Journal of Radioanalytical and Nuclear Chemistry (2025) 334:4663–4673
https://doi.org/10.1007/s10967-025-10170-7

Streamlined approach for radium isotopes quantification in water samples by α and γ-spectrometry

M. Gongora[1] · J. Martínez[1] · A. Peñalver[1] · C. Aguilar[1] · F. Borrull[1]

Received: 6 February 2025 / Accepted: 7 May 2025 / Published online: 27 May 2025

Abstract
A radiochemical method has been developed for the simultaneous isolation and sequential determination of ^{226}Ra and ^{228}Ra in water samples. The procedure involves coprecipitation with Pb(Ba)SO_4, microprecipitation and sequential analysis using alpha- and gamma-spectrometry, avoiding lengthy ingrowth periods and offering a faster and more cost-effective alternative. Optimal conditions for 0.5 L of sample (200 mg of Pb^{2+}, 500 µg of Ba^{2+}, 10 mL of EDTA) were established through ANOVA. Method verification with spiked samples and IAEA reference water samples demonstrated high precision and accuracy. The method complies with Spanish regulatory requirements and is suitable for routine monitoring and emergency applications.

Keywords Radium · Lead sulfate · Microprecipitation · Drinking water · Alpha spectrometry · Gamma spectrometry

Introduction

Radium (Ra) is a naturally occurring radioactive element, with isotopes ranging from ^{206} to ^{230}Ra, all of which are radioactive. Of these isotopes, only four (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) occur naturally [1, 2]. The most abundant naturally occurring isotopes are ^{226}Ra, an alpha emitter with a half-life of 1600 years [3], and ^{228}Ra, a beta emitter with a half-life of 5.75 years [4]. These isotopes are decay products of uranium (^{238}U) and thorium (^{232}Th), respectively, and are among the most radiotoxic [1, 5].

Determining Ra isotopes in environmental samples is crucial for health physics and environmental protection [6, 7]; because: (1) large Ra activities can be produced or accumulated in waste products from the phosphate industry, the mining and processing of metal ores, oil and gas extraction, and the coal mining and combustion industries [6]; (2) Ra isotopes that dissolve in water or enter the food chain are bioavailable and, due to their chemical similarity to calcium, accumulate primarily in the bones when ingested [8, 9]; and (3) production of radioactive progeny is rapid following their decay [6].

Ra isotopes are routinely analyzed in drinking water because they can contribute to radiation dose exposure in humans [10]. Ra is typically present in environmental samples at very low activity concentrations (0.1–1000 mBq·L^{-1}) and is often accompanied by other radionuclides and interferents [11]. Preconcentration and radiochemical isolation are therefore essential steps for ensuring accurate measurement [1]. Spanish Royal Decree 3/2023 mandates the quantification of ^{226}Ra and ^{228}Ra in drinking water when gross alpha or beta activities exceed 0.1 Bq·L^{-1} or 1 Bq·L^{-1}, respectively [12]. This regulation sets detection limits of 0.04 Bq·L^{-1} for ^{226}Ra and 0.02 Bq·L^{-1} for ^{228}Ra. Sensitive analytical methods are therefore required.

Several analytical methods have been developed to determine ^{226}Ra and ^{228}Ra, each of with advantages and limitations. These methods include alpha spectrometry [5, 13], gamma spectrometry [14, 15], liquid scintillation counting (LSC) [16–18] and inductively coupled plasma mass spectrometry (ICP-MS) [19–21].

Alpha spectrometry, which is commonly used for ^{226}Ra detection, offers high sensitivity and low background noise, which makes it ideal for environmental samples with low radioisotope activity concentrations. However, it often requires extensive sample preparation and long counting times. Gamma spectrometry, though non-destructive, enables the direct quantification of ^{228}Ra by measuring its decay product, ^{228}Ac, at

✉ C. Aguilar
carme.aguilar@urv.cat

[1] Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili Unitat de Radioquímica Ambiental i Sanitària (URAIS), Consorci d'Aigües de Tarragona (CAT), Ctra. Nacional 340, Km. 1094, 43895 L'Ampolla, Tarragona, Spain

911.1 keV. As outlined by Medley et al. [22] and Sahin et al. [23], this approach reduces ingrowth time but can exhibit lower sensitivity than alpha spectrometry in certain applications. LSC offers a high and rather constant efficiency facilitated by a 4π arrangement, convenient sample source preparation, and fast-batch measurement capability. Coupling LSC with a pulse-shape analyzer (PSA) has been used as a simple and accurate way to determine ^{226}Ra or ^{228}Ra, since the ingrowth of Ra progeny is not required [24]. ICP-MS provides extremely low detection limits, ensures reliable and reproducible results, enables faster analysis, is able to measure multiple isotopes of radium simultaneously in a single run (thus enhancing efficiency), requires small sample volumes, simplifies sample preparation, reduces radioactive waste, and can meet stringent regulatory requirements. ICP-MS and accelerator mass spectrometry (AMS) have been used on account of their high precision and low detection limits. However, as reported by Guerin et al. [25], they involve expensive instrumentations and labor-intensive sample preparation, which makes them less practical for routine environmental monitoring.

Given the limitations of existing methodologies, such as long preparation times and the need for ingrowth periods, this study aims to develop an improved radiochemical procedure that combines the strengths of alpha and gamma spectrometry while significantly reducing sample handling and analysis time. Specifically, it aims to establish a protocol for the simultaneous isolation and sequential determination of ^{226}Ra and ^{228}Ra in water samples. The innovative aspects of the method include the optimization of microcoprecipitation conditions, specifically the volumes of EDTA and the mass of Ba^{2+}, to maximize radium recovery and improve the resolution of the alpha spectrum. Additional improvements involve the refinement of Pb^{2+} concentration during coprecipitation and the implementation of an enhanced sample preparation protocol. These modifications are addressed to achieve lower detection limits, ensuring compliance with the regulatory thresholds for both ^{226}Ra and ^{228}Ra established by Spanish Royal Decree 3/2023. By overcoming the main limitations of conventional methods, such as lengthy preparation times and the need for extended ingrowth periods, the proposed procedure aims to provide a robust, streamlined and cost-effective analytical solution suitable for both routine monitoring of drinking water or radiological emergencies, where timely and accurate quantification for radium isotopes is crucial.

Experimental

Reagents

All chemicals used in this study were of analytical grade. The reagents included nitric acid (HNO_3, 65%), sulfuric acid (H_2SO_4, 95–97%), barium chloride dihydrate ($BaCl_2{\cdot}2H_2O$), lead nitrate ($Pb(NO_3)_2$), sodium sulfate (Na_2SO_4) and acetic acid (CH_3COOH) all supplied by J.T. Baker® (Deventer, The Netherlands). Ammonium hydroxide (NH_4OH, 25%) was purchased from Honeywell Fluka™ (Seelze, Germany), and EDTA disodium salt dihydrate was purchased from PanReac AppliChem (Darmstadt, Germany). Hydrogen sodium sulfate ($NaHSO_4$) and citric acid were obtained from Chem-Lab (Zedelgem, Belgium). Perchloric acid ($HClO_4$, 70%), as well as the indicators methyl orange and phenolphthalein were purchased from Merck (Darmstadt, Germany). All solutions were prepared using Milli-Q water from a Milli-Q® Reference Water Purification System (Millipore SAS, France) and filtered through 0.45 µm membrane filters (Filter-Lab®, Spain) to remove any insoluble materials. Standard solutions of ^{226}Ra and ^{133}Ba, as well as a gamma-ray radionuclide cocktail (7.8 ± 0.2 Bq of ^{241}Am, 27 ± 0.7 Bq of ^{54}Mn, 77.1 ± 1.9 Bq of ^{65}Zn, 9.5 ± 0.2 Bq of ^{57}Co, 27 ± 0.7 Bq of ^{60}Co, 9.6 ± 0.2 Bq of ^{137}Cs, 42.3 ± 1.1 Bq of ^{113}Sn, 7.8 ± 1.9 Bq of ^{88}Y), were supplied by the Ionising Radiation Metrology Laboratory at Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT, Madrid, Spain).

Instruments

^{226}Ra activity was measured using an Octete Plus® Alpha Spectroscopy Workstation equipped with eight 450 mm^2 ULTRA-AS ion-implanted silicon detectors (AMETEK/ORTEC, Inc., Oak Ridge, TN, USA). Data acquisition and analysis were performed using Maestro software. Detector efficiency calibration was carried out with a standard alpha source containing ^{226}Ra in sulfate form (0.111 Bq) on a polypropylene Resolve® filter (0.1 µm, 25 mm diameter) (Triskem, France) mounted on a stainless-steel disk with a diameter of 25 mm and a thickness of 0.63 mm at a source-detector distance of 5 mm.

^{228}Ra and ^{133}Ba measurements were performed with a high-purity germanium detector (HPGe) (model 2020, Canberra Industries, Meriden, USA) equipped with a standard multichannel analyzer. The measurements were taken under a voltage of 4000 V, and data analysis was conducted using Genie 2000 software (Canberra Industries, Meriden, USA). A gamma-ray radionuclide cocktail covering an energy range of 59.54–1836.07 keV and ^{133}Ba (1.67 Bq) were used to perform the energy and efficiency calibration.

Samples

The method performance was evaluated using 0.5 and 5 L spiked water samples containing known concentrations of

^{226}Ra (0.221 Bq·L^{-1} and 0.0221 Bq·L^{-1}) and a water sample from an intercomparison exercise (IAEA-TEL-2019) organized by the International Atomic Energy Agency (IAEA) with reference activities of 7.5 ± 0.25 Bq·kg^{-1} of ^{226}Ra and 22.08 ± 1.0 Bq·kg^{-1} of ^{228}Ra were used as reference materials. Following verification, the method was applied to analyze bottled mineral water samples from Catalonia (Spain) to determine ^{226}Ra and ^{228}Ra activity concentrations.

Procedure for the coprecipitation and radiochemical isolation of ^{226}*Ra and* ^{228}Ra

The procedure for determining ^{226}Ra and ^{228}Ra was adapted from the Goldin method [26] and optimized to enhance the resolution of alpha spectrometry. As Fig. 1 shows, this process involved three main steps (1) preconcentration, (2) microprecipitation and (3) filtration. Spiked water samples of ^{226}Ra (0.221 Bq·L^{-1} and 0.0221 Bq·L^{-1}) in Milli-Q water with 60 µL of a certified standard solution of ^{226}Ra (1,847 ± 81 Bq·L^{-1}) and a ^{133}Ba tracer (1.67 Bq) were tested to evaluate the radiochemical recovery. After preconcentration, the supernatant was discarded, and the precipitate was transferred to a centrifuge tube using H_2SO_4 0.05 M. To remove interferences from other radionuclides, the precipitate was rinsed with HNO_3 65% and Milli-Q water, and then centrifuged. Microprecipitation was conducted using a seeding suspension of $BaSO_4$ prepared as described by Medley et al. [27]. The filtration process conducted using on Resolve® filters and disposable funnels in a vacuum box system at a flow rate of 5 mL·min^{-1}. After drying, the samples were counted by alpha spectrometry to determine ^{226}Ra and by gamma spectrometry to determine ^{228}Ra and ^{133}Ba with a counting time of 300,000 s per measurement technique.

Optimization of the coprecipitation and microprecipitation conditions

Coprecipitation and microprecipitation conditions were optimized to improve the recovery of ^{226}Ra and the resolution of the alpha spectrum. A three-way ANOVA test was used to evaluate the effects of three factors by measuring the recovery of ^{226}Ra in 0.5 L of spiked Milli-Q water samples with 60 µL of a standard solution of ^{226}Ra (1,847 ± 81 Bq·L^{-1}). The independent factors evaluated were: (1) the mass of Pb^{2+} (factor A) with a = 3 levels (100 mg, 150 mg and 200 mg), (2) the mass of Ba^{2+} (factor B) with b = 2 levels (300 µg and 500 µg) and (3) the volume of EDTA (factor C) with c = 2 levels (10 mL and 20 mL), while assuming an alpha level of 5% for statistical significance. The goal was to maximize radium recovery and resolution of the alpha spectrum. The number of observations for each experiment was n = 2, for a total of N = 24 experiments in the twelve treatment groups or combinations between factors. Seven sets of hypotheses (Table 1) were therefore assessed. In the factorial design 3×2×2, the behavior of the response variable Y (recovery and measured activity of ^{226}Ra) can be described as an effect model where µ represents the overall mean [28].

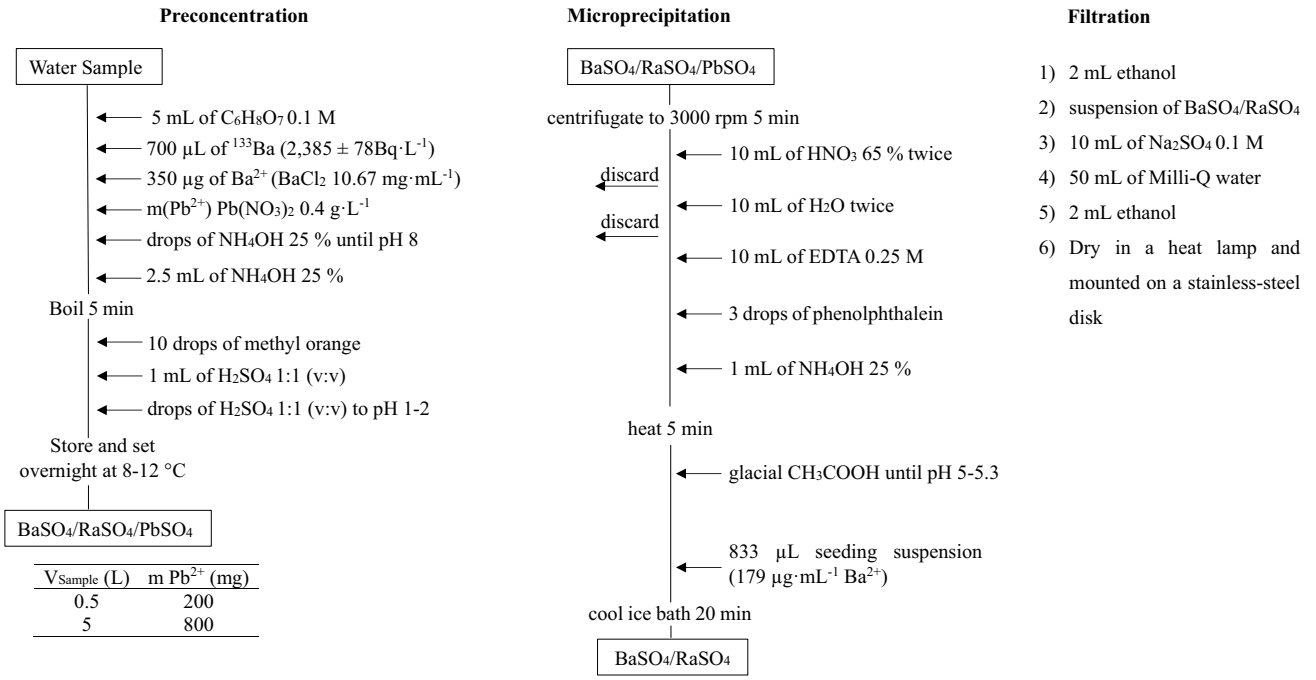

Fig. 1 Scheme of the preconcentration, microprecipitation and filtration steps of the developed method

Counting and activity calculations

Determination of chemical recovery

Chemical recovery (R_{chem}) was calculated by measuring the activity of the ^{133}Ba tracer by gamma spectrometry. For this, the net peak areas of the ^{133}Ba energy lines at 81 keV (34.06%), 302.85 keV (18.33%), 356.02 keV (62.05%) and 383.85 keV (8.94%), were used to calculate the detection efficiency. The counting time was 300,000 s for each sample. The chemical recovery of the analyzed samples was calculated using Eq. (1):

$$R_{chem} = \frac{N_{Ba-133}}{t_s \varepsilon A_{Ba-133}} \quad (1)$$

where $N_{Ba\text{-}133}$ is the net peak area of the ^{133}Ba energy lines, t_s is the sample counting time (s), $A_{Ba\text{-}133}$ is the activity of ^{133}Ba (Bq) and ε is the ^{133}Ba detection efficiency (%). Chemical recovery was averaged over all ^{133}Ba energy lines for each sample to ensure consistency in the calculations.

Alpha and gamma spectrometric analysis and calculation of ^{226}Ra and ^{228}Ra activity concentrations

^{226}Ra activity concentration was determined by alpha spectrometry. To assess the counting efficiency of the detector, a source was prepared following the coprecipitation procedure to obtain Ra in sulfate form. The net peak areas of the ^{226}Ra energy lines at 4784.3 keV (94.07%) and 4601 keV (5.93%) were used to calculate the efficiency and activity concentration in the water samples.

The activity concentration of ^{226}Ra was determined using Eq. (2):

$$A_{Ra-226} = \frac{N_{Ra-226}}{t_s \varepsilon V R_{chem}} \quad (2)$$

where $N_{Ra\text{-}226}$ is the net peak area of the overlapping ^{226}Ra energy lines, t_s is the sample counting time (s), ε is the detector efficiency for ^{226}Ra (26.01%), V is the sample volume (L) and R_{chem} is the chemical recovery (%). The sample counting times ranged from 150,000 to 500,000 s depending on the recovery and the intensity of the peak.

For ^{228}Ra, the activity concentration was determined using gamma spectrometry. The 911.21 keV (26.6%) gamma-ray line of ^{228}Ac was used for this purpose, while taking advantage of the secular equilibrium between ^{228}Ra and ^{228}Ac after a waiting period of approximately three days. The activity concentration of ^{228}Ra in the water sample was determined using Eq. (3):

$$A_{Ra-228} = A_{Ac-228} = \frac{N_{Ac-228}}{t_s \varepsilon f_\gamma V R_{chem}} \quad (3)$$

where $N_{Ac\text{-}228}$ is the net peak area of the 911.21 keV (26.6%) gamma-ray line of ^{228}Ac, t_s is the sample counting time (s), ε is the detector efficiency (%), f_γ is the emission probability of the 911.21 keV gamma-ray line (26.6%), V is the sample volume (L) and R_{chem} is the chemical recovery (%). The measurement time was fixed at 300,000 s.

The uncertainties associated with the ^{226}Ra and ^{228}Ra measurements were calculated considering the main contributors to the uncertainty budget: counting statistics, full energy peak efficiency, chemical recovery, emission probability and the volume of sample.

Minimum detectable activity

Minimum detectable activity (MDA) for both alpha and gamma spectrometry, was calculated using a procedure blank prepared according to the proposed methodology. MDA was calculated following Currie [29] using Eq. (4):

$$MDA = \frac{2.71 + 4.65\sqrt{B}}{t_s \varepsilon V R_{chem}} \quad (4)$$

where B are the background counts in the region of interest (ROI) selected, t_s is the sample counting time (s), R_{chem} is the chemical recovery (%), ε is the detection efficiency (%) and V is the sample volume (L).

Table 1 Sets of hypotheses evaluated

Factors	Null hypothesis (H_0)	Alternative hypothesis (H_a)
A	$\mu_{A1} = \mu_{A2} = \mu_{A2}$	At least one mean difference
B	$\mu_{B1} = \mu_{B2}$	$\mu_{B1} \neq \mu_{B2}$
C	$\mu_{C1} = \mu_{C2}$	$\mu_{C1} \neq \mu_{C2}$
Interactions (AB, AC, BC, ABC)	There is no interaction between the factors	There is an interaction between the factors

Results and discussion

This section presents the optimization of conditions for determining ^{226}Ra and ^{228}Ra in water samples from a three-way ANOVA test and method verification using spiked water samples and a water sample from the IAEA intercomparison exercise. The initial conditions were established according to the classical method used in the URAIS laboratory (Goldin method) [26] for quantifying ^{226}Ra by ZnS(Ag) and modified

in order to develop this method. The optimized method has been applied to bottled mineral water samples.

Optimization of the coprecipitation and microprecipitation conditions

The coprecipitation and microprecipitation steps were optimized to enhance radium recovery and improve resolution of the alpha spectrum. A three-way ANOVA was performed to evaluate the effects of (1) the mass of Pb^{2+} (100 mg, 150 mg and 200 mg), (2) the mass of Ba^{2+} (300 µg and 500 µg) and (3) the volume of EDTA (10 mL and 20 mL) on ^{226}Ra recovery. A total of 24 spiked Milli-Q water samples (0.5 L each with an activity concentration of 0.221 $Bq{\cdot}L^{-1}$ of ^{226}Ra) were analyzed to assess the effects of these factors and their interactions. Table 2 shows the statistical results for each factor and their interactions, including Sum of Squares (SS), degrees of freedom (d_f), Mean Squares (MS), F-ratios, F-critic provided by the FDIST function (normal distribution function) and p-values calculated with a 95% confidence interval.

The null hypothesis was evaluated using the F-test and p-value to determine whether it should be accepted or rejected. The null hypothesis proposed that the total mean for all treatments is equal, which would indicate no variation in treatment means. The alternative hypothesis predicted that at least one treatment will significantly differ on average. ANOVA results showed that the first two critical factors – the mass of Pb^{2+} (effect A) and the mass of Ba^{2+} (effect B) – as well as their interactions (effect AB), significantly influenced recovery, as was indicated by the F-ratios being greater than the critical F-value and the p-value being lower than 0.05.

The null hypothesis was therefore rejected. The interaction graph in Fig. 2 illustrates the combined effect of the Pb^{2+} and Ba^{2+} masses. It shows that the optimal conditions for the highest recovery were achieved with 200 mg of Pb^{2+} and 500 µg of Ba^{2+}, which yielded recoveries of between 50 and 60%. This result aligns with the findings of Guerin et al. [5], who reported similar dependencies of radium recovery on coprecipitation mass. However, our study further demonstrated that while a higher Pb^{2+} mass enhanced recovery, excessive barium could lead to broader alpha peaks due to self-absorption effects. This emphasizes the need to balance these parameters for optimal performance. Other studies, such as that by Sahin et al. [13] used a lower Pb concentration (0.01 $g{\cdot}L^{-1}$) but their small precipitate size increased the risk of loss during handling, which compromises reliability.

The third critical factor examined in our study is the volume of EDTA. As Fig. 2B and 2C show, using either 10 mL or 20 mL of EDTA along with the optimal conditions for the best recovery (200 mg of Pb^{2+} and 500 µg of Ba^{2+}), did not significantly affect the recovery value but did significantly affect spectrum resolution. Our results align with previous research by Guerin et al. [3], who found a linear decrease in Ra recovery with increasing EDTA volumes in the 10–50 mL range, with 10 mL being the optimal volume.

As Fig. 3A and 3B show, the alpha spectra deteriorated when the EDTA volume was increased from 10 to 20 mL, both measured over 300,000 s. This could be attributed to the formation of a thicker layer of microprecipitate on the filter, which leads to the energy attenuation of alpha particles. Based on these findings, 10 mL of EDTA was selected as the optimal volume for this study.

To sum up, for 0.5 L volume samples, the optimal conditions for maximizing ^{226}Ra recovery and obtaining alpha spectra with good resolution were 200 mg of Pb^{2+}, 500 µg of Ba^{2+}, and 10 mL of EDTA. Based on the ANOVA results from the 0.5 L samples, for 5 L volume samples the optimal conditions were adjusted to 800 mg of Pb^{2+}, 500 µg of Ba^{2+}, and 20 mL of EDTA. These adjustments helped to obtain lowers MDA values for both ^{226}Ra and ^{228}Ra.

Method verification

The presented method was verified through duplicate analyses of 0.5 L and 5 L spiked water samples with ^{226}Ra and water samples from an intercomparison exercise organized

Table 2 Three-way ANOVA results for the recovery response (%)

Source	SS	d_f	MS	F-calculated	F-critic	p-value	Significance
Effect A	3559.2	2	1779.6	24.11	3.8853	0.0001	Significant
Effect B	399.3	1	399.3	5.41	4.7472	0.0384	Significant
Effect C	51.9	1	51.9	0.70	4.7472	0.4181	Not significant
Effect AB	688.6	2	344.3	4.66	3.8853	0.0317	Significant
Effect AC	33.5	2	16.7	0.23	3.8853	0.8004	Not significant
Effect BC	70.7	1	70.7	0.96	4.7472	0.3472	Not significant
Effect ABC	182.5	2	91.3	1.24	3.8853	0.3250	Not significant
Error	885.8	12	73.8				
Total	5871.5	23					

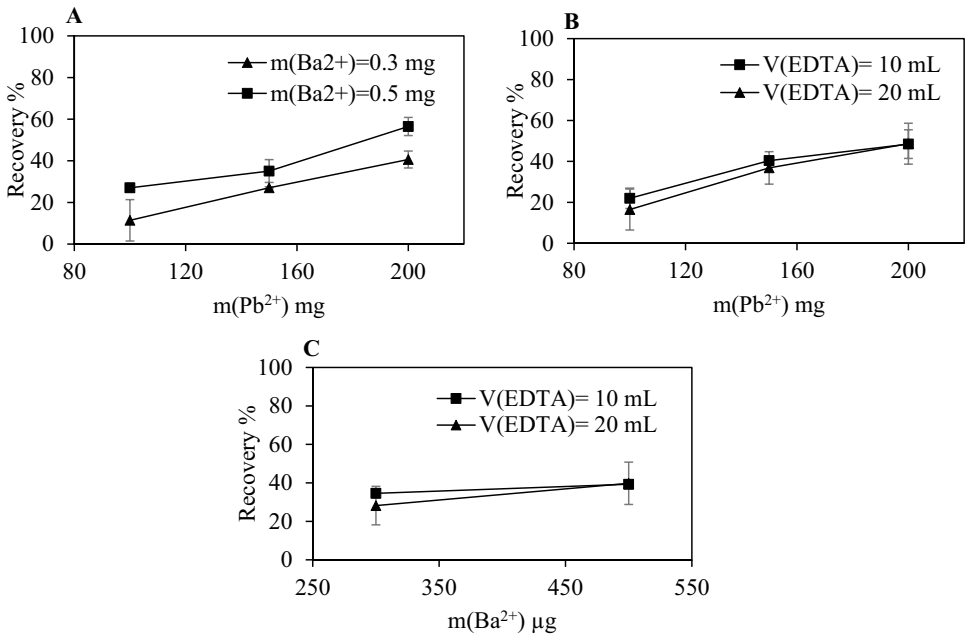

Fig. 2 Recovery response from the interaction between factors. **A** interaction graph effect AB (mass of Pb^{2+} and Ba^{2+}); **B** interaction graph effect AC (mass of Pb^{2+} and V(EDTA)); and **C** interaction graph effect BC (mass of $Ba.^{2+}$ and V(EDTA))

by IAEA in 2019 containing ^{226}Ra and ^{228}Ra in different ranges of activity concentrations. These reference materials used, although not certified, provided traceable and well-characterized values suitable for method verification. The IAEA intercomparison sample was diluted at 1:50 and 1:500 ratios to simulate environmental radium activity concentrations.

Method performance was evaluated in terms of precision, accuracy, and MDA, with results summarized in Table 3. Precision and accuracy were calculated using relative standard deviation (RSD) and relative bias (RB), respectively. The MDA was calculated according to the Currie criteria (Eq. 4). Results were analyzed according to the acceptance criteria for precision and accuracy established by the URAIS laboratory and taking into account the assay characteristics [30]. Values of 30% for an activity concentration of 1–10 MDA ($Bq{\cdot}L^{-1}$) and 25% for an activity concentration above 10 MDA ($Bq{\cdot}L^{-1}$) were used as the acceptance criteria for method verification [30].

According to RSD and RB values, all results were in the range for the acceptance criteria established by the URAIS laboratory (< 25%) [30]. A sample volume of 5 L used to determine ^{226}Ra and ^{228}Ra significantly improved the MDA values, which is especially important for ensuring that the analysis satisfies the regulatory limits set by Spanish Royal Decree 3/2023. This approach therefore satisfies the required detection thresholds for both radionuclides in drinking water samples from sequential analysis of the same sample and a sample counting time of 300,000 s for α and γ-spectrometry. These metrics are comparable to those reported by Sahin et al. [13], who obtained MDA values of 0.3 $mBq{\cdot}L^{-1}$ and 87 $mBq{\cdot}L^{-1}$ for radiochemical analyses of ^{226}Ra and ^{228}Ra in water samples by microprecipitation with $BaSO_4$ without using a seeding suspension.

These results were lower than those obtained by Guérin et al. [5] and higher than our results, but with a lower of the alpha spectrum resolution compared to obtained using the method developed in this study. By enabling simultaneous quantification of both isotopes, our method reduces analysis time and complexity. Moreover, the low MDA shows that it is also a sensitive tool for the routine and regulatory monitoring of drinking water, especially in low-activity scenarios.

Evaluation of the results by comparing methods

To further evaluate this method's efficacy, an analysis was conducted to compare this method with the one traditionally used in our laboratory and based on the modified Goldin method. Specifically, the method's performance was assessed in water samples labeled IAEA 1, IAEA 2 and IAEA 3 (dilutions of a water sample from an IAEA intercomparison exercise, as shown in Table 3). The results of this assessment were compared to those when the modified Goldin method was applied to the same undiluted IAEA intercomparison water sample (IAEA 4). In this case, ^{226}Ra was determined using ZnS(Ag), and ^{228}Ra was determined by directly measuring a 0.5 L-sample in a Marinelli vessel using gamma spectrometry. The statistical parameters used to perform this comparative analysis between these two methods (Z-score, u-value and RB in accordance with IAEA criteria for accepting measurements results) are shown in Fig. 4 for ^{226}Ra and in Fig. 5 for ^{228}Ra. Figures 4A and 5A show Z-scores resulting from the determination of ^{226}Ra and ^{228}Ra using these methods. These Z-scores ranged from

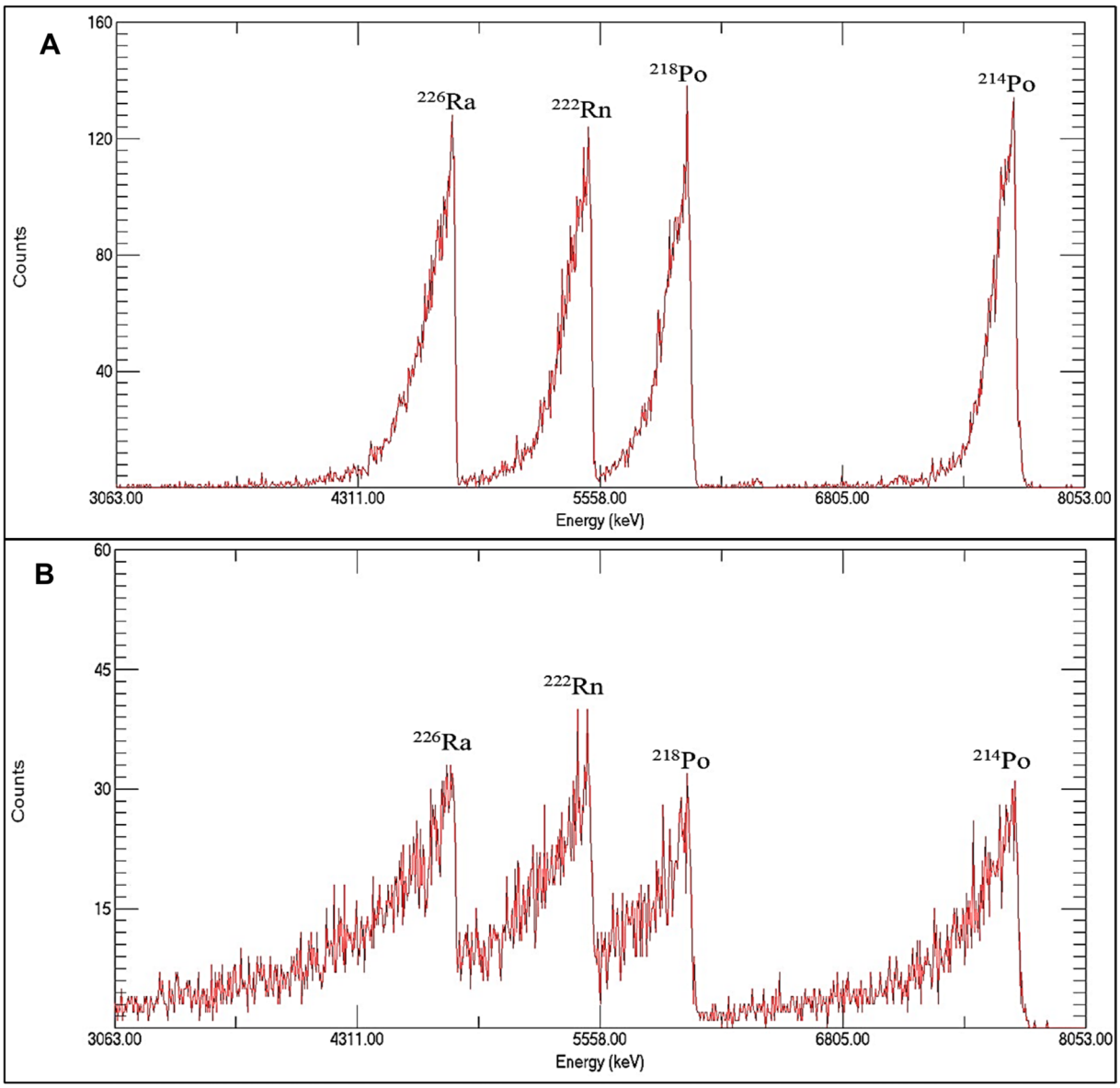

Fig. 3 Alpha spectrum of a spiked sample of Milli-Q water, m(Pb^{2+}) = 200 mg, m(Ba^{2+}) = 500 µg, V_{sample} = 0.5 L and **A** 10 mL of EDTA and **B** 20 mL of EDTA

−0.57 to 1.23 for ^{226}Ra and from −0.58 to −0.3 for ^{228}Ra. According to the acceptance criteria (Z-scores between −2 and +2), these results indicate that both the method developed in this study as well as the classical method are suitable since they provide satisfactory performance. Figures 4B and 5B show the *u*-values calculated from the ^{226}Ra and ^{228}Ra determination for each method. These ranged from 0.25 to 1.21 for ^{226}Ra and from 0.22 to 0.46 for ^{228}Ra. Since the acceptance criteria require u-values of ≤2.58, the results from both methods again meet the required accuracy standards. Finally, Figs. 4C and 5C show the RB values, which indicate the deviation from reference values of the results obtained when determining ^{226}Ra and ^{228}Ra with each method. Since all RB values were below 25%, the results fell within the laboratory's acceptance criteria for each method [30]. Both methods are therefore suitable for determining ^{226}Ra and ^{228}Ra. However, the method we present in this study has several advantages: (1) a relatively fast assay (two days 'preparation time), (2) shorter counting times for both radionuclides measured by alpha and gamma spectrometry (300,000 s), and (3) a smaller sample volume of 5 L. With the classical method, on the other hand, more preparation time is required since the measurements are performed from different assays of the sample (two days for ^{226}Ra sample preparation and three days for ^{228}Ra). Longer counting times are also required (10 days for ^{226}Ra because ^{224}Ra

Table 3 Results of method verification for determining ^{226}Ra and ^{228}Ra in water samples

Sample (n = 2)	Volume (L)	Radionuclide	Certified activity (mBq·L^{-1})	Measured activity (mBq·L^{-1})	R_{chem} (%)	RSD (%)	RB (%)	MDA (mBq·L^{-1})
Spiked 1	0.5	^{226}Ra	221 ± 7	218 ± 5	53 ± 4	2	–2	0.7 ± 0.2
Spiked 2	5		22 ± 1	17 ± 2	55.4 ± 0.1	12	–23	0.06 ± 0.01
IAEA 1[a]	0.5		15.0 ± 0.5	13 ± 2	60.6 ± 0.3	12	–12	0.42 ± 0.02
IAEA 2[b]	0.5		150 ± 5	187 ± 14	52 ± 3	8	24	0.92 ± 0.03
IAEA 3[a]	5		15.0 ± 0.5	16.4 ± 0.8	54 ± 2	5	9	0.11 ± 0.02
IAEA 1[a]	0.5	^{228}Ra	44 ± 2	< MDA	60.6 ± 0.3	-	-	194 ± 47
IAEA 2[b]	0.5		442 ± 20	429 ± 90	52 ± 3	21	–3	195 ± 1
IAEA 3[a]	5		44 ± 2	44 ± 9	54 ± 2	20	–2	24 ± 2

[a]Samples obtained by diluting IAEA-2019-TEL sample to 1:500

[b]Sample obtained by diluting IAEA-2019-TEL sample to 1:50

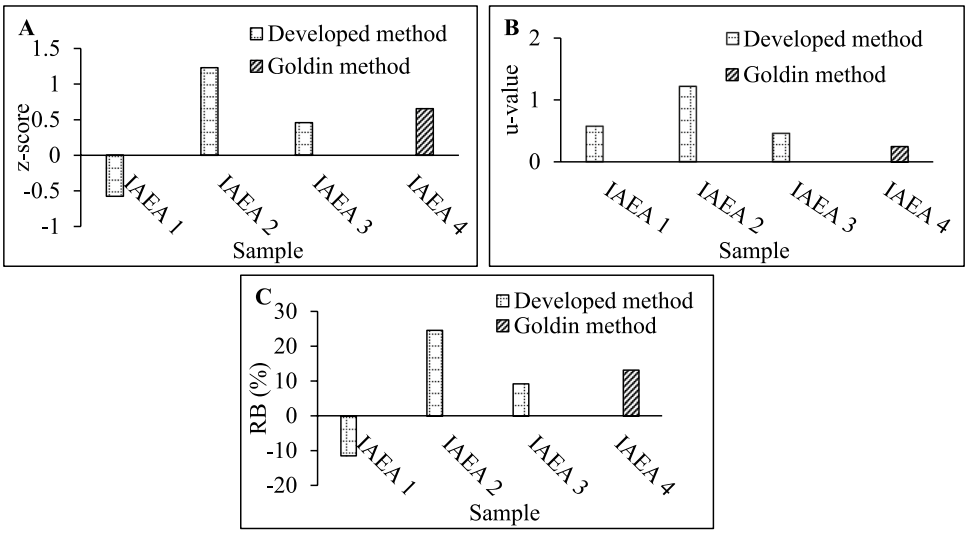

Fig. 4 Graphic view of **A** z-scores, **B** *u*-values and **C** RB for ^{226}Ra determined in IAEA intercomparison water samples by the developed method and the modified Goldin method

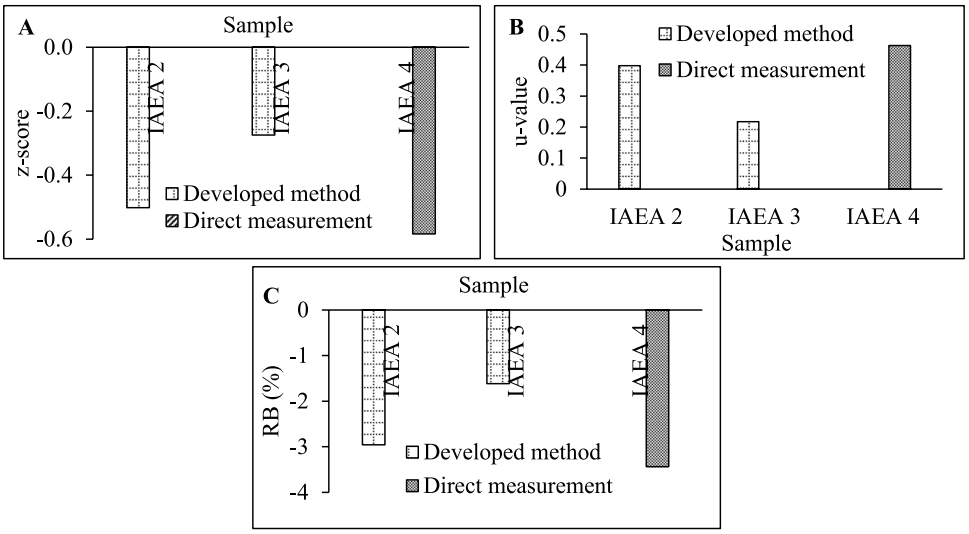

Fig. 5 Graphic view of **A** z-scores, **B** *u*-values and **C** RB for ^{228}Ra determined in IAEA intercomparison water samples by the developed method and the modified Goldin method. Sample IAEA 1 was not assessed in this figure because ^{228}Ra activity was below MDA

determination by ZnS(Ag) is required first, and seven days for ^{228}Ra measurement by gamma spectrometry). The classical method also uses a larger sample volume: 0.5 L for ^{226}Ra and 6 L for ^{228}Ra.

Compared to other radium quantification methods, the method developed in this paper offers several advantages while also addressing key limitations of existing approaches for the simultaneous or sequential determination of ^{226}Ra and ^{228}Ra in water samples [13, 18, 31–35]. Classical methods usually require lengthy ingrowth periods to enable equilibrium between ^{226}Ra and ^{222}Rn, which significantly delays analysis. Similarly, ^{226}Ra by gamma ray spectrometry [31, 32] is measured indirectly by analyzing the photopeaks of the radon daughters ^{214}Bi and ^{214}Pb. As this requires a secular equilibrium, a waiting period of roughly one month is needed before counting. These time constraints make such methods impractical for routine or emergency applications. LSC is often used in environmental samples for simultaneously measuring ^{226}Ra and ^{228}Ra radioisotopes [36]. However, it has drawbacks such as quenching, low energy resolution, relatively high background radiation, acceptable detection limits and the need for a large sample. In the method developed in this paper, no specialized resins are needed because Pb(Ba)SO_4 coprecipitation and $BaSO_4$ microprecipitation are simple and cost-effective and avoid dependence on a single source supplier, unlike methods that use resins [33–35].

Unlike the classical methods, this method achieves lower MDA values for the determination of ^{226}Ra (0.11 mBq·L^{-1}) and ^{228}Ra (24 mBq·L^{-1}) from 5 L water samples and does not require long periods for the ingrowth of radioactive materials, thus enabling rapid quantification from a relatively cheap and accurate procedure for concentration and sample measurement. Lower time measurements are required by LSC and GPC (gas proportional counting), but the availability of the resins limits the use of these methods.

Application of the method in mineral water samples

Applicability of the method developed in this paper was demonstrated by analyzing 10 bottled mineral water samples from different brands in Catalonia (Spain) that exceeded the gross alpha parametric value (0.1 Bq·L^{-1}). These samples were selected based on a previous study in our laboratory by Martínez et al. [37], that focused on the radiological characterization of bottled mineral water samples under Spanish Royal Decree 3/2023, from Catalan aquifers with different lithological (sedimentary, metamorphic or granitic) characteristics and purchased from local supermarkets in the Tarragona area.

Table 4 presents the results only for analyzed bottled natural mineral water samples with the highest levels of ^{226}Ra. The activity concentration of ^{226}Ra in the samples ranged from 13.0 to 18.1 mBq·L^{-1} and RSD was below 5.7%, which demonstrates the method's precision when applied to real samples. No detectable activity concentration of ^{228}Ra was found in these samples, as their activities were below the MDA of 20 mBq·L^{-1}, which is in compliance with the regulatory limits established by Spanish Royal Decree 3/2023. These results are consistent with previous findings from Martínez et al. [37] and Palomo et al. [38] in bottled drinking water samples from similar regions of Catalonia.

Table 4 Results of the determination of ^{226}Ra and ^{228}Ra in drinking water samples

Sample (n = 2)	^{226}Ra activity (mBq·L^{-1})	RSD (%)	^{228}Ra activity (mBq·L^{-1})
S1.1[a]	13.0 ± 0.7	5.5	< MDA
S1.2[a]	13.7 ± 0.8	5.2	< MDA
S2	18.1 ± 0.1	5.7	< MDA

[a]Results from two batches from the same brand purchased 6 month apart

Conclusions

The effect of critical parameters: m(Pb^{2+}), m(Ba^{2+}) and V(EDTA) in the coprecipitation and microprecipitation steps were studied and optimized using a three-way ANOVA assay to improve radium recovery and alpha spectrum resolution. During the ANOVA based optimization phase, the recovery range varied relatively widely between 35–60%. This result was found to be mainly influenced by the mass of lead and barium used in the procedure. Following method optimization, recovery results consistently ranged between 50–60% in both reference materials and mineral water samples, highlighting the method's reproducibility and robustness.

The method developed addresses several challenges in radium isotope analysis, and offers a rapid, cost-effective and environmentally sustainable alternative to traditional methods. Its ability to achieve MDA lower than those required by Spanish Royal Decree 3/2023 without requiring lengthy ingrowth periods, makes it particularly valuable for routine drinking water monitoring and emergency response scenarios.

Acknowledgements The authors would like to thank the Consorci d'Aigües de Tarragona (CAT) for their invaluable collaboration. These results are part of the project PIA 2023-148939 NB-I00.

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature.

Declarations

Conflict of interest The authors declare that there are no conflicts of interest regarding the publication of this article.

References

1. Thakur P, Ward AL, González-Delgado AM (2021) Optimal methods for preparation, separation, and determination of radium isotopes in environmental and biological samples. J Environ Radioact 228:1–22. https://doi.org/10.1016/j.jenvrad.2020.106522
2. Suárez-Navarro JA, Expósito-Suárez VM, Crespo MT, Sánchez-Castaño B, Suárez-Navarro MJ, Gascó C, Barragán M, Gascón JL, Pecker R (2022) Improvements in the radiochemical method for separating 226Ra in solid samples through coprecipitation with BaSO4. Appl Radiat Isot 187:110321. https://doi.org/10.1016/j.apradiso.2022.110321
3. LNE-LNHB/CEA-Table de radionucléides, 226Ra. http://www.lnhb.fr/nuclides/Ra-226_tables.pdf. Accessed 06 May 2025
4. LNE-LNHB/CEA-Table de radionucléides, 228Ra. http://www.lnhb.fr/nuclides/Ra-228_tables.pdf. Accessed 06 May 2025
5. Guérin N, Behm D, Leppinen J, Gagné A (2023) Determination of 226Ra in environmental samples by alpha spectrometry: a new separation method based on the rapid co-precipitation of 226Ra with PbSO4. J Radioanal Nucl Chem 332:4311–4323. https://doi.org/10.1007/s10967-023-09130-w
6. Jia G, Jia J (2012) Determination of radium isotopes in environmental samples by gamma spectrometry, liquid scintillation counting and alpha spectrometry: a review of analytical methodology. J Environ Radioact 106:98–119. https://doi.org/10.1016/j.jenvrad.2011.12.003
7. Vukanac I, Šešlak B, Kandić A, Čeliković I, Nikolić NM, Milanović T, Obradović Z, Đurašević M (2022) A comparison of alpha-particle and gamma-ray spectrometry methods for determination of 235U, 238U and 226Ra activity concentration in samples of coal, slag and fly-ash. Radiat Phys Chem 193:1–7. https://doi.org/10.1016/j.radphyschem.2021.109933
8. Vasile M, Benedik L, Altzitzoglou T, Spasova Y, Wätjen U, González de Orduña R, Hult M, Beyermann M, Mihalcea I (2010) 226Ra and 228Ra determination in mineral waters—Comparison of methods. Appl Radiat Isot 68:1236–1239. https://doi.org/10.1016/j.apradiso.2009.11.018
9. Rodríguez R, Borràs A, Leal L, Cerdà V, Ferrer L (2016) MSFIA-LOV system for 226 Ra isolation and pre-concentration from water samples previous radiometric detection. Anal Chim Acta 911:75–81. https://doi.org/10.1016/j.aca.2016.01.004
10. Zawadzki A, Cook M, Cutmore B, Evans F, Fierro D, Gedz A, Harrison JJ, Loosz T, Medley P, Mokhber-Shahin L, Mullins S, Sdraulig S (2017) Comparison of radium-228 determination in water among Australian laboratories. J Environ Radioact 178–179:411–418. https://doi.org/10.1016/j.jenvrad.2017.05.012
11. Carvalho FP, Fesenko S, Harbottle AR, Lavrova T, Mitchell NG, Payne TE, Rigol A, Thorne MC, Ulanowski A, Vidal M, Voitsekhovych O, West JM, Yankovich T (2023) The Environmental Behaviour of Uranium. International Atomic Energy Agency, Vienna
12. RD 3/2023 (2023) Real Decreto 3/2023, de 10 de enero, por el que se establecen los criterios técnico-sanitarios de la calidad del agua de consumo, su control y suministro. Boletín Oficial del Estado, número 9. Madrid 12 de enero de 2023.
13. Şahin M, Dikmen H (2023) Validation of a newly adopted chemical method for determination of 226Ra and 228Ra activities in water and shrimp samples. J Radioanal Nucl Chem. https://doi.org/10.1007/s10967-023-09126-6
14. Suárez-Navarro JA, Benavente JF, Expósito-Suárez VM, Caño A, Hernaiz G, Alonso MM (2024) 226Ra activity concentration determined directly from the 186 keV photopeak using gamma spectrometry and a neural network. Radiat Phys Chem 217:1–11. https://doi.org/10.1016/j.radphyschem.2023.111486
15. Vuong LQ, Chuong HD, Nguyen VH, Hung NQ, Thanh TT, Van Tao C (2017) Revision of nuclear data of 235U and 226Ra for the 186-keV gamma-ray peak for the determination of activity in environmental samples. J Radioanal Nucl Chem 314:1273–1277. https://doi.org/10.1007/s10967-017-5461-1
16. Zheng Q, Zhang Y, Yin L, Qian Y, Ji Y (2024) Simultaneous determination of 226Ra and 228Ra in food samples using liquid scintillation counting. Food Chem 438:1–9. https://doi.org/10.1016/j.foodchem.2023.137998
17. Canepa C, Benzi P, Marabello D (2022) The dynamics of the detection of 226Ra in water by scintillation counting in nonequilibrium conditions. J Environ Radioact 251–252:1–7. https://doi.org/10.1016/j.jenvrad.2022.106970
18. Xia M-M, Liang Y-G, Yu G-B, Zhu J-P, Cheng S-S, Tian C, Xu T, Wu Y-R (2020) Simultaneous determination of Ra-226 and Ra-228 in water using spectrum stripping method by LSC. J Radioanal Nucl Chem 326:115–120. https://doi.org/10.1007/s10967-020-07291-6
19. Roulier M, Baya PA, Roberge S, Larivière D (2024) Comparison of radium-226 separation methods based on chromatographic and extraction resins for its determination by ICP-MS in drinking waters. J Mass Spectrom 59:1–10. https://doi.org/10.1002/jms.5005
20. Yuan L, Cai P, Jiang X, Geibert W, Cheng Y, Chen Y (2023) Precise measurement of 226Ra/230Th disequilibria in deep-sea sediments by high-sensitivity ICP-MS. Chem Geol 620:1–9. https://doi.org/10.1016/j.chemgeo.2023.121351
21. Boudias M, Gourgiotis A, Montavon G, Cazala C, Pichon V, Delaunay N (2022) 226Ra and 137Cs determination by inductively coupled plasma mass spectrometry: state of the art and perspectives including sample pretreatment and separation steps. J Environ Radioact 244–245:1–34. https://doi.org/10.1016/j.jenvrad.2022.106812
22. Medley P, Martin P, Bollhöfer A, Parry D (2015) 228Ra and 226Ra measurement on a BaSO4 co-precipitation source. Appl Radiat Isot 95:200–207. https://doi.org/10.1016/j.apradiso.2014.09.015
23. Şahin M, Dirican A, Şahin NK (2017) Radiochemical separation and determination of radium-228 in bottled mineral waters by low level gamma spectrometry and its committed effective dose. Environ Earth Sci. https://doi.org/10.1007/s12665-017-7147-y
24. Abbasi A (2018) A review of the analytical methodology to determine Radium-226 and Radium-228 in drinking waters. Radiochim Acta 106:819–829. https://doi.org/10.1515/ract-2018-2967
25. Guérin N, McMullin D, Fabian X, Kramer-Tremblay S, Gagné A, Gale A (2019) Routine method for the determination of trace

amounts of 226Ra in urine by alpha spectrometry. Radiat Prot Dosimetry 187:174–182. https://doi.org/10.1093/rpd/ncz152
26. Goldin AS (1961) Determination of Dissolved Radium. Anal Chem 33:406–409. https://doi.org/10.1021/ac60171a030
27. Medley P, Bollhöfer A, Iles M, Martin P (2005) Barium sulphate method for radium-226 analysis by alpha spectrometry. Internal Report 501, June, Supervising Scientist Darwin
28. Bathke A (2004) The ANOVA F test can still be used in some balanced designs with unequal variances and nonnormal data. J Stat Plan Inference 126:413–422. https://doi.org/10.1016/j.jspi.2003.09.010
29. Currie LA (1968) Limits for qualitative detection and quantitative determination. Application to radiochemistry. J Anal Chem 40:586–593
30. Ortiz Moragón J (2012) Criterios desarrollados para la validación de procedimientos. In: VII Jornadas sobre Calidad en el Control de la Radiactividad Ambiental. Tarragona, pp 135–144
31. Ho PL, Minh VT, Hung LD, Trung DQ, Chinh DV, Thanh TT, Tao CV (2019) Assessment of annual effective dose from radium isotopes in groundwater samples in households along the lower Mekong River. J Radioanal Nucl Chem 322:503–511. https://doi.org/10.1007/s10967-019-06699-z
32. Bhangare RC, Sahu SK, Maity S, Ajmal PY, Rathod TD, Tiwari M, Pandit GG (2017) Method for determination of radium in seawater using MnO2 co-precipitation technique. J Radioanal Nucl Chem 313:597–601. https://doi.org/10.1007/s10967-017-5308-9
33. Fons-Castells J, Oliva J, Tent-Petrus J, Llauradó M (2017) Simultaneous determination of 226Ra, 228Ra and 210Pb in drinking water using 3M Empore™ RAD disk by LSC-PLS. Appl Radiat Isot 124:83–89. https://doi.org/10.1016/j.apradiso.2017.03.016
34. Vasile M, Loots H, Jacobs K et al (2016) Determination of 210Pb, 210Po, 226Ra, 228Ra and uranium isotopes in drinking water in order to comply with the requirements of the EU "Drinking Water Directive." Appl Radiat Isot 109:465–469. https://doi.org/10.1016/j.apradiso.2015.11.076
35. Maxwell SL (2006) Rapid method for 226 Ra and 228 Ra analysis in water samples. J Radioanal Nucl Chem 270:651–655
36. Wallner G, Herincs E, Ayromlou S (2008) Determination of natural radionuclides in drinking water from the Waldviertel, Austria. In: J Eikenberg, M Jäggi, H Beer, H Baehrle (eds) LSC 2008, advances in liquid scintillation spectrometry. Radiocarbon, pp 345–352
37. Martínez J, Peñalver A, Riu J et al (2024) Radiological characterization related to lithology and risk assessment of bottled natural mineral water. Environ Monit Assess 196:1169. https://doi.org/10.1007/s10661-024-13353-z
38. Palomo M, Peñalver A, Borrull F, Aguilar C (2007) Measurement of radioactivity in bottled drinking water in Spain. Appl Radiat Isot 65:1165–1172. https://doi.org/10.1016/j.apradiso.2007.04.022