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Destructive and Nondestructive Determination of ^{226}Ra and ^{228}Ra in Drinking Water by Gamma Spectrometry

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Abstract

The Safe Drinking Water Act (SDWA) mandates that the drinking water should be monitored for ^{226}Ra and ^{228}Ra isotopes and establishes the Maximum Contaminant Level of 185 mBq/L (5 pCi·L^{-1}) for the sum. In addition, SDWA regulates the Detection Limit (DL) of 37.0 mBq/L (1 pCi/L) for each isotope. The purpose of this work is to develop a working method for the determination of radium isotopes in drinking water satisfying the regulatory requirements of U.S. Environmental Protection Agency by utilizing our extensive experience in low-background gamma spectrometry at this laboratory. Two versions of the method were studied: destructive and non-destructive. Destructive method used the $BaSO_4$ coprecipitation as well as ^{133}Ba tracer for chemical recovery. We have used three gamma spectrometers: low-background 102% and 134% efficient with top muon guards, as well as an ultra-low-background 140% efficient with full muon guard. We obtained a range of DLs from 5.3 to 22.6 mBq/L for ^{226}Ra and from 7.4 to 30.4 mBq/L for ^{228}Ra using the destructive method. For non-destructive method, the DL range was 26.0 to 26.9 mBq/L for ^{226}Ra and 27.6 to 28.6 mBq/L for ^{228}Ra using the 140% detector. To verify the methods, 7 to 10 laboratory control samples were spiked with both ^{226}Ra and ^{228}Ra at two different activities of 37.0 and 185 mBq/L. The results were evaluated by performing a combined location/variance chi-square test at a right-tail significance of 0.01 (99% Confidence Level), as stipulated by EPA. The verification results passed the chi-square tests at both activity levels. The destructive method can be accomplished using low-background gamma spectrometry, whereas non-destructive method requires ultralow-background gamma spectrometry.

Keywords

Radioactive Pollution, Germanium Detector, Detection Limit, Chi-Square Test

1. Introduction

Radium is present naturally in soil, minerals, groundwater, and can incorporate in foodstuffs, and several common materials, including many used in construction. Exposure to radium isotopes by ingestion can lead to significant committed radiation dose considering their affinity to bone structures as well as rapid series equilibrium of the progeny resulting in several alpha-emitting radionuclides [1]. This radiation dose is known to cause bone cancer [2]. Owing to solubility of radium found naturally in rocks and soil and the alpha-recoil mechanism, it can get into groundwater supplies [3]. In communities where wells are used, drinking water can be an important source of radium ingestion to the public. According to the U.S. Environmental Protection Agency (EPA), long-term consumption of water containing 185 mBq/L (5 $pCi{\cdot}L^{-1}$) radium may cause 44 additional cancer deaths for every million people exposed [4]. The risk increases as the level of radium increases. Therefore, radium isotopes are considered listed contaminants in drinking water in many countries. From the regulatory health perspective, ^{226}Ra ($T_{1/2}$ = 1600 y) from the uranium series and ^{228}Ra ($T_{1/2}$ = 5.75 y) from the thorium series are the most significant radionuclides. ^{224}Ra is already included in the thorium series as a progeny of ^{228}Ra; it has also been studied separately as it can deviate from the series equilibrium [5] [6]. In detailed studies, ^{223}Ra from the actinium series has also been investigated [7], and its main significance is in geochemistry. For these reasons, we investigate ^{226}Ra and ^{228}Ra only in this work.

There exist several methods for the determination of radium isotopes in water, the ones utilizing gamma spectrometry with Germanium (Ge) detectors are the most efficient among them. The sensitivity of radium determination by gamma spectrometry depends on several sample-related factors, such as sample volume [8], preconcentration on Mn-based medium [9] [10], coprecipitation with $BaSO_4$ [11] [12], coprecipitation with $PbSO_4$ [6] or nondestructive analysis [5]. On the instrumental side, the sensitivity depends on the efficiency of the Ge spectrometer, extent and purity of shielding materials, use of active cosmic-muon rejection [13], Compton suppression [14], as well as counting time.

Under the Safe Drinking Water Act, the U.S. Environmental Protection Agency (EPA) has promulgated maximum contaminant level goals (MCLGs) as zero for radioactivity in drinking water. However, the maximum contamination level (MCL) for combined ^{226}Ra and ^{228}Ra in drinking water is equal to 185 mBq/L (5 $pCi{\cdot}L^{-1}$) and both radium isotopes are required to be measured separately [4].

Among many methods for Ra determination, it is sometimes not clear how sensitive they are. In this work, we use the Currie's detection limit [15] as a measure of detection capability, also referred to as the minimum detectable activity (MDA) by the National Environmental Laboratory Accreditation Conference Institute Standard [16]. On the other hand, the EPA approved methods for radium require regulatory detection limit (DL) of 37 mBq/L (1 $pCi{\cdot}L^{-1}$) as a measure of detection capability [4]. This required DL is only five times smaller than the MCL. Even if a given detection capability can be calculated from the data, it does not necessarily follow that this capability can be achieved in repetitive analytical measurements. In order to verify the achieved DL, a Chi-square test has been recommended [17].

The purpose of the present work was to develop a method for the determination of two major natural radium isotopes: ^{226}Ra and ^{228}Ra in drinking satisfying the regulatory requirements. At the New York State Department of Health, we have been performing low-background gamma spectrometry for more than three decades laboratory [13]. The applied uses of gamma spectrometry include monitoring of environment, food, air, and water, and surveillance of energy and manufacturing facilities, as well as health physics and radiological emergency applications. Low-background gamma spectrometry is applicable to very low activity matrices, such as water or chemically separated samples. Specific projects include mandated analysis of radium in drinking water and monitoring of radioactive iodine and cesium at nuclear facilities. In this work we have investigated two radium detection methods in drinking water, referred as destructive and non-destructive. We described in detail the achieved MDA and DL using the newly developed procedures [18], supported by the newly developed methods for Chi-square testing [19].

2. Experimental and Calculation Procedures

2.1. Gamma Spectrometry

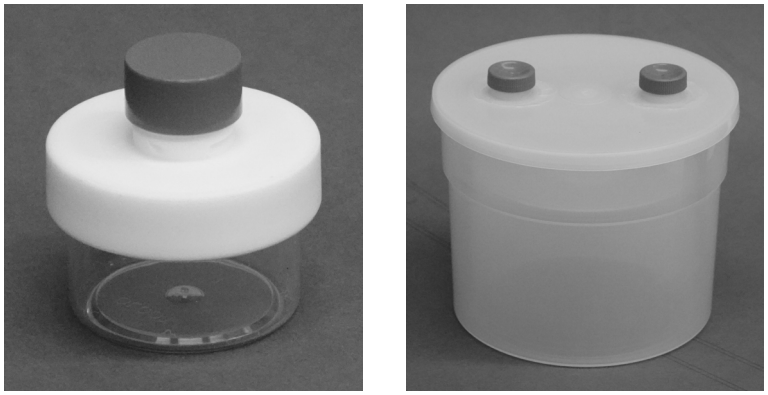
In this study, we have utilized p-type high purity Germanium (HPGe) detectors having 102% relative efficiency (Model GC10020) and 134% relative efficiency (Model GC13021), as well as an XtRa-type 140% Ge detector (Model GX13023), all by Mirion Technologies (Canberra) Inc. (Meriden, CT, USA). The spectrometers are situated inside a 15-cm-thick wall steel room made of pre-World War II steel (Dixie Manufacturing Co., Baltimore, MD, USA), which is located under a 47-story building providing 33 meters of water-equivalent (mwe) shielding from cosmic rays in the vertical direction. The 102% and 134% detectors have general low-background lead shields and are equipped with custom active muon shields made of plastic scintillators positioned on the top, which reduce cosmic muon background by a factor of 2. The 140% detector has a custom 3-layer ultra-low background lead shield of a 17 cm total thickness, which is surrounded by plastic scintillators for muon rejection [13]. This spectrometer has an integrated background rate of 2.4 counts per min (cpm) in the gamma-ray energy

range between 50 - 2700 keV, corresponding to a background rate of 15 counts $ks^{-1} \cdot kg^{-1}$ Ge. This background compares well with the lowest-background gamma spectrometers in the world [20].

Considering the facilities at this institution, we refer to low-background gamma spectrometry when using the 102% and 134% detectors, and to ultra-low background gamma spectrometry when using the 140% detector.

2.2. Radium Detection Methods

In this work we investigate two radium detection methods, referred to as destructive and nondestructive. In the destructive method, we start with a 2.5 L of water sample and coprecipitate radium isotopes with $BaSO_4$ carrier with an addition of ^{133}Ba recovery tracer, as reported elsewhere [11] [12]. The precipitate was settled, centrifuged, dissolved in ethylenediaminetetraacetic acid (EDTA) solution, and transferred to a 50-mL counting jar [**Figure 1(a)**] calibrated for gamma spectrometry. After allowing 4 weeks for to reach secular equilibrium with ^{222}Rn and progeny, ^{226}Ra was measured and assayed by means of a 609.3-keV gamma peak from ^{214}Bi (I_γ = 0.4549). While it is possible to use and average other peaks of lower intensity, we did not include them because they are often poorly defined in the spectrum for low-level applications. It is also possible to degas ^{222}Rn prior to its ingrowth from the sample [5], which enables calculation of ingrowth factor and shorter waiting time. This procedure, however, decreases the sensitivity while earlier reporting has not been necessary for radium monitoring at this institution. Therefore, we waited 30 days for full equilibrium. ^{228}Ra activity was assayed using a 911.2-keV gamma peak from its progeny, ^{228}Ac (I_γ = 0.258), which reaches equilibrium in less than 3 days. Similarly, we did not include less intense peaks. The chemical recovery was determined with a ^{133}Ba tracer ($T_{1/2}$ = 10.6 y), using a 356.0-keV gamma peak (I_γ = 0.6205). This peak and its Compton continuum do not interfere with the detection of either ^{214}Bi or ^{228}Ac. The measured chemical recoveries for ^{133}Ba tracer varied between 0.75 and 0.96.



(a) (b)

Figure 1. (a) 50-mL jar for destructive, and (b) 800-mL Marinelli beaker for non-destructive, ^{226}Ra and ^{228}Ra measurements.

In the nondestructive method, 800 mL of the sample was transferred to 800-mL Marinelli beaker [**Figure 1(b)**] without any processing and counted after waiting 30 days for equilibrium. The counting time for gamma spectrometry measurements of either 50-mL or 800-mL geometry was 1000 min for the sample spectrum and 4000 min for the background spectrum.

The absolute efficiencies for the 50-mL and 800-mL geometries were calibrated using a mild acidic solution spiked with a mixed-gamma standard traceable to the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) as described elsewhere [21]. Since the calibration standards and samples were water solutions, no density corrections were applied. The coincidence-summing corrections calculated using the Gespecor software [22] ranged from 0.95 to 0.96.

2.3. Sample Containers

It is well recognized that radon distributes between air and water by a ratio of 3 to 1, according to Henry's law [23]. Therefore, to maintain counting geometry for the 50-mL and 800-mL containers described in Section 2.2, they must be filled with water with no air gap above the solution. This creates practical problems with filling procedure and leaking of both radon and water. Several techniques were developed for sealing of counting containers using a variety of sealants [24] [25].

In this work, we modified common sample containers in house to prevent leaks. The 50-mL jar screw lid (white in [**Figure 1(a)**]) was made of Teflon, and an aluminized washer was inserted between the lid and the container. Then, the rim of the lid was sealed with a silicone rubber. The solution entry port on the top had a screw cap with a Teflon washer. A standard 800-mL Marinelli baker's lid was modified by thermal fusing two ports to it with screw caps equipped with Teflon washers [**Figure 1(b)**]. One port is for filling the solution, and the second port for degassing. The lid was then sealed to the beaker with the silicone rubber.

A radon leak test was performed on the smaller container, which was filled with water saturated with ^{222}Rn gas from a historical radium-ore Revigator [26]. After establishing equilibrium with the progeny, the decay of radon was followed on a gamma spectrometer for 45 days.

2.4. Calculation Procedures

Define As described in the Introduction, in this work we study quantitative measures of sensitivity of ^{226}Ra and ^{228}Ra detection in drinking water. One such measure is MDA [15] [16]. We calculated MDA using Genie 2000 algorithms in the gamma spectrometry software (Mirion Technologies (Canberra), Inc.). Another measure of sensitivity is the EPA's DL defined as a "concentration which can be counted with a precision of plus or minus 100 percent at the 95 percent confidence level (1.96σ, where σ is the standard deviation of the net counting rate of the sample) [4]". The formula for calculation of DL is given in

[17] for paired counting. In gamma spectrometry, its calculation is more complicated as it involves gamma peak fitting and subtraction of background spectrum [12]. We have recently revised the formula for DL by better quantifying Poisson fluctuations in the counting data [18] and use it in this investigation.

It has been guided by EPA (2017) [17] to verify detection performance at the required DL using a Chi-square test. We provide the verifications at the regulatory DL of 37 mBq/L (1 pCi·L^{-1}) as well as MCL of 185 mBq/L (5 pCi·L^{-1}). From 7 to 10 samples were spiked with NIST-traceable standards of ^{226}Ra and ^{228}Ra at activities close to the above levels. Then either destructive or nondestructive procedures were followed. The results were evaluated with a combined location/variance right-tail (RT) Chi-square test at 0.01 significance (99% confidence level, CL), as described elsewhere [19]. The observed Chi-square variable is defined as $\sum\left[\left(x_i-\mu\right)/\sigma_i\right]^2$, where x_i is the measured activity, μ is known spike activity, and σ_i is the measured uncertainty, for $i=1,\cdots,n$, where n is the number of measurements. The calculated Chi-square is performed using standard algorithm in Excel (Microsoft) for n degrees of freedom, since there are no constraints in the data.

Another measure of verification is the E_n score defined as $\left(\overline{x}-\mu\right)\Big/\left(k\sqrt{\sigma_x^2+\sigma_\mu^2}\right)$, where $\overline{x}$ is mean measured activity, σ_x is sample standard deviation, σ_μ is spike standard deviation, and $k=1.960$ is the coverage factor for 95% CL [27].

3. Results and Discussion

The results of radon leak test from the 50-mL jar are shown in [**Figure 2**]. The measured counting rates are depicted as points. The fitted curve consisted of an exponential term and a constant term for background. The fit resulted in the best estimate for ^{222}Rn half-life of 3.8079 days, slightly smaller than the literature value of $T_{1/2}$ = 3.8235 days [28], indicating at most a minor leak. However, it affects the relative saturation factor in 30 days by about 10^{-4} and, therefore, can be

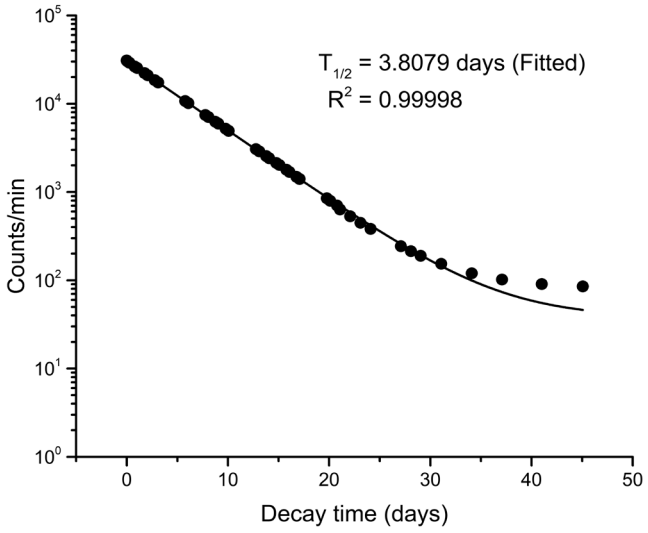


Figure 2. ^{222}Rn decay curve for leak testing of the 50-mL container.

neglected. Radon leak has not been explicitly tested on the 800-mL Marinelli beaker. Nevertheless, the verification experiments described below do not indicate any leaks.

The results of the DL calculations are given in Table 1, which is subdivided into two major groups by destructive and nondestructive methods. The DL results are given in mBq/L. They were obtained for 2.5 L of sample, 1000 min sample counting time, 4000 min background counting time, and 30-day radon ingrowth period. The DL values were calculated using statistical methods on statistical data, including variability in chemical recovery for the destructive method, therefore some variability in the results is expected.

It is seen that, for the destructive method and low-background detectors (102% and 134%), the DL values range from 14.9 to 22.6 mBq/L for ^{226}Ra from 28.4 to 30.4 mBq/L for ^{228}Ra. All these values are below 37 mBq/L, therefore they satisfy the regulatory DL under these experimental conditions for both radionuclides. Significantly lower detection limits were calculated for the destructive method and the ultralow-background detector (140%) with the DL values of 5.3 and 6.2 mBq/L for ^{226}Ra as well as 7.4 and 9.7 mBq/L for ^{228}Ra. Since they are significantly lower than the required DL, there is room for decreasing of the sample quantity and decreasing counting time, as reported earlier [18], or for shorter radon ingrowth time. Also given in Table 1 are the MDA results. It is seen that they are slightly higher than DL, which is the result of different definition.

Within the nondestructive-method group in Table 1, none of the low-background detectors satisfied the required DL, with the values between 68.1 and 77.9 mBq/L for ^{226}Ra as well as 80.7 and 97.7 mBq/L for ^{228}Ra. These

Table 1. Detection limits for ^{226}Ra and ^{228}Ra in method blanks by low-level gamma spectrometry (T-top muon shield, F-full muon shield).

Method	Detector rel. eff. (%)	DL (mBq/L)		MDA (mBq/L)	
		^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
Destructive	102-T	18.6	29.2	22.2	38.1
	102-T	20.3	28.9	23.0	37.9
	134-T	22.6	28.4	31.7	31.0
	134-T	14.9	30.4	21.1	31.0
	140-F	5.3	7.4	6.0	7.2
	140-F	6.2	9.7	8.4	12.4
Non-Destructive	102-T	71.8	126.8	84.6	165.8
	102-T	68.1	121.3	86.4	150.0
	134-T	77.9	111.2	97.7	148.9
	134-T	69.5	104.1	80.7	129.2
	140-F	26.9	27.6	36.5	51.3
	140-F	26.0	28.6	33.9	45.4

results could be lowered by increasing sample volume to over 4 L, as done by earlier study [18], and/or by increasing sample counting time above 1000 min. However, using the ultralow-background gamma spectrometry we obtained satisfactory results of 26.0 and 26.9 mBq/L for ^{226}Ra as well as 27.6 and 28.6 mBq/L for ^{228}Ra. In addition, the nondestructive method used only 0.8-L sample instead of 2.5 L.

The performance of the developed methods was tested by spiking 7 to 10 samples simultaneously with ^{226}Ra and ^{228}Ra at the levels close to the DL or MCL in separate experiments. The actual spiking activities and their standard deviations are given in the heading of **Table 2** for the destructive method and of **Table 3** for the nondestructive method. The measured mean activities and their standard deviations are reported in **Table 2** and **Table 3** as well.

A simple measure of performance verification is the E_n score, as defined in Section 2.4. It is seen that for both destructive and nondestructive methods, the E_n scores are between −1.0 and +1.0. This verifies the performance of both methods at the two spiking levels, at 95% CL. A more sophisticated performance verification is the Chi-square test. A version of Chi-square was adopted which tests for a combined location and variance, as described in Section 2.4. The observed Chi-square values were below the calculated Chi-square values for all cases including two radium isotopes, destructive and nondestructive methods, as well as two spiking levels, as listed in **Table 2** and **Table 3**. Therefore, the Chi-square tests passed at 99% CL, and the methods in question are considered verified.

Table 2. Verifications of ^{226}Ra and ^{228}Ra determinations using destructive low-level gamma spectrometry (T-top muon shield, F-full muon shield).

Det. Efficiency (%)	102-T	134-T	140-F	102-T	134-T	140-F
Parameter	^{226}Ra					
	37.0 ± 1.0 (mBq/L)			187.4 ± 5.0 (mBq/L)		
Measured mean (mBq/L)	34.0	35.5	33.9	186.2	178.5	177.1
Measured std. dev. (mBq/L)	9.0	7.7	4.5	18.0	8.5	9.9
E_n score (95% CL)	−0.17	−0.10	−0.35	−0.03	−0.46	−0.47
Degrees of freedom	7	8	7	8	8	9
Observed χ^2	8.7	9.2	12.5	13.7	8.1	17.8
Calculated χ^2	18.5	20.1	18.5	20.1	20.1	21.7
Parameter	^{228}Ra					
	37.0 ± 0.8 (mBq/L)			176.8 ± 4.0 (mBq/L)		
Measured mean (mBq/L)	39.8	39.1	36.5	186.3	188.9	174.8
Measured std. dev. (mBq/L)	7.7	7.2	3.5	17.0	8.6	12.5
E_n score (95% CL)	0.19	0.15	−0.02	0.28	0.65	−0.08
Degrees of freedom	7	8	8	10	10	9
Observed χ^2	2.2	4.1	3.3	8.6	5.8	15.9
Calculated χ^2	18.5	20.1	20.1	23.2	23.2	21.7

Table 3. Verifications of ^{226}Ra and ^{228}Ra determinations using non-destructive ultra-low-level gamma spectrometry for 140% detector with full muon shield.

Parameter	^{226}Ra (mBq/L)		^{228}Ra (mBq/L)	
	37.0 ± 1.0	185.0 ± 5.0	34.9 ± 0.8	174.3 ± 3.9
Measured mean (mBq/L)	36.8	182.6	37.9	187.1
Measured std. dev. (mBq/L)	5.6	23.3	9.0	12.5
E_n score (95% CL)	−0.02	−0.05	0.17	0.49
Degrees of freedom	8	10	9	7
Observed χ^2	1.2	11.1	3.0	2.9
Calculated χ^2	20.1	23.2	21.7	18.5

4. Summary and Conclusions

In this work, we have developed a method for the determination of both ^{226}Ra and ^{228}Ra for the purpose of regulatory radium monitoring in drinking water. We used two approaches to the method: destructive, based on coprecipitation of barium sulfate, as well as nondestructive. Both versions utilized gamma spectrometry. While coprecipitation and gamma spectrometry have been studied extensively in the literature, the sensitivities of many investigations vary and/or are difficult to judge. Therefore, we paid emphases to rigorously quantifying the results in terms of DL and MDA. In addition, we used statistical measures such as E_n score and Chi-square test to verify performance at DL and MCL.

It was shown that by using a 2.5-L sample quantity, 1000 min of sample counting, 4000 min of background counting, and allowing for a full 30-day radon ingrowth, we were able to achieve the regulatory DL of 37 mBq/L (1 pCi·L^{-1}), as stipulated by the U.S. EPA, with the destructive method which involved low-background gamma spectrometry. The DL obtained using the ultra-low-background gamma spectrometry is significantly lower than the required DL. Therefore, in the ultralow-background gamma spectrometry technique, there is room for decreasing of the sample quantity and/or decreasing sample counting time, or for shorter radon ingrowth time.

For the nondestructive version of the method, only ultralow-background gamma spectrometry was able to achieve the regulatory DL, and as such for 0.8-L sample volume only, whereas the low-background gamma spectrometry failed to do so under the experimental conditions studied.

The verifications performed at two spiking levels: around DL and MCL were followed for the destructive method as well as low-background and ultra-low-background gamma spectrometry. For the nondestructive method, the verifications were performed using ultralow-background gamma spectrometry only. All the verifications described above passed using sophisticated statistical tests such as E_n score as well as location/variance Chi-square.

The methods developed here are judged fit for radium monitoring as required by the SDWA.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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