

Scientific paper

Uncertainty Budget for ^{226}Ra Activity Concentration in Water by Alpha Spectrometry

Yana Spasova,* Stefaan Pommé,
Ljudmila Benedik, Uwe Wätjen

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements,
Retieseweg 111, B-2440 Geel, Belgium

* Corresponding author: E-mail: yana.spasova@ec.europa.eu

Received: 04-06-2007

Abstract

Alpha-particle spectrometry is the most frequently used technique for the activity determination of alpha emitters, such as radium, uranium, plutonium, americium and thorium in environmental samples. In this paper an extensive uncertainty budget is presented for a typical alpha-particle spectrometry measurement of the ^{226}Ra activity concentration in drinking water. The most influential parameters contributing to the uncertainty are investigated. The set-up used is a common alpha-spectrometry system for environmental samples using PIPS detectors. In particular, the influence of geometrical parameters as well as the activity distribution in the measured sources on the solid angle is scrutinised.

Keywords: Uncertainty, alpha-particle spectrometry, solid angle

1. Introduction

Alpha-particle spectrometry provides the best information about alpha emitters such as radium, uranium, plutonium, americium and thorium in environmental samples because of its high energy resolution, reasonably good counting efficiency and low background. However, the preparation of alpha-spectrometric sources requires long chemical procedures to isolate the studied isotopes. The sample preparation and the quality of the source with respect to uniformity influence the measurement results.

In recent years more attention is paid to the evaluation of the measurement uncertainty and to the preparation of an uncertainty budget. However, there is no common procedure on how to estimate realistic uncertainties. When calculating the combined uncertainty on the results obtained by alpha spectrometry, several components have to be taken into account in the uncertainty budget, such as the sample preparation and the chemical recovery, spectral deconvolution, system dead time and solid angle.

In this work, we evaluate the uncertainty propagation of dimensional parameters, such as the detector radius R_D , the source-detector distance d , the source radius R_S and the eccentricity of the source material. The corresponding equations can be used for the evaluation of the uncertainty budget for the solid angle subtended by the detector.

An example is taken from the analyses of ^{226}Ra activity concentration which were carried out in the frame of an intercomparison exercise organised by the Institute for Reference Materials and Measurements (IRMM) on determination of ^{226}Ra , ^{228}Ra , ^{234}U and ^{238}U in mineral water.¹ The experimental set-up used is a common alpha spectrometry system for environmental samples which consists of an alpha detector (PIPS) in a vacuum chamber, where the source is deposited on a flat substrate that is placed in a parallel plane, centred at the symmetry axis of the detector.

All uncertainties mentioned below refer to standard deviations.

1. 1. Uncertainty Due to Sample Preparation and Chemical Recovery

For measuring ^{226}Ra by alpha-particle spectrometry, each water sample needs extensive chemical separation prior to counting in order to remove interferences from other alpha emitters. In this work, a co-precipitation procedure was used for the preparation of the radium sources, using BaSO_4 as a carrier.^{1,2} ^{133}Ba was added as a tracer for the determination of the chemical yield of the radiochemical procedure and its activity concentration in the sample was determined by gamma-ray spectrometry with a high-

purity germanium detector (HPGe).^{1,2} The detector end-cap has a 0.15 mm thick Be window. The gamma-ray peak analysis was done with the GammaVision-32 software.

The chemical yield was determined by relative measurements based on the comparison of the measured peak areas of the ¹³³Ba tracer in the water samples ($N_{Ba-133sample}$) and a ¹³³Ba standard source ($N_{Ba-133Std}$) that was prepared in the same manner.¹ The recovery factor of the standard ($R_{Ba-133Std}$) was determined by measuring the activity left in the filtrate and the washing solution after the filtration of BaSO₄.

The chemical yield R_{chem} was calculated from:

$$R_{chem} = \left(\frac{N_{Ba-133sample}}{t_{Ba-133sample} \cdot m_{Ba-133sample}} \right) \cdot \left(\frac{t_{Ba-133Std} \cdot m_{Ba-133Std}}{N_{Ba-133Std}} \right) \cdot R_{Ba-133Std} \quad (1)$$

in which N_{Ba-133} is the net area of ¹³³Ba in the sample and the standard source, respectively; t_{Ba-133} is the counting time of the sample and the standard source measurements; m_{Ba-133} mass of added ¹³³Ba in the sample and in the barium standard source, respectively; $R_{Ba-133Std}$ is the recovery factor of the standard source.

In evaluating the uncertainty due to the sample preparation and the chemical yield, the contributions of the weighing of the tracer, geometrical reproducibility and peak area determination have to be taken into account. Also the use of ¹³³Ba for yield correction must be taken with caution, as one may suspect a different microscopic chemical behaviour between radium and barium. It has been shown in literature² that the yield ratio Y_{Ra-226}/Y_{Ba-133} is slightly higher than 1 (≈ 1.04), with a typical uncertainty of 8%. This is the major uncertainty component in the chemical procedure.

An independent, squared sum was made of the components due to the sample preparation and the chemical recovery, including uncertainty on the standard (2%), weighing (1%), counting uncertainty (1%) and yield ratio uncertainty (8%), leading to a 8% total uncertainty for the chemical yield.

1. 2. Uncertainty on the Solid Angle

1. 2. 1. Point Source Approximation

The detection efficiency is obtained directly from the relative solid angle, i.e. the ratio of the solid angle to 4π steradian. The simplest configuration is that of a point source on the symmetry axis of the circular detector. The solid angle Ω corresponds to:

$$\Omega = 2\pi(1 - \cos \theta) \quad (2)$$

$$\theta = \arctg\left(\frac{R_D}{d}\right) \quad (3)$$

in which R_D represents the radius of the detector and d is the distance between the source and detector. One can easily verify that, as a rule of thumb, the relative uncertainty on the solid angle is about twice that of the polar angle. The uncertainty on the polar angle will generally be calculated from the relative uncertainties on the distance d and the detector radius R_D . Varying these dimensions would correspond to the following relative uncertainties:

$$\frac{\sigma(\Omega)}{\Omega} = \left[\frac{(\cos \theta)^3}{1 - \cos \theta} (\text{tg} \theta)^2 \right] \cdot \sqrt{\frac{\sigma^2(R_D)}{R_D^2} + \frac{\sigma^2(d)}{d^2} - 2\rho \frac{\sigma(R_D)}{R_D} \frac{\sigma(d)}{d}} \quad (4)$$

in which ρ is a correlation coefficient.

Positively correlated changes of the dimensions due to variations in temperature tend to cancel out. If the detector and distance tube have the same coefficient of expansion, then the correlation factor is one, hence the corresponding uncertainty increase is nil.

In this work, we used a 450 mm² PIPS detector ($R_D = 11.95 \pm 0.05$ mm) and put the source at a distance (varying a bit amongst chambers) of about 5.0 ± 0.5 mm. Propagation of the estimated uncertainties on R_D and d via Eq. 4, leads to 5% standard uncertainty on Ω .

1. 2. 2. Co-axial Homogeneous Disk Source

The approximation for a point source is too rough in our case, considering that the radius of the active part of the measured sources was about 11 mm. A further step in increasing the accuracy of solid angle determination is by representing the source as a flat disk with a radius R_S , assuming a homogeneous distribution of the active material and perfect alignment of source and detector on a common symmetry axis. It has been shown that the corresponding solid angle can be rigorously calculated from:^{3,4}

$$\Omega = \frac{2\pi R_D}{n R_S} \sum_{i=1}^n \frac{\sin^2 \varphi}{\sqrt{x - \cos \varphi} (\sqrt{y} + \sqrt{x - \cos \varphi})} \quad (5)$$

in which $x = \frac{R_S^2 + R_D^2 + d^2}{2R_S R_D}$, $y = \frac{d^2}{2R_S R_D}$, $\varphi = (i - 0.5)\pi/n$ and n is an integer value of choice (e.g. $n = 50$).

This Eq. 5 can easily be differentiated for the different geometrical parameters. The uncertainty on the source radius, for example, leads to the following relative uncertainty:

$$\frac{\sigma(\Omega)}{\Omega} = \frac{\sigma(R_S)}{R_S} \frac{R_S}{\Omega} \frac{2\pi}{n} \left[\sum_{i=1}^n \frac{\partial}{\partial R_S} \left[\frac{R_D}{R_S} T(n) \right] \right] \quad (6)$$

$$= \frac{\sigma(R_S)}{R_S} \frac{1}{\Omega} \frac{2\pi R_D}{n R_S} \left[\sum_{i=1}^n -T(n) + \frac{\partial T(n)}{\partial x} \frac{\partial x}{\partial R_S} R_S + \frac{\partial T(n)}{\partial y} \frac{\partial y}{\partial R_S} R_S \right]$$

in which we define $T^{(n)} = \frac{\sin^2 \varphi}{\sqrt{x - \cos \varphi} (\sqrt{y} + \sqrt{x - \cos \varphi})}$.

Taking an uncertainty of 1 mm on the radius R_S , one finds 5% uncertainty on Ω . In a similar manner, one derives better uncertainty propagation for R_D and d , resulting now to 6% (compared to 5% in the case of a point source).

1. 2. 3. Eccentric Disk or Point Source

One should also consider the possibility that the source is not well centred under the detector, i.e. its centre being at a distance a away from the symmetry axis of the detector. Conway has shown that the solid angle can be calculated from the following equation:⁴

$$\Omega = 4\pi \frac{R_D}{R_S} \int_0^\infty \frac{J_0(sa)J_1(sR_D)J_1(sR_S)}{s} e^{-sh} ds \quad (7)$$

in which J_0 and J_1 are Bessel Functions of the first kind.

Assuming a possible eccentricity of $a = 2$ mm (for $R_D = 11.95$ mm, $R_S = 11$ mm, $d = 5$ mm), one finds 2% uncertainty on Ω , by comparing MathCad calculations for $a = 0$ and $a = 2$.

1. 2. 4. Non-homogeneous, Realistic Source

Realistic sources are somewhat inhomogeneous and out-of-centre. At IRMM, autoradiographs are sometimes taken of the sources, in order to assess their activity distribution.^{5,6} For calculation purposes, the source is virtually divided in concentric rings with constant solid angle. Their contribution to the total solid angle is weighted according to the relative amount of activity in the ring. Thus, any deviation from a homogeneous disk source is taken into account, including variations on the source radius and the eccentricity of the source material on its substrate, however not the eccentricity of the source holder. The solid angle of a ring source can e.g. be derived from a linear combination of solid angles for disk sources (Eq. 4) with the corresponding inner and outer diameter.⁵

$$\Omega_{\text{ring}} = \frac{R_{\text{out}}^2 \Omega_{\text{out}} - R_{\text{in}}^2 \Omega_{\text{in}}}{R_{\text{out}}^2 - R_{\text{in}}^2} \quad (8)$$

Fig. 1 shows the autoradiograph of three sources, together with corresponding radial activity distribution. Obviously the sources are not as homogeneous and of reproducible geometry as would be desired. The activity is sometimes concentrated in the centre or in ‘moon shaped’ structures.

In Fig. 2 the solid angle is shown for sixteen ²²⁶Ra sources prepared by BaSO₄ co-precipitation. The variation in the calculated Ω ($s(\Omega) = 3\%$) is completely due to a different activity distribution within the sources. Yet, the

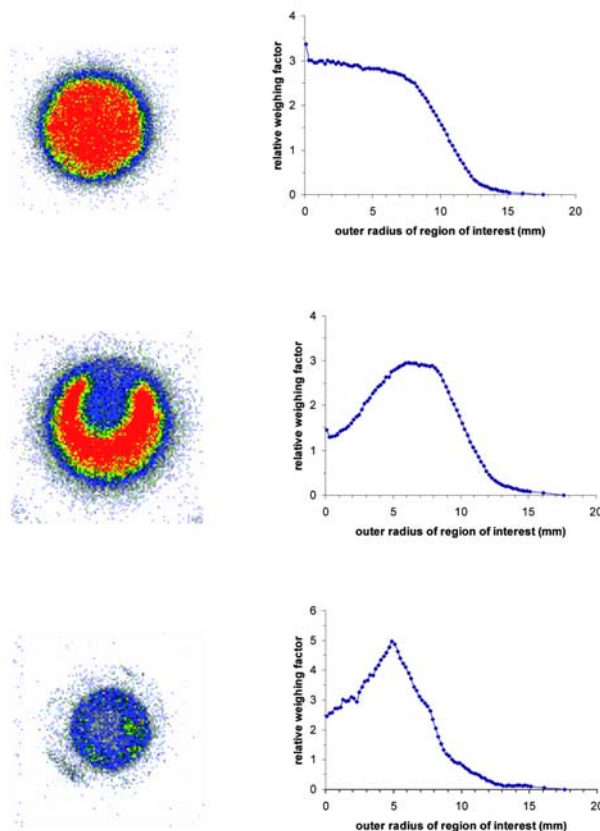


Fig. 1 Autoradiographs (left) and radial activity distributions (right) for ²²⁶Ra samples prepared by BaSO₄ co-precipitation. A perfectly homogeneous source should have a flat radial activity distribution.

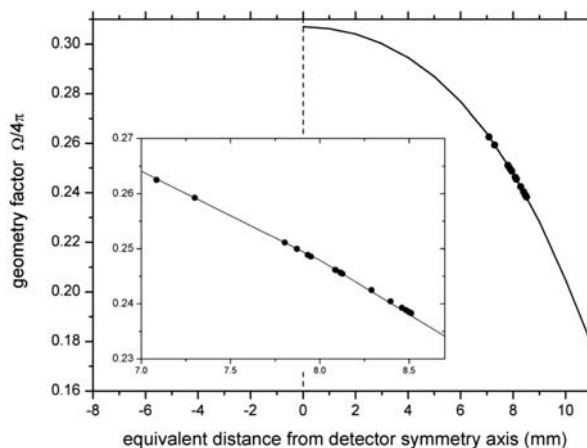


Fig. 2 Calculated solid angle subtended by a circular PIPS detector with radius $R_D = 11.95$ mm for real sources at a distance of 5 mm. The variation in the solid angle amongst the sources is completely due to differences in their activity distribution. The solid line corresponds to a point source with eccentricity between $a = 0$ and $a = 11$ mm. (For the sources, virtual radii were assigned in accordance with their respective Ω -value.)

variation is not too dramatic, considering that the variation of Ω for a point source with eccentricity between $a = 0$ and $a = 11$ mm is as high as 72%.

1. 2. 5. Total Uncertainty Budget for the Solid Angle

The eventual value of the source-to-detector distance, was evaluated from the measurement of a reference ^{226}Ra source with known activity (standardised at IRMM within 0.2% by defined solid angle counting) and similar geometry, and taking into account possible variation amongst sources, an estimated uncertainty value of 2% was assigned to d ($\approx 5\text{mm}$). The uncertainty caused by a possible tilt of the source or detector is considered to be negligible compared to the other uncertainty components. An independent, squared sum was made of the components due to the radial activity distribution (incl. source inhomogeneity, internal eccentricity and source radius) (3%), distance d (1.2%), detector radius and tilt (0.5%), external eccentricity (1mm) (1%), leading to a 3.4% total uncertainty of the solid angle.

1. 3. Uncertainty Due to Spectral Deconvolution

Alpha spectra were obtained using Canberra alpha spectrometer chambers (Model 7401 VR) and PIPS detectors with 450 mm^2 sensitive area. The data acquisition and analysis was done using the Genie-2000 Alpha Analysis Software and Alpha Analyst Control Application V.2.1.

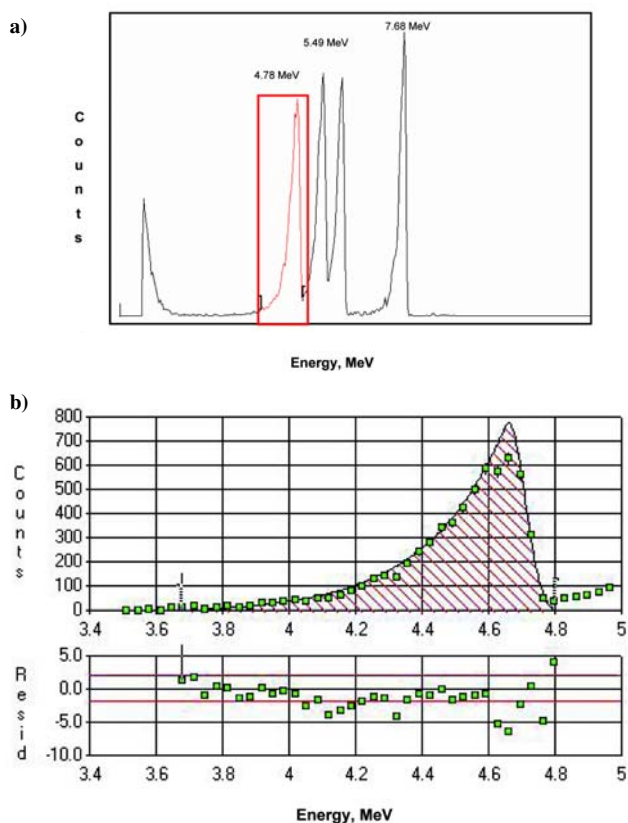


Fig. 3 α -particle spectrometry of ^{226}Ra (A.): measured (points) and fitted (filled area) peak at 4.78 MeV (B.).

Whereas the software reports an uncertainty on the fitted peak areas, one has to be cautious not to underestimate the true uncertainty. The fit has been restricted to the energy region (3.7–4.8 MeV) around the ^{226}Ra peak (Fig. 3B), hereby not fully subtracting the tailing of the daughter peaks situated at higher energy (Fig. 3A). The residuals of the fit show systematic structure, whereas for the uncertainty calculations to be valid it is required that the residuals are randomly distributed.⁷ Moreover, one should also be aware that using the number of counts of Poisson distributed data as their relative weight in the fit, leads to a bias towards lower values.⁸

As an alternative to the fit, one can calculate the net area (N) by taking the numerical integral of the number of counts in the peak region (N_g) instead and correcting for background (B) and subtracting the low-energy tail of the interfering peak at 5.49 MeV (T):

$$N = N_g - T - B \quad (9)$$

A tail-to-peak ratio (ca. $T/N \sim 0.05$) was derived from the well isolated peak at the end of the spectrum (7.68 MeV) and this ratio was applied to subtract the tailing from the 4.78 MeV peak (Fig. 3A). The uncertainty was calculated from the sum of the counting uncertainties (Poisson) and an additional, estimated 10% uncertainty on the tailing:

$$u(N) = \sqrt{N_g + B + T + (T/10)^2} \quad (10)$$

which is only slightly higher than the uncertainty delivered by the software. A typical relative uncertainty is 1–1.5%.

1. 4. Uncertainty Budget for ^{226}Ra Activity Concentration in Water

In the total uncertainty budget for ^{226}Ra in mineral water the typical uncertainties for a single measurement of a sample at the 1s level are included (Table 1). The individual uncertainty contributions are combined to the total uncertainty (9%) by taking the square root of the sum

Table 1. Uncertainty budget for ^{226}Ra in mineral water. The uncertainty budget shows the typical uncertainties for a single measurement of a sample at the 1s level. The combined uncertainty is the quadratic sum of all components ($k = 1$).

Component	Uncertainty (%)
Chemical yield	8.0
Solid angle	3.4
Counting statistics (incl. background)	1.5
Counting time	0.005
Dead time	0.005
Half-life ($T_{1/2} = 1600\text{ a}$)	9.3E-05
Combined uncertainty (quadratic sum)	9.0

of the squared uncertainty components. The major contributions come from the sample preparation and the chemical recovery (8%) and the solid angle determination (3.4%). The uncertainties due to system dead time, counting time and decay correction (i.e. half-life) are considered to be negligible compared to the other uncertainty components (in total <0.1% of the total uncertainty). In the example presented, the uncertainty on the counting statistics is a minor uncertainty contribution (1.5%).

2. Conclusions

A detailed uncertainty budget for ^{226}Ra activity concentration in water determined by alpha-particle spectrometry was presented. The total combined uncertainty is 9% ($k = 1$). Since in this case, the main uncertainty contribution comes from the sample preparation and the chemical recovery (8%), significant improvement to the uncertainty budget can only be made by determining the yield ratio $Y_{\text{Ra-226}}/Y_{\text{Ba-133}}$, which is now taken from literature,² with smaller uncertainty in the future. The procedure presented for estimating the uncertainty on the solid angle, however, has general value and can be applied to the determination of other alpha-particle emitting radionuclides as well.

Povzetek

Spektrometrija alfa je najbolj pogosto uporabljena tehnika za določanje aktivnosti sevalcev alfa kot so radij, uran, plutonij, americij in torij v vzorcih iz okolja. V prispevku je predstavljen izračun merilne negotovosti pri določanju koncentracij aktivnosti ^{226}Ra v pitni vodi. Ovrednoteni so vsi parametri, ki vplivajo na izračun merilne negotovosti celotnega postopka. Za meritve z alfa spektrometri najpogosteje uporabljamo detektorje PIPS, ki zahtevajo natančno poznavanje vplivov oddaljenosti izvora od detektorja, kakor tudi homogenosti oz. porazdelitve radionuklida v izvoru žarkov alfa.

3. References

1. L. Benedik, U. Wätjen, Y. Spasova, *Determination of ^{226}Ra in drinking water as regards the requirements of the EU directive*, 15th International Symposium "Spectroscopy in Theory and Practice", 18–21 April 2007, Nova Gorica, Slovenia.
2. J. C. Lozano, F. Fernandez, J. M. G. Gomez, *J. of Radioanal. Nucl. Chem.*, **1997**, 223 (1–2), 133–137.
3. S. Pommé, J. Paepen, *Nucl. Instr. and Meth.*, **2007**, A579, 272–274.
4. J. T. Conway, *Nucl. Instr. and Meth.*, **2006**, A562, 146–153.
5. S. Pommé, A new algorithm for the solid angle calculation applied in alpha-particle counting, Internal Report IRMM, GE/R/RN/08/01, **2001**.
6. G. Sibbens, S. Pommé, L. Johansson, B. Denecke, *Nucl. Instr. and Meth.*, **2003**, A205, 277–281.
7. S. Pommé, Applied Modeling and Computations in Nuclear Science, in T. M. Semkow, S. Pommé, S. M. Jerome and D. J. Strom (Eds.), ACS Symposium Series 945. American Chemical Society, Washington, DC, **2007**, ISBN 0-8412-3982-7, pp. 282–292.
8. S. Pommé, J. Keightley, Applied Modeling and Computations in Nuclear Science, in T. M. Semkow, S. Pommé, S. M. Jerome and D. J. Strom (Eds.), ACS Symposium Series 945. American Chemical Society, Washington, DC, **2007**, ISBN 0-8412-3982-7, pp. 316–334.