

# The influence of method precision on assessing radiological hazards for patients using radium water in balneotherapy

Joanna Lemańska <sup>(D)</sup>, Krzysztof Isajenko, Karol Wiatr <sup>(D)</sup>, Barbara Piotrowska, Agnieszka Matysiak, Maciej Norenberg, Slawomir Jednorog <sup>(D)</sup>

**Abstract.** The influence of uncertainty on the method adopted for the determination of radioactive radium concentration in water was analyzed due to the assessment of the radiation hazards of balneotherapy. For the calculation, we considered the influence of the bath in radioactive water containing only <sup>226</sup>Ra. <sup>226</sup>Ra concentration was determined with two  $\gamma$ -spectrometers armed with HPGe detectors with different relative efficiencies. Both spectrometers were energy-efficiency calibrated with a calibration source and based on numerical simulations. Different methods for qualitative  $\gamma$ -spectrum analysis were adopted. The emanation method and the liquid scintillation method were also used. The uncertainty of humans hazard assessment linearly depends on the adopted radiometric method precision. For effective dose calculation, two models were adopted: the model of external exposure proposed by ICRP Publication 144 and the Reference Men model proposed by ICRP Publication 23, respectively.

Keywords: Balneotherapy • Radiation hazard • Radium water

# Introduction

This research aims to demonstrate the impact of technical precision on assessing radiological risks for patients receiving balneotherapy with radium water.

Sanatorium treatments and SPA services are popular in Poland for patients who have finished hospital treatments and for outpatients. According to the Ministry of Health, there are currently 49 sanatorium complexes in Poland, comprising 286 individual sanatoria. These facilities have the capacity to accommodate thousands of individuals.

Southern Polish health spas, particularly those located in the Sudety Mountains, utilize radioactive mineral waters containing radium and radon. Resorts such as Kamienica, Świeradów Zdrój, and Ciepłowody offer radon-enriched water with a minimum activity level of 74 Bq/L [1, 2].

Previous studies predominantly concentrated on monitoring the preservation of therapeutic properties in medicinal water through the measurement of <sup>222</sup>Rn activity concentration [3]. Limited information is available regarding the effects of bathing in waters containing <sup>226</sup>Ra on external exposure [4].

This study compared several methods for determining the concentration of  $^{226}$ Ra in water, including  $\gamma$ -spectrometry using both medium-efficiency

0029-5922 © 2024 The Author(s). Published by the Institute of Nuclear Chemistry and Technology. This is an open access article under the CC BY-NC-ND 4.0 licence (http://creativecommons.org/licences/by-nc-nd/4.0/).

J. Lemańska<sup>⊠</sup>, K. Isajenko, K. Wiatr, B. Piotrowska, A. Matysiak, M. Norenberg, S. Jednorog Central Laboratory for Radiological Protection Konwaliowa 7 St., 03-194 Warsaw, Poland E-mail: j.lemanska@clor.waw.pl

Received: 3 October 2023 Accepted: 22 April 2024 and high-efficiency high purity germanium (HPGe) detectors, as well as the emanation and the liquid scintillation counting (LSC) methods.

To calculate the radiation hazard, two ICRP models were adopted: (1) the model of Reference Men [5] and (2) the model of external exposure [6]. The adopted model uses coefficients for transforming activity concentration in water into an effective dose in humans.

The report explores the accuracy of evaluating radiation hazards, with a particular focus on the significance of technique uncertainty. When it comes to measuring radiation, accuracy is extremely important because of the potential dangers it poses to both human health and the environment. However, a certain degree of tolerance is also accepted.

## Material and methods

# <sup>226</sup>Ra – nuclear properties

Radium isotopes are short-lived and stem from the ongoing decay of <sup>238</sup>U. <sup>226</sup>Ra nuclei undergo  $\alpha$  decay, yielding progeny radionuclides that emit  $\alpha$ ,  $\beta$ , and  $\gamma$  radiation [7].

As a result, radioactive <sup>226</sup>Ra occurs in conjunction with its progeny radionuclides. This is particularly evident in the  $\gamma$ -spectrometry method used for determining its activity (refer to Fig. 1).

Detecting <sup>226</sup>Ra using its spectrometric line at an energy of 186.211 keV and intensity of 3.57% presents hurdles while appearing simple [8, 9].

# Collection and distribution of water samples

Brine waters exhibiting elevated <sup>226</sup>Ra concentrations were gathered from a sanatorium situated in southern Poland and promptly conveyed to the Central Laboratory for Radiological Protection. Subsequently, they were segregated based on the particular radiometric technique employed. Waters designated for  $\gamma$ -spectrometric analysis were transferred directly into 500 ml Marinelli beakers. The remaining waters underwent additional processing in accordance with the specific requirements of each respective method.

## Metrology of radium in water

#### *γ*-Spectrometry with HPGe detectors

For the  $\gamma$ -spectrometry of radium water, two HPGe detectors with distinct numerical characteristics were employed. The first detector has a relative efficiency of 40%, while the second has 25% efficiency. The resolution of both detectors is full width at half maximum (FWHM) ( $E_{\gamma} = 1332.49 \text{ keV}$ ) = 1.75 keV. Both detectors underwent experimental and mathematical calibration specific to the measurement geometry of the samples. The difference between the aforementioned efficiency calibration methods is smaller than 0.1%, as evidenced by previous experiences [10].

The Marinelli beaker containing water was digitally described using Geometry Composer, while



Fig. 1. γ-ray spectrogram of radium water.

LabSOC software was employed to calculate photon registration efficiency.

Radium radioactivity was quantified using algorithms within the Genie2000 software package, which incorporates both efficiency calibration methods and directly utilizes net peak area for specific full energy absorption peaks (FEAPs). The  $\gamma$ -ray spectrum is intricate, involving functions that delineate various physical phenomena, including interaction with detector materials, particle interactions influencing peak shape, non-linear photon registration efficiency, energy calibration, and detector resolution. Deconvolution, a technique used to analyze the spectrum for specific radionuclide presence and quantity, disentangles these functions. The Genie2000 package employs Nuclide Identification (NID) along with interference correction for deconvolution.

When the net count rate of <sup>235</sup>U is too low to detect, the amount of <sup>226</sup>Ra can be indirectly calculated by using the unaffected FEAPs of its descendant radionuclides, particularly <sup>214</sup>Pb and <sup>214</sup>Bi. Measuring the unique  $\gamma$ -ray FEAP intensity emitted by <sup>214</sup>Pb and <sup>214</sup>Bi allows for estimating the concentration of <sup>226</sup>Ra. Radioactive equilibrium permits the determination of <sup>226</sup>Ra concentration by analyzing its decay product concentrations, as illustrated in Eq. (1) [11].

(1)  

$$A \Big[ {}^{226} \operatorname{Ra} \Big( E_{\gamma} = 186.2 \text{ keV} \Big) \Big]$$

$$= A \Big[ {}^{214} \operatorname{Pb} \Big( E_{\gamma 1} = 295.2 \text{ keV} \Big) \Big]$$

$$A \Big[ {}^{214} \operatorname{Pb} \Big( E_{\gamma 2} = 351.5 \text{ keV} \Big) \Big]$$

$$= A \Big[ {}^{214} \operatorname{Bi} \Big( E_{\gamma} = 609.8 \text{ keV} \Big) \Big]$$

# Liquid scintillator counting method

The activity concentration of <sup>226</sup>Ra was determined using the LSC technique. A radiochemical sample was prepared and mixed with a scintillation cocktail to facilitate direct interaction. The interaction between  $\alpha$  particles and the scintillation cocktail produces light flashes, which are subsequently detected and converted into electrical pulses. These pulses are then shown as a spectrum. The study used a sophisticated methodology to concurrently identify the presence of <sup>226</sup>Ra and <sup>228</sup>Ra in potable water [12]. The 120-min measurement is performed within a time frame of 16 h following sample preparation in order to prevent the accumulation of decay products of <sup>226</sup>Ra. The Quantulus GCT 6220 counter, produced by Packard Canberra, is utilized for the purpose of conducting the analysis.

### Emanation method

The emanation method quantifies the quantity of  $^{226}$ Ra by detecting the  $\alpha$ -radiation produced by its offspring,  $^{222}$ Rn.  $^{226}$ Ra is separated from other components by coprecipitation with Ba<sup>2+</sup>, using ammonium sulfate as the precipitating agent. The Ba(Ra)SO<sub>4</sub> precipitate is dissolved in 0.25 M ethylenediamine-tetraacetic acid (EDTA) with ammonium hydroxide.

The solution is transferred to a bubbler and flushed with argon gas to remove the accumulated <sup>222</sup>Rn. The bubbler efficiency is ~99.5% when the carrier gas volume exceeds the sample volume four times. After sealing, the sample is left to achieve <sup>226</sup>Ra–<sup>222</sup>Rn equilibrium. <sup>222</sup>Rn is quantitatively transferred to a Lucas-type scintillation chamber. The chambers are made of polymethyl methacrylate covered with activated zinc sulfide in chloroform [13, 14].

Chambers containing the sample are placed within the ALFA spectrometer, produced by TD Electronics. Chambers are checked for impermeability and adjusted using a reference solution containing <sup>226</sup>Ra. Calibration samples are prepared from a standard solution with an activity of 9.4 Bq/mL, within an error tolerance of 0.5%, so that the activity concentration falls within the range of 1.5–2.5 Bq/L.

### Estimation of radiation hazards during balneotherapy

<sup>226</sup>Ra activity concentration in therapeutic water is utilized to estimate external effective doses for patients undergoing balneotherapy. The ICRP models were utilized for the calculations [5, 6]. The calculated radiation hazard only accounted for external exposure through the skin and did not factor in the effects of <sup>226</sup>Ra decay products or interior exposure from ingestion and/or inhalation. The effective doses were estimated (nSv) by multiplying the relevant coefficients [6], the specific activity of <sup>226</sup>Ra (), and an exposure period of 18 000 s, which is the result of 10 baths lasting 30 in each.

(2) 
$$E_{\rm H} = 2.14^{-6} \cdot A_{_{226}\rm Ra} \cdot t$$

where: 2.14<sup>-6</sup> [nSv·L·(Bq·s)<sup>-1</sup>] coefficient adopted for conversion of water activity on effective dose,  $A_{226_{Ra}}$  (Bq) radioactive concentration of <sup>226</sup>Ra in water, *t* (s) exposition time.

#### **Result and discussion**

The concentration of <sup>226</sup>Ra, as estimated through several methods, is presented in Table 1, together with the associated radiation hazard for patients undergoing balneotherapy.

The most precise methods are the  $\gamma$ -spectrometry techniques, albeit with some reservations outlined below. Their precision ranges from 2.2% to 5.0%. Uncertainty in  $\gamma$ -spectrometry is mostly due to measurement errors and errors related to energy and efficiency calibration execution. The ultimate error is contingent on the approach used for efficiency calibration. For mathematical calibration, the accuracy is approximately 1% or less. The value of calibration using a source relies on the precision of preparing the calibration standard and is around 3%.

The results obtained from direct and indirect calculations using both HPGe detectors show a few differences. The outcome from the 40% relative efficiency detector overestimated values when compared with the other detector, as well as the LSC and

| Measurement<br>method   | Energy-efficiency<br>calibration | Calculation<br>method   | Radioactivity<br>(Bq/L) | Effective<br>dose E <sub>H</sub><br>(nSv) | Uncertainty<br>(%) |
|---|----------------------------------|---|-------------------------|---|--------------------|
| γ-Spectrometry<br>with HPGe detector<br>medium efficiency<br>detector | Calibration source               | Genie2000   | 56.4                    | 2.44                                      | 2.2                |
|   |                                  | Evaluation of 186.2 keV FEAP                                      | 54.5                    | 2.35                                      | 5.0                |
|   |                                  | Evaluation of $^{\rm 214}{\rm Pb}$ and $^{\rm 214}{\rm Bi}$ FEAPs | 51.1                    | 2.21                                      | 5.0                |
|   | LabSOCS                          | Genie2000   | 53.2                    | 2.30                                      | 2.6                |
|   |                                  | Evaluation of 186.2 keV FEAP                                      | 51.4                    | 2.22                                      | 4.0                |
|   |                                  | Evaluation of $^{\rm 214}{\rm Pb}$ and $^{\rm 214}{\rm Bi}$ FEAPs | 51.0                    | 2.20                                      | 4.0                |
| γ-Spectrometry<br>with HPGe detector<br>high-efficiency<br>detector   | Calibration source               | Genie2000   | 68.0                    | 2.94                                      | 4.3                |
|   |                                  | Evaluation of 186.2 keV peak                                      | 71.2                    | 3.08                                      | 4.2                |
|   |                                  | Evaluation of <sup>214</sup> Pb and <sup>214</sup> Bi FEAPs       | 59.0                    | 2.55                                      | 2.8                |
|   | LabSOCS                          | Genie2000   | 65.8                    | 2.84                                      | 3.4                |
|   |                                  | Evaluation of 186.2 keV peak                                      | 68.9                    | 2.98                                      | 4.2                |
|   |                                  | Evaluation of <sup>214</sup> Pb and <sup>214</sup> Bi FEAPs       | 56.8                    | 2.45                                      | 2.6                |
| Liquid scintillation  | -                                |   | 57.9                    | 2.50                                      | 10.4               |
| Emanation method  | _                                |   | 51.1                    | 2.21                                      | 16.3               |
|   |                                  |   |                         |   |                    |

Table 1. Humans hazard and its uncertainty

FEAP, full energy absorption peak.

emanation methods. The absence of hermetic sealing in Marinelli beakers was considered a potential primary factor contributing to the observed difference. However, a procedure was implemented to confirm or refute this hypothesis, involving the hermetic sealing of Marinelli beakers using silicone glue.

Nevertheless, certain disparities between the Genie2000 calculation method and the techniques based on evaluating FEAPs are noticeable, particularly in the results from the medium efficiency HPGe detector. This suggests that the Genie2000 method might not be the most precise choice in this specific scenario. The direct measurement approach for <sup>226</sup>Ra has the benefit of fast sample preparation and measurement, eliminating the requirement for progeny ingrowth. The drawbacks of this approach principally stem from the low emission probability (3.57%) of the gamma photopeak and the presence of the interfering primary gamma emission of <sup>235</sup>U at 185.7 keV and intensity of 57.24% [9].

The measurement uncertainty of the emanation method is 16% and was calculated using Eq. (3):

(3) 
$$\frac{u(A)}{A} = \sqrt{\frac{\frac{u^2(N_p) + u^2(N_t)}{(N_p - N_t)^2} + \left(\frac{u(K)}{K}\right)^2 + \left(\frac{u(F)}{F}\right)^2}{+\left(\frac{u(Y)}{Y}\right)^2 + \left(\frac{u(V)}{V}\right)^2}}$$

The main factor contributing to the total uncertainty is the first component, which determines the standard uncertainty of the counting, where  $N_p$ represents the sample counting with background (imp/min),  $N_t$  denotes the background counting (imp/min),  $t_p$  and  $t_i$  are sample and background measurement times (min):

(4) 
$$u(N_p) = \sqrt{\frac{N_p}{t_p}}$$

(5) 
$$u(N_t) = \sqrt{\frac{1}{2}}$$

The overall uncertainty is influenced by various factors, including the uncertainty of the total correction factor, which considers the buildup and decay of <sup>222</sup>Rn{[u(F)]/F<sup>2</sup>, as well as the uncertainty of the sample volume {[u(V)]/V<sup>2</sup>, chamber calibration factor {[u(K)]/K}, and efficiency {[u(Y)]/Y<sup>2</sup>. These components have a lesser impact than the measurement error of the counting frequency.

According to observations in the literature, such a range of uncertainty (10–20%) is typical for this type of measurement [14].

Radon emission counting is a favorable choice when there is a need for achieving low detection limits. This method is characterized by its simplicity and insensitivity to sample mineralization, chemical composition, or the presence of contaminants. However, ensuring the tightness of the measurement system poses a challenge, and the necessity of <sup>222</sup>Rn equilibrium may restrict the application of this method when rapid determinations are required [13].

For the LSC method, the estimated relative uncertainty of the standard radioactive concentration, as per Eq. (6), is 10%, primarily attributed to counting  $u(N_0)$  and efficiency  $u(\varepsilon)$  errors, which constitute the main sources of uncertainty:

(6) 
$$u(A) = \sqrt{\left(\frac{A}{N_0}\right)^2 \times u(N_0)^2 + \left(\frac{A}{\varepsilon}\right)^2 \times u(\varepsilon)^2} + \left(\frac{A}{V_p}\right)^2 \times u(\varepsilon)^2 + \left(\frac{A}{V_p}\right)^2 \times u(v_p)^2}$$
(7) 
$$u(\varepsilon) = \sqrt{\left(\frac{\varepsilon}{N_0}\right)^2 \times u(N_0)^2 + \left(\frac{\varepsilon}{A_W}\right)^2 \times u(A_W)^2} + \left(\frac{\varepsilon}{V_W}\right)^2 + u(V_W)^2}$$
(8) 
$$u(N_0) = \sqrt{\left(\frac{N_p}{t}\right)^2 + \left(\frac{N_t}{t}\right)^2}$$

where  $N_p$  represents the sample counting with background (imp/s),  $N_t$  is the background counting (imp/s),  $N_0$  is the net counting (imp/s),  $V_p$  is volume of sample (L),  $V_W$  is volume of standard solution (mL), t is measurement time (s),  $u(A_W)$  is working solution activity error (Bq/mL).

Additionally, potential interferences, such as chemiluminescence and photoluminescence, can lead to elevated background levels, thereby reducing measurement precision. The simplicity of execution and the ability to quickly analyze samples enable effective utilization of the LSC method. Although sample preparation involves multiple steps and necessitates special reagents like scintillation cocktails – whose composition significantly impacts counting efficiency – the continual refinement of calibration procedures works to alleviate uncertainties and interferences, thus enhancing the efficacy and dependability of results [12, 13].

# Conclusion

The study established a direct proportionality between the effective dose and the concentration of <sup>226</sup>Ra in water. Furthermore, the applied method's uncertainty intricately ties into the precision of the effective dose measurement.

It is worth noting that  $\gamma$ -spectrometry techniques have demonstrated the highest precision, ranging from 2.2% to 5.0%. However, the discrepancies observed between computational methods and measurement techniques underscore the need for careful consideration when selecting the most suitable approach for specific scenarios.

In circumstances where the radiation hazard nears the dose limit, all methods outlined in the study were deemed applicable. It is noteworthy that the determined values correspond to exceedingly small doses.

Our investigation demonstrates the complex interplay between radium determination methods, accurate dose estimations, and their influence on the assessment of radiation exposure. Comprehending these techniques is crucial for efficient risk mitigation, particularly when approaching dosage limits. Our efforts in providing information for decision-making in exposure monitoring and control directly contribute to safeguarding public health and the environment.

## ORCID

*S. Jednorog* b http://orcid.org/0000-0003-4996-6917 *J. Lemańska* b http://orcid.org/0009-0002-4699-1586 *K. Wiatr* b http://orcid.org/0000-0003-1072-6430

# References

- 1. Bilska, I. (2016). The impact of radioactive radon and its decay products on human health. *Medycyna Środowiskowa*, 19(1), 51–56.
- Kozłowska, B., Walencik-Łata, A., Dorda, J., & Zipper, W. R. (2010). Radon in groundwater and dose estima-

tion for inhabitants in Spas of the Sudety Mountain area, Poland. *Appl. Radiat. Isot.*, 68, 854–857. https://doi.org/10.1016/j.apradiso.2009.12.016.

- Walczak, K., & Zmyślony, M.(2013). Estimation of effective doses derived from radon in selected spa centers that use geothermal waters based on the information of radon concentrations. *Medycyna Pracy*, 64(2), 193–198. https://doi.org/10.13075/ mp.5893/2013/0015.
- Karpińska, M., Kapała, J., Raciborska, A., & Mnich, S. (2020). Assessment of effective dose from radioactive isotopes contained in mineral waters received by patients during hydrotherapy treatments. *Water*, 12(1), 97. https://doi.org/10.3390/w12010097.
- 5. International Commission on Radiological Protection. (1975). *Report of the Task Group on Reference Man*. Oxford: Pergamon Press. (ICRP Publication 23).
- International Commission on Radiological Protection. (2020). Dose coefficients for external exposures to environmental sources. (ICRP Publication 144). *Ann. ICRP*, 49(2).
- Decay Radiation Database. (2023, August). NuDat3. [computer software]. National Nuclear Data Center. Retrieved August 10, 2023, from https://www.nndc. bnl.gov/nudat3/indx\_dec.jsp.
- De Corte, F., Umans, H., Vandenberghe, D., De Wispelaere, A., & Van Den Haute, P. (2005). Direct gammaspectrometric measurement of the <sup>226</sup>Ra 186.2 keV line for detecting <sup>238</sup>U/<sup>226</sup>Ra disequilibrium in determining the environmental dose rate for the luminescence dating of sediments. *Appl. Radiat. Isot.*, 63 (5/6), 589–598. https://doi.org/10.1016/j.apradiso.2005.05.008.
- Federal Ministry for the Environment, Nature Conservation and Consumer Protection. (2018). Procedures manual for monitoring of radioactive substances in the environment and of external radiation. Federal Office for Radiation Protection (BfS) & Physikalisch-Technische Bundesanstalt (PTB).
- Jednorog, S., Szydłowski, A., Scholz, M., Paduch, M., & Bieńkowska, B. (2012). Preliminary determination of the angular distribution of neutrons emitted from the PF-1000 facility by indium activation. *Nukleonika*, 57(4), 563–568.
- Lasheen, Y. F., El-Zakla, T., Seliman, A. F., & Abdel-Rassoul, A. A. (2008). Direct gamma-ray measurement of different radionuclides in the surface water of Suez Canal. *Radioprotection*, 43(2), 255–272. DOI: 10.1051/radiopro:2008002.
- International Atomic Energy Agency. (2014). A procedure for the rapid determination of <sup>226</sup>Ra and <sup>228</sup>Ra in drinking water by liquid scintillation counting. Vienna: IAEA. (Analytical Quality in Nuclear Application Series no. 39).
- Köhler, M., Preusse, W., Gleisberg, B., Schäfer, I., Heinrich, T., & Knobus, B. (2002). Comparison of methods for the analysis of <sup>226</sup>Ra in water samples. *Appl. Radiat. Isot.*, 56(1/2), 387–392. https://doi. org/10.1016/s0969-8043(01)00219-6.
- U.S. Environmental Protection Agency, & EMSL. (1980). Method 903.1: Radium-226 in drinking water radon emanation technique. Prescribed procedures for measurement of radioactivity in drinking water. (EPA/600/4/80/032).