Original Article

A comparative study of different radiometric methodologies for the determination of ^{226}Ra in water

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ABSTRACT

An evaluation of various radiometric methods to analyze ^{226}Ra in water has been employed on a set of 10 standard solutions of different concentrations in the range of $1-10$ Bq/L^{-1}. The analysis was carried out using well-established procedures by means of gamma-ray, alpha-particle and liquid scintillation spectrometry. The feasibility of the various methods has been quantified in terms of relative standard error and percentage error. Correlations between the various methods have been presented and discussed. In general, good agreement was found in the results of various methodologies, which assures the accuracy of the methods and allows for the validation of instrumentation and procedures. Of the different methods adopted here, a combined procedure for the determination of ^{226}Ra along with ^{228}Ra using Quantulus 1220 ultra-low level background liquid scintillation counting gave the most accurate results.

1. Introduction

Water is one of the prime elements for radiometric investigations and consequent assessment of health impact. Among natural radionuclides, ^{226}Ra is the most common one that can be present in water, either natural or surface, in a wide range of concentrations. The concern about ^{226}Ra stems from the fact that it has been identified as a significant source of environmental pollution caused by nuclear and/or nonnuclear applications. ^{226}Ra has high radiotoxicity, long half-life, permanent presence in nature, and high dose conversion factor [1]. ^{226}Ra is an alpha-emitter, belonging to the natural series of uranium, with main emissions of 4.7844 MeV (94.45%), 4.6011 MeV (5.55%), and many other minor emissions, besides its gamma-ray emission at 186.1 keV (3.5%). Like other radium isotopes, ^{226}Ra can be easily incorporated into bones because of its physiological and chemical similarity to calcium and barium [2]. Thus, consumption of food or water contaminated with radium leads to accumulation of short-lived progenies of ^{226}Ra in the human body [3,4] and contributes to radiological dose.

Moreover, ^{226}Ra is an important key radionuclide to be evaluated for water supplies from a radiological point of view (US EPA 2003, [5]). This motivates research to determine the activity concentration of ^{226}Ra along with those of other radionuclides in water and other environmental samples.

Usually, monitoring of the ^{226}Ra radiation exposure risk along the water pathway requires accurate determination close to the detection limit. A survey of the literature shows that several techniques have been employed to determine ^{226}Ra concentration in water. Commonly used methodologies are based on direct measurements by α-particle (e.g., [6–8]; and/or γ-ray emissions of ^{226}Ra (e.g., [9–11]). Moreover, measurements of α-particle (^{222}Rn, ^{218}Po, and ^{214}Po), β-particle (^{214}Pb and ^{214}Bi), and γ-ray emissions (^{214}Pb and ^{214}Bi) allow indirect determinations of ^{226}Ra (e.g., [12–14]) via its progenies when radioactive equilibrium has occurred.

In the present study, the application of various methodologies to determine ^{226}Ra concentration in water by means of alpha-particle, gamma-ray, and liquid scintillation spectrometry has been investigated. The use of standard solutions containing ^{226}Ra at known concentrations is appropriate to test the validity and performance of the analytical method. Therefore, the prescribed procedures have been applied to standard solutions of various concentrations of

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226Ra. The results of these methodologies have been validated by comparing them with each other and with the theoretical concentrations in the investigated standard solutions. This comparison was carried out in terms of activity concentrations, minimum activity concentration, relative standard deviation (RSD), and percentage error (PE). The motivation to conduct these experiments was to check the accuracy of the methods, results, and adequate operation of the equipment. The suitability of each analytical approach used in this work has also been explored.

2. Sample preparation of 226Ra

A 3-L bottle of distilled water was spiked with a high-purity 226Ra standard source of 20 Bq/mL^{-1} activity, procured from the National Institute for Standards and Technology (NIST), USA, and the solution was homogenized. For 226Ra analysis, 10 standard solutions were prepared with an activity range of 1–10 Bq/L^{-1} and uncertainty less than 10%. Table 1 shows the activity concentration of each 226Ra standard solution. Appropriate aliquots of each standard solution were distributed using the various analytical methods, depending on the method used to measure 226Ra.

3. Methods of 226Ra determination

3.1. Determination of 226Ra using alpha spectrometry

As an α-particle emitter, 226Ra can be directly measured by alpha spectrometry. In the literature, it was reported that α spectrometry after chemical separation is one of the best techniques for 226Ra analysis in terms of accuracy and minimum detection limit [11]. The method of 226Ra determination by alpha spectrometry (referred to as "α-226Ra") adopted here is rapid (3 days) and direct. Following the procedure developed by Chalupnik and Lebecka [6] and used previously by Alkhomashi et al. [8], about 250 mL of each standard solution was taken in a 400 mL glass beaker and preserved by adding 10M of HCl (pH: 1.5–3) and 1 mL aliquot of the tracer 133Ba. The sample was then evaporated on a hot plate to about 40 mL, and drops (about 3 mL) of 1:1 sulfuric acid (H_2SO_4) and 5 g of potassium sulfate (K_2SO_4) were added to the sample while it was on the heater at 120°C with stirring to dissolve materials and yield a clear solution. After that, 3 mL of lead carrier perchlorate $Pb(ClO_4)_2$ was slowly added 1 mL by 1 mL with stirring while on hot plate until a cloudy solution appeared. The solution was left on the heater for some time until it precipitated to the bottom of the beaker. The supernatant with the precipitate was then transferred to a centrifuge for 10 minutes at 3000 rpm. The precipitate formed in the last process was dissolved in 3 mL of 0.1M of alkaline diethylenetriaminepentaacetic acid. In case the solution is acidic and not dissolved, drops of 10M of NaOH were added. To obtain a yellow

color of the alkaline medium, an indicator of methyl red (about 12 μg) was added to the solution and then 100 μL of barium carrier and drops of 1:1 acetic acid were also added. The sample was then kept in cold water and ice for about 30 minutes and filtered using a 0.10 μm polyethylene membrane filter; it was then analyzed for 226Ra activity (at 4.776 MeV) using an alpha spectrometer. The chemical recovery of 226Ra was calculated by using an High purity Germanium (HPGe) detector to count the photopeak (at 356 keV) of the 133Ba tracer produced from the centrifuging process.

After chemical separation, 226Ra was directly determined by means of an ORTEC alpha spectrometry system that consists of 16 Si(Au) surface barrier detectors, which have the advantage of having low-background efficiencies ranging from 24.78% to 27.75% and high sensitivity. The lower limit of detection (LLD) achieved for a counting time of 18 h and sample size of 100 mL was 0.019 Bq/L^{-1}, calculated based on Curie's method [15].

3.2. Determination of 226Ra by HPGe spectrometry

The gamma-ray spectrometry system used for 226Ra determination was an HPGe detector (CANBERRA, USA) coupled with a digital multichannel analyzer (MCA Emulation software MAESTRO-32). The gamma detector, which has a relative efficiency of 40% and a resolution of 1.88 keV at 1.33 MeV, was housed in a low-background lead shield. 0.5 L of each standard solution was transferred to a Marinelli beaker for analysis. To cover the desired energy range of 46–1864 keV, the system was calibrated using a multienergy mixed standard source (22Na, 57Co, 137Cs, 133Ba, and 241Am) supplied by Amersham International plc. (UK). The efficiency calibration was performed using a mixed radionuclide source, which has the same geometry as the real samples, prepared at the NIST (USA). Data analysis was performed using software Genie 2000 (CANBERRA, Meriden, CT, USA). Calculations of the minimum detectable activity at the 95% level of confidence were performed based on the Curie method [15].

3.3. Evaluation of 226Ra by liquid scintillation counting

Liquid scintillation counting (LSC) coupled with extractive techniques and alpha−beta discrimination allows rapid and relatively simple determination of all radiometric parameters relevant to dose evaluation, namely gross alpha and beta activity, uranium and radium isotopes.

In this study, three different methodologies have been employed for the determination of 226Ra by means of liquid scintillation technique. The first one (referred to as "Rn-LSC-28") is based on the method by Prichard and Gessel [16] and Cooper et al. [17] and was also used by Aliessa et al., Escobar et al., and Zouridakis et al. [18−20]. In this procedure, 8 mL of each standard

Table 1
Theoretical values of 226Ra activity concentrations and the results of alpha-particle and gamma-ray spectrometry.

Samples' ID	Theoretical	α-226Ra			γ-1764 KeV			γ-186 KeV		
	A ± 1σ	A ± 1σ	RSD (%)	PE (%)	A ± 1σ	RSD (%)	PE (%)	A ± 1σ	RSD (%)	PE (%)
STD-1	0.98 ± 0.08	1.00 ± 0.06	5.90	2.39	0.90 ± 0.26	29.47	8.41	0.16 ± 0.92	569.24	83.50
STD-2	1.96 ± 0.15	1.83 ± 0.10	5.57	6.84	2.14 ± 0.29	13.48	9.38	1.77 ± 0.79	44.89	9.71
STD-3	2.94 ± 0.23	2.72 ± 0.15	5.46	7.61	2.95 ± 0.33	11.23	0.27	2.15 ± 0.98	45.73	27.01
STD-4	3.92 ± 0.31	3.87 ± 0.21	5.30	1.18	3.67 ± 0.38	10.23	6.46	2.58 ± 0.97	37.51	34.19
STD-5	4.90 ± 0.38	4.66 ± 0.26	5.50	4.83	4.16 ± 0.39	9.29	15.18	3.81 ± 0.81	21.35	22.33
STD-6	5.88 ± 0.46	5.87 ± 0.31	5.21	0.16	5.07 ± 0.42	8.21	13.79	5.31 ± 0.83	15.64	9.71
STD-7	6.86 ± 0.54	6.91 ± 0.37	5.35	0.67	6.40 ± 0.49	7.71	6.73	6.13 ± 0.83	13.53	10.62
STD-8	7.84 ± 0.61	7.94 ± 0.41	5.17	1.24	7.27 ± 0.58	8.02	7.30	5.27 ± 0.95	18.00	32.81
STD-9	8.82 ± 0.69	8.95 ± 0.48	5.33	1.45	8.04 ± 0.59	7.39	8.86	9.03 ± 1.30	14.41	2.38
STD-10	9.80 ± 0.77	9.38 ± 0.51	5.44	4.30	7.33 ± 0.57	7.74	25.23	7.41 ± 0.98	13.18	24.36

PE, percentage error; RSD, relative standard deviation.

solution was transferred to a high-density polyethylene vial, covered with a Teflon cap to prevent radon from escaping, and preloaded with 12 mL of an insoluble high-efficiency mineral oil scintillation cocktail (PerkinElmer, Boston, MA, USA) so as to avoid white precipitate formation. Prior to evaluating ^{226}Ra, the samples were kept for 28 days in a refrigerator to allow equilibrium between ^{222}Rn and ^{226}Ra to be reached. During the storage period, precautions were taken to prevent radon release and to avoid oxygen–cocktail contact, as O_2 can destroy the sensitive ingredients in the cocktail.

The second method (referred to as "^{228}Ra-LSC") is based on a combined procedure for the determination of ^{226}Ra along with ^{228}Ra and ^{224}Ra isotopes using a pulse-shape analyzer for α/β discrimination counting mode [8]. Following the procedure by Chalupnik and Lebecka [21]; 1 L of each standard solution was transferred to a 2 L glass beaker and 10 mL of $C_6H_8O_7$ (1M), 10 mL of NH_3 (6M), 20 mL of $BaCl_2$ (0.05M), and 1 mL of $Pb(NO_3)_2$ (0.5M) were added. The mix was heated to boiling and then a few drops of methyl orange indicator and H_2SO_4 (1:1) were added drop by drop until the solution changed color. After waiting for the precipitate to settle, the supernatant solution was decanted and the precipitate was transferred to a centrifuge tube, where it was centrifuged and rinsed with distilled water at a pH up to 7. Then, 60 mL of EDTA (0.125M) and 9 mL of NH_3 (6M) were added. The sample was then heated in a water bath with stirring to dissolve the precipitate. Additional portions of di-sodium salt (EDTA) and ammonia were added when necessary to obtain a clear solution. After cooling the sample, 6 mL of glacial acetic acid per each portion of EDTA and ammonia were added to precipitate radium and barium again as sulfates. The supernatant was then centrifuged and decanted. After rinsing the precipitate with distilled water, it was transferred to a liquid scintillation vial and centrifuged again. Water was mixed with the precipitate to a total volume of 6 mL; then 10 mL of gelling scintillator was added, and the mixture was vigorously shaken to obtain a homogenous gel medium. The resultant sample was evaluated for ^{226}Ra after 28 days. It is worth mentioning that, in the case of ^{228}Ra determination, the sample should be measured for 1 hour at 24 hours after preparation.

The third method (referred to as "Rn-LSC-Evaporation") is based on radon extraction from the water phase into the organic phase containing the scintillation cocktail, leaving ^{226}Ra in the water. In this procedure, 10 mL of each standard solution was pipetted into a low-diffusion polyethylene (Teflon coated—PTFE) LSC vial containing 10 mL of a water-immiscible cocktail based on a mineral oil in trimethyl benzene. The vial was capped, vigorously shaken to extract radon and then opened to let radon evaporate. The vial was then retained for a minimum of 20 days in a refrigerator for ingrowth of radon from the ^{226}Ra in the sample until the "unsupported" radon decayed below the LLD and ^{226}Ra came to be in equilibrium with its short-lived daughters. The vials were then measured for 500 minutes from the alpha spectrum channel alone; any radon detected then must have originated from the decay of ^{226}Ra. It is worth mentioning that this procedure can also be used to determine radon concentration by direct and initial evaluation of the vials before equilibrium is reached.

The three liquid scintillation (LS) methods mentioned above were carried out by means of two LSC apparatuses under alpha and beta settings. The first one is a PerkinElmer (Turku, Finland) Quantulus 1220 ultra-low level background LSC equipped with a pulse-shape analyzer for the proper setting of the α/β discrimination parameter. The calibration was done in two different ways. First, to study the stability of the detectors, the manufacturers' standard source, supplied by PerkinElmer (Turku, Finland), containing high-energy beta (^{14}C) and low-energy beta (^{3}H) nuclides was used. The second calibration method was performed

using an internal (in house) mixed standard source containing pure alpha (^{241}Am) and pure beta (^{90}Sr) radionuclides, obtained from the NIST in the USA. The LLD was calculated using the Curie equation and found to be between 0.11 and 0.35 Bq/L^{-1} for alpha and beta activities, respectively. This LLD was achieved under the condition of 8 mL-sample size, 1000 minutes of counting time, and efficiency of 99%.

The second LSC apparatus used for ^{226}Ra determination was a Hidex 300 SL (Hidex, Finland). Calibration with Hidex 300 SL was also performed using the two previously mentioned methods. Using the manufacturer' standard solution, the efficiency levels achieved were 98% and 73% for alpha and beta evaluation, respectively. On the other hand, the internal (mixed ^{214}Am–^{90}Sr) standard source with pulse length index was used for the discrimination of alpha and beta at 6. The triple-to-double coincidence ratio, which is the same as the efficiency, was 100% for alpha and 99.75% for beta counting. To set window for evaluation of ^{226}Ra, a standard source of ^{226}Ra activity of 2 Bq/mL^{-1} was prepared in the laboratory. The total area under the window from 550 to 750 with triple-to-double coincidence ratio of 300% was used because this window covers ^{222}Rn, ^{218}Po, and ^{214}Po radionuclides.

4. Results and discussion

All spectra obtained from the various methods were analyzed to determine the ^{226}Ra activity concentrations in the 10 standard solutions. The individual analytical results are listed in Tables 1–3, along with the theoretical values of ^{226}Ra. The uncertainty 1σ (95% confidence), also presented in Tables 1–3, was derived from uncertainties associated with the counting and weight statistics for individual standard solutions. The RSD is derived from the ratio of the standard deviation to the individual ^{226}Ra concentration, whereas the PE is the percentage difference between the experimental and theoretical values. The values of RSD and PE are also included in Tables 1–3 as these values can be used to evaluate the precision and accuracy of the measurements. It is worth mentioning that an analysis of variance test was performed to compare the results of ^{226}Ra activity concentration obtained by the various techniques applied to each of the standard solutions. These analysis of variance tests showed no significant differences between the concentrations obtained by either of the two methods. This reveals a general agreement between the various radiometric techniques applied in this study.

For comparison, Table 1 presents the results of alpha and gamma spectrometry together. For the alpha spectra, the use of a ^{133}Ba tracer that has no alpha-particle emitters has the result that interference with ^{226}Ra, which is chemically very similar to the tracer, is not created in the alpha spectrum. The results proved that the α-^{226}Ra method is an accurate technique for the determination of the activity concentrations, as can be seen from the low values of RSD, ranging from 5.17% to 5.90%, and the values of PE, ranging from 0.16% to 7.61%.

On the other hand, the nondestructive method of gamma-ray spectral analysis is recommended as it permits simultaneous measurement of various radionuclides in a single sample with minimal preparation steps. However, because of the relatively large sample volume, poor detection limits, and numerous types of interference and attenuation that may be encountered, gamma-ray spectrometry is not the best choice to attain accurate and reliable results. Nevertheless, this approach has been used by several laboratories because of its relatively simple preparation methods and direct counting procedure. In this study, the gamma-ray spectrometry determination of ^{226}Ra was performed both by direct measurement (referred to as "γ-186 keV") of its principal photopeak at 186.26 keV, which has a low emission probability of

Table 2
Theoretical values of [226]Ra activity concentrations and the results of the three techniques using Quantulus 1220 ultra-low level background LSC.

Samples' ID	Theoretical	Rn-LSC-28			[228]Ra-LSC			Rn-LSC-Evaporation		
	A ± 1σ	A ± 1σ	RSD (%)	PE (%)	A ± 1σ	RSD (%)	PE (%)	A ± 1σ	RSD (%)	PE (%)
STD-1	0.98 ± 0.08	1.01 ± 0.07	7.28	3.18	0.86 ± 0.04	4.29	14.09	1.02 ± 0.01	1.27	4.32
STD-2	1.96 ± 0.15	1.89 ± 0.09	4.80	3.67	1.83 ± 0.08	4.29	0.22	1.92 ± 0.02	1.00	1.82
STD-3	2.94 ± 0.23	2.95 ± 0.11	3.77	0.20	2.80 ± 0.12	4.27	3.26	2.83 ± 0.03	0.93	3.60
STD-4	3.92 ± 0.31	3.96 ± 0.13	3.28	1.12	3.70 ± 0.16	4.27	4.48	3.93 ± 0.03	0.75	0.23
STD-5	4.90 ± 0.38	5.05 ± 0.14	2.84	3.08	4.80 ± 0.20	4.26	3.01	4.72 ± 0.04	0.74	3.66
STD-6	5.88 ± 0.46	6.00 ± 0.15	2.55	2.05	5.44 ± 0.23	4.26	7.35	5.38 ± 0.04	0.70	8.49
STD-7	6.86 ± 0.54	7.18 ± 0.17	2.33	4.72	6.56 ± 0.28	4.26	5.04	6.71 ± 0.05	0.73	2.24
STD-8	7.84 ± 0.61	8.21 ± 0.19	2.25	4.70	7.95 ± 0.34	4.26	0.19	7.61 ± 0.05	0.66	2.96
STD-9	8.82 ± 0.69	8.91 ± 0.19	2.09	1.03	9.00 ± 0.38	4.26	0.57	8.27 ± 0.05	0.65	6.23
STD-10	9.80 ± 0.77	9.82 ± 0.20	2.00	0.25	9.88 ± 0.42	4.26	5.34	9.23 ± 0.06	0.61	5.78

LSC; liquid scintillation counting; PE, percentage error; RSD, relative standard deviation.

Table 3
Theoretical values of [226]Ra activity concentrations and the results of the three techniques using Hidex 300 SL.

| Samples' ID	Theoretical	Rn-Hidex-28			[228]Ra-Hidex			Rn-Hidex-Evaporation		
	A ± 1σ	A ± 1σ	RSD (%)	PE (%)	A ± 1σ	RSD (%)	PE (%)	A ± 1σ	RSD (%)	PE (%)
STD-1	0.98 ± 0.08	0.99 ± 0.07	7.44	1.03	0.86 ± 0.01	0.63	12.07	0.88 ± 0.01	1.47	9.88
STD-2	1.96 ± 0.15	1.94 ± 0.09	4.66	0.80	1.93 ± 0.01	0.56	1.61	1.67 ± 0.02	1.11	14.96
STD-3	2.94 ± 0.23	2.78 ± 0.11	4.00	5.51	2.71 ± 0.01	0.54	7.89	2.83 ± 0.03	0.92	3.81
STD-4	3.92 ± 0.31	3.68 ± 0.13	3.52	6.11	3.85 ± 0.02	0.53	1.86	3.79 ± 0.03	0.76	3.41
STD-5	4.90 ± 0.38	4.63 ± 0.14	3.09	5.47	4.93 ± 0.03	0.52	0.58	4.60 ± 0.03	0.69	6.19
STD-6	5.88 ± 0.46	5.52 ± 0.15	2.77	6.04	5.40 ± 0.03	0.52	8.17	5.37 ± 0.03	0.65	8.59
STD-7	6.86 ± 0.54	6.81 ± 0.17	2.45	0.80	6.52 ± 0.03	0.52	4.91	6.77 ± 0.04	0.60	1.28
STD-8	7.84 ± 0.61	7.51 ± 0.18	2.45	4.16	7.61 ± 0.04	0.52	2.96	7.44 ± 0.04	0.58	5.12
STD-9	8.82 ± 0.69	8.73 ± 0.19	2.13	1.07	8.64 ± 0.04	0.51	2.07	8.27 ± 0.05	0.56	6.28
STD-10	9.80 ± 0.77	8.96 ± 0.20	2.21	8.59	9.69 ± 0.05	0.51	1.10	9.75 ± 0.05	0.55	0.48

PE, percentage error; RSD, relative standard deviation.

3.59%, and indirectly (referred to as "γ-1764 keV") by using the emission of the radon daughter [214]Bi at 1764.54 keV, which has an intensity of 15.4% [22]. Direct measurement has the advantage of immediate counting of the sample directly after preparation. But, the quantification of [226]Ra using its own 186.26 keV peak is subject to interference and potential bias. This happens because of the presence of interfering gamma emission of [235]U at 185.72 keV, which has a higher photo emission probability (57.24%) and constitutes an irresolvable doublet photopeak in the vicinity of 186 keV, causing false [226]Ra results in gamma-ray spectral analysis. However, [235]U is not present in our standard samples, and thus there is no need to apply deconvolution analysis to resolve the doublet and determine the respective contribution of each radionuclide, as should be done with real samples. On the other hand, the photopeak of [214]Bi at 1764.54 keV requires the existence of radioactive equilibrium between [226]Ra and [222]Rn. This was assured by using a radon-tight sealed Marinelli beaker and a waiting period of one month or more to achieve secular equilibrium prior to counting. The results obtained by the two gamma-ray spectrometry methods are tabulated in Table 1. The high RSD and PE values associated with the γ-186-[226]Ra results relative to those associated with the γ-1764-[226]Ra results, particularly for low [226]Ra concentrations, reflect the lower accuracy and precision in the measurements using the 186 gamma peak. Nevertheless, both measurements showed the ability to determine [226]Ra concentrations in water samples. To verify this, comparison of the activity concentrations of [226]Ra obtained by both methods were performed using linear regression analysis (Fig. 1A). As can be seen in this figure, the agreement between the two gamma-ray spectrometry methods is obvious, with linear correlation of slope 1.03 ± 0.06 and correlation coefficient R = 98.7% (p < 0.0001). Hence, [226]Ra activity concentration measured using the 186 keV peak also gives reliable values except at low concentrations near

the minimum detectable activity limit, at which concentrations of the activity is difficult to measure. Similar results were reported by Völgyesi et al. [23]; who studied the [238]U-[226]Ra secular equilibrium in coal slag samples from Hungary.

Further, Fig. 1B displays a comparison between α-[226]Ra results and both gamma-ray spectrometric results for the 10 standard solutions. The fitting indicates a strong correlation between α and both γ results, with correlation coefficients of R = 98.9% and 97.6% for the cases of 1764 and 186 keV, respectively. This shows that the agreement between the α and γ results is high. However, the slopes of the fitted straight lines of values 0.88 ± 0.05 and 0.95 ± 0.07, respectively, indicate a tendency to obtain higher [226]Ra concentrations by alpha-particle spectrometry than by gamma-ray spectrometry for most of the standard solutions. From this result, a general conclusion can be drawn that gamma-ray determination of [226]Ra is underestimated due to some small [222]Rn diffusion from the sample and low abundance of the peak at 186 keV. Besides this, the tendency of underestimation by the gamma-ray spectrometric analysis could be caused by the self-absorption factor [24–25]. Nevertheless, this comparison proves that gamma-ray spectrometry with suitable shielding can be considered as a good alternative to alpha-particle spectrometry for [226]Ra analysis in water samples when lower detection limits are not required.

Tables 2 and 3 show the results of the three LSC techniques using the Quantulus 1220 ultra-low level background LSC and the Hidex 300 SL, respectively. The differences in the results obtained using the three techniques with the two LSC apparatus cannot be attributed to consistent overestimation or underestimation, but are rather random. In fact, LSC, with its alpha/beta separation feature, has the advantage of high efficiency, which can reach 100% for alpha and high-energy beta emitters; as such, drawbacks, including quenching, loss of energy resolution of alpha peaks, and relatively high background [12], can be avoided. It turns out that
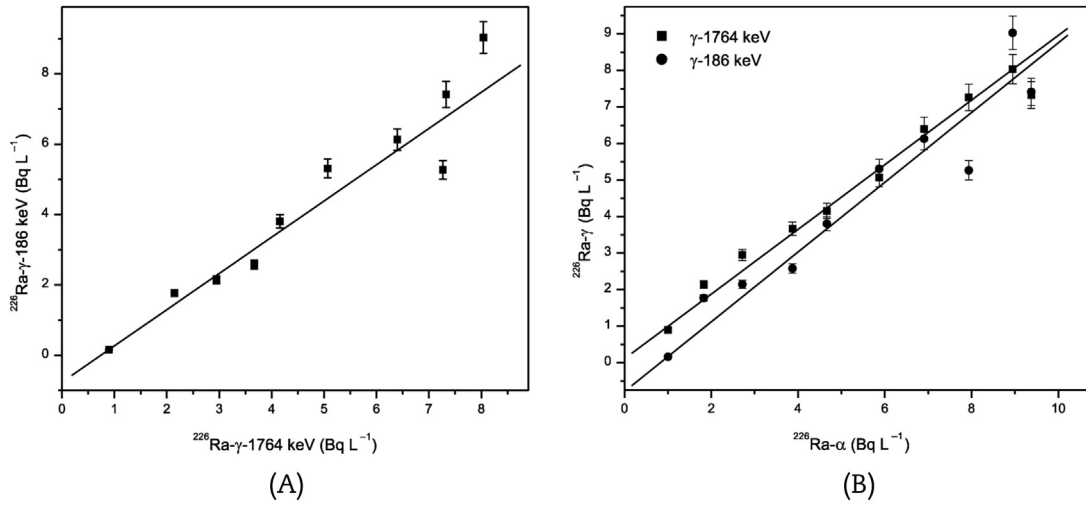
Fig. 1. [226]Ra activity in the ten standard solutions measured by its own peak at 186 keV versus the peak of Bi at 1764 keV and alpha-particle spectrometry versus gamma-ray spectrometry. (**A**) Relationship between results of [226]Ra-γ-186 and [226]Ra-γ-1764. (**B**) Relationship between [226]Ra-α and both gamma-ray spectrometry results. Error bars of 95% confidence level are also shown.
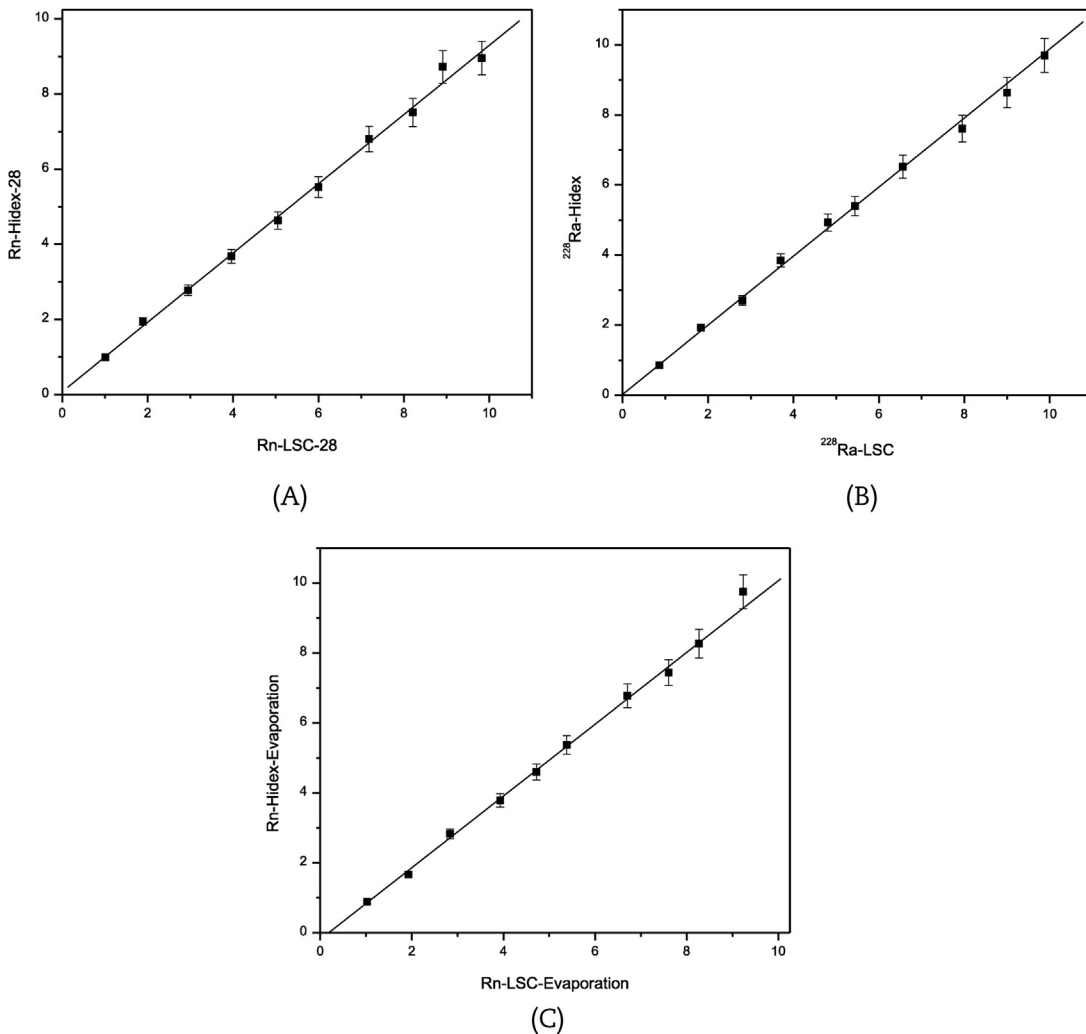
Fig. 2. (**A**) Relationship between results of Rn-LSC-28 and Rn-Hidex-28. (**B**) Relationship between results of [228]Ra-LSC and [228]Ra-Hidex. (**C**) Relationship between results of Rn-LSC-Evaporation and Rn-Hidex-Evaporation. Error bars of 95% confidence level are also shown.

the [226]Ra results of the three techniques using Quantulus 1220 LSC lie within one standard deviation of the theoretical values of most of the standard solutions. Based on this, it can be concluded that LSC spectrometry techniques are the most accurate techniques applied in this investigation. Based on the RSD and PE values, the most accurate Quantulus 1220 LSC technique is the "[226]Ra-LSC" method, whereas the "Rn-LSC-Evaporation" method is the least accurate one (Table 2). The same can be said about the results obtained from the three techniques using the Hidex 300 SL, but the values are slightly higher (Table 3). The main reason for this is that the difference between the Quantulus 1220 LSC and the Hidex 300 LS; the Quantulus 1220 LSC has a much thicker asymmetrical lead shield, and thus lower background rate, than the Hidex 300 SL.

The correlation between the [226]Ra results of the two LSC apparatuses, the Quantulus 1220 LSC and the Hidex 300 SL, using the three abovementioned techniques, was determined and compiled in Fig. 2A–C. In this figure, and for each standard solution, the results of one technique using the Quantulus 1220 LSC were plotted against those of the same technique using the Hidex 300 SL, allowing a meaningful comparison. The figures show strong linearity in the range of 1–10 Bq/L^{-1}, with correlation coefficients exceeding 99% ($p < 0.0001$) for the three techniques. From the values of slope of 0.92 ± 0.01, 0.98 ± 0.02, and 1.02 ± 0.02 for the "Rn-28", "228Ra", and "Rn-Evaporation" methods, respectively, the agreement between the results of the two scintillation counters is obvious. Thus, it can be concluded that both counters can be applied to analyze [226]Ra in water samples.

5. Conclusions

The various analytical methodologies applied for the determination of [226]Ra activity concentration in water samples are reliable and specific radiometric techniques for a wide range of concentrations. Well-established techniques based on alpha, gamma, and liquid scintillation spectrometry have been included in this study. The results obtained by the various detection instruments led us to conclude that the methods performed could be applied to environmental water samples. In addition, the methods adopted in this study proved to be sufficiently sensitive, with different levels of accuracy, to determine [226]Ra concentration in water. In general, using the various methods, no considerable discrepancies in [226]Ra concentrations in water were found, but it should be emphasized that determination of [226]Ra combined with [228]Ra using Quantulus 1220 ultra-low level background LSC gives the most accurate results.

Conflicts of interest

The authors have no conflicts of interest to declare.

Acknowledgment

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