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Determination of ^{226}Ra in natural water samples by liquid scintillation counting

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Abstract

A relatively fast, simple and reliable method has been developed for determination of ^{226}Ra from natural water samples, using radiochemical separation and liquid scintillation counting (LSC). This method is based on the usage of ^{133}Ba as tracer, sorption on MnO$_2$ Resin® and precipitation of Ba(Ra)SO$_4$. Ba(Ra)SO$_4$ was converted into Ba(Ra)CO$_3$, solubilized, and then measured by LSC. The ^{133}Ba tracer and the ^{226}Ra analyte were determined parallel using the same LSC measurement. Analyzing model solutions and real samples, 60(±15)% average recovery and 10 mBq of limit of detection were observed. (Detection time was 100 min.) This method was successfully used for analysis of bottled mineral waters, medicinal thermal waters and natural surface waters.

Highlights

- A method has been developed for determination of ^{226}Ra from natural water samples.
- The method is relatively fast, simple and reliable.
- The method is based on radiochemical separation and LSC measurement.
- Activities of ^{133}Ba and ^{226}Ra were determined from the same LSC measurement.
- ^{226}Ra in natural water samples was analyzed.

Keywords: Ra-226, LSC, MnO$_2$ Resin®, natural water

Introduction

Determination of ^{226}Ra in drinking waters, natural waters and other environmental samples is an important task due to its high radio-toxicity. ^{226}Ra can be determined directly or via its progenies (e. g. ^{222}Rn, ^{214}Po). According to the newest comprehensive papers (IAEA, 2010; Jia and Jia, 2012), α-spectrometry, γ-spectrometry, liquid scintillation spectrometry (LSC) and mass spectrometry are mostly used as measurement techniques for determination of ^{226}Ra. However, in another recent comprehensive paper (Vasile et al., 2010) only α-spectrometry, γ-spectrometry and Rn emanation technique are referred, while LSC is only mentioned as a technique for determination of ^{228}Ra.

Method

Figure 1 shows the sample preparation procedure used. 0.5-1.5 L sample was taken, filtered through a 0.45 µm filter and pH was adjusted to 4-7 using 1 M HNO$_3$ or 1 M NaOH. After that 4 Bq ^{133}Ba tracer and 1.25 g MnO$_2$ Resin® were added. (As Ba/Ra divergence does not seem to be an issue using this method, ^{133}Ba was chosen as tracer. Its activity was chosen to be much higher as that of β-emitter ^{228}Ra, possibly also present in drinking and natural waters.) The sample was stirred for at least 1 hour, and the resin was allowed to settle (preferably for a night). The supernatant was decanted, the resin was centrifuged and the supernatant was discarded. Ba and Ra were eluted from the resin using 12 mL 6 M HCl, 1 drop 30% H$_2$O$_2$ was added to make the solution colorless, then it was filtered through a 0.45 µm filter. (Application of MnO$_2$ Resin® for concentration of Ra and Ba from natural waters was developed and published by Moon et al. (2003).) 100 µL 1:1 acetic acid was added to make complex with Pb^{2+}. 19 mg Ba(NO$_3$)$_2$ and 5 mL 40% (saturated) Na$_2$SO$_4$-solution were added. The sample was slightly warmed and stirred for 30 minutes to form BaSO$_4$ precipitate, then it was centrifuged (3000 rpm, 5 min) and the supernatant was discarded. The precipitate was suspended in 2 mL saturated K$_2$CO$_3$ solution and it was evaporated with 3x2 mL distilled water to dryness to convert BaSO$_4$ to BaCO$_3$. (This is a well-known procedure, see for example Kirby and Salutsky (1964).) 30-40 mL distilled water was added, and the slurry was centrifuged. This step was repeated until the pH of the supernatant reached 7 (typically 3 times). The BaCO$_3$ precipitate was dissolved in 1 mL 0.5 M HNO$_3$, 1 drop 30% H$_2$O$_2$ was added to make it colorless. The solution was transferred into a 20 mL plastic LSC vial, 16 mL Ultima Gold LLT cocktail was added and LSC measurement was performed using a Tri-Carb 2900TR (Packard, USA) equipment.

| Sampling |
| Addition of ^{133}Ba tracer |
| Sorption of Ba and Ra on MnO$_2$ Resin® |
| Elution (6 M HCl) |
| Co-precipitation with BaSO$_4$ |
| Conversion into Ba(Ra)CO$_3$ using saturated K$_2$CO$_3$ |
| LSC source preparation |
| LSC measurement |

Figure 1
Flowchart of the procedure

Discussion 1: Evaluation of LSC measurements

Focal point of this method is that the same LSC measurement was used for determination of activity of ^{133}Ba tracer as well as that of ^{226}Ra analyte (see Figure 2), as proposed by Tinker and Smith (1996).

Figure 2
LSC spectrum of ^{226}Ra and ^{133}Ba. The peak in the α-spectrum correspond to ^{226}Ra (4784 keV). The β-spectrum consists of counts from ^{133}Ba tracer and spillover of α counts of ^{226}Ra. As these spectra were acquired right after separation, progenies of ^{226}Ra are not present.

To optimize the pulse decay discriminator setting of the LSC analyzer, ^{241}Am standard was used as pure α-emitter (as the α-emitter ^{226}Ra has some β-emitter progenies) and ^{133}Ba standard was used as "pure β-emitter". ^{133}Ba decays by electron capture but its γ-rays, X-rays, Auger electrons and conversion electrons can be counted by LSC as β-counts (Chylinski and Radoszewski, 1993). The crossover point was at 125 ns, but 140 ns discrimination time was used to reduce the spillover of ^{133}Ba counts into the α-counting region.

Activity of ^{133}Ba was calculated on the basis of the β-LSC spectrum. Counting efficiency (f_β) of ^{133}Ba was calculated using the formula:

$$f_\beta = \frac{I_{cal}^\beta - I_{bg}^\beta}{A_{cal}} \qquad (1)$$

where I_{cal}^β stands for measured β-intensity of a calibration sample (containing known A_{cal} activity of ^{133}Ba) and I_{bg}^β stands for measured β-intensity of a background sample of the same composition as real samples.

Adding different amounts of 65% HNO$_3$ to the calibration samples, the effect of quench was also studied. Counting efficiency of ^{133}Ba (using channels 0-2000 of the β-LSC spectrum) was found to be 118% and independent on quench. (As not only the Auger and conversion electrons but even some γ- and X-particles are detected via their Compton electrons, counting efficiency can be higher than 100%.)

Either channels 0-2000 or channels 10-250 of the β-LSC spectrum can be used for determination of recovery (R) of ^{133}Ba. According to our results, there is no significant difference between the recoveries calculated using the different regions. In some cases, recoveries were checked and confirmed by determining the activity of ^{133}Ba by γ-spectrometry. When analyzing samples whose activity of ^{228}Ra is commensurate with that of ^{133}Ba tracer, channels 40-250 can be used as well (as the β-endpoint of ^{228}Ra is 40 keV), but this increases the uncertainty of recovery too much – this is why in such cases it is advisable to use another method.

Recovery of ^{226}Ra was assumed to be the same as that of ^{133}Ba. Activity of ^{226}Ra (A_{sample}) was calculated using channels 90-500 of the α-LSC spectrum subtracting spillover of ^{133}Ba counts into the α-counting region ($I_{cal}^\alpha/I_{cal}^\beta$; typically 0.2%-0.5%) by the formula:

$$A_{sample} = \frac{I_{sample}^\alpha - \frac{I_{cal}^\alpha}{I_{cal}^\beta} I_{sample}^\beta}{f_\alpha} \qquad (2)$$

where I_{sample}^α is α-intensity of the sample,
I_{cal}^α is α-intensity of the calibration sample,
I_{sample}^β is β-intensity of the sample and
f_α is detection efficiency of α-particles (95%).

In the region mentioned above, peaks of all α-emitter progenies of ^{226}Ra (namely ^{222}Rn, ^{218}Po and ^{214}Po) are present (as shown in Figure 3). Their in-growth was taken into account using a calibration curve based on the results and equations described by Fons et al. (2013):

$$A_{sample}^\alpha(t) = \left\{ 1 + 3 \cdot \left[1 - exp\left(-\frac{\ln(2) \cdot t}{91.68\ hours} \right) \right] \right\} \cdot A_{sample}(t=0) \qquad (3)$$

where $A_{sample}(t=0)$ is the ^{226}Ra-activity of sample at separation,
$A_{sample}^\alpha(t)$ is the α activity of sample at t hours after separation and
91.68 hours is half-life of ^{222}Rn.

Figure 3
LSC spectrum of ^{226}Ra and its progenies (without ^{133}Ba tracer). The peaks in the α-spectrum correspond (from left to right) to ^{226}Ra (4784 keV), ^{222}Rn (5490 keV), ^{218}Po (6002 keV) and ^{214}Po (7687 keV). As no ^{133}Ba tracer is present, the β-spectrum consists of β counts from β-emitter progenies of ^{226}Ra (^{214}Pb and ^{214}Bi) as well as of spillover of α counts.

Results

Some results of 38 analyzed water samples (bottled mineral waters, medicinal thermal waters and natural surface waters) can be seen in Tables 1 and 2. Our experiments have showed that the average chemical recovery was 60(±15)%, and we could not find correlation between recovery and sample composition (alkaline earth content).

According to 2.2 cpm background between channels 90-500 of the α-LSC spectrum and applying 100 min detection time, typically 10 mBq of minimal detectable activity (MDA) was achieved. Therefore, analyzing a sample of 0.5-1.5 L, the limit of detection described in the Council Directive 2013/51/Euratom [3] (namely 40 mBq/L for drinking water) is easily achievable. Typical relative uncertainty of results (in cases they were over MDA) was 8%, calculated using a coverage factor of 1 (k=1).

Discussion 2: Method reliability

To check the reliability of the method, 2 water samples of a proficiency test (Determination of activity concentration of ^{3}H, ^{226}Ra, ^{241}Am, ^{239}Pu in food and environmental samples; Institute of Nuclear Chemistry and Technology (INCT), Warsaw, Poland 2014-14) were analyzed. The results show acceptable agreement with the reference values (see Table 1).

The well-known medicinal thermal waters of Spa Rudas were also analyzed, results are reported in Table 2. The result of sample 'Hungária' was checked and confirmed by γ-spectrometry. A 20 L aliquot was evaporated and the residue was ashed. According to the γ-spectrum of the ash, activity concentration of ^{226}Ra in the original sample was 447±17 mBq L^{-1}. Earlier results are also presented in Table 2, taking into account their high variability, the results reported in this paper are acceptable.

Results of analysis of some popular bottled mineral waters (selected randomly) are reported in Table 3. Differences between older and newer values can be explained by changes in exploitation or processing technology (e. g. changing of the spring).

Sample code	Measured value	Reference value
R1/13.	< 24	50 ± 10
R2/13.	432 ± 37	440 ± 60

Table 1
Activity concentration of ^{226}Ra (mBq L^{-1}) in two intercomparison samples. The uncertainty is given using a coverage factor of 1 (k=1).

Name of spring	Measured value	Earlier results
Hungária	452 ± 45	993 ± 96 (Baradács, 1999)
		699 ± 69 (Baradács, 2002)
		532 (Baradács, 2002)
Attila	729 ± 57	2150 (Szerbin, 1996)
		1650 ± 30 (Kasztovszky et al., 1996)
		912 ± 89 (Baradács, 1999)
		834 ± 81 (Baradács, 2002)
		500 (Baradács, 2002)
Juventus	708 ± 61	710 ± 67 (Baradács, 1999)
		646 ± 64 (Baradács, 2002)
		522 (Baradács, 2002)

Table 2
Activity concentration of ^{226}Ra (mBq L^{-1}) in medicinal thermal waters of Spa Rudas. The uncertainty is given using a coverage factor of 1 (k=1).

Brand name	Measured value	Earlier results
Balfi	< 10	85 (Baradács et al., 2001)
		< 200 (Ugron, 2010)
Borsec [sparkling; Romania]	343 ± 38	
Borsec [still; Romania]	41 ± 9	
Fonyódi	< 10	
Kereki Theodora	< 10	
Kékkúti Theodora	< 10	270 (Szerbin és Köteles, 1999)
		77 (Baradács et al., 2001)
		< 170 (Ugron, 2010)
Mizse	< 10	
Natur Aqua	< 10	
Óbudai Gyémánt	100 ± 9	110 (Baradács et al., 2001)
		68 ± 29 (Guczi, 2005)
		128 ± 17 (Guczi, 2005)
		92 ± 33 (Ugron, 2010)
Szentkirályi	< 10	
Visegrádi	159 ± 14	204 (Baradács et al., 2001)
		< 129 (Guczi, 2005)
		< 180 (Ugron, 2010)

Table 3
Activity concentration of ^{226}Ra (mBq L^{-1}) in some popular Hungarian (and Rumanian) bottled mineral waters (purchased from local supermarkets). The uncertainty is given using a coverage factor of 1 (k=1).

Conclusions

A relatively fast, simple and reliable method has been developed for determination of ^{226}Ra from natural water samples, using radiochemical separation and LSC measurement. Activities of ^{133}Ba (for determination of the chemical yield of the procedure) and ^{226}Ra were determined from the same LSC measurement.

As no extra gamma-spectrometry was used for measurement of ^{133}Ba, the overall time consumption of this method (about 20 hours) is comparable with that of methods based on α-spectrometry and more convenient than that of methods based on ^{222}Rn in-growth. (However, presence of ^{228}Ra increases the uncertainty of recovery.)

This method was successfully applied for analysis of bottled mineral waters, medicinal thermal waters and natural surface waters.

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