to reduce the volume of the sample to be analysed so that the total content of Ba in the sample does not exceed 50 mg.

### 8.1. SEPARATION OF RADIUM BY PRECIPITATION

- (1) Acidify 0.5 L of the water sample to approximately pH 2 using drops of 10M HCl.
- (2) Add 2 mL of Pb carrier and 2 mL of Ba carrier to the solution. In case that the total content of Ba in the sample solution is 50 mg or higher, it is not necessary to add Ba carrier to the sample.
- (3) Add 4 mL of 9M  $\text{HSO}_4$  and 5 g of ammonium sulphate accurately weighed.
- (4) Stir the solution to ensure that all solids are dissolved, allow the precipitate to form and then let the precipitate settle.
- (5) Decant the supernatant without disturbing the precipitate, leaving less than 30 mL of liquid in the glassware.
- (6) Quantitatively transfer the precipitate and the limited amount of liquid to a 50 mL HDPE or PP centrifuge tube rinsing the beaker with de-ionized water to avoid loss of precipitate.
- (7) Centrifuge the solution for five minutes at 3500 rpm.
- (8) Decant the excess supernatant carefully without disturbing the precipitate.

### 8.2. PURIFICATION OF RADIUM

- (1) Dissolve the precipitate in 10 mL of hot 0.25M EDTA solution (the solution volume is changeable, depending on total contents of Ca and Ba in the sample, and is given in Table 1 in Appendix III) and 3 mL of 25%  $\text{NH}_3$  solution. Carefully agitate the solution to dissolve the precipitate.
- (2) Add 5 mL of 10% ammonium sulphate and adjust the pH to 4.2-4.5 using 96% glacial acetic acid. As the pH is lowered, the precipitate should begin to re-form.
- (3) Boil the solution in the HDPE or PP centrifuge tube in a water bath at  $80^\circ\text{C}$  for two minutes, cool it with cold tap water, then centrifuge for five minutes at 3500 rpm. The resulting precipitate is purified barium (radium) sulphate precipitate. Discard the supernatant.
- (4) Dissolve the precipitate in 10 mL of hot 0.25M EDTA solution (the solution volume is changeable, depending on total content of Ba in the sample, and is given in Table 2 in Appendix III) and agitate the solution carefully to dissolve the precipitate into solution. This may require the use of a vortex.
- (5) Add 3 mL of 10% ammonium sulphate solution to the solution and adjust the pH to 4.5 using the 96% glacial acetic acid. The precipitate should begin to re-form. Separate the precipitate by centrifugation for five minutes at 3500 rpm. (Precaution: don't leave the precipitate for overnight and don't allow it to dry. Prepare the source as soon as the precipitate has been prepared).



### 8.3. SOURCE PREPARATION

- (1) Wash the precipitate twice with 20 mL of de-ionized water, shake well, centrifuge and discard the supernatant to ensure removal of any residual solvents.
- (2) Add 3 mL of hot 0.25M EDTA to suspend the precipitate. Make sure to break up the precipitate at this point either through vortex or suction through a transfer pipette.
- (3) Heat the suspension in a water bath at a moderate temperature (30-50°C) for a minimum of 30 minutes.
- (4) Vortex the sample to ensure the precipitate gets well suspended and no cluster of precipitate is visible in the suspension. Steps (3) and (4) may need to be repeated for obtaining a homogeneous suspension and the absence of cluster of precipitate.
- (5) Quantitatively transfer the solution including partially dissolved BaSO<sub>4</sub> precipitate to a 20 mL plastic liquid scintillation vial using a transfer pipette
- (6) Rinse the HDPE or PP centrifuge tube with another 1 mL of hot 0.25M EDTA solution to ensure that no analyte remains in the tube.
- (7) Add 14 mL of Optiphase Hisafe 3 liquid scintillation cocktail to the source solution and vortex or shake well until the solution appears homogenous. (Precaution: the addition of the cocktail should be done all at once or in large portions to avoid any reaction with the source solution that could cause a cloudy, inhomogenous mixture).
- (8) Seal and shake the LSC source until the suspension appears homogenous.
- (9) Clean the vial with an alcohol wipe to remove any static interference.

Precaution: Sample stability is determined by the suspension of the precipitate. If the precipitate is not well reacted with the EDTA solution, it will fall out more easily and quickly. It is suggested to break up the precipitate in the EDTA solution either through vortex, shaking or continued suction and expulsion through a transfer pipette for stubborn precipitates.

Heat is also a major factor in the reaction between the precipitate and the EDTA solution. If a good suspension is difficult to achieve, heating in a water bath for a further 30 minutes followed by vortex/shaking will help force the reaction. This should be repeated until the sample can be held still without any settling occurring within a few minutes.

The grade of the ammonium sulphate used also has a bearing on the quality of the precipitate. Reagent grade ammonium sulphate produces a precipitate that is slightly chunkier and stickier and therefore harder to suspend during source preparation. Analytical grade ammonium sulphate produces a precipitate that is much easier to work with.

### 8.4. MEASUREMENT CONDITIONS SETTING AND DETERMINATION OF COUNTING EFFICIENCY

#### 8.4.1. Source preparation for alpha/beta discrimination setting

- (1) Add 2 mL of barium carrier to two 50 mL volume HDPE or PP centrifuge tubes.
- (2) Add 3 mL of 10% ammonium sulphate solution and 1 mL of 25% NH<sub>3</sub> solution to each solution to obtain the BaSO<sub>4</sub> precipitates. Separate the precipitates by centrifuging for five minutes at 3500 rpm.

- (3) Dissolve the precipitates in 4 mL of hot 0.25M EDTA solutions and agitate the solutions carefully to dissolve and suspend the precipitates into solution. This may require the use of a vortex.
- (4) Follow section 8.3 steps (5) to (7).
- (5) Add 10–100 Bq of alpha and beta emitters, respectively (e.g.  $^{241}\text{Am}$  or  $^{210}\text{Po}$  or  $^{242}\text{Pu}$  and  $^{90}\text{Sr}/^{90}\text{Y}$ ) in 50  $\mu\text{L}$  volume solutions.
- (6) Follow section 8.3 steps (8) to (9).

#### **8.4.2. Alpha/beta discrimination setting**

The discrimination factor integrates the tail of the pulse and compares it with the total charge in the pulse. The higher the discrimination factor setting is, the more pulses will be directed into the short pulse category (beta) and vice versa. This allows the simultaneous determination of alphas and betas.

The determination of an optimum discrimination factor requires two standards, one pure alpha and one pure beta emitter,  $^{241}\text{Am}$  or  $^{210}\text{Po}$  or  $^{242}\text{Pu}$  and  $^{90}\text{Sr}/^{90}\text{Y}$  respectively. These radionuclides are used rather than  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , as the latter are accompanied by progeny in-growth, which creates uncertainty in the determination of a discrimination factor. To arrive at the optimum setting, each standard is counted individually at a range of discrimination factor settings and the percent misclassification of alphas into the beta channel and vice versa are plotted against discrimination factor on the same graph. The point of minimum cross-over is selected as the optimum discrimination factor value.

As can be seen in Table 3 in Appendix IV, for testing of the method, a range of discrimination factors from 80 to 150 was chosen. Two blank samples were made following the above procedure, one spiked with  $^{241}\text{Am}$  and one with  $^{90}\text{Sr}/^{90}\text{Y}$  after source preparation. The activity concentrations of these spikes do not need to be documented as it is the raw count spillover that is being determined and not a final activity concentration. These samples were counted for 60 minutes each at each discrimination factor within the selected range. The region of interest used to analyse these samples utilised the full range of the instrument from channel 0 to channel 1024. The alpha and beta counts of each sample are then tabulated and the number of betas in the alpha MCA and vice versa is calculated, as can be seen in Table 3 in Appendix IV. These values are then graphed to determine the optimum discrimination factor as can be seen in Fig. 3 in Appendix IV. The optimum discrimination factor for this laboratory was calculated to be 130. The optimum discrimination factor has to be determined at each laboratory performing this procedure.

#### **8.4.3. Region of interest (ROI) setting**

The setting of multichannel analysers (MCA) and windows for the measurement of radium is performed using the standard Alpha/Beta configuration. This involves the first MCA analysing all beta events in the first half and all alpha events in the second half, as determined by the discrimination factor. The second MCA then analyses all guard anticoincidence events in the first half and all guard coincidence events in the second half. These guard events are not considered as true sample events. Any liquid scintillation analyser with the ability to discriminate between alpha and beta events will have a standard Alpha/Beta configuration for use with this method.

The lower and upper limits of the analysis windows are set using the known emission energies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , approximately 4500–5000 keV and 0–50 keV, respectively. When using channels in the MCA, this converts to approximately 600–640 and 50–300, respectively. Each liquid scintillation counter should be calibrated for radium analysis, including setting of regions, prior to any analysis.

Regions of interest are set specifically to contain only the analyte of interest. The range of each region has been set following the width of the FWHM of each peak. This enables a greater accuracy when calculating specific activity. It also negates the use of spillover calculations to correct for interfering peaks in the ROI as the difference in the number of counts lost and gained in each region is negligible as shown in Fig. 4 to 7 in Appendix V.

#### 8.4.4. Counting efficiencies of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ and chemical recovery

##### 8.4.4.1. Counting efficiencies of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ determined by direct measurement of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ standard sources

The counting efficiencies of the liquid scintillation counter for  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  were determined using two blank samples, resulting from the  $\text{BaSO}_4$  precipitates in de-ionized water. The samples were spiked after preparation of  $\text{BaSO}_4$  precipitates, one with  $^{226}\text{Ra}$  and one with  $^{228}\text{Ra}$ . Spiking of the samples after preparation eliminates the chemical recovery variable. For the determination, each spiked sample was counted seven times. This provided a reasonable data set for calculations. The counting efficiencies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  were calculated using equations (1) and (2):

$$\mathcal{E}_{226\text{Ra}} = \frac{n_{226\text{Ra}}^s}{A_{226\text{Ra}} \times m_{s-226\text{Ra}} \times e^{-\lambda_{226\text{Ra}} \times t_{s-226\text{Ra}}}} \quad (1)$$

$$\mathcal{E}_{228\text{Ra}} = \frac{n_{228\text{Ra}}^s}{A_{228\text{Ra}} \times m_{s-228\text{Ra}} \times e^{-\lambda_{228\text{Ra}} \times t_{s-228\text{Ra}}}} \quad (2)$$

The counting efficiencies were determined to be 1.03 and 0.646 with 6% and 10% of relative standard deviation for  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  respectively, as shown in Fig. 8 in Appendix VI.

##### 8.4.4.2. Overall efficiencies of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ determined by analysis of quality control samples with known activities of $^{226}\text{Ra}$ and $^{228}\text{Ra}$

The overall efficiency describes the ability of the method to extract radium as well as the ability of the instrument to detect it. These parameters are known as chemical recovery and counting efficiency. This ensures that all factors of sample preparation have been taken into account. As part of a thorough validation process, these parameters have been considered separately.

A quality control sample (spiked sample with known activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ) was used for the determination of the overall efficiency of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ . Overall efficiencies for both  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  were calculated using equations (3) and (4).

$$\mathcal{E}_{226\text{Ra}}^c = \frac{n_{226\text{Ra}}^t}{A_{226\text{Ra}}^t \times m_{t-226\text{Ra}} \times e^{-\lambda_{226\text{Ra}} \times t_{t-226\text{Ra}}}} \quad (3)$$

$$\mathcal{E}_{228\text{Ra}}^c = \frac{n_{228\text{Ra}}^t}{A_{228\text{Ra}}^t \times m_{t-228\text{Ra}} \times e^{-\lambda_{228\text{Ra}} \times t_{t-228\text{Ra}}}} \quad (4)$$

The control chart for overall efficiencies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  is shown in Fig. 9 in Appendix VI. The overall efficiencies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  were determined to be 0.908 and 0.516 with 6.6 % and 18.9 % of relative standard deviation for  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , respectively.

#### 8.4.4.3. Chemical recovery

Using counting efficiency and overall efficiency data, the chemical recovery was determined using equations (5) and (6).

$$R_{226\text{Ra}} = \frac{\mathcal{E}_{226\text{Ra}}^c}{\mathcal{E}_{226\text{Ra}}} \quad (5)$$

$$R_{228\text{Ra}} = \frac{\mathcal{E}_{228\text{Ra}}^c}{\mathcal{E}_{228\text{Ra}}} \quad (6)$$

The chemical recovery was calculated indirectly using this method instead of the conventional gravimetric or tracer techniques due to the chemistry of the procedure and the technique of source preparation used. The addition of  $^{133}\text{Ba}$  as a tracer has previously shown inconsistent recovery, possibly due to the chemistry used during the procedure, and it is therefore not suitable. Gravimetric determination requires drying of the precipitate, which causes inconsistent source preparation and is therefore not suitable. In this procedure, the chemical recovery was not used for the calculation of specific activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in the sample, but used for quality control purpose only. The chemical recoveries of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  ranged from 78–90%.

#### 8.4.4.4. Measurement

Samples are counted using a liquid scintillation counter with pulse shape analysis for 60 minutes each including quality control and blank samples. The spectra should be inspected for reasonable alpha peak resolution and any visible quenching (movement of spectra outside regions of interest). Those are shown in Appendix V. For quality assurance purpose, a quality control sample and a blank were analysed for every set of samples. Samples should be counted immediately after source preparation to avoid extensive in-growth of progeny and the degradation of alpha spectrum due to the formation of flakes of precipitation.

As illustrated in Figs. 10–11 in Appendix VI, samples have a period of approximately 4 hours of stability within 2% of the variation of the overall efficiency of  $^{226}\text{Ra}$  in a shaken source and 12% in an unshaken source due to in-growth of progeny and sinking of the  $\text{BaSO}_4$  precipitate.

High selectivity of the method is provided by chemical separation and the ability of pulse shape analysis afforded by liquid scintillation counting. However, possible interferences cannot be excluded. If the solid precipitate is not completely suspended in EDTA, alpha peak broadening can occur due to the inability of alpha particles contained within unsuspended precipitate to fluoresce efficiently.

## 9. EXPRESSION OF RESULTS

### 9.1. CALCULATION OF MASSIC ACTIVITIES OF $^{226}\text{Ra}$ AND $^{228}\text{Ra}$ AT THE SAMPLING DATE

Activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in water sample were expressed in the procedure as units of massic activity ( $\text{Bq}\cdot\text{kg}^{-1}$ ). In case the activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are expressed as units of activity concentration ( $\text{Bq}\cdot\text{L}^{-1}$ ), the density of the sample should be measured to convert the unit of massic activity to activity concentration. All nuclear data used for the calculation of massic activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  were taken from the recommended data of the DDEP database from the Laboratoire National Henri Becquerel [16] and Nudat 2.5 [17].

Massic activities of both  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are calculated using the counts per minute as given by the spectral analysis software, separate efficiency factors as determined from the validation process and the background count rate as specified by the blank sample data.

The peak resolution using this method is good and therefore the use of spillover calculations is not necessary. This is due to the fact that the ROI is very specific and the difference between counts lost and gained in each region is negligible. Any background counts produced due to the environment or chemiluminescence is also corrected for, since blank/background samples are always run simultaneously.

In this procedure, massic activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in water sample are calculated based on the overall efficiencies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  obtained from the analysis of the quality control sample with known activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  as shown in equations (7) and (8).

$$a_{226\text{Ra}} = \frac{n_{226\text{Ra}}}{\epsilon_{226\text{Ra}}^c \times m_S} \times e^{\lambda_{226\text{Ra}} \times t_{226\text{Ra}}} \quad (7)$$

$$a_{228\text{Ra}} = \frac{n_{228\text{Ra}}}{\epsilon_{228\text{Ra}}^c \times m_S} \times e^{\lambda_{228\text{Ra}} \times t_{228\text{Ra}}} \quad (8)$$

It is therefore recommended that real samples should be analysed with minimum one quality control sample and one blank sample at the same time. The analyst should pay attention to the quality control of overall efficiencies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , because they are changeable; testing showed changes within a relative standard deviation of 7% for  $^{226}\text{Ra}$  and 19% for  $^{228}\text{Ra}$ , as shown in Fig. 9 in Appendix VI. It is advised that the analyst prepares control charts for counting efficiency and overall efficiency of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , similar to the ones shown in Figs. 8–9 in Appendix VI.

## 9.2. CALCULATION OF INDIVIDUAL UNCERTAINTY AND COMBINED UNCERTAINTY

The combined uncertainty is calculated according to the guide to the expression of uncertainty in measurement [18], and is described in Appendix VII.

An example of spreadsheets for the measurement of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  is given in Table 4 in Appendix VII. It can be noticed that the overall efficiencies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are a dominant contributor (90%) to the combined uncertainty of the measurement result.

## 9.3. DECISION THRESHOLD

In accordance with ISO 11929:2010, the decision threshold,  $x_x^*$ , is obtained from the following equation (9):

$$x_x^* = k_{1-\alpha} \times u(0_x) \quad (9)$$

$u(0_x)$  is the uncertainty of the measurement when the activity of the analyte is equal to zero, and  $k_{1-\alpha} = 1.65$  is chosen referring to the probability that error of the first kind (wrongly rejecting the hypothesis that the analyte is present) is not greater than 5%.

$u(0_x)$  can be quantified as:

$$u(0_x) = \frac{1}{\varepsilon_x \times m_S} \times \sqrt{\frac{r_{0-x}}{T_{s-x}} + \frac{r_{0-x}}{t_{0-x}}} \quad (10)$$

## 9.4. DETECTION LIMIT

In accordance with ISO 11929:2010, the detection limit,  $\xi_x^*$ , is calculated by the following equations (11) and (12), assuming  $\alpha = \beta$  then  $k_{1-\alpha} = k_{1-\beta} = k$ ,

$$\xi_x = 2 \times q_x \quad (11)$$

$$q_x = k_{1-\alpha} \times u(0_x) + \frac{1}{2} \times \frac{k_{1-\alpha}^2}{a_x} \times [u^2(a_x) - u^2(0_x)] \quad (12)$$

$a_x$  is the massic activity of the analyte and  $u(0_x)$  is the uncertainty of the measurement when the activity of the analyte is equal to zero and  $k_{1-\alpha} = 1.65$  is chosen.

The detection limit of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in the procedure are  $0.01 \text{ Bq}\cdot\text{kg}^{-1}$  and  $0.06 \text{ Bq}\cdot\text{kg}^{-1}$ , respectively for a 1 hour counting time in a low background liquid scintillation spectrometer with 0.5 kg of sample.

## 10. VALIDATION OF THE PROCEDURE

For the validation of the procedure, four types of spiked water samples with different activity ratios of  $^{228}\text{Ra}/^{226}\text{Ra}$ , used as quality control samples, and a blank were prepared. One of the quality control samples was used for testing the reproducibility and the other three quality control samples were used for repeatability and trueness testing. The repeatability, reproducibility and trueness of the procedure were tested according to ISO-5725 and ISO/TS-21748.

The following parameters were established via the validation process:

- Linear response range;
- Trueness;
- Precision;
- Repeatability;
- Reproducibility;
- Detection limit.

Quality control samples are run to ensure the accuracy of both the method and the instrumentation. Blank samples are run to monitor reagent radiological purity and ensure that there is no cross-contamination during the procedure. This also includes the monitoring of the background to ensure that there is no excess background activity being counted by the instrumentation that could affect the results.

### 10.1. LINEARITY, RANGE OF MEASUREMENT

The linear range of measurement of the method was tested by measuring the  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  activities at various activity concentrations in de-ionized water. Results of measurements as a function of reference values have been tabulated and graphed in Fig. 12 in Appendix VIII. Linearity of the method was proven in the range  $0\text{--}100 \text{ Bq}\cdot\text{kg}^{-1}$  for both  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ .

It is very likely that the method can be used in a wider range, from detection limit to approximately  $1000 \text{ Bq}\cdot\text{kg}^{-1}$ . This makes this method suitable for  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  massic activities determination ranging from detection limit to higher than environmental levels.

### 10.2. TRUENESS OF THE METHOD

The trueness of the procedure was tested using twelve replicates of three types of quality control samples and calculated using equation (13).

$$\delta(\%) = \frac{C_x - \overline{X}_x}{C_x} \times 100 \quad (13)$$

Trueness of the method for the three types of quality control samples is given in Tables 5–7 in Appendix VIII.

### 10.3. PRECISION OF THE METHOD

The precision index was determined using twelve replicates of three types of quality control samples and calculated using the equation (14):

$$PI\% = 100 \times \sqrt{\frac{u(C_x)^2}{C_x^2} + \frac{u(a_x)^2}{a_x^2}} \quad (14)$$

Precision of the method for the three types of quality control samples is given in Tables 5 to 7 in Appendix VIII.

### 10.4. REPEATABILITY

The repeatability limit was estimated by analysing twelve replicates of three types of quality control samples with known activity concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in repeatability conditions. The repeatability limit is calculated using equation (15):

$$r_L = S_r \times 2.8 \quad (15)$$

The results of repeatability testing in one laboratory are shown in Tables 5 to 7 in Appendix VIII. The procedure provides 7% of relative repeatability standard deviation ( $S_r$ ) for 1–2 Bq·kg<sup>-1</sup> of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  activity level, as shown in Table 7 in Appendix VIII.

### 10.5. REPRODUCIBILITY

The reproducibility limit was estimated by analysing ten replicates of a quality control sample with known activity concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in five laboratories. The reproducibility limit is calculated using the equation (16):

$$R_L = S_R \times 2.8 \quad (16)$$

The results of reproducibility testing obtained from an inter-laboratory exercise with five laboratories are shown in Table 8 in Appendix VIII. The relative reproducibility standard deviation is determined to be 17% for  $^{226}\text{Ra}$  and 15% for  $^{228}\text{Ra}$  at 0.5 Bq·kg<sup>-1</sup> activity level of both isotopes in inter-laboratory comparison exercise.

### 10.6. ACCEPTANCE CRITERIA

According to the criteria of ISO/TS 21748:2004, the test results meet the requirements if:

- the absolute mean bias  $|\delta|$  in the repeatability test is smaller than the repeatability limit ( $r_L$ ):  $|\delta| < r_L$ ;
- the absolute mean bias  $|\delta|$  in the reproducibility test is smaller than the reproducibility limit ( $R_L$ ):  $|\delta| < R_L$ ;
- $PI < 25\%$ .

According to these criteria, the procedure for the rapid determination of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in drinking water samples performs well.



## 11. TEST REPORT

The test report shall conform to ISO 17025 requirements and shall contain the following information:

- Sample code;
- Sample description;
- Sampling date (if known);
- Analysis request code;
- Responsible person;
- Reference to the measurement and evaluation procedure used;
- Test result;
- Units in which the test result is expressed;
- Date to which the test result has been corrected.

Unless otherwise required, the test result should be stated together with the expanded uncertainty [19] calculated using a coverage factor  $k = 2$ .

The following form is recommended:  $a_x \pm u(a_x)$  with the associated  $k$  value.

## 12. CONCLUSION

A procedure was developed and tested for the rapid determination of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in drinking water using liquid scintillation counting. Radium is radiochemically separated from interfering elements using co-precipitation steps. The analysis time for chemical separation and source preparation of radium for a set of samples (3 samples, one blank and one quality control sample) is about 8 hours.

According to the repeatability and reproducibility tests, the measurement process is considered to perform adequately.

The method can be used for the rapid determination of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in drinking water, both for screening of activity levels in emergency situations and for routine environmental monitoring purposes.

## APPENDIX I. U AND TH DECAY SERIES

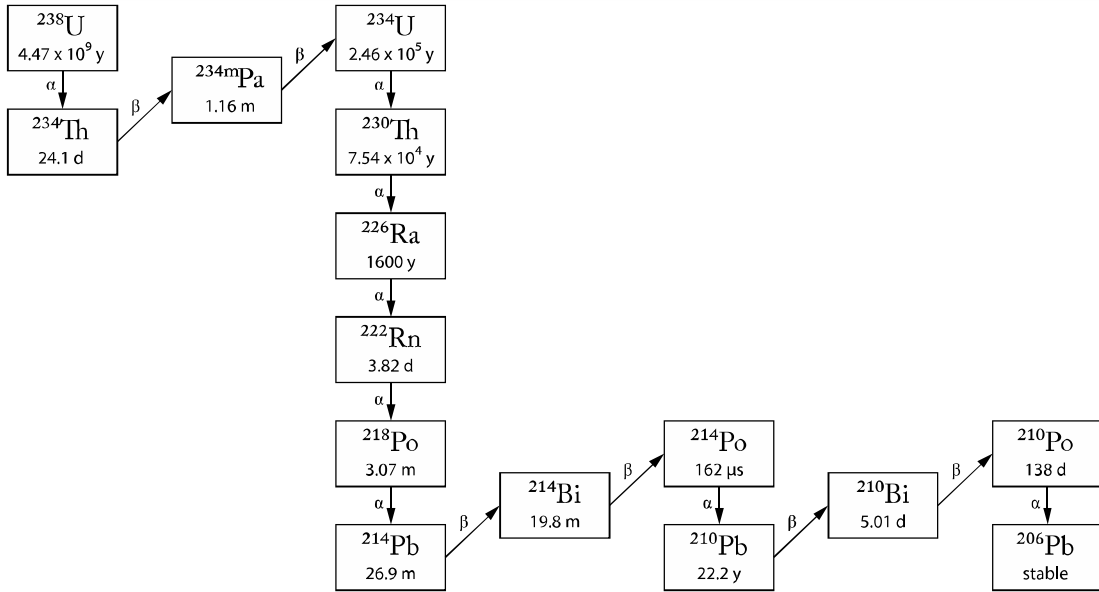


FIG. 1.  $^{226}\text{Ra}$  is a member of the  $^{238}\text{U}$  decay series [17].

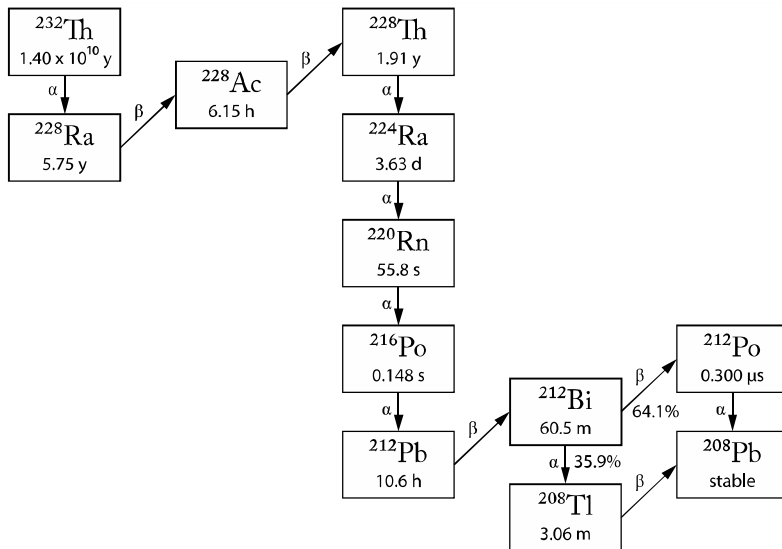
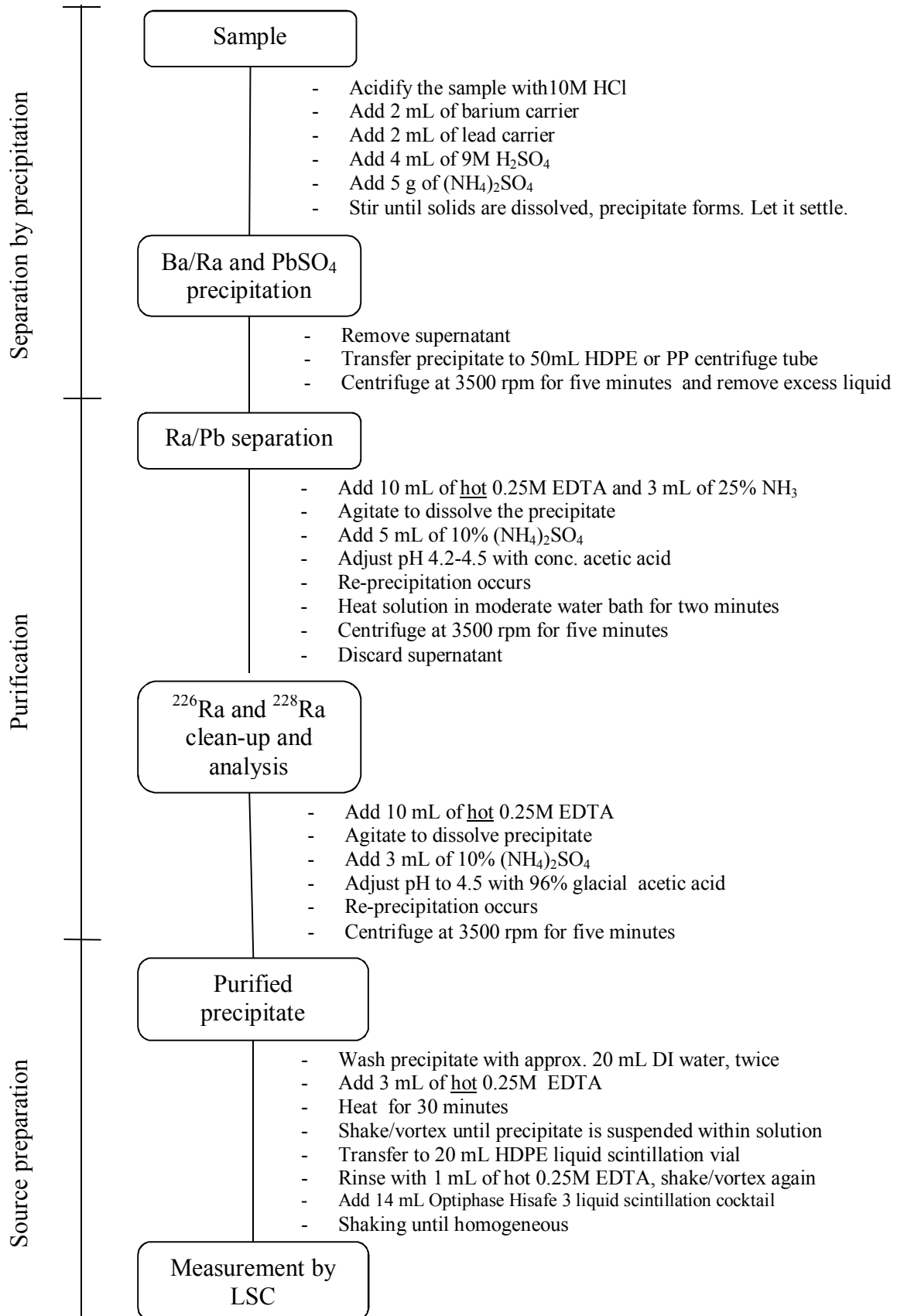


FIG. 2.  $^{224}\text{Ra}$  and  $^{228}\text{Ra}$  are members of the  $^{232}\text{Th}$  decay series [17].



## APPENDIX II. FLOW CHART FOR CHEMICAL SEPARATION OF RADIUM





**APPENDIX III. EXPERIMENTAL CONDITIONS AS A FUNCTION OF MATRIX CONTENT**

TABLE 1. VOLUME OF 0.25M EDTA SOLUTION REQUIRED DEPENDING ON CONTENTS OF CALCIUM AND BARIUM IN THE SAMPLE AT THE FIRST DISSOLUTION STEP OF BaSO<sub>4</sub> PRECIPITATE (8.2. STEP 1)

| Contents of Ca and Ba in the sample (mg) |     | Volume of 0.25 M EDTA solution (mL) |
|--|-----|-------------------------------------|
| Ca                                       | Ba  |                                     |
| 0  | 50  | 15                                  |
| 0  | 75  | 26                                  |
| 0  | 100 | 35                                  |
| 300                                      | 30  | 52                                  |
| 400                                      | 30  | 65                                  |
| 500                                      | 30  | 75                                  |

TABLE 2. VOLUME OF 0.25M EDTA SOLUTION REQUIRED DEPENDING ON THE CONTENT OF BARIUM IN THE SAMPLE SOLUTION AT THE SECOND DISSOLUTION STEP OF BaSO<sub>4</sub> PRECIPITATE (8.2. STEP 4)

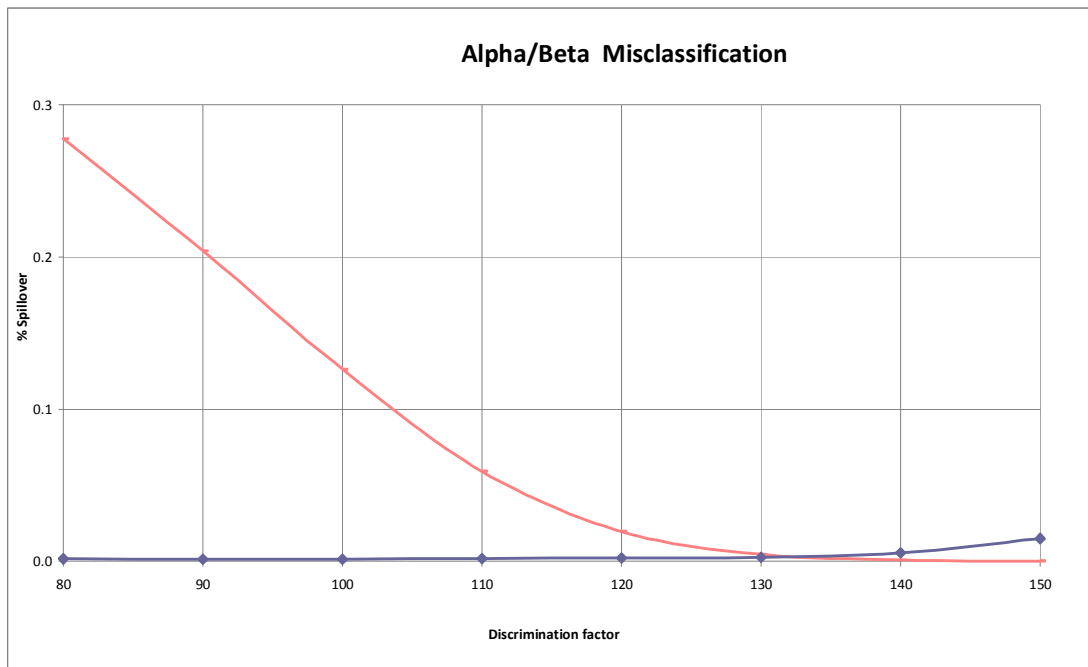
| Content of Ba in the sample (mg) | Volume of 0.25M EDTA solution (mL) |
|----------------------------------|------------------------------------|
| 50                               | 10                                 |
| 75                               | 15                                 |
| 100                              | 25                                 |



## APPENDIX IV. ALPHA/BETA DISCRIMINATION SETTING

TABLE 3. RESULTS OF OPTIMUM ALPHA/BETA DISCRIMINATION SETTING

| Discrimination factor | Alpha counts |          | Beta counts |          | Total alpha counts | Total beta counts | Alpha spillover | Beta spillover |
|-----------------------|--------------|----------|-------------|----------|--------------------|-------------------|-----------------|----------------|
|                       | Alpha MCA    | Beta MCA | Alpha MCA   | Beta MCA |                    |                   |                 |                |
| 80                    | 4596         | 7.49     | 10193       | 26500    | 4603               | 36693             | 0.277783        | 0.001628       |
| 90                    | 4627         | 6.43     | 7823        | 30505    | 4633               | 38328             | 0.204105        | 0.001388       |
| 100                   | 4622         | 6.94     | 5032        | 34832    | 4628               | 39864             | 0.126225        | 0.001499       |
| 110                   | 4608         | 8.86     | 2514        | 39945    | 4617               | 42459             | 0.059216        | 0.001919       |
| 120                   | 4591         | 10.1     | 909         | 45474    | 4601               | 46384             | 0.019608        | 0.002201       |
| 130                   | 4609         | 11.8     | 231         | 49241    | 4621               | 49472             | 0.004677        | 0.002553       |
| 140                   | 4606         | 25.8     | 45.6        | 50674    | 4632               | 50720             | 0.000899        | 0.005564       |
| 150                   | 4546         | 69.6     | 11.3        | 50783    | 4616               | 50795             | 0.000223        | 0.015072       |



*FIG. 3. Correlation between spillover and discrimination factor.*





## APPENDIX V. TYPICAL SPECTRA OF $^{226}\text{Ra}$ AND $^{228}\text{Ra}$

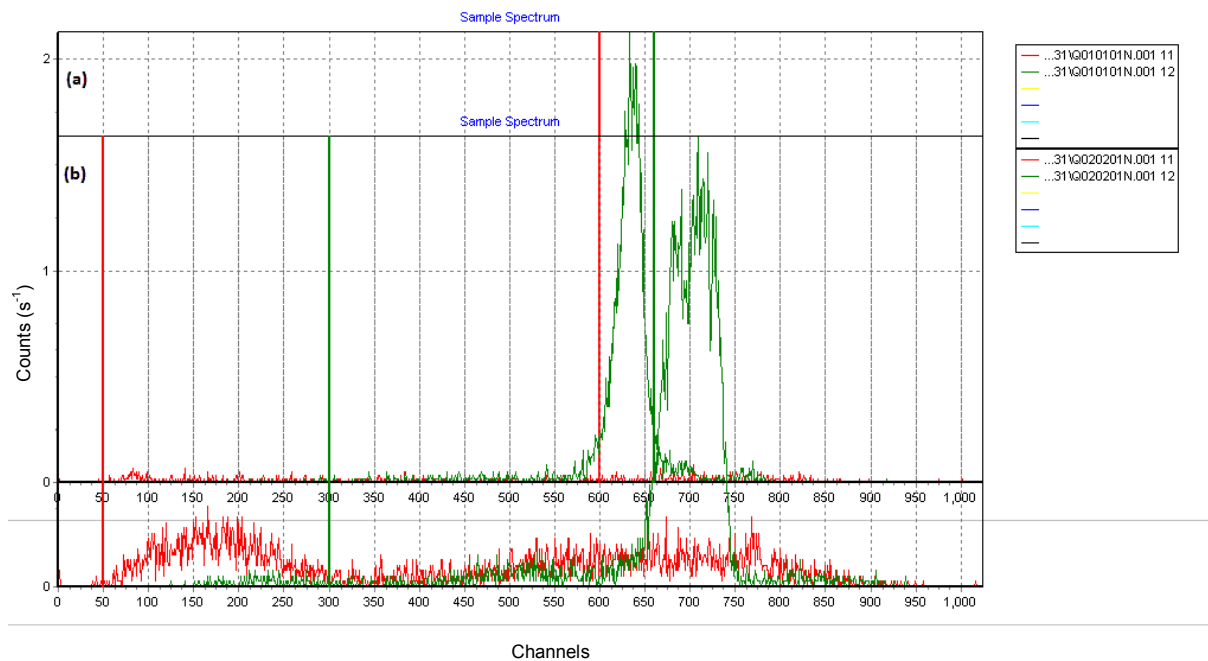


FIG. 4. Negligible spectral overlap of (a)  $^{226}\text{Ra}$  spectra and (b)  $^{228}\text{Ra}$  spectra.

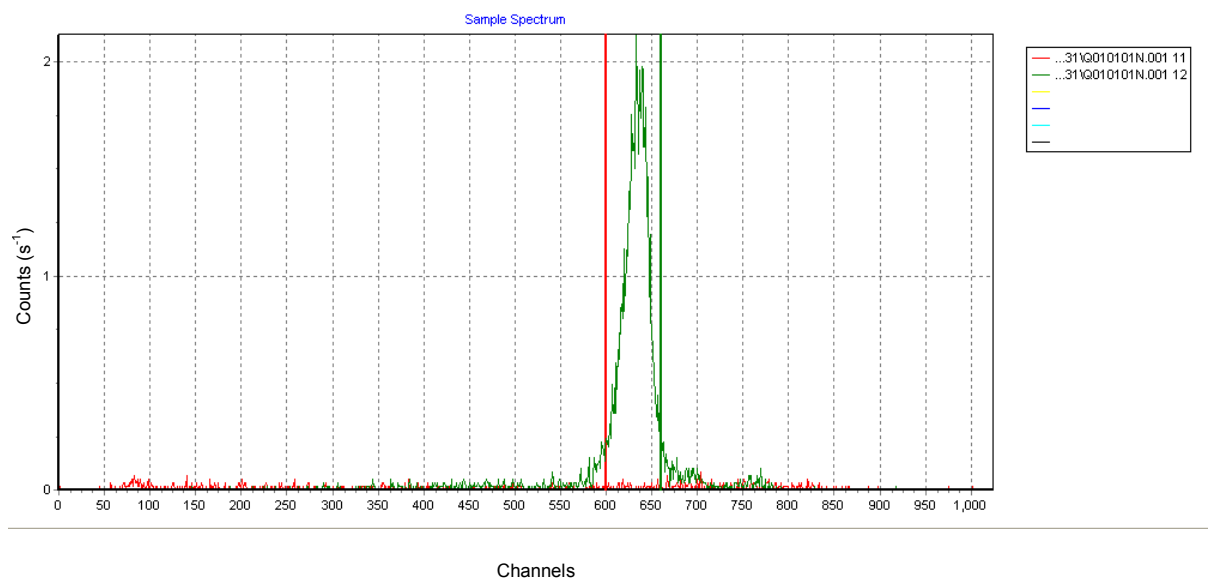


FIG. 5.  $^{226}\text{Ra}$  spectra and counting window as shown in spectral analysis software.

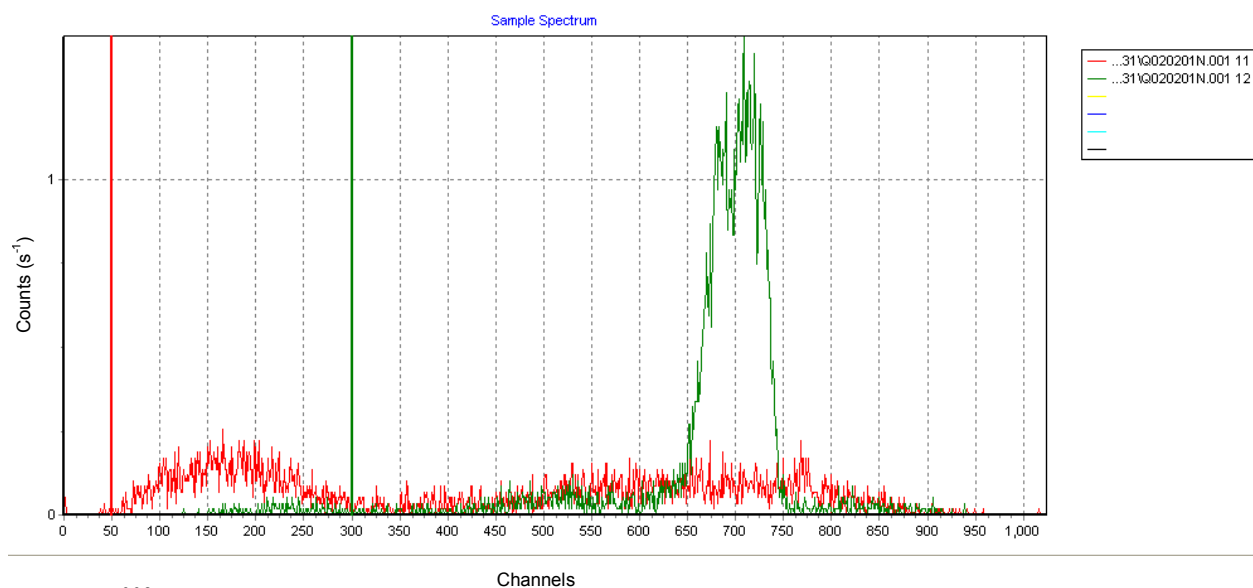


FIG. 6.  $^{228}\text{Ra}$  spectra and counting window as shown in spectral analysis software, alpha peaks are  $^{228}\text{Ra}$  decay progeny.

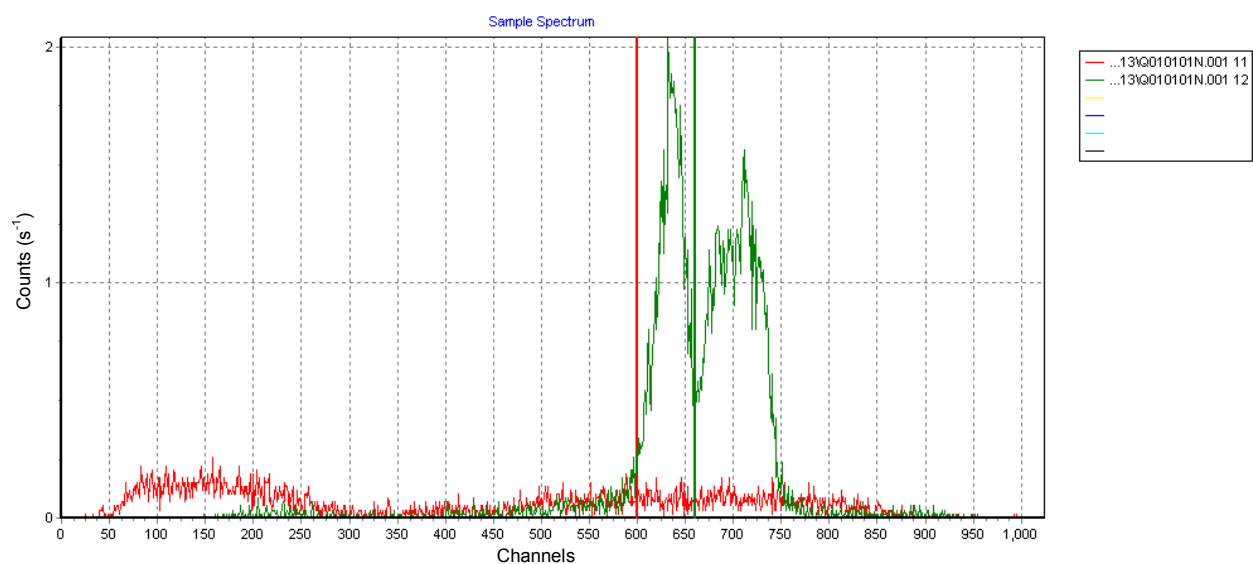


FIG. 7. Combined spectra of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  as shown in spectral analysis software.

## APPENDIX VI. COUNTING EFFICIENCIES AND OVERALL EFFICIENCIES

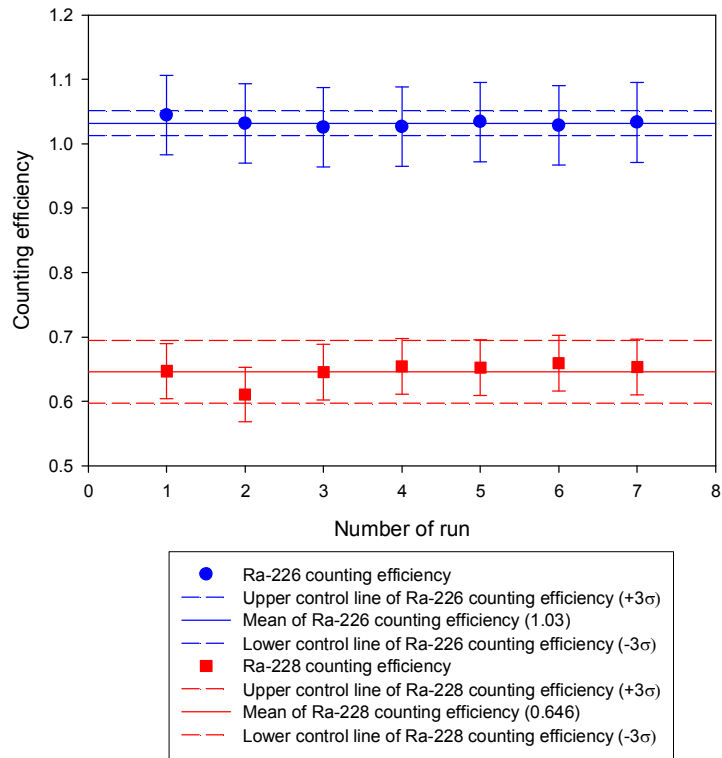


FIG. 8. Control chart for counting efficiencies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ .

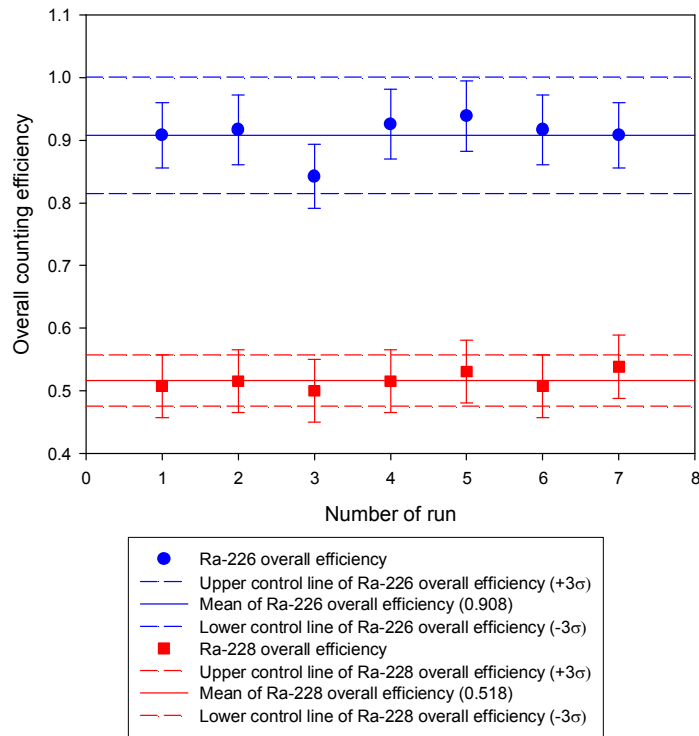


FIG. 9. Control chart for overall efficiencies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ .

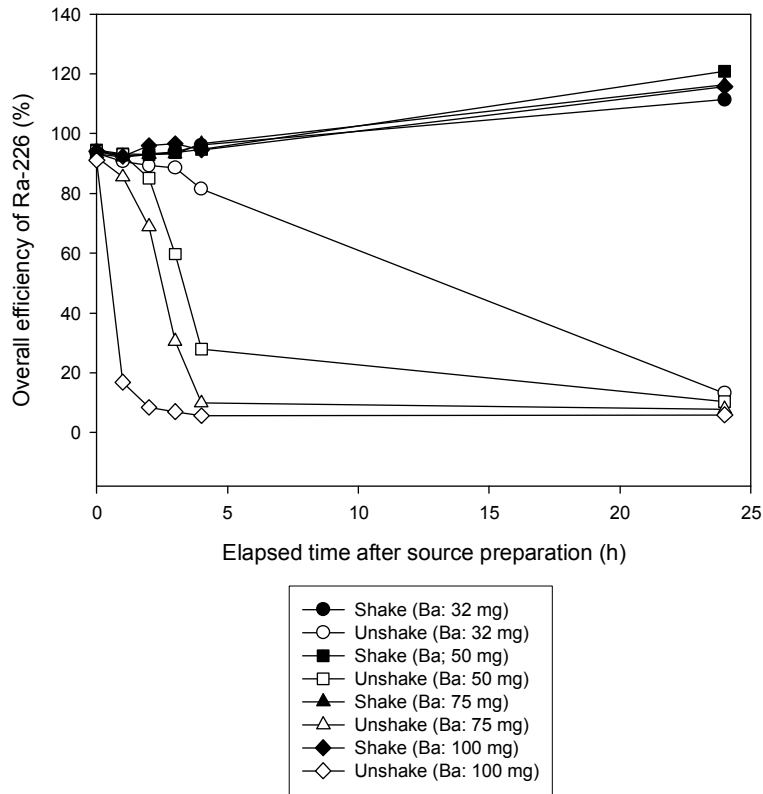


FIG. 10. Variation of overall efficiency for  $^{226}\text{Ra}$  with elapsed time after source preparation.

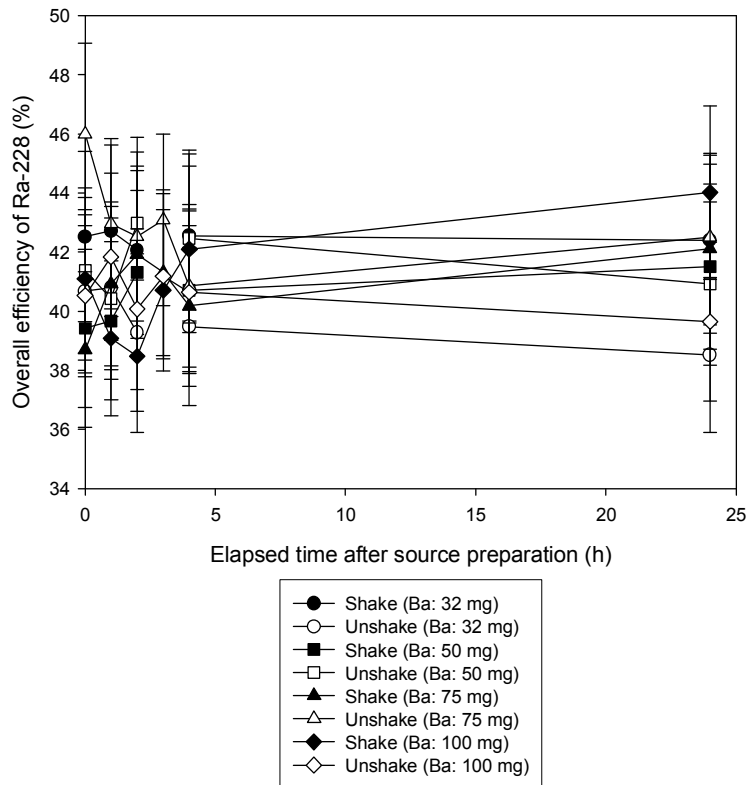


FIG. 11. Variation of overall efficiency for  $^{228}\text{Ra}$  with elapsed time after source preparation.

## APPENDIX VII. CALCULATION OF INDIVIDUAL UNCERTAINTY AND COMBINED UNCERTAINTY OF ACTIVITY CONCENTRATION OF <sup>226</sup>Ra AND <sup>228</sup>Ra IN WATER SAMPLES

### VII.1. Uncertainty in weighing the sample mass

The uncertainty associated with the mass of sample is estimated using the data from the calibration certificate of the analytical balance and the manufacturer's recommendations on the uncertainty estimation of the balance. If it is assumed that a balance with  $u_{mb}$  mass uncertainty is used for weighing the sample and the linearity distribution is assumed to show a triangular distribution, the standard uncertainty in the weighing of the sample mass can be calculated as:

$$u_{\text{single weighing}} = \frac{u_{mb}}{\sqrt{3}} \quad (17)$$

The contribution for the linearity has to be accounted for twice, once for the tare and once for the gross mass (tare + sample), leading to an uncertainty  $u(m_s)$  according to equation (18):

$$u(m_s) = \sqrt{2 \times \left( \frac{u_{mb}}{\sqrt{3}} \right)^2} \quad (18)$$

### VII.2. Uncertainty of net counts of <sup>226</sup>Ra and <sup>228</sup>Ra in standard solution, spiked sample and real sample

The uncertainty of net count rates at ROIs of <sup>226</sup>Ra and <sup>228</sup>Ra in LSC spectra can be calculated as follows:

$$n_{226Ra}^s = r_{g-226Ra}^s - r_{0-226Ra} \quad \text{and} \quad u(n_{226Ra}^s) = \sqrt{\left( \frac{r_{g-226Ra}^s}{T_{s-226Ra}} \right)^2 + \left( \frac{r_{0-226Ra}}{t_{0-226Ra}} \right)^2} \quad (19)$$

$$n_{228Ra}^s = r_{g-228Ra}^s - r_{0-228Ra} \quad \text{and} \quad u(n_{228Ra}^s) = \sqrt{\left( \frac{r_{g-228Ra}^s}{T_{s-228Ra}} \right)^2 + \left( \frac{r_{0-228Ra}}{t_{0-228Ra}} \right)^2} \quad (20)$$

$n_{226Ra}^t$ ,  $u(n_{226Ra}^t)$ ,  $n_{228Ra}^t$  and  $u(n_{228Ra}^t)$  for spiked sample, and  $n_{226Ra}$ ,  $u(n_{226Ra})$ ,  $n_{228Ra}$  and  $u(n_{228Ra})$  for real sample can be calculated in the same way with  $n_{226Ra}^s$  and  $u(n_{226Ra}^s)$  for standard solution.

### VII.3. Uncertainties of counting efficiency and overall efficiency of $^{226}\text{Ra}$ and $^{228}\text{Ra}$

The uncertainty of the counting efficiency  $u(\varepsilon_{226\text{Ra}})$  can be calculated based on equation (1). Differentiating equation (1), each partial derivative can be calculated as follows:

$$\frac{\partial \varepsilon_{226\text{Ra}}}{\partial n_{226\text{Ra}}^s} = \frac{\varepsilon_{226\text{Ra}}}{n_{226\text{Ra}}^s} \quad (21)$$

$$\frac{\partial \varepsilon_{226\text{Ra}}}{\partial A_{226\text{Ra}}} = \frac{\varepsilon_{226\text{Ra}}}{A_{226\text{Ra}}} \quad (22)$$

$$\frac{\partial \varepsilon_{226\text{Ra}}}{\partial m_{s-226\text{Ra}}} = \frac{\varepsilon_{226\text{Ra}}}{m_{s-226\text{Ra}}} \quad (23)$$

$$\frac{\partial \varepsilon_{226\text{Ra}}}{\partial \lambda_{226\text{Ra}}} = -\varepsilon_{226\text{Ra}} \times t_{s-226\text{Ra}} \quad (24)$$

$$\frac{\partial \varepsilon_{226\text{Ra}}}{\partial t_{s-226\text{Ra}}} = \varepsilon_{226\text{Ra}} \times \lambda_{226\text{Ra}} \quad (25)$$

The uncertainty of counting efficiency ( $u(\varepsilon_{226\text{Ra}})$ ) can be calculated from the law of error propagation as follows:

$$\begin{aligned} u(\varepsilon_{226\text{Ra}})^2 &= \left( \frac{\varepsilon_{226\text{Ra}}}{n_{226\text{Ra}}^s} \right)^2 \times u(n_{226\text{Ra}}^s)^2 + \left( \frac{\varepsilon_{226\text{Ra}}}{A_{226\text{Ra}}} \right)^2 \times u(A_{226\text{Ra}})^2 + \left( \frac{\varepsilon_{226\text{Ra}}}{m_{s-226\text{Ra}}} \right)^2 \times u(m_{s-226\text{Ra}})^2 \\ &+ (\varepsilon_{226\text{Ra}} \times t_{s-226\text{Ra}})^2 \times u(\lambda_{226\text{Ra}})^2 + (\varepsilon_{226\text{Ra}} \times \lambda_{226\text{Ra}})^2 \times u(t_{s-226\text{Ra}})^2 \end{aligned} \quad (26)$$

The uncertainty of the counting efficiency  $u(\varepsilon_{228\text{Ra}})$  can be calculated based on equation (2). Differentiating equation (2), each partial derivative can be calculated as follows:

$$\frac{\partial \varepsilon_{228\text{Ra}}}{\partial n_{228\text{Ra}}^s} = \frac{\varepsilon_{228\text{Ra}}}{n_{228\text{Ra}}^s} \quad (27)$$

$$\frac{\partial \varepsilon_{228\text{Ra}}}{\partial A_{228\text{Ra}}} = \frac{\varepsilon_{228\text{Ra}}}{A_{228\text{Ra}}} \quad (28)$$

$$\frac{\partial \varepsilon_{228\text{Ra}}}{\partial m_{s-228\text{Ra}}} = \frac{\varepsilon_{228\text{Ra}}}{m_{s-228\text{Ra}}} \quad (29)$$

$$\frac{\partial \varepsilon_{228Ra}}{\partial \lambda_{228Ra}} = \varepsilon_{228Ra} \times t_{s-228Ra} \quad (30)$$

$$\frac{\partial \varepsilon_{228Ra}}{\partial t_{s-228Ra}} = \varepsilon_{228Ra} \times \lambda_{228Ra} \quad (31)$$

The uncertainty of counting efficiency ( $u(\varepsilon_{228Ra})$ ) can be calculated from the law of error propagation as follows:

$$\begin{aligned} u(\varepsilon_{228Ra})^2 = & \left( \frac{\varepsilon_{228Ra}}{n_{228Ra}^s} \right)^2 \times u(n_{228Ra}^s)^2 + \left( -\frac{\varepsilon_{228Ra}}{A_{228Ra}} \right)^2 \times u(A_{228Ra})^2 + \left( -\frac{\varepsilon_{228Ra}}{m_{s-228Ra}} \right)^2 \times u(m_{s-228Ra})^2 \\ & + (\varepsilon_{228Ra} \times t_{s-228Ra})^2 \times u(\lambda_{228Ra})^2 + (\varepsilon_{228Ra} \times \lambda_{228Ra})^2 \times u(t_{s-228Ra})^2 \end{aligned} \quad (32)$$

Overall efficiency uncertainties of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ,  $u(\varepsilon_{226Ra}^c)$  and  $u(\varepsilon_{228Ra}^c)$  can be calculated in the same way with calculation of counting efficiency uncertainties,  $u(\varepsilon_{226Ra})$  and  $u(\varepsilon_{228Ra})$ . The uncertainties of  $t_{s-226Ra}$  and  $t_{s-228Ra}$  are regarded negligible.

#### VII.4. Uncertainty of chemical recovery

Uncertainties of chemical recovery of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are calculated as follows:

$$u(R_{226Ra}) = \frac{\varepsilon_{226Ra}^c}{\varepsilon_{226Ra}} \times \sqrt{\left( \frac{u(\varepsilon_{226Ra}^c)}{\varepsilon_{226Ra}^c} \right)^2 + \left( \frac{u(\varepsilon_{226Ra})}{\varepsilon_{226Ra}} \right)^2} \quad (33)$$

$$u(R_{228Ra}) = \frac{\varepsilon_{228Ra}^c}{\varepsilon_{228Ra}} \times \sqrt{\left( \frac{u(\varepsilon_{228Ra}^c)}{\varepsilon_{228Ra}^c} \right)^2 + \left( \frac{u(\varepsilon_{228Ra})}{\varepsilon_{228Ra}} \right)^2} \quad (34)$$

#### VII.5. Combined uncertainty in the determination of the analyte at the sampling date

The combined uncertainty of the specific activity of  $^{226}\text{Ra}$  in the sample is calculated based on equation (7) using the general formula given elsewhere [18, 19]. Differentiating equation (7), each partial derivative can be calculated as follows:



$$\frac{\partial a_{226Ra}}{\partial n_{226Ra}} = \frac{a_{226Ra}}{n_{226Ra}} \quad (35)$$

$$\frac{\partial a_{226Ra}}{\partial \varepsilon_{226Ra}} = -\frac{a_{226Ra}}{\varepsilon_{226Ra}} \quad (36)$$

$$\frac{\partial a_{226Ra}}{\partial m_s} = -\frac{a_{226Ra}}{m_s} \quad (37)$$

$$\frac{\partial a_{226Ra}}{\partial \lambda_{226Ra}} = a_{226Ra} \times t_{226Ra} \quad (38)$$

$$\frac{\partial a_{226Ra}}{\partial t_{226Ra}} = a_{226Ra} \times \lambda_{226Ra} \quad (39)$$

The uncertainty of counting efficiency ( $u(\varepsilon_{226Ra})$ ) can be calculated from the law of error propagation as follows:

$$\begin{aligned} u(a_{226Ra})^2 &= \left( \frac{a_{226Ra}}{n_{226Ra}} \right)^2 \times u(n_{226Ra})^2 + \left( -\frac{a_{226Ra}}{\varepsilon_{226Ra}} \right)^2 \times u(\varepsilon_{226Ra})^2 + \left( -\frac{a_{226Ra}}{m_s} \right)^2 \times u(m_s)^2 \\ &+ (a_{226Ra} \times t_{226Ra})^2 \times u(\lambda_{226Ra})^2 + (a_{226Ra} \times \lambda_{226Ra})^2 \times u(t_{226Ra})^2 \end{aligned} \quad (40)$$

The uncertainty of  $t_{226Ra} \times u(\lambda_{226Ra})$  is often regarded negligible.

The combined uncertainty of the specific activity of  $^{228}\text{Ra}$  on the sampling date can be calculated by the same way with that of  $^{226}\text{Ra}$ .

TABLE 4. EXAMPLE OF SPREADSHEETS FOR THE MEASUREMENT UNCERTAINTIES OF  $^{226}\text{Ra}$  AND  $^{228}\text{Ra}$  IN SPIKED WATER SAMPLE

| Components  | Value of variable | Standard uncertainty | Percent contribution to combined standard uncertainty |
|---|-------------------|----------------------|---|
| $^{226}\text{Ra}$                                     |                   |                      |   |
| $r_{g-226\text{Ra}}$ (cps)                            | 0.651             | 0.014                | 10  |
| $r_{0-226\text{Ra}}$ (cps)                            | 0.00113           | 0.00057              |   |
| $\epsilon_{226\text{Ra}}$                             | 0.908             | 0.060                | 90  |
| Half-life of $^{226}\text{Ra}$ (y)                    | 1600              | 7                    | negligible  |
| $m_s$ (kg)  | 0.508             | 0.00008              | negligible  |
| $a_{226\text{Ra}}$ ( $\text{Bq}\cdot\text{kg}^{-1}$ ) | 1.41              | 0.09                 |   |
| $^{228}\text{Ra}$                                     |                   |                      |   |
| $r_{g-228\text{Ra}}$ (cps)                            | 0.1986            | 0.0075               | 8   |
| $r_{0-228\text{Ra}}$ (cps)                            | 0.040             | 0.0034               | 2   |
| $\epsilon_{228\text{Ra}}$                             | 0.516             | 0.097                | 90  |
| Half-life of $^{228}\text{Ra}$ (y)                    | 5.75              | 0.04                 | negligible  |
| $m_s$ (kg)  | 0.508             | 0.00008              | negligible  |
| $a_{228\text{Ra}}$ ( $\text{Bq}\cdot\text{kg}^{-1}$ ) | 0.599             | 0.100                |   |



## APPENDIX VIII. VALIDATION RESULTS OF THE PROCEDURE

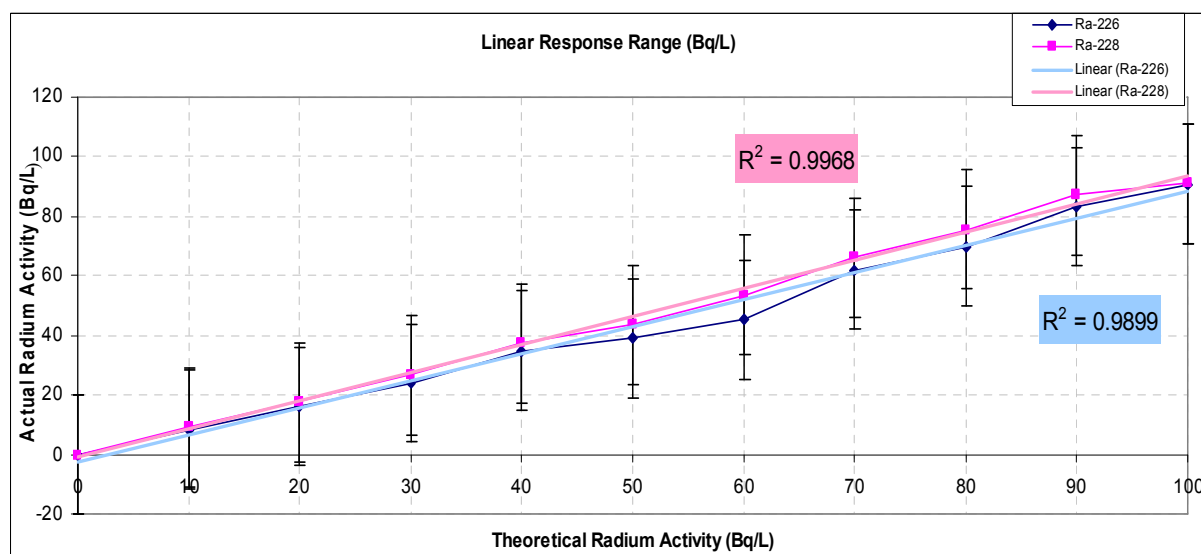


FIG. 12. Linear ranges of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ .

TABLE 5. REPEATABILITY TESTING RESULTS FOR  $^{226}\text{Ra}$  AND  $^{228}\text{Ra}$  IN QUALITY CONTROL SAMPLE 1

| Number of run                                       | $^{226}\text{Ra}$                                     |                   |                 | $^{228}\text{Ra}$                                     |                   |                 |
|---|---|-------------------|-----------------|---|-------------------|-----------------|
|   | massic activity<br>( $\text{Bq}\cdot\text{kg}^{-1}$ ) | relative bias (%) | precision index | massic activity<br>( $\text{Bq}\cdot\text{kg}^{-1}$ ) | relative bias (%) | precision index |
| 1   | 1.39±0.09   | -9.7              | 6.5             | 0.69±0.07   | -5.5              | 10.5            |
| 2   | 1.52±0.09   | -1.3              | 6.0             | 0.79±0.07   | 8.2               | 9.3             |
| 3   | 1.52±0.09   | -1.3              | 6.0             | 0.81±0.07   | 11.0              | 9.1             |
| 4   | 1.54±0.09   | 0.0               | 5.9             | 0.81±0.07   | 11.0              | 2.7             |
| 5   | 1.52±0.09   | -1.3              | 6.0             | 0.80±0.07   | 9.6               | 9.2             |
| 6   | 1.47±0.09   | -4.5              | 6.2             | 0.84±0.07   | 15.1              | 8.8             |
| 7   | 1.47±0.09   | -4.5              | 6.2             | 0.81±0.07   | 11.0              | 9.1             |
| 8   | 1.35±0.08   | -12.3             | 6.0             | 0.87±0.07   | 19.2              | 8.5             |
| 9   | 1.38±0.08   | -10.4             | 5.8             | 0.87±0.07   | 19.2              | 8.5             |
| 10  | 1.30±0.08   | -15.6             | 6.2             | 0.89±0.07   | 21.9              | 8.3             |
| 11  | 1.33±0.08   | -13.6             | 6.0             | 0.84±0.07   | 15.1              | 9.9             |
| 12  | 1.40±0.10   | -9.1              | 7.2             | 0.80±0.07   | 9.6               | 12.8            |
| Mean  | 1.43  |                   |                 | 0.82  |                   |                 |
| Absolute mean bias                                  | 0.11  |                   |                 | 0.09  |                   |                 |
| Repeatability standard deviation ( $S_r$ )          | 0.08  |                   |                 | 0.05  |                   |                 |
| Relative repeatability standard deviation $S_r$ (%) | 5.59  |                   |                 | 6.10  |                   |                 |
| Repeatability limit ( $r_L$ )                       | 0.22  |                   |                 | 0.20  |                   |                 |
| Assigned value at reference date                    | 1.54±0.03*  |                   |                 | 0.73±0.02*  |                   |                 |

\*: coverage factor (k=1)

TABLE 6. REPEATABILITY TESTING RESULTS FOR  $^{226}\text{Ra}$  AND  $^{228}\text{Ra}$  IN QUALITY CONTROL SAMPLE 2

| Number of run                                       | $^{226}\text{Ra}$                                     |                   |                 | $^{228}\text{Ra}$                                     |                   |                 |
|---|---|-------------------|-----------------|---|-------------------|-----------------|
|   | massic activity<br>( $\text{Bq}\cdot\text{kg}^{-1}$ ) | relative bias (%) | precision index | massic activity<br>( $\text{Bq}\cdot\text{kg}^{-1}$ ) | relative bias (%) | precision index |
| 1   | 1.01±0.07   | 0.0               | 7.0             | 1.56±0.09   | 6.1               | 6.7             |
| 2   | 1.00±0.07   | -1.0              | 7.1             | 1.62±0.09   | 10.2              | 6.5             |
| 3   | 1.01±0.07   | 0.0               | 7.0             | 1.60±0.10   | 8.8               | 7.1             |
| 4   | 1.03±0.07   | 2.0               | 6.9             | 1.50±0.09   | 2.0               | 3.4             |
| 5   | 0.98±0.07   | -3.0              | 7.2             | 1.54±0.09   | 4.8               | 6.8             |
| 6   | 1.01±0.07   | 0.0               | 7.0             | 1.56±0.09   | 6.1               | 6.7             |
| 7   | 0.99±0.07   | -2.0              | 7.1             | 1.54±0.09   | 4.8               | 6.8             |
| 8   | 0.97±0.07   | -4.0              | 7.3             | 1.60±0.10   | 8.8               | 7.1             |
| 9   | 0.95±0.07   | -5.9              | 7.4             | 1.60±0.10   | 8.8               | 7.1             |
| 10  | 0.98±0.07   | -3.0              | 7.2             | 1.50±0.09   | 2.0               | 6.9             |
| 11  | 1.02±0.07   | 1.0               | 6.9             | 1.53±0.09   | 4.1               | 6.8             |
| 12  | 1.00±0.1  | -1.0              | 10.0            | 1.60±0.20   | 8.8               | 13.0            |
| Mean  | 1.00  |                   |                 | 1.56  |                   |                 |
| Absolute mean bias                                  | 0.01  |                   |                 | 0.09  |                   |                 |
| Repeatability standard deviation ( $S_r$ )          | 0.02  |                   |                 | 0.04  |                   |                 |
| Relative repeatability standard deviation $S_r$ (%) | 2.00  |                   |                 | 2.56  |                   |                 |
| Repeatability limit ( $r_L$ )                       | 0.06  |                   |                 | 0.11  |                   |                 |
| Assigned value at reference date                    | 1.01±0.01*  |                   |                 | 1.47±0.05*  |                   |                 |

\*: coverage factor ( $k=1$ )

TABLE 7. REPEATABILITY TESTING RESULTS FOR  $^{226}\text{Ra}$  AND  $^{228}\text{Ra}$  IN QUALITY CONTROL SAMPLE 3

| Number of run                                       | $^{226}\text{Ra}$                                     |                   |                 | $^{228}\text{Ra}$                                     |                   |                 |
|---|---|-------------------|-----------------|---|-------------------|-----------------|
|   | massic activity<br>( $\text{Bq}\cdot\text{kg}^{-1}$ ) | relative bias (%) | precision index | massic activity<br>( $\text{Bq}\cdot\text{kg}^{-1}$ ) | relative bias (%) | precision index |
| 1   | 2.0±0.1   | 2.0               | 5.0             | 2.5±0.1   | 8.2               | 5.0             |
| 2   | 2.1±0.1   | 2.9               | 4.8             | 2.4±0.1   | 3.9               | 5.2             |
| 3   | 2.0±0.1   | 2.0               | 5.0             | 2.3±0.1   | 0.4               | 5.3             |
| 4   | 2.0±0.1   | 2.0               | 5.0             | 2.5±0.1   | 8.2               | 3.0             |
| 5   | 2.0±0.1   | 2.0               | 5.0             | 2.5±0.1   | 8.2               | 5.0             |
| 6   | 1.7±0.1   | 16.7              | 5.9             | 2.3±0.1   | 0.4               | 5.3             |
| 7   | 1.8±0.1   | 11.8              | 5.6             | 2.5±0.1   | 8.2               | 5.0             |
| 8   | 1.8±0.1   | 11.8              | 5.6             | 2.8±0.1   | 21.2              | 4.7             |
| 9   | 1.8±0.1   | 11.8              | 5.6             | 2.7±0.1   | 16.9              | 4.8             |
| 10  | 1.7±0.1   | 16.7              | 5.9             | 2.7±0.1   | 16.9              | 4.8             |
| Mean  | 1.89  |                   |                 | 2.52  |                   |                 |
| Absolute mean bias                                  | 0.15  |                   |                 | 0.21  |                   |                 |
| Repeatability standard deviation ( $S_r$ )          | 0.14  |                   |                 | 0.17  |                   |                 |
| Relative repeatability standard deviation $S_r$ (%) | 7.41  |                   |                 | 6.75  |                   |                 |
| Repeatability limit ( $r_L$ )                       | 0.39  |                   |                 | 0.48  |                   |                 |
| Assigned value at reference date                    | 2.04±0.01*  |                   |                 | 2.31±0.07*  |                   |                 |

\*: coverage factor ( $k=1$ )

TABLE 8. REPRODUCIBILITY TEST RESULTS FOR THE DETERMINATION OF  $^{226}\text{Ra}$  AND  $^{228}\text{Ra}$  IN A QUALITY CONTROL SAMPLE BY INTER-LABORATORY COMPARISON EXERCISE WITH 5 LABORATORIES (UNIT:  $\text{Bq}\cdot\text{kg}^{-1}$ )

| Factors                                    | $^{226}\text{Ra}$ | $^{228}\text{Ra}$ |
|--|-------------------|-------------------|
| Mean of measurement results at target date | 0.55              | 0.54              |
| Assigned value at target date              | $0.40\pm 0.02^*$  | $0.52\pm 0.02^*$  |
| Absolute mean bias                         | 0.15              | 0.02              |
| Repeatability variance ( $S_r^2$ )         | 0.002             | 0.001             |
| Between laboratory variance ( $S_L^2$ )    | 0.002             | 0.001             |
| Reproducibility variance ( $S_R^2$ )       | 0.004             | 0.003             |
| Repeatability limit ( $r_L$ )              | 0.13              | 0.11              |
| Reproducibility limit ( $R_L$ )            | 0.17              | 0.15              |

\*: coverage factor ( $k=1$ )





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