

*A Procedure for the Rapid  
Determination of Ra-226 and Ra-  
228 in Drinking Water by Prompt  
Liquid Scintillation Counting*

DRAFT

## FOREWORD

Reliable, comparable and 'fit for purpose' results are an essential requirement for any decision based on analytical measurements. For the analyst, the availability of tested and validated analytical procedures is an extremely important tool for production of such analytical measurements. For maximum utility, such procedures should be comprehensive, clearly formulated, and readily available to both the analyst and the customer for reference.

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. For establishing a recommended rapid procedure for  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in water samples by liquid scintillation counting, about 300 papers from scientific literature were reviewed. Based on this review, a candidate method was selected for testing, refinement and validation in accordance with ISO guidelines. A comprehensive methodology for calculation of results including quantification of measurement uncertainty was developed. This report presents the rapid procedure which was developed based on that work.

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DRAFT

## 1. INTRODUCTION

Radium is a radioactive element for which no stable isotope is known. The mass numbers of the known isotopes range from 206 to 230. Among them, two radium isotopes,  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are very significant from a radiological protection viewpoint due to their relatively long half-lives, presence in nature, and high dose conversion factors. Radium isotopes 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 produce 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 nuclides, contributing to radiological dose.

Radium isotopes 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 around NORM and TENORM industries, radium isotopes have been measured by several techniques, gamma-spectrometry, alpha-spectrometry, liquid scintillation counting (LSC) and mass-spectrometry.

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

Gamma 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 complicated 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].

Liquid scintillation counting (LSC) is often used for the determination of radium isotopes in environmental samples, especially in liquids [4, 5]. LSC methods can provide high sample throughput, and acceptable detection limits for several radium isotopes [6, 7, 8]. There are disadvantages in LSC including quenching, poor energy resolution and relatively high background, especially in comparison with alpha particle spectrometry [9, 10].

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 years). The main advantages of mass spectrometric methods are high sensitivity and short analytical 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 [11].

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 report introduces a procedure for rapid determination of both isotopes to be used for emergency situations and routine monitoring. This procedure could be used for screening of activity levels of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in drinking water. The procedure was validated in accordance with ISO guidelines.

## 2. SCOPE

This procedure is based on the method published in paper [12]. The procedure describes the use of a barium sulfate co-precipitation with the removal of lead and separation of radium from its aqueous media enabling analysis by liquid scintillation counting. The procedure was prepared based on 0.5 kg of drinking water sample and can be applied to other type of water samples where the Ba concentration is less than  $100 \text{ mg kg}^{-1}$ . The procedure provides 7% of relative repeatability standard deviation ( $S_r$ ) for  $1\text{--}2 \text{ Bq kg}^{-1}$  of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  activity level. The relative reproducibility standard deviation is determined to be 16% for  $^{226}\text{Ra}$  and 11% for  $^{228}\text{Ra}$  at  $0.5 \text{ Bq kg}^{-1}$  activity level of both isotopes in inter-laboratory exercise. The detection limit is  $0.01 \text{ Bq kg}^{-1}$  and  $0.06 \text{ Bq kg}^{-1}$  for  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  respectively for a 1 hour counting time in a low background liquid scintillation spectrometer with 0.5 kg of sample. The relative standard uncertainty is 6% and 17% for  $1.5 \text{ Bq kg}^{-1}$  of  $^{226}\text{Ra}$  and  $0.6 \text{ Bq kg}^{-1}$  of  $^{228}\text{Ra}$  respectively. The analysis time (chemical separation and source preparation) of radium for a set of samples (3 samples, one blank and one quality control sample) is about 8 hr. In case more precise results are required, other analytical techniques (e.g. alpha-spectrometry or mass-spectrometry) are recommended.

## 3. NORMATIVE REFERENCES

- ISO 11929-7, 2005. Determination of the detection limit and decision threshold for ionizing radiation measurement – Part 7: Fundamentals and general applications.
- ISO/TS 21748, 2004. Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation
- ISO/IEC Guide 98-3:2008. Guide to the expression of uncertainty in measurement.
- 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 5725-1, 1994. Accuracy (trueness and precision) of measurement methods and results - Part 1: General principles and definitions
- 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, 1993. Control charts – General guide and introduction
- ISO 7966, 1993. Acceptance control charts

#### 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 internal rules for chemical and radiological safety is obligatory.

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

ROI: region of interest

MCA: multi channel analyser

FWHM: full width half maximum

rpm: revolutions per minute

HDPE: high density polyethylene

EDTA: ethylenediaminetetraacetic acid

MDL: minimum detectable limit

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

$A_x$  and  $u(A_x)$ : the certified massic activity of the analyte on the reference date [ $\text{Bq g}^{-1}$ ]

$A_x^t$  and  $u(A_x^t)$ : the massic activity of the analyte in the quality control sample on the reference date [ $\text{Bq g}^{-1}$ ]

$a_x$  and  $u(a_x)$ : the massic activity of the specific analyte on the sampling date [ $\text{Bq kg}^{-1}$ ]

$C_x$  and  $u(C_x)$ : the target massic activity of the specific analyte in the quality control sample prepared for the validation of the procedure [ $\text{Bq kg}^{-1}$ ]

$m_{s-x}$  and  $u(m_{s-x})$ : the mass of the certified standard solution taken for the analysis of the specific analyte [g]

$m_{t-x}$  and  $u(m_{t-x})$ : the mass of the quality control sample taken for the analysis of the specific analyte [g]

$m_s$  and  $u(m_s)$ : the mass of sample [kg]

$n_x^s$  and  $u(n_x^s)$ : net count rates of the specific analyte in the certified standard solution [ $\text{counts s}^{-1}$ ]

$n_x^t$  and  $u(n_x^t)$ : net count rates of the specific analyte in the quality control sample [ $\text{counts s}^{-1}$ ]

$n_x$  and  $u(n_x)$ : net count rates of the specific analyte in the sample [ $\text{counts s}^{-1}$ ]

$PI$ : precision index [%]

$R_{226}$  and  $u(R_{226})$ : the chemical recovery of  $^{226}\text{Ra}$

$R_{228}$  and  $u(R_{228})$ : the chemical recovery of  $^{228}\text{Ra}$

$R_L$ : reproducibility limit [ $\text{Bq kg}^{-1}$ ]

$r_L$ : repeatability limit [ $\text{Bq kg}^{-1}$ ]

$r_{g-x}^s$  and  $u(r_{g-x}^s)$ : gross count rates of the specific analyte in standard solution [ $\text{counts s}^{-1}$ ]

$r_{g-x}^t$  and  $u(r_{g-x}^t)$ : gross count rates of the specific analyte in the quality control sample [ $\text{counts s}^{-1}$ ]

$r_{g-x}$  and  $u(r_{g-x})$ : gross count rates of the specific analyte in the sample [ $\text{counts s}^{-1}$ ]

$r_{0-x}$  and  $u(r_{0-x})$ : gross count rates of the specific analyte in blank sample [ $\text{counts s}^{-1}$ ]

$S_r$ : standard deviation of repeatability [ $\text{Bq kg}^{-1}$ ]

$S_R$ : standard deviation of reproducibility [ $\text{Bq kg}^{-1}$ ]

$T_{s-x}$ : the counting time of the specific analyte in the sample [s]

$t_{0-x}$ : the 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 [a]

$t_{t-x}$ : time interval between the measurement date and the reference date of the specific analyte in the quality control sample [a]

$t_x$ : time interval between the measurement date and the sampling date [a]

$\varepsilon_x$  and  $u(\varepsilon_x)$ : counting efficiency of specific analyte

$\varepsilon_x^c$  and  $u(\varepsilon_x^c)$ : overall efficiency of specific analyte in the quality control sample

$\lambda_x$  and  $u(\lambda_x)$ : decay constant of the specific analyte [ $\text{a}^{-1}$ ]

$\overline{X}_x$ : the mean of all measured values of the specific analyte in the quality control sample for the validation of the procedure [ $\text{Bq kg}^{-1}$ ]

$x_x^*$ : decision threshold of the specific analyte [ $\text{Bq kg}^{-1}$ ]

$\xi_x$ : detection limit of the specific analyte [ $\text{Bq kg}^{-1}$ ]

$\delta$ : the relative bias of the method [%]



$u_{mb}$  : uncertainty of analytical balance [g]

## 6. PRINCIPLE

Barium co-precipitation is used as a method of radium analysis 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 in this procedure is achieved by suspending the  $\text{BaSO}_4$  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 rather than a gel-forming cocktail.

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. CHEMICAL REAGENTS AND EQUIPMENT

### 7.1. Chemical reagents

- Lead carrier: 2.397 g  $\text{Pb}(\text{NO}_3)_2$ , 0.5 mL  $\text{HNO}_3$  made up to 100 mL with de-ionized water.
- Barium 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 deionised water.
- 0.25 MEDTA
- 32% hydrochloric acid
- 9 M sulfuric acid
- Analytical grade ammonium sulphate (solid)
- 10% ammonium sulphate solution

- 96% glacial acetic acid
- 25% ammonium hydroxide solution
- $^{226}\text{Ra}$  certified reference material
- $^{228}\text{Ra}$  certified reference material

## 7.2. Equipment

- 500 mL beakers
- 50 mL HDPE centrifuge tubes
- Analytical balance with accuracy of 0.1 mg
- Low background liquid scintillation counter (LSC)
- Vortex
- 5 mL and 10 mL Eppendorf pipettes
- Block heater equipped with  $\text{N}_2$  blow down (or equivalent evaporation system)

## 8. PRECAUTIONS

In this procedure, massic activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in the 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 Eqs. (7) and (8).

Therefore, it is recommended that real samples should be analyzed with a minimum of 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  $^{228}\text{Ra}$  (see Figure IV-3). This is therefore a dominant contributor (90%) to the combined uncertainty of the measurement result (see Table V-1).

It is recommended that the analyst should prepare control charts for counting efficiency and overall efficiency of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  (see Figures IV-2 and IV-3). Prior to start the analysis of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in the sample, it is recommended to check if the Ba concentration in the sample is higher than  $100 \text{ mg kg}^{-1}$ . If the Ba concentration is higher than the limit ( $100 \text{ mg kg}^{-1}$ ), it is recommended to so reduce the volume of the sample to be analysed that the total content of Ba in the sample does not exceed 50 mg. In the case that the total content of Ba in the sample solution is 50 mg, it is not necessary to add Ba carrier to the sample. If this procedure is applied to other type of water samples than drinking water, the Ba content in the sample should be check using an appropriate technique such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma-mass spectrometry (ICP-MS) before analysing  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ .

The 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.

Samples should be counted immediately after source preparation to avoid extensive in-growth of progeny (see Figures III-5 and III-6) and the degradation of the alpha spectrum due to formation of the flakes of precipitation. 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 a unshaken source that caused by in-growth of progeny and sinking of the  $\text{BaSO}_4$  precipitate (see Figures IV-4 and IV-5).

## 9. PROCEDURE

### 9.1. Separation of radium by precipitation (See Appendix I)

1. Acidify the sample (0.5 kg) with 32% hydrochloric acid to approximately pH 2.
2. Add both the lead carrier (2 mL) and barium carrier (2 mL) to the solution.
3. Add 9M sulfuric acid (4 mL) and ammonium sulphate (5 g).
4. Stir the solution to ensure all solids are dissolved then allow the precipitate to form and settle.
5. Decant the supernatant without disturbing the precipitate, leaving less than 30 mL of liquid in the glassware.
6. Quantitatively transfer the precipitate to a 50 mL HDPE tube rinsing the beaker with deionised 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.

### 9.2. Purification of radium

1. Dissolve the precipitate in hot 0.25 M EDTA solution (10 mL, but the solution volume is variable depending on total contents of Ca and Ba in the sample: see Table I-1) and ammonium hydroxide (3 mL). Carefully agitate the solution to dissolve the precipitate.
2. Add 10% ammonium sulphate (5 mL) and adjust the pH to 4.2-4.5 using glacial acetic acid, while stirring. As the pH is lowered, the precipitate should begin to re-form.
3. Boil the solution in the HDPE tube in a water bath at 80°C for two minutes then centrifuge for five minutes at 3500 rpm. The resulting precipitate is purified barium (radium) sulphate. Discard the supernatant.

4. Dissolve the precipitate in hot 0.25 M EDTA solution (10 mL, but the solution volume is variable depending on total content of Ba in the sample: see Table I-2) and agitate the solution carefully to dissolve the precipitate into solution. This may require the use of a vortex.
5. Add 10% ammonium sulphate solution (3 mL) to the solution and adjust the pH to 4.5 using the concentrated acetic acid. The precipitate should begin to re-form. Separate the precipitate by centrifuge for five minutes at 3500rpm. (Precaution: don't leave the precipitate overnight and don't allow it to dry. Prepare the source as soon as the BaSO<sub>4</sub> precipitate has been prepared).

### 9.3. Source Preparation

1. Wash the precipitate twice with 20 mL deionised water, shake well, centrifuge and discard the supernatant to ensure removal of any residual solvents.
2. Carefully remove the supernatant and add 3 mL of hot 0.25 M 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 each sample to ensure the precipitate gets suspended well and no clusters of precipitate are visible in the suspension.
5. Quantitatively transfer the solution including partially dissolved BaSO<sub>4</sub> precipitate to a 20mL plastic liquid scintillation vial using a transfer pipette
6. Rinse the HDPE tube with another 1mL of hot 0.25 M EDTA solution to ensure that no analyte remains in the tube.
7. Add 14mL 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, inhomogeneous mixture).
8. Seal and shake the LSC source until the suspension appears homogeneous.
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 waterbath 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.

## **9.4. Measurement condition setting and determination of counting efficiency**

### **9.4.1. Source preparation for alpha/beta discrimination setting**

1. Take 2 mL barium carrier (2 mL) in two 50 mL volume of HDPE tube.
2. Add 10 % ammonium sulphate solution (3 mL) and 1mL 25%  $\text{NH}_3(\text{aq})$  solution to the solution to perform the  $\text{BaSO}_4$  precipitate. Separate the precipitate by centrifuging for five minutes at 3500 rpm.
3. Dissolve the precipitate in hot 0.25 M EDTA solution (4 mL) and agitate the solution carefully to dissolve and suspend the precipitate into solution. This may require the use of a vortex.
4. Follow section 9.3 steps 5)–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 a small volume (50 microliter) solution.
6. Follow section 9.3 steps 8)–9).

### **9.4.2. 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, 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 emitter ( $^{241}\text{Am}$  or  $^{210}\text{Po}$  or  $^{242}\text{Pu}$ ) and one pure beta emitter ( $^{90}\text{Sr}/^{90}\text{Y}$ ). These radionuclides rather than  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , as the latter are accompanied by progeny ingrowth 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 II-1, 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 0–1024. 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 II-1. These values are then graphed to determine the optimum discrimination factor as can be seen in Figure II-1. The optimum discrimination factor for this laboratory was calculated to be 130.

### 9.4.3. Region of Interest (ROI) Setting

The setting of multi channel analysers (MCA) and windows for the measurement of radium is done 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 massic activity. It also negates the use of spill over 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 Figure III-1.

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

#### 9.4.4.1. 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 efficiency of the liquid scintillation counter was determined using two blank samples, the resulting  $\text{BaSO}_4$  precipitate of deionised water. The samples were spiked after preparation of  $\text{BaSO}_4$  precipitate, one with  $^{226}\text{Ra}$  and one with  $^{228}\text{Ra}$ . Spiking of the sample after preparation eliminates the variable of chemical recovery. For the determination, two blank samples were prepared and each was counted seven times. This provided a reasonable data set for calculations. The counting efficiencies of  $^{226}\text{Ra}$  and one with  $^{228}\text{Ra}$  were calculated by following equations:

$$\mathcal{E}_{Ra226} = \frac{n_{226}^s}{A_{Ra226} \cdot m_{s-226} \cdot e^{-\lambda_{226} \cdot t_{s-226}}} \quad (1)$$

$$\mathcal{E}_{Ra228} = \frac{n_{228}^s}{A_{Ra228} \cdot m_{s-228} \cdot e^{-\lambda_{228} \cdot t_{s-228}}} \quad (2)$$

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 Figure IV-2 of Appendix IV.

9.4.4.2. *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 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).

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

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

The control chart for overall efficiencies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  is shown in Figure IV-3 of Appendix IV. 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.

9.4.4.3. *Chemical recovery*

Using counting efficiency and overall efficiency data, the chemical recovery was determined using equations (5) and (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 is unsuitable. Gravimetric determination requires drying of the precipitate which causes inconsistent source preparation and therefore is unsuitable. In this procedure the chemical recovery was not used for the calculation of massic activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in the sample but used for only quality control purpose. The chemical recoveries of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  ranged from 78 % to 90 %.

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

$$R_{228} = \frac{\mathcal{E}_{Ra228}^c}{\mathcal{E}_{Ra228}} \quad (6)$$

#### 9.4.4.4. Measurement

Samples are counted using a liquid scintillation counter with pulse shape analysis for 60 minutes each including quality assurance and blank samples. The spectra should be inspected for reasonable alpha peak resolution and any visible quenching (movement of spectra outside regions of interest) (Figures III-2, III-3 and III-4). For quality control, a quality sample and a blank were analyzed for every set of samples.

## 10. EXPRESSION OF RESULTS

### 10.1. Calculation of massic activities of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ on the sampling date

Activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in water sample were expressed as unit of massic activity ( $\text{Bq kg}^{-1}$ ) in the procedure. In case the activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are expressed as units of activity concentration ( $\text{Bq L}^{-1}$ ), 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 cited from the recommended data of LNHB [13] and Nudat 2.5 [14].

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 afforded this method is good and therefore the use of spill over calculations is negated. 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 as blank/background samples are always run simultaneously.

$$a_{Ra226} = \frac{n_{226}}{\mathcal{E}_{Ra226}^c \cdot m_S} \cdot e^{\lambda_{226} \cdot t_{226}} \quad (7)$$

$$a_{Ra228} = \frac{n_{228}}{\mathcal{E}_{Ra228}^c \cdot m_S} \cdot e^{\lambda_{228} \cdot t_{228}} \quad (8)$$

### 10.2. Calculation of individual uncertainty and combined uncertainty

According to the guide to the expression of uncertainty in measurement [15], the combined uncertainty is calculated and described in Appendix V.



### 10.3. Decision threshold

In accordance with ISO 11929-7, the decision threshold,  $x_x^*$ , is obtained from the following equation (9):

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

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

If  $\alpha=0.05$  is selected i.e. the probability of the error of the first kind is 5 % then  $k_{1-\alpha} = 1.65$  according to the distribution function of the standardized normal distribution, what is often chosen as default.

### 10.4. Detection limit

In accordance with ISO 11929-7, the detection limit,  $\xi_x^*$ , is calculated by the following equations (11) and (12):

Assuming  $\alpha = \beta$  then  $k_{1-\alpha} = k_{1-\beta} = k$ ,

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

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

The detection limit of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in the procedure are  $0.01 \text{ Bq kg}^{-1}$  and  $0.06 \text{ Bq kg}^{-1}$ , respectively.

## 11. METHOD VALIDATION

For the validation of the procedure, four kinds of spiked water samples (so called quality control sample) with different activity ratios of  $^{228}\text{Ra}/^{226}\text{Ra}$  and a blank were prepared. A quality control sample was used for testing the reproducibility and 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, ISO/TS 21748 and ISO 5725-2.

The following parameters were established via the validation process:

- Trueness
- Repeatability
- Reproducibility

- Detection limit
- Linear response range
- Precision index

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 there is no cross-contamination during the procedure. This also includes the monitoring of the background to ensure there is no excess background activity being counted by the instrumentation that could affect results.

### 11.1. Linearity, range of measurement

The method was tested by the determination of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  isotopes at varying activity concentrations in deionised water. Results of measurements as a function of reference values have been tabulated and graphed (Figure IV-1). Linearity of the method was proven in the range 0–100 Bq kg<sup>-1</sup> in both  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ . It is very likely that the method can be used in a wider range starting from the detection limit to higher than environmental levels.

The recommended range of the method for  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  isotopes is 0–100 Bq kg<sup>-1</sup>.

### 11.2. Trueness of the method (relative bias of the method)

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

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

### 11.3. Precision of the method

The precision index (PI %) is calculated for the twelve replicates of three kinds of quality control samples. PI % were calculated by following equations:

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

### 11.4. Repeatability limit (within-run precision)

The repeatability limit is estimated by analysing twelve replicates of three kinds of quality control samples with known activity concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in repeatability conditions.

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

The results of repeatability testing in one laboratory are shown in Tables IV-1, IV-2 and IV-3.

### 11.5. Reproducibility limit

The reproducibility limit is estimated by analyzing 10 replicates of a quality control sample with known activity concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in 5 laboratories. The reproducibility limit is calculated by equation (17).

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

The results of reproducibility by inter-laboratory exercise with 5 laboratories are shown in Tables IV-4.

### 11.6. Acceptance criteria

The procedure performed well both in repeatability and reproducibility tests. The test results met the requirements of repeatability, reproducibility and trueness.

- 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 ( $R_L$ ):  $|\delta| < R_L$
- $\text{PI}\% < 25\%$

According to the criteria of ISO/TS 21748:2004, the procedure for the rapid determination of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in water samples performs well in repeatability and reproducibility tests for each radioisotope.

## 12. 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 [4] calculated using a coverage factor  $k = 2$ . The following form is recommended:

$a_x \pm u(a_x)$  with the associated  $k$  value.

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# APPENDIX I. FLOW CHART FOR CHEMICAL SEPARATION OF RADIUM

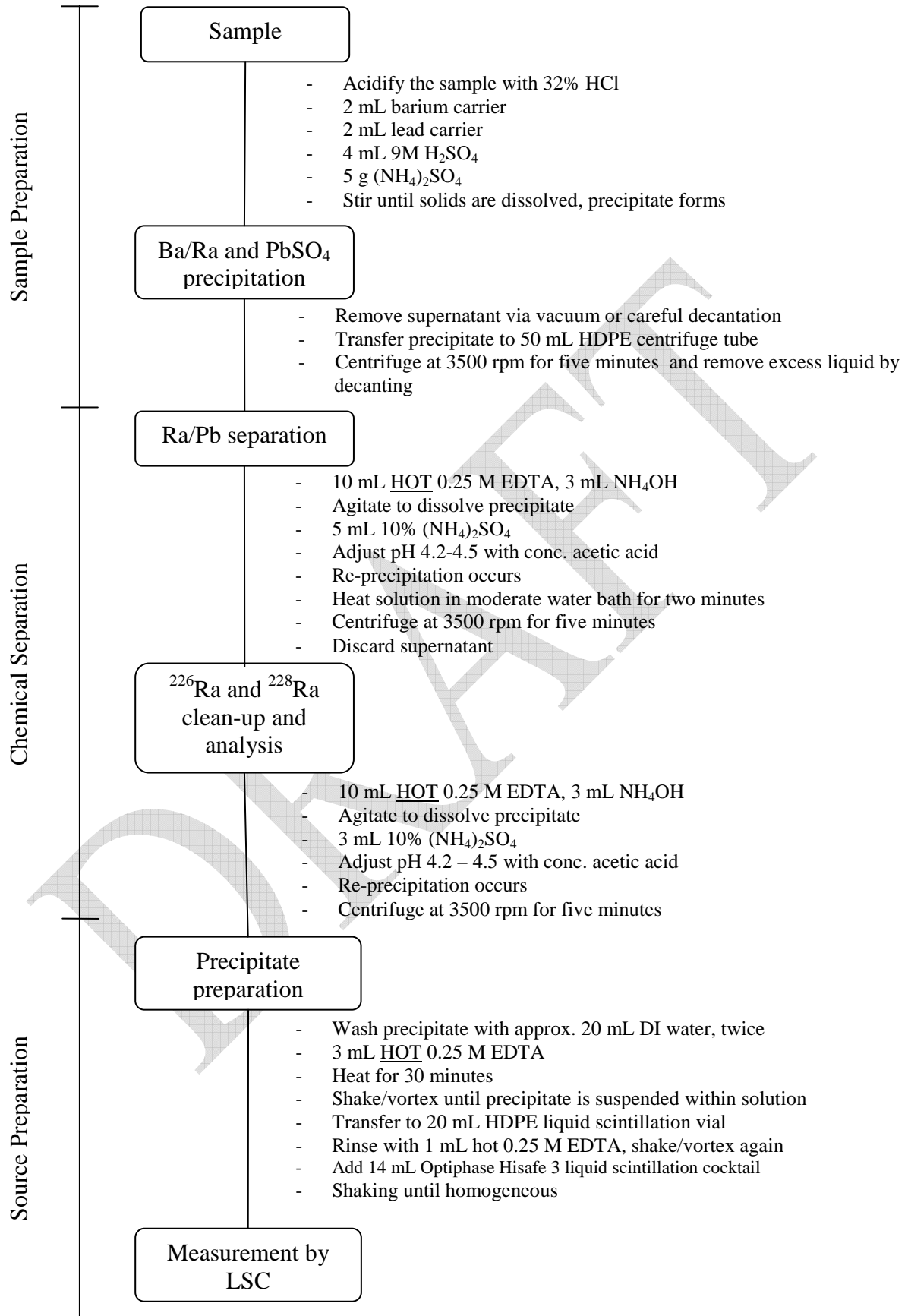


TABLE I-1. THE VOLUME OF 0.25M EDTA SOLUTION REQUIRED DEPENDING ON CONTENTS OF CALCIUM AND BARIUM IN THE SAMPLE AT THE FIRST DISSOLUTION STEP OF BaSO<sub>4</sub> PRECIPITATE (9.2. STEP 1)

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 I-2. THE 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 (9.2. STEP 4)

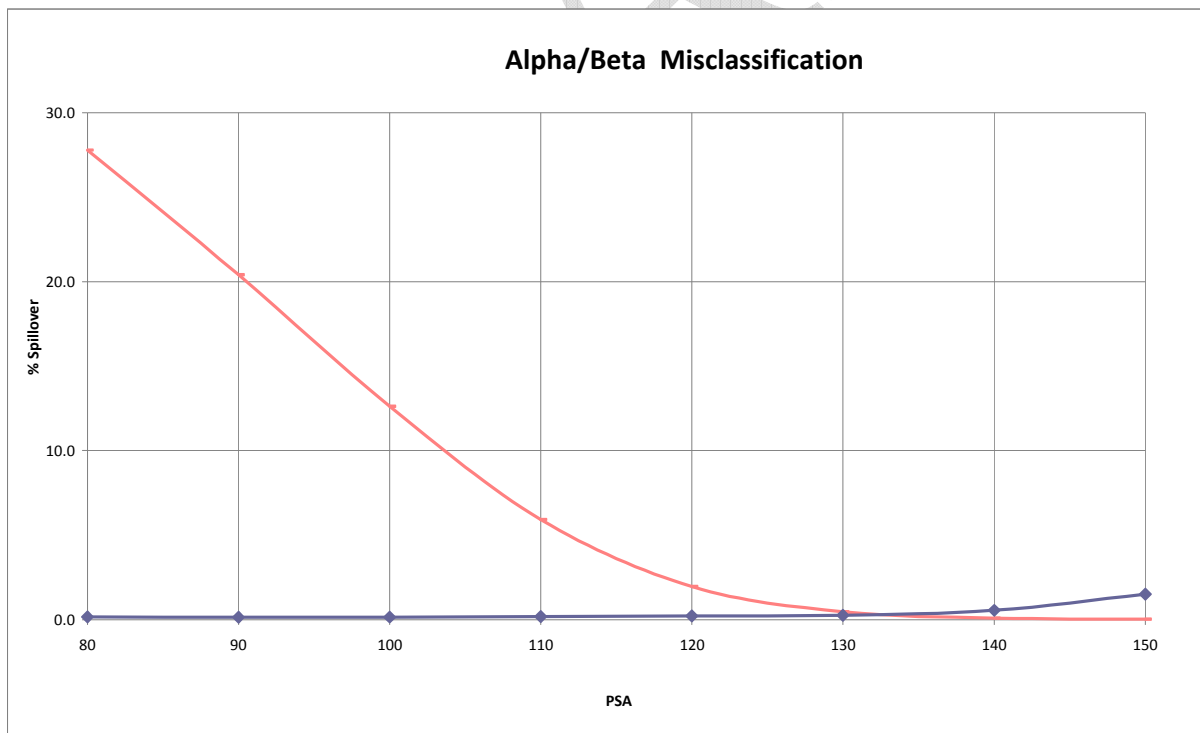
Content of Ba in the sample (mg)	Volume of 0.25 M EDTA solution (mL)
50	10
75	15
100	25



## APPENDIX II. ALPHA/BETA DISCRIMINATION SETTING

TABLE II-1. 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	27.778288	0.162775
90	4627	6.43	7823	30505	4633	38328	20.410501	0.138787
100	4622	6.94	5032	34832	4628	39864	12.622533	0.149855
110	4608	8.86	2514	39945	4617	42459	5.921567	0.191899
120	4591	10.1	909	45474	4601	46384	1.960807	0.220077
130	4609	11.8	231	49241	4621	49472	0.467706	0.255294
140	4606	25.8	45.6	50674	4632	50720	0.089911	0.556369
150	4546	69.6	11.3	50783	4616	50795	0.022269	1.507196



*FIG. II-1. Correlation between spillover and discrimination factor*

### APPENDIX III. $^{226}\text{Ra}$ AND $^{228}\text{Ra}$ SPECTRA

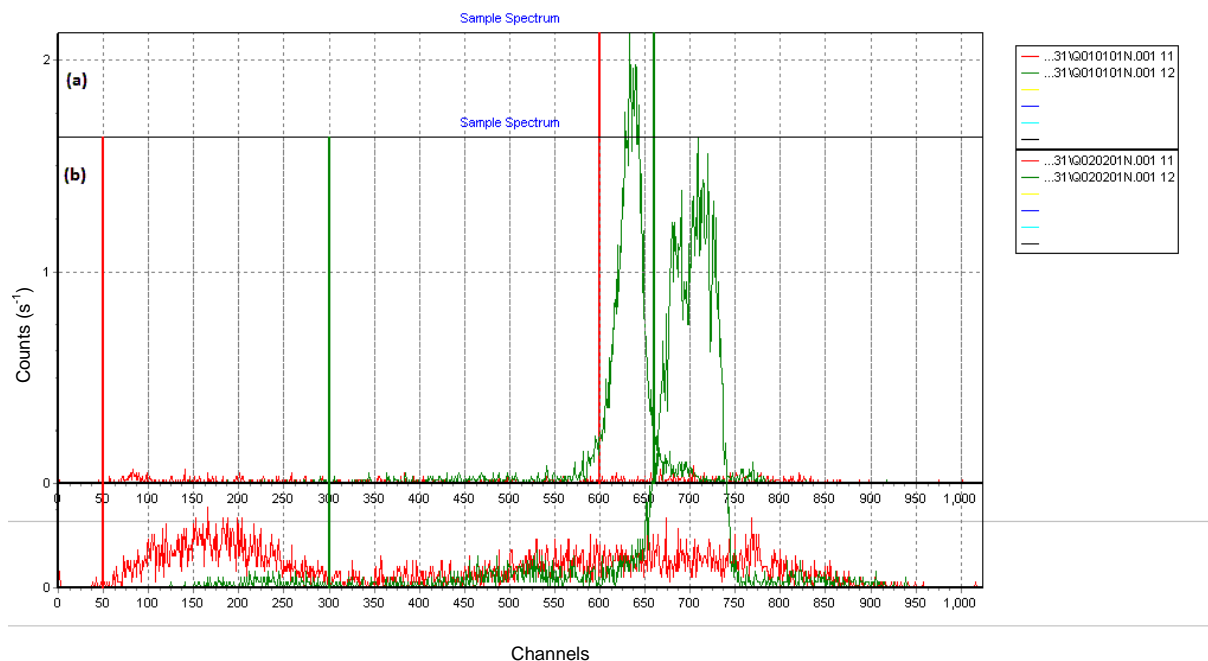


FIG. III-1. Negligible spectral overlap of (a)  $^{226}\text{Ra}$  spectra and (b)  $^{228}\text{Ra}$  spectra (for fresh source)

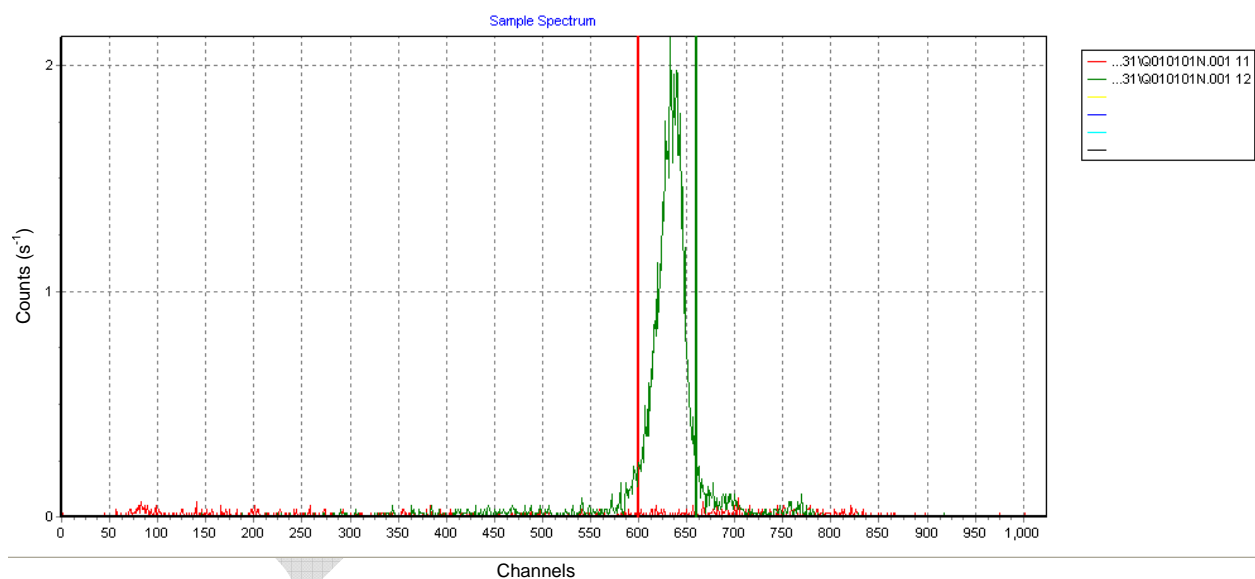


FIG. III-2.  $^{226}\text{Ra}$  spectra (for fresh source) and counting window as shown in spectral analysis software

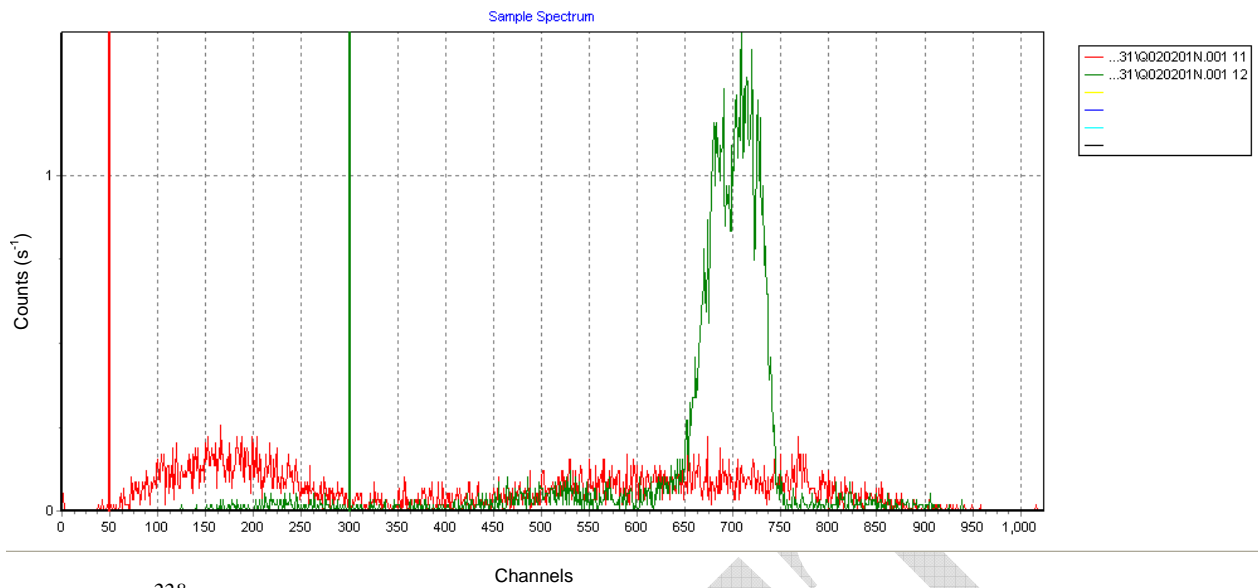


FIG. III-3.  $^{228}\text{Ra}$  spectra and counting window as shown in spectral analysis software, alpha peaks are  $^{228}\text{Ra}$  decay progeny

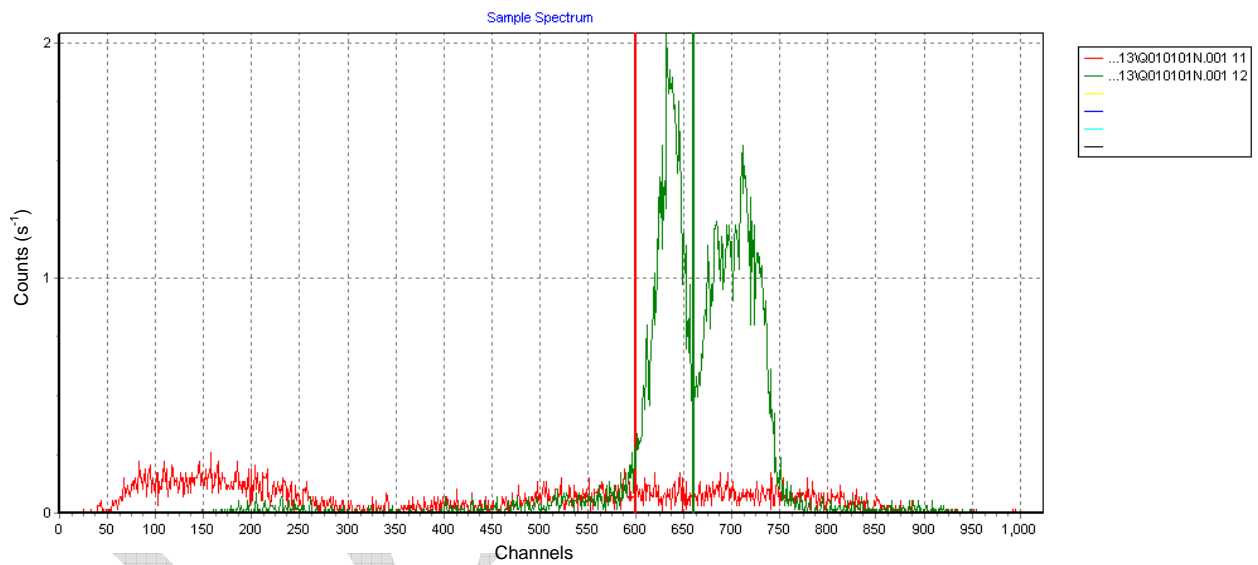


FIG. III-4. Combined spectra of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  (for fresh source) as shown in spectral analysis software

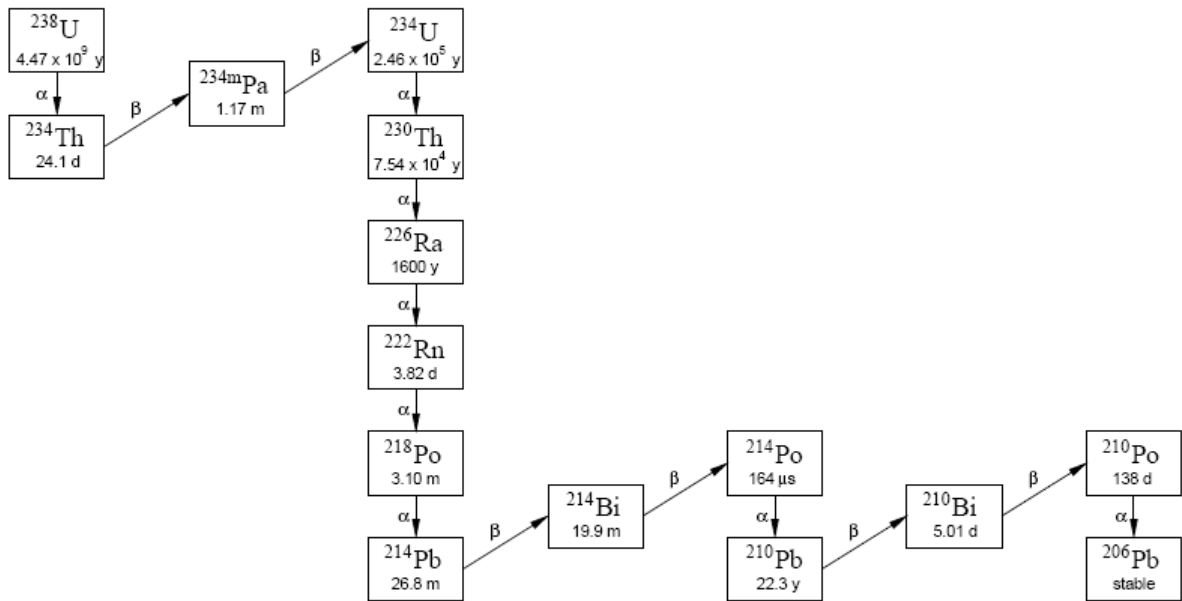


FIG. III-5.  $^{226}\text{Ra}$  is a member of the uranium ( $^{238}\text{U}$ ) decay series [17].

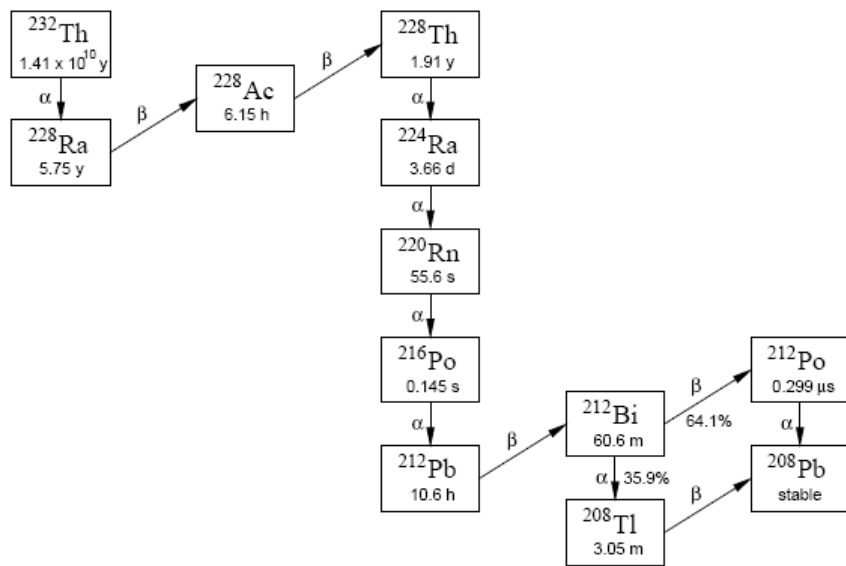
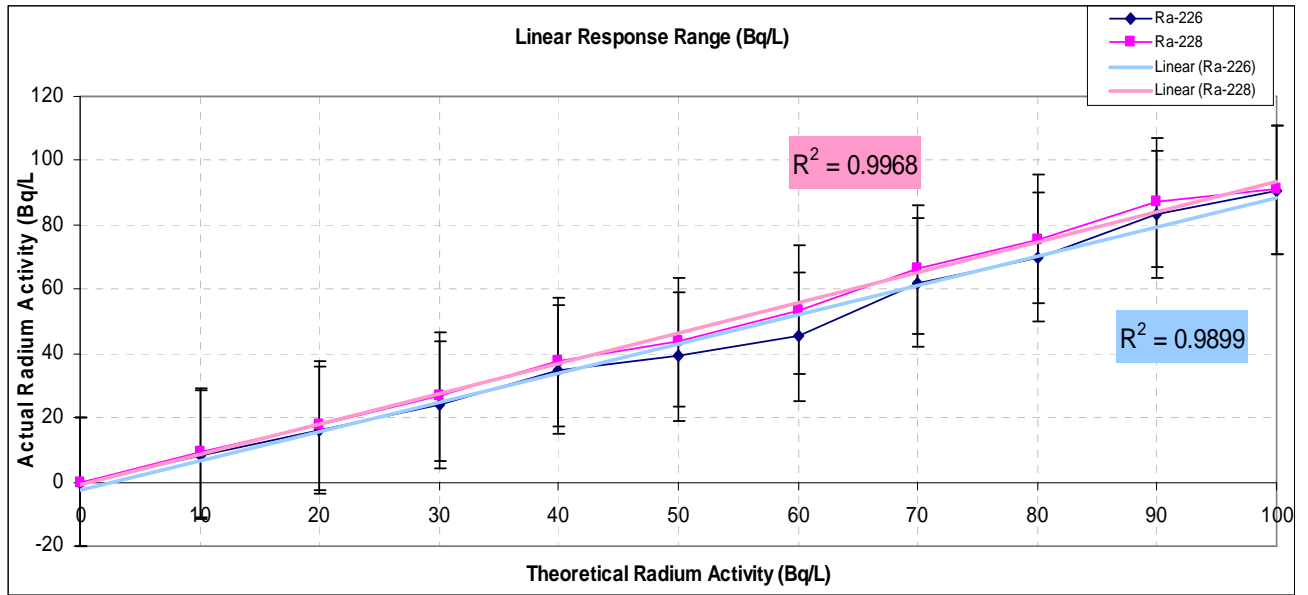
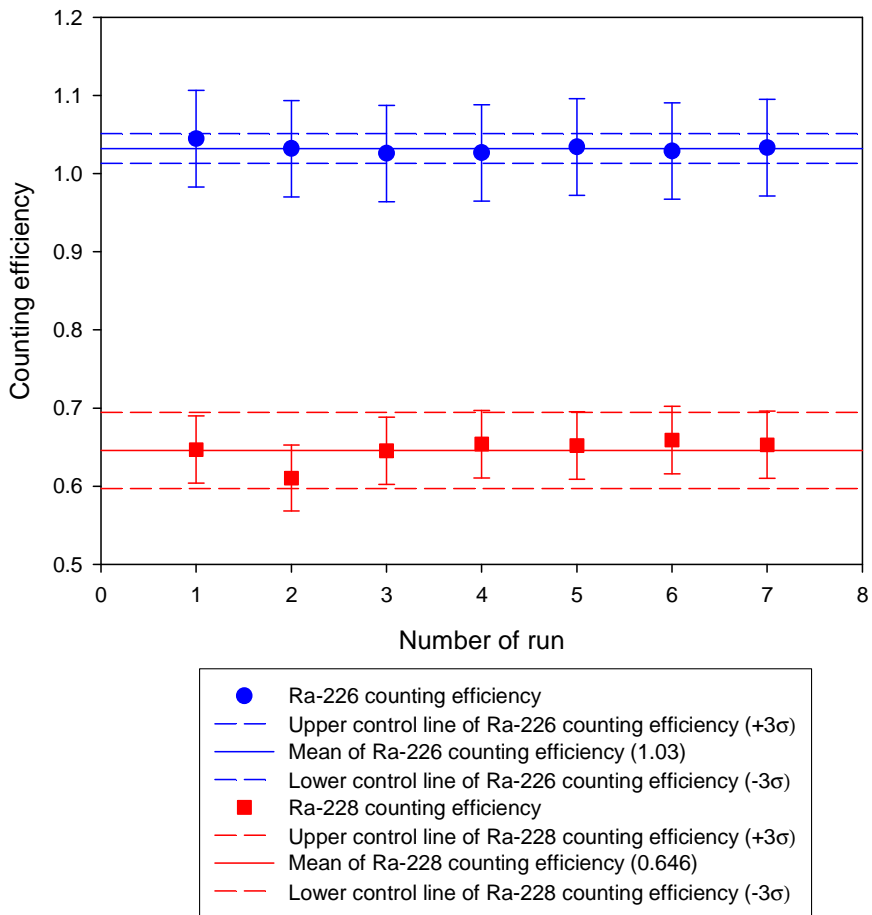


FIG. III-6.  $^{228}\text{Ra}$  and  $^{224}\text{Ra}$  are members of the thorium ( $^{232}\text{Th}$ ) decay series [17].

## APPENDIX IV. VALIDATION DATA OF THE PROCEDURE



*Fig. IV-1. linear ranges of <sup>226</sup>Ra and <sup>228</sup>Ra*



*Fig. IV-2. Control chart for counting efficiencies of <sup>226</sup>Ra and <sup>228</sup>Ra*

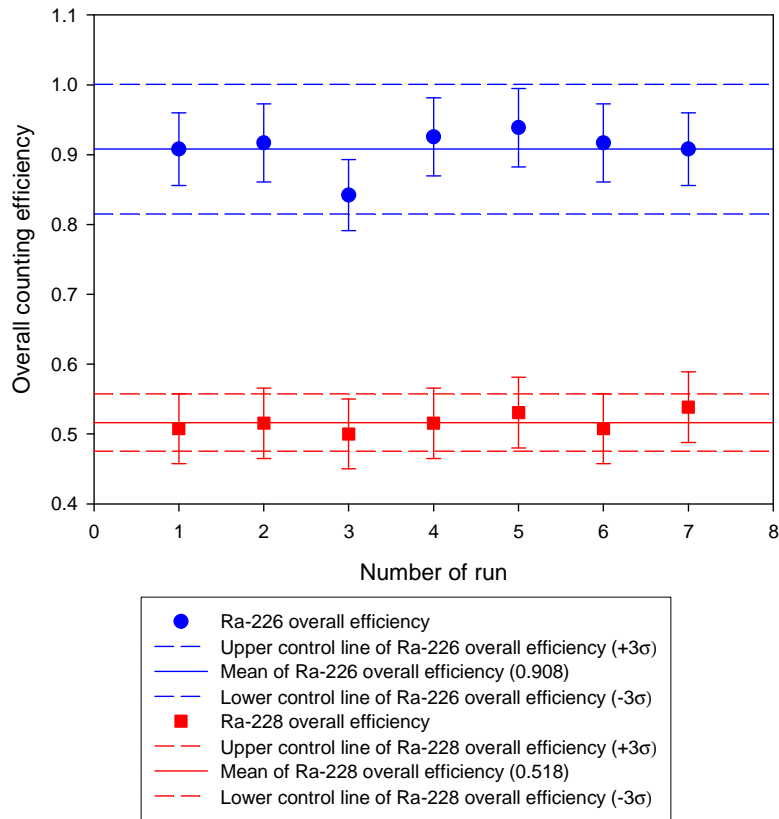


Fig. IV-3. Control chart for overall efficiencies of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$

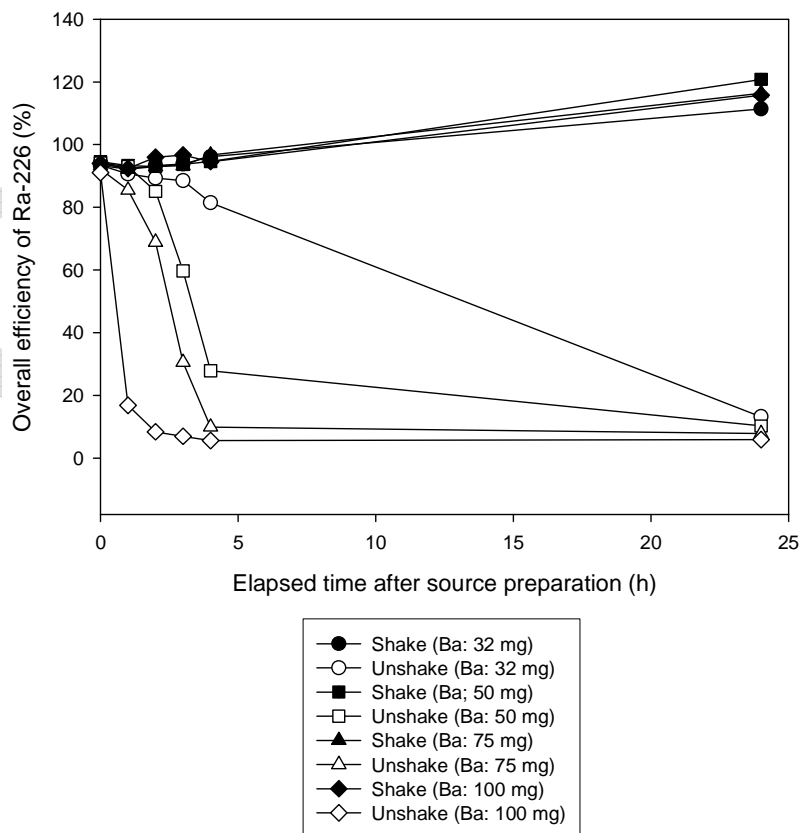


Fig. IV-4. Variation of overall efficiency for Ra-226 with elapse time after source preparation

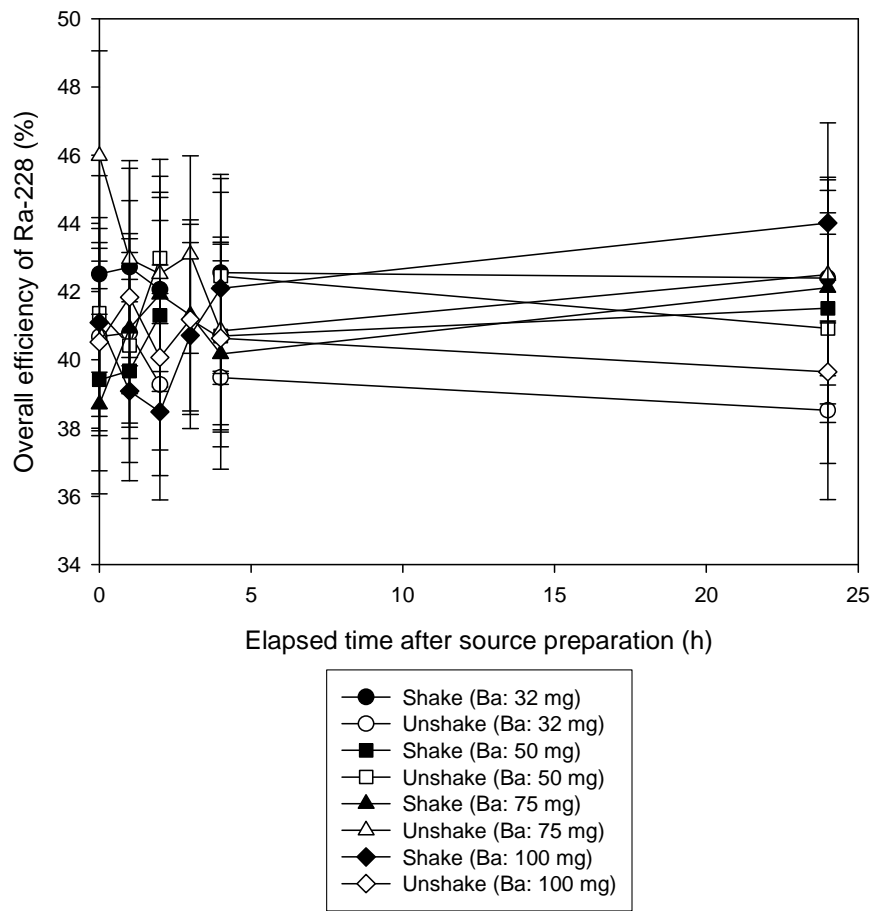


Fig. IV-5. Variation of overall efficiency for Ra-228 with elapse time after source preparation

TABLE IV-1. REPEATABILITY TESTING RESULTS FOR Ra-226 AND Ra-228 IN QUALITY CONTROL SAMPLE 1

Number of run	Ra-226			Ra-228		
	massic activity (Bq kg <sup>-1</sup> )	relative bias (%)	precision index	massic activity (Bq kg <sup>-1</sup> )	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 <sub>r</sub> )	0.08			0.05		
Relative repeatability standard deviation S <sub>r</sub> (%)	5.59			6.10		
Repeatability limit (r <sub>1</sub> )	0.22			0.20		
Assigned value at reference date	1.54±0.03*			0.73±0.02*		

\*: coverage factor (k =1)



TABLE IV-2. REPEATABILITY TESTING RESULTS FOR Ra-226 AND Ra-228 IN QUALITY CONTROL SAMPLE 2

Number of run	Ra-226			Ra-228		
	massic activity (Bq kg <sup>-1</sup> )	relative bias (%)	precision index	massic activity (Bq kg <sup>-1</sup> )	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 <sub>r</sub> )	0.02			0.04		
Relative repeatability standard deviation S <sub>r</sub> (%)	2.00			2.56		
Repeatability limit (r <sub>L</sub> )	0.06			0.11		
Assigned value at reference date	1.01±0.01*			1.47±0.05*		

\*: coverage factor (k =1)

TABLE IV-3. TABLE IV-1. REPEATABILITY TESTING RESULTS FOR Ra-226 AND Ra-228 IN QUALITY CONTROL SAMPLE 3

Number of run	Ra-226			Ra-228		
	massic activity (Bq kg <sup>-1</sup> )	relative bias (%)	precision index	massic activity (Bq kg <sup>-1</sup> )	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 <sub>r</sub> )	0.14			0.17		
Relative repeatability standard deviation S <sub>r</sub> (%)	7.41			6.75		
Repeatability limit (r <sub>L</sub> )	0.39			0.48		
Assigned value at reference date	2.04±0.01*			2.31±0.07*		

\*: coverage factor (k =1)

TABLE IV-4. REPRODUCIBILITY TEST RESULTS FOR THE DETERMINATION OF Ra-226 AND Ra-228 IN A QUALITY CONTROL SAMPLE BY INTER-LABORATORY EXERCISE WITH 5 LABORATORIES (UNIT: Bq kg<sup>-1</sup>)

Factors	<sup>226</sup> Ra	<sup>228</sup> Ra
Mean of measurement results at target date	0.55	0.54
Assigned value at target date	0.40±0.02*	0.52±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)

## APPENDIX V. CALCULATION OF INDIVIDUAL UNCERTAINTY AND COMBINED UNCERTAINTY OF ACTIVITY CONCENTRATION OF RA-226 AND RA-228 IN WATER SAMPLES

Equations that are used to calculate the massic activity of the analyte at the separation time and the sampling date as well as the chemical recovery and the counting efficiency are described in chapters 9 and 10. The same formulas are used to calculate the combined uncertainties. Individual uncertainty components are discussed in detail in the present chapter.

### V.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

$$\text{calculated as } \frac{u_{mb}}{\sqrt{3}} \quad (17)$$

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  $u(m_s)$  of Eq.18:

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

### V.2. Uncertainty of net counts of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ in standard solution, spiked sample and real sample

The uncertainty of net count rates at ROIs of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in LSC spectra can be calculated as follows:

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

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

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

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

The uncertainty of the counting efficiency  $u(\varepsilon_{\text{Ra}226})$  can be calculated based on equation (1).

Differentiating equation (1), each partial derivative can be calculated as follows:

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

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

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

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

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

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

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

The uncertainty of the counting efficiency  $u(\varepsilon_{\text{Ra}228})$  can be calculated based on equation (2).

Differentiating equation (2), each partial derivative can be calculated as follows:

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

$$\frac{\partial \varepsilon_{Ra228}}{\partial A_{Ra228}} = -\frac{\varepsilon_{Ra228}}{A_{Ra228}} \quad (28)$$

$$\frac{\partial \varepsilon_{Ra228}}{\partial m_{s-228}} = -\frac{\varepsilon_{Ra228}}{m_{s-228}} \quad (29)$$

$$\frac{\partial \varepsilon_{Ra228}}{\partial \lambda_{228}} = \varepsilon_{Ra228} \cdot t_{s-228} \quad (30)$$

$$\frac{\partial \varepsilon_{Ra228}}{\partial t_{s-228}} = \varepsilon_{Ra228} \cdot \lambda_{228} \quad (31)$$

The uncertainty of counting efficiency ( $u(\varepsilon_{Ra228})$ ) can be calculated from the law of error propagation as follows:

$$u(\varepsilon_{Ra228})^2 = \left(\frac{\varepsilon_{Ra228}}{n_{228}^s}\right)^2 \cdot u(n_{228}^s)^2 + \left(-\frac{\varepsilon_{Ra228}}{A_{Ra228}}\right)^2 \cdot u(A_{Ra228})^2 + \left(-\frac{\varepsilon_{Ra228}}{m_{s-228}}\right)^2 \cdot u(m_{s-228})^2 + (\varepsilon_{Ra228} \cdot t_{s-228})^2 \cdot u(\lambda_{228})^2 + (\varepsilon_{Ra228} \cdot \lambda_{228})^2 \cdot u(t_{s-228})^2 \quad (32)$$

Overall efficiency uncertainties of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ,  $u(\varepsilon_{Ra226}^c)$  and  $u(\varepsilon_{Ra228}^c)$  can be calculated in the same way with calculation of counting efficiency uncertainties,  $u(\varepsilon_{Ra226})$  and  $u(\varepsilon_{Ra228})$ .

The uncertainties of  $t_{s-226}$  and  $t_{s-228}$  are regarded negligible.

#### V.4. Uncertainty of chemical recovery

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

$$u(R_{226}) = \frac{\varepsilon_{Ra226}^c}{\varepsilon_{Ra226}} \cdot \sqrt{\left(\frac{u(\varepsilon_{Ra226}^c)}{\varepsilon_{Ra226}^c}\right)^2 + \left(\frac{u(\varepsilon_{Ra226})}{\varepsilon_{Ra226}}\right)^2} \quad (33)$$

$$u(R_{228}) = \frac{\varepsilon_{Ra228}^c}{\varepsilon_{Ra228}} \cdot \sqrt{\left(\frac{u(\varepsilon_{Ra228}^c)}{\varepsilon_{Ra228}^c}\right)^2 + \left(\frac{u(\varepsilon_{Ra228})}{\varepsilon_{Ra228}}\right)^2} \quad (34)$$

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

The combined uncertainty of the massic activity of  $^{226}\text{Ra}$  in the sample is calculated based on equation (7) using the general formula given elsewhere [15 and 16].

Differentiating equation (7), each partial derivative can be calculated as follows:

$$\frac{\partial a_{Ra226}}{\partial n_{226}} = \frac{a_{Ra226}}{n_{226}} \quad (35)$$

$$\frac{\partial Ra_{226}}{\partial \varepsilon_{Ra226}} = -\frac{a_{Ra226}}{\varepsilon_{Ra226}} \quad (36)$$

$$\frac{\partial a_{Ra226}}{\partial m_s} = -\frac{a_{Ra226}}{m_s} \quad (37)$$

$$\frac{\partial a_{Ra226}}{\partial \lambda_{226}} = a_{Ra226} \cdot t_{226} \quad (38)$$

$$\frac{\partial a_{Ra226}}{\partial t_{226}} = a_{Ra226} \cdot \lambda_{226} \quad (39)$$

The uncertainty of counting efficiency ( $u(\varepsilon_{Ra226})$ ) can be calculated from the law of error propagation as follows:

$$u(a_{Ra226})^2 = \left(\frac{a_{Ra226}}{n_{226}}\right)^2 \cdot u(n_{226})^2 + \left(-\frac{a_{Ra226}}{\varepsilon_{Ra226}}\right)^2 \cdot u(\varepsilon_{Ra226})^2 + \left(-\frac{a_{Ra226}}{m_s}\right)^2 \cdot u(m_s)^2 + \left(a_{Ra226} \cdot t_{226}\right)^2 \cdot u(\lambda_{226})^2 + \left(a_{Ra226} \cdot \lambda_{226}\right)^2 \cdot u(t_{226})^2 \quad (40)$$

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

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

TABLE V-1. EXAMPLE OF SPREAD SHEETS FOR THE MEASUREMENT UNCERTAINTIES OF Ra-226 AND Ra-228 IN SPIKED WATER SAMPLE

Components	Value of variable	Standard uncertainty	Percent contribution to combined standard uncertainty
<b><sup>226</sup>Ra</b>			
$r_{g-226}$ (cps)	0.651	0.014	10
$r_{0-226}$ (cps)	0.00113	0.00057	
$\epsilon_{Ra226}$	0.908	0.060	90
Half-life of <sup>226</sup> Ra (a)	1600	7	negligible
$m_s$ (kg)	0.508	0.00008	negligible
<hr/>			
$a_{Ra226}$ , (Bq kg <sup>-1</sup> )	1.41	0.09	
<b><sup>228</sup>Ra</b>			
$r_{g-228}$ (cps)	0.1986	0.0075	8
$r_{0-228}$ (cps)	0.040	0.0034	2
$\epsilon_{Ra228}$	0.516	0.097	90
Half-life of <sup>228</sup> Ra (a)	5.75	0.04	negligible
$m_s$ (kg)	0.508	0.00008	negligible
<hr/>			
$a_{Ra228}$ , (Bq kg <sup>-1</sup> )	0.599	0.100	



## CONTRIBUTORS TO DRAFTING AND REVIEW

Chmielewska, I.	Central Mining Institute, Katowice, Poland
Cook, M	Queensland Health, Brisbane, Australia
Gaigl, F. A.	IAEA Terrestrial Environment Laboratory, Seibersdorf, Austria
Kleinschmidt, R.	Queensland Health, Brisbane, Australia.
Kim, C. K.	IAEA Terrestrial Environment Laboratory, Seibersdorf, Austria
Kim, Y. J.	Korea Institute of Nuclear Safety, Daejeon, Korea, the Republic of
Kis-Benedek, G.	IAEA Terrestrial Environment Laboratory, Seibersdorf, Austria
Kožar logar, J.	Jožef Stefan Institute, Ljubljana, Slovenia
Martin, P.	Health Physics Section, Australian Radiation Protection and Nuclear Safety Agency (ARPANSA), Yallambie, Victoria, Australia
Maurizio, F.	Lombardia, Agenzia Regionale per la Protezione dell'Ambiente della Lombardia, Italy
Rusconi, R.	Lombardia, Agenzia Regionale per la Protezione dell'Ambiente della Lombardia, Italy
Sansone, U.	IAEA Terrestrial Environment Laboratory, Seibersdorf, Austria
Sanada, T.	Japan Chemical Analysis Center, Japan
Tarján, S.	Central Agricultural Office Food and Feed Safety Directorate, Radioanalytical Reference Laboratory of Food and Feed Safety Directorate, Hungary