Technical paper

Evaluation of the Uncertainty Budget for ^{226}Ra Analysis in Water Samples

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Abstract

An alpha spectrometric method for the rapid determination of ^{226}Ra isotope in water samples is presented. The method is based on the co-precipitation of (Ba)(Ra)SO_4 for source preparation. The parameters contributing to the uncertainty budget are investigated. Geometry factor (solid angle / 4π) was used instead of ^{226}Ra standard disc for the determination of detector efficiency. The analytical method has been successfully applied to the determination of ^{226}Ra for water samples in proficiency tests organized by International Atomic Energy Agency (IAEA) and National Physical Laboratory (NPL). The proposed method also showed high reproducibility.

Keywords: Radium-226, barium-133, alpha-particle spectrometry, uncertainty budget, solid angle

1. Introduction

^{226}Ra, ^{223}Ra, ^{224}Ra and ^{228}Ra are the four radium isotopes present in the natural decay series of uranium, actinium and thorium. ^{226}Ra is one of the most important and most toxic isotopes to be determined among the naturally occurring nuclides in water samples due to its long half-life (about 1600 years) and radiological effects on human health.[1,2] ^{226}Ra is mainly accumulated in the bones when ingested, thus increasing the internal radiation dose of individuals.[3] Therefore, the activity concentration of ^{226}Ra has to be determined in order to evaluate its potential contribution to the internal dose. Moreover, according to World Health Organization (WHO) guideline, ^{226}Ra is one of the recommended analyses for drinking waters with gross alpha activity above 0.5 Bq/L.[4]

Various analytical methods have been proposed for the detection of ^{226}Ra, based on different physical and chemical principles. These methods include gamma ray spectrometry,[5] alpha-particle spectrometry,[6,7] radon emanation method,[8] Cerenkov counting,[9] liquid scintillation counting,[10–12] TIMS or Multi collector-ICP/MS.[13,14] Among these methods alpha-particle spectrometry in combination with radiochemical separation is one of the most sensitive techniques and allows determining very low activity concentration of ^{226}Ra in water. In alpha spectrometric technique, it is not necessary to await the equilibrium of ^{226}Ra with its daughters. In this technique, radiochemical separation is necessary to obtain high energy resolution α-spectra and minimize peak overlap. A number of separation methods for radium have been reported, but the preparation of sources with high spectrometric quality is usually laborious, time-consuming and complex to perform. These methods include adsorption of radium on a MnO_2 coated disc,[15] purification of radium by cation exchange chromatography and source preparation by electrodeposition,[7] and preparation by microcoprecipitation of Ba(Ra)SO_4,[16] preconcentration of radium isotopes using MnO_2 Resin,[17] co-precipitation of radium with $BaCrO_4$[18] and radium separation by using ion-selective membrane technology.[19] Among these separation methods co-precipitation as (Ba)(Ra)SO_4 is one of the most frequently used and useful analytical methods for the preparation of thin sources for α- spectrometric measurements.

In this paper, we used (Ba)(Ra)SO_4 co-precipitation method for the preparation of ^{226}Ra sources.[20,21] We applied some modifications to this method by calculating the geometry factor instead of using a ^{226}Ra standard source for the determination of the detector efficiency. An uncertainty budget including all possible uncertainty elements are presented. The method was applied to the analysis of water samples of proficiency tests organized by International Atomic Energy Agency "IAEA-CU-2008-03 World-wide open proficiency test on the determination of natural radionuclides in phosphogypsum and spiked water", "IAEA-CU-2010-03 World-wide open proficiency test on the determination of natural radionuclides in water and Ra-226 in soil", "IAEA-CU-2010-04 World-wide open proficiency test on the determination of natural radionuclides in water and Ra-226 in soil" and National Physical Laboratory "NPL Environmental Radioactivity PTE-2009".

2. Experimental

2. 1. Instrumentation and Calibration

The activity concentration of radium was determined by using alpha spectrometer from Canberra, USA and the silicon surface barrier detector (PIPS) with a surface area of 600 mm^2. The counting efficiency of the alpha detector was determined by calculating the geometry factor of the source-detector geometry. An electroplated mixed alpha standard source containing ^{238}U: 1.67 Bq (± 5.2 %), ^{234}U: 1.63 Bq (± 4.9 %), ^{239}Pu: 1.91 Bq (± 5.5 %) and ^{241}Am: 1.81 Bq (± 5.5 %) was used for the energy calibration of the alpha spectrometer. This source was purchased from Eckert & Ziegler Isotope Products. A High Purity Germanium (HPGe) gamma detector from Ortec Instruments was used for the determination of the chemical recovery.

2. 2. Sample Description

A spiked water sample of IAEA-CU-2008-03 Proficiency Test Exercise, two spiked water samples of IAEA-CU-2010-03, two spiked water samples of IAEA-CU-2010-04 Proficiency Test Exercises and Alpha High (AH) sample of NPL Environmental Radioactivity Proficiency Test Exercise 2009 were used.

2. 3. Reagents and Tracer

All reagents used in this study were of analytical grade and used without further purification. H_2SO_4, $Pb(NO_3)_2$, $BaCl_2.2H_2O$, Na_2SO_4, EDTA, NaOH, CH_3COOH and pH indicator solution (pH 0–5) were supplied from Merck. ^{133}Ba standardized solution with an activity concentration of 3.715 kBq/g ± 0.015 % (k=1) was purchased from Isotope Products Lab. SRM 1443-59-1. This standardized solution was diluted with 0.1 M HCl for reducing the activity concentration to ~30 Bq/mL. Ba-133 standard disc was prepared by drop deposition on a polypropylene filter.

2. 4. Radiochemical Procedure

The chemical separation procedure is based on coprecipitation of $Pb(Ra)(Ba)SO_4$ from acidified water samples.[20,21] ^{133}Ba radioisotope is added to the water sample as a tracer. 10 mL of concentrated H_2SO_4 and 0.5 mL of Pb^{2+} (10 mg/mL) were added to the sample to co-precipitate Ba and Ra on $PbSO_4$. After centrifugation at 3000 rpm for 5 minutes, the supernatant was discarded, and the precipitate dissolved in 4 mL of 0.1 M EDTA / 0.5 M NaOH. The radium was co-precipitated with $BaSO_4$ by adding 0.3 mL of Ba^{2+} carrier (30 mg/mL), 1 drop pH indicator, 1 mL acetic acid to adjust the pH to 4.5, 4 mL of saturated Na_2SO_4 solution and 0.3 mL of a barium sulphate seeding suspension (10 mg/mL). The precipitate was left to stand for at least 30 min and then filtered through a 0.1 mm polypropylene filter. The filter was mounted on a stainless steel disc and measured by α-particle spectrometry for determination of ^{226}Ra activity concentration. The chemical yield was evaluated by means of comparing the net peak area of ^{133}Ba at 356.0134 (7) keV in gamma energy spectrum of sample and standard (disc) source.

2.5. Spectrometric Analysis

2.5.1. α-Spectrometric Analysis and Calculation of ^{226}Ra Activity Concentration

The ^{226}Ra peak area, in the 3700–4800 keV energy region of the alpha-particle spectrum, was determined and corrected by subtracting the ambient background and reagent background. The geometry factor calculation method was used in order to determine the counting efficiency, ε, of the α-particle spectrometer instead of a relative measurement to a ^{226}Ra source. The radius of radioactive source (Rs) and source to detector distance (d) were measured by using a caliper and found to be 11.20 ± 0.15 mm and 11.00 ± 0.13 respectively. The uncertainty of measurements were calculated according to the method described by Flack.[22] We used PIPS detector with 600 mm^2 active surface area (R_D = 13.8 mm). The corresponding solid angle was calculated using algorithms and software developed by Pommé,[23] Pommé and Paepen[24] and Pommé et al.[25] The detection efficiency was obtained directly from the geometry factor.

The activity concentration of the ^{226}Ra in the water sample was determined using Equation 1.

$$A_{^{226}Ra} = \frac{N_{^{226}Ra}}{t * \varepsilon * V * R_{chem}} \tag{1}$$

Where; $N_{^{226}Ra}$ is net peak area of ^{226}Ra, t is time of measurement (s), V is volume of water samples (L), ε is detector efficiency and R_{chem} is chemical recovery of the ^{226}Ra material.

2. 5. 2. γ - Spectrometric Analysis and Determination of the Chemical Yield

A ^{133}Ba standard disc was prepared for the calibration of the gamma-ray spectrometer. The same amount of ^{133}Ba that was added into the samples as a tracer was dropped onto the disc by using polyethylene pycnometer. Active solution dispensed directly on a polypropylene filter. The dispensed amount is derived from two weightings of the pycnometer on a microbalance, calibrated with SI-traceable weights.[20,21,26] The net peak area of ^{133}Ba (356.0134 (7) keV) in sample and standard disc was determined using GENIE 2000 software for the peak evaluation. The chemical recovery was calculated by using Equation 2.

$$R_{chem} = \frac{N_{^{133}Ba-sample} * t_{^{133}Ba-std} * m_{^{133}Ba-std}}{t_{^{133}Ba-sample} * m_{^{133}Ba-sample} * N_{^{133}Ba-std}} \qquad (2)$$

Where; $N_{^{133}Ba-sample}$ and $N_{^{133}Ba-std}$ are peak area of tracer (^{133}Ba) in the spectrum of sample and barium standard disc, $t_{^{133}Ba-sample}$ and $t_{^{133}Ba-std}$ are counting time of sample and barium standard disc, $m_{^{133}Ba-sample}$ and $m_{^{133}Ba-std}$ are mass of ^{133}Ba tracer in sample and barium standard disc, respectively.

3. Results and Discussion

In this study, the parameters contributing to the uncertainty budget such as detector efficiency, spectral deconvolution, chemical recovery, volume of sample, mass of Ba-133 in sample and standard disc are discussed in detail.

3. 1. Uncertainty of Detector Efficiency

The relative solid angle calculation method was used in order to determine the counting efficiency of the α-particle spectrometer. The detector efficiency (ε) was calculated as 0.159 ± 0.008 by using algorithms and software.[23–25] This value was used to calculate the activity concentration of the ^{226}Ra in the water samples according to Equation 1. The values and absolute uncertainties of the radius of radioactive source (Rs) and detector (R_D) and source to detector distance (d) were used as 11.20 ± 0.40 mm, 13.80 ± 0.05 mm and 11.00 ± 0.30 mm, respectively. The uncertainty due to the detector efficiency was calculated by using these values and presented in Table 1.

The uncertainty in detector efficiency consists of the measurement of source and detector radius and source to detector distance, as well as source homogeneity and centering on the symmetry axis.[27] The sum of the squares of components due to the radial activity distribution including source inhomogeneity and source radius (3.6%), distance (2.7%) and detector radius (0.4%), external eccentricity taken as 1% for 1mm leading to a combined uncertainty of 5.0% for the geometry factor.

3. 2. Uncertainty of Spectral Deconvolution

Radium measurements were made considering the alpha discriminated spectrum component (channels range 3700–4800). The spectrum was deconvoluted in the energy region from 4200 to 4800 keV with the Visual Basic

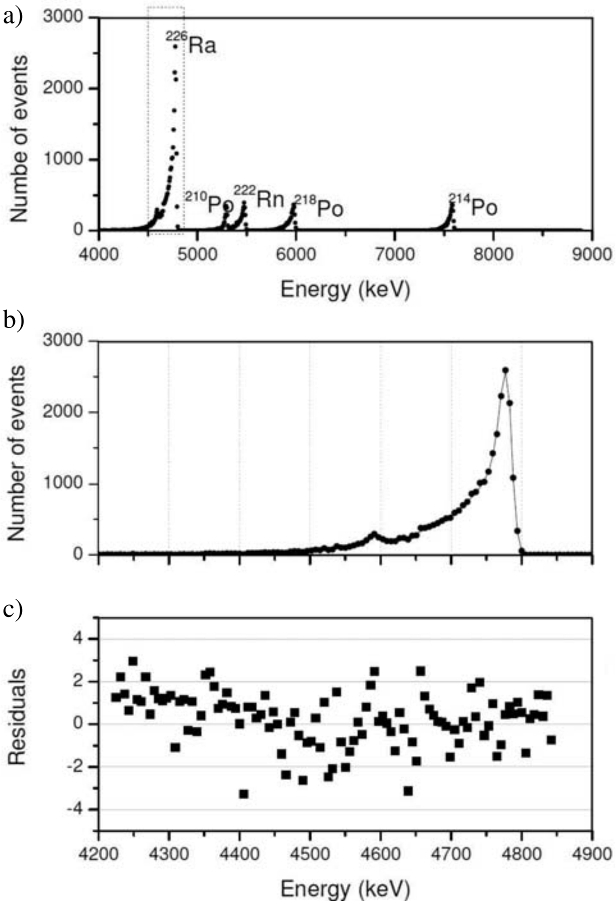

Figure 1. α-particle spectrometry of ^{226}Ra (a), measurement results and fitted peak area at 4.78 keV (b) and residuals (c). The residuals show the difference between measurement and fit in units of one standard deviation of the channel contents.

Table 1. Uncertainty budget of detector efficiency (ε) (*k = 1*)

Quantity	**Value and Standard Uncertainty, u(x)**	**Relative Standard Uncertainty, u(x)/x (%)**
h (Distance from detector)	11.00 (30)	2.7
r_d (Detector radius)	13.80 (5)	0.4
r_s (Source radioactivity distribution)	11.20 (40)	3.6
Combined uncertainty (quadratic sum) (%)	5.0	
ε (Detector efficiency)	0.159	

application ALPHA-version 7.0 within a spreadsheet [28–30] (Fig. 1). The fit has been restricted to the energy region 4200–4800 keV around the ^{226}Ra peak. The corrected net peak area 27806 counts and the related uncertainty 167 counts were evaluated from Poisson distribution. The uncertainty was calculated from the sum of the counting uncertainties (Poisson) and an additional, estimated 0.3% uncertainty on background. Interfering peak wasn't observed above 4.8MeV. A typical relative uncertainty is 1.2%.

3. 3. Uncertainty of Chemical Recovery

The contributions of volume of added Ba-133 in barium standard disc and sample and peak area of Ba-133 in the standard disc and sample have been taken into account for the calculation of uncertainty of the chemical recovery. The calculated uncertainties are presented in Table 2. The uncertainties due to the peak areas of sample and standard are reported as the major components in the combined uncertainty of chemical recovery. This uncertainty only represents the uncertainty of chemical recovery of Ba-133.

The possible uncertainty caused by sample preparation (include reagent blanks) was 7.0%. The sum of combined standard uncertainty of chemical recovery was 1.5%. The sum of uncertainties in sample preparation and chemical recovery was calculated as 8.5%.

3. 4. Total Uncertainty

Uncertainty associated with the volume of sample was estimated to be of the order of 0.05 mL on a sam-

Table 2. Uncertainty budget of radiochemical yield (recovery) (k = 1)

Quantity	**Value and Standard Uncertainty, u(x)**	**Relative Standard Uncertainty, u(x)/x (%)**
$N_{\text{Ba-133 Sample (net peak area)}}$	8749 (91)	1.0
$m_{\text{Ba-133 Sample}}$	1.000 (3)	0.3
$m_{\textit{Ba-133 std}}$	1.000 (3)	0.3
$N_{\text{Ba-133 std (net peak area)}}$	10300 (102)	1.0
$t_{\text{Ba-133 Sample}}$ *(s)*	3600	
$t_{\text{Ba-133 std}}$ *(s)*	3600	
Combined uncertainty (quadratic sum) (%)	1.5	
R_{chem}	0.85	

Table 3. Uncertainty budget of ^{226}Ra activity concentration in sample (k = 1).

Quantity	**Value and Standard Uncertainty, u(x)**	**Uncertainty (%)**
$N_{Ra\text{-}226}$ (counts)	27806 (167)	1.2
V_{sample} (mL)	55.00 (5)	0.1
R_{chem} and sample preparation	0.85	8.5
ε	0.159	5.0
$t_{Ra\text{-}226}$ (s)	237269	
Combined uncertainty (quadratic sum) (%)	9.9	
$A_{Ra\text{-}226}$ (Bq/L)	0.016 (2)	

Table 4. ^{226}Ra results obtained with the method presented in this paper in proficiency tests organized by IAEA and NPL.

Proficiency test governing institution	**Sample Name**	**This work (Bq/kg)**	**Reference Value (Bq/kg)**	**Z-Score**
IAEA	IAEA-Cu-2008-03 Spike water 01	0.762 (80)	0.690 (4)	1.04
	IAEA-Cu-2008-03 Spike water 02	2.13 (18)	1.93 (9)	1.03
IAEA	IAEA-CU-2010-03 S02	0.93 (11)	0.86 (2)	0.19
	IAEA-CU-2010-03 S03	1.84 (21)	1.57 (4)	0.37
NPL	AH	16.4 (18)	15.90 (21)	0.53

ple volume 55.00 mL. The uncertainty due to decay correction (half-life) is considered to be negligible compared to the other uncertainty components. Thus, this parameter is not taken into account for the calculation of the total uncertainty. The corrected 27806 net peak area counts and 167 related uncertainty counts were evaluated from Poisson distribution. The total uncertainty due to all parameters is presented in Table 3. Combined standard uncertainty of sample was calculated as a 9.9%

The major contributions come from the chemical recovery, geometry factor, counting statistics and sample volume.

3. 5. Sample Application

The accuracy and precision of the recommended procedure for analyses of ^{226}Ra were checked by analyzing the water samples of IAEA and NPL proficiency tests (Table 4). The results are evaluated in terms of Z-score. The validity of proposed method was satisfactory if the Z-scores was less than or equal to 2. Thus, the validity of proposed method was satisfactory according to the Z-scores. It is clear from the table that the results of the analytical method presented were consistent with the reference values.

4. Conclusion

In this study, solid angle calculation method was successfully used to determine detector efficiency instead of using a ^{226}Ra standard. The procedure was tested with reference materials from IAEA and NPL proficiency tests and the results were favorable. This indicates that the solid angle calculation method is an effective method and provided good accuracy and precision, without needing of preparation and measurement of a ^{226}Ra standard. The parameters contributing to the uncertainty budget were re-evaluated and the total relative uncertainty was found to be 9.9% ($k = 1$). The main uncertainty contribution comes from the chemical recovery and sample preparation (8.5%).

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Povzetek

Predstavljamo alfa-spektrometrično metodo za hitro določitev izotopa ^{226}Ra v vodnih vzorcih. Metoda je osnovana na soobarjanju (Ba)(Ra)SO_4 za pripravo vira. Raziskali smo dejavnike, ki prispevajo k skupni negotovosti. Namesto standardnega ^{226}Ra diska smo za določitev učinkovitosti detektorja uporabili geometrijski faktor (prostorski kot / 4π). Analizno metodo smo uspešno uporabili za določitev ^{226}Ra v vodnih vzorcih pri testiranju usposobljenosti, ki sta ga organizirala Mednarodna agencija za jedrsko energijo (IAEA) in Nacionalni fizikalni laboratorij (NPL). Predlagana metoda se je pokazala tudi za zelo obnovljivo.