Validation of $^{226}$Ra and $^{228}$Ra Measurements in Water Samples Using Gamma Spectrometric Analysis

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ABSTRACT

Radium isotopes can be analyzed by different analytical methods based on gamma spectrometric measurements or alpha spectrometry. An improved method was developed to determine radium isotopes from water using gamma spectrometry after radiochemical separation. The Radium was selectively extracted from acidified samples using co-precipitation procedure with iron hydroxide and followed by precipitation of radium as radium sulphate Ba(Ra)SO₄. The precipitate Ba(Ra)SO₄ was filtered through the Millipore filter paper, dried and weighed to calculate chemical yield. $^{226}$Ra and $^{228}$Ra activities were measured using low-background gamma spectrometry in water samples. Radium was pre-concentrated from environmental samples by co-precipitation with BaSO₄. The amounts of $^{226}$Ra and $^{228}$Ra on the sample were obtained by gamma-ray spectrometry for the 351 keV $\gamma$-ray from $^{214}$Pb and for the 911 keV $\gamma$-ray from $^{228}$Ac, both in radioactive equilibrium with precursors, respectively. The accuracy, selectivity, traceability, applicability and Minimum Detectable Activity (MDA) of the technique were discussed. Also, the effect of physical and chemical characteristics of the water samples such as TDS, pH, soluble species, sulphate and bicarbonate that effect on the radium determination were taking into consideration. The method has been validated with a certified reference material supplied by the International Atomic Energy Agency and reliable results were obtained. The radiochemical yields for radium were 70% - 90% and recovery was 97% and 80% for $^{226}$Ra and $^{228}$Ra, respectively.

Keywords: Radium Isotopes; Gamma-Ray Spectrometry; Water Analysis

1. Introduction

Radium (Ra) isotopes are important from the viewpoints of radiation protection and environmental protection. Their high toxicity has stimulated the continuing interest in methodology research for determination of Ra isotope in various media. Radium is a radioactive element for which no stable isotope is known. The mass numbers of the known isotopes range from 206 to 230. Among them, two radium isotopes, $^{226}$Ra and $^{228}$Ra are very significant from a radiological protection viewpoint due to their relatively long half-lives, presence in nature, and high dose conversion factors. Radium isotopes are important because they can be easily incorporated into bones due to having similar properties to other elements from Group II (i.e. calcium) and produce short lived radionuclides of high massic activity [1]. Gamma spectrometry is a useful non-destructive method that permits the simultaneous determination of many radionuclides in a bulk sample [2,3], without the need for complicated and time consuming radiochemical separations as undertaken for alpha spectrometry. However, it is limited by the weak emission probabilities of many potentially useful emission lines, the relatively poor efficiency of the High Purity Germanium (HPGe) detectors over a wide range of energy, the difficult task of precisely calibrating the efficiency of the detector, and the need to evaluate self-absorption effects [4].

Barium co-precipitation is used as a method of radium analysis due to the very similar chemical properties of barium and radium. The exploitation of the ability of barium to react with an excess of sulphate ions to produce a precipitate allows the quantitative analysis of environmental activity concentrations of radium in water [5].

In this study, rapid radiochemical separation technique for determination of isotope $^{226}$Ra and $^{228}$Ra in water samples using co-precipitation with iron hydroxide is applied. The co-precipitation with iron hydroxide acts as a separator to remain radium and barium in the solution.
(as radium barium sulphate) and remove the interfering radionuclides such as 210Pb and 210Po and matrix constituents with additional co-precipitation. The activity of 226Ra and 228Ra on filter paper is determined by γ-ray spectrometry. Uncertainties associated with the 226Ra and 228Ra activities were determined.

2. Experimental

2.1. Instrumentation

All samples were prepared in the same size Marinilli beaker to obtain the similar counting geometry. Gamma-spectrometry based on hyper-pure germanium detectors was used. The HPGe detector has a relative efficiency of 40% and full width at half maximum (FWHM) of 1.95 keV for 60Co gamma energy line at 1332 keV and operated with Canberra Genie 2000 software for gamma acquisition and analysis. 226Ra was then quantified by gamma counting for its 186-keV gamma emission, 351.9, 0.46 for 609.3 keV γ-ray from 214Bi, respectively. The activity concentration of 228Ra can also be calculated for 911.2 keV and 583 of the 228Ac progeny.

\[
A_i = \left[ \frac{1}{0.037 \gamma Y D_s \varepsilon} \right] \left( \frac{R}{F_i} \right)
\]

where:
- \(A_i\): The concentration of 226Ra or 228Ra in pCi/L,
- \(Y_i\): Chemical yield determined for the sample,
- \(D_s\): Ingrowth factor (1 - e^{-\lambda t}) = \frac{1}{\lambda} \ln(2) \text{ half life of } 222Rn \text{ of } 3.82 \text{ d},
- \(R\): Net counts per s for the gamma-ray under consideration (background and Compton contributions have been subtracted; the uncertainty or error reported for that gamma ray should be noted),
- \(F_i\): Branching ratio of γ-rays under consideration; 0.358 for 351.9, 0.46 for 609.3, 0.309 for 583 and 0.29 for 911.
- \(\varepsilon\): Counting efficiency of specific gamma ray and
- \(V\): Sample volume L.

The activity concentration of 226Ra can be calculated from the following equation for the 351.9 keV γ-ray from 214Pb and the 609.3 keV γ-ray from 214Bi, respectively. The activity concentration of 228Ra can also be calculated for 911.2 keV and 583 of the 228Ac progeny.

\[
Y_s = \frac{\text{Final mass of barium sulphate}}{\text{initial mass of barium sulphate}}
\]

where:
- \(Y_s\): Chemical yield determined for the sample, Equation (2).

The error associated with any particular counting result is determined by the use of the following equation [9]:

\[
\sigma = \frac{\sqrt{N}}{t} = \sqrt{\frac{N}{t}} = \frac{N}{\sqrt{t}}
\]

where:

\(N\): Net counts of the gamma ray under consideration.
\( r \): The net count rate.

In this case we are interested in subtracting one count from another (gross counts minus background counts) and determining the resulting \% error of the NCPs (Net Count Per Second) based on the standard deviation \( \sigma \) value. Counting instruments typically have a confidence interval of 95\%. Thus equation (2) is written as:

\[
\sigma_{r} = \sqrt{\frac{r_{bg}^2}{t_{bg}} + \frac{r_{st}^2}{t_{st}}}
\]

(4)

Where:

- \( r_{0Y}, r_{sY} \): The net count rate at the gamma line (Y) for the background and the sample respectively,
- \( t_{0}, t_{s} \): The real counting time of the background and the sample respectively.

### 2.4. Method Validation

Comparison of the chemical recovery obtained through HPGe spectrometer provides an additional QA process. The calibration of high resolution gamma spectrometers allows for accurate determination of chemical recovery in samples for \(^{226}\)Ra analysis where \(^{226}\)Ra activity levels are very high. The energy and efficiency calibration were validated by using the Certified Reference Materials (CRM), IAEA-423 and IAEA-426, present in the same counting geometry. All the samples (including standard) were counted directly in the system with a suitable counting time. The precision and accuracy of the method were also determined. The precision achieved was 6.7\% for Ra isotopes. Typical lower limits of detection for the gamma measurements were 1.6 mBq/l for \(^{226}\)Ra and 1.8 mBq/l for \(^{228}\)Ra.

### 3. Results and Discussion

Analysis of \(^{226}\)Ra and \(^{228}\)Ra via this developed technique showed suitability for relatively rapid, cheap and accurate analysis of drinking water for the assessment of drinking water. The filter samples were analyzed using HpGe and the results were obtained from the analysis reports of the different sample spectra. Background spectrum was determined and the intensities of the major peaks were recorded to subtract from the peaks recorded for filter samples. A number of spectra were analyzed taking the formation of secular equilibrium between \(^{226}\)Ra and its daughters \(^{214}\)Pb and \(^{214}\)Bi for obtaining activity concentrations for \(^{226}\)Ra and secular equilibrium between \(^{228}\)Ra and its daughter \(^{228}\)Ac for obtaining activity concentrations for \(^{228}\)Ra.

Results for both \(^{226}\)Ra and \(^{228}\)Ra activity concentrations were presented in Table 1. The results indicated that the concentration of \(^{226}\)Ra ranged from 1.02 - 8.1 and 3.1 - 7.9 mBq L\(^{-1}\) of analyzed water samples (spiked and reference samples).

### Table 1. Activity concentration of \(^{226}\)Ra and \(^{228}\)Ra in water samples.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>(^{226})Ra-St.</th>
<th>(^{228})Ra-St.</th>
<th>Mixed-St.</th>
<th>IAEA-426</th>
<th>IAEA-423</th>
<th>Spiked Ba-133 backgroud</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample volume (V)</td>
<td>Liter</td>
<td>Liter</td>
<td>Liter</td>
<td>Liter</td>
<td>Liter</td>
<td>Liter</td>
</tr>
<tr>
<td>Chemical yield fraction (Y) %</td>
<td>76 ± 60</td>
<td>88 ± 0.90</td>
<td>70 ± 1.90</td>
<td>85 ± 1.20</td>
<td>88 ± 1.60</td>
<td>1.00</td>
</tr>
<tr>
<td>Ingrowth factor (D)</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Ra-226</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ra-228</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Activity calculated Bq/L</td>
<td>1.11 ± 0.07</td>
<td>-</td>
<td>1.0 ± 0.06</td>
<td>6.44 ± 0.2</td>
<td>8.1 ± 0.40</td>
<td>N.D</td>
</tr>
<tr>
<td>(^{226})Ra</td>
<td>609.3 keV</td>
<td>351.9 keV</td>
<td>0.92 ± 0.03</td>
<td>-</td>
<td>0.90 ± 0.06</td>
<td>6.35 ± 0.3</td>
</tr>
<tr>
<td>(^{228})Ra</td>
<td>338.3 keV</td>
<td>911.2 keV</td>
<td>1.11 ± 0.07</td>
<td>-</td>
<td>1.0 ± 0.06</td>
<td>6.44 ± 0.2</td>
</tr>
<tr>
<td>Mean Activity calculated Bq/L</td>
<td>1.02 ± 0.05</td>
<td>0.95 ± 0.06</td>
<td>0.95 ± 0.06</td>
<td>6.39 ± 0.25</td>
<td>7.94 ± 0.21</td>
<td>N.D</td>
</tr>
<tr>
<td>(^{226})Ra</td>
<td>351.9 keV</td>
<td>609.3 keV</td>
<td>0.92 ± 0.03</td>
<td>-</td>
<td>0.90 ± 0.06</td>
<td>6.35 ± 0.3</td>
</tr>
<tr>
<td>(^{228})Ra</td>
<td>338.3 keV</td>
<td>911.2 keV</td>
<td>1.11 ± 0.07</td>
<td>-</td>
<td>1.0 ± 0.06</td>
<td>6.44 ± 0.2</td>
</tr>
<tr>
<td>Activity in pCi/L</td>
<td>226Ra</td>
<td>27.54 ± 1.35</td>
<td>25.65 ± 1.62</td>
<td>91.53 ± 6.75</td>
<td>214.38 ± 5.67</td>
<td>N.D</td>
</tr>
<tr>
<td>228Ra</td>
<td>-</td>
<td>150.39 ± 9.99</td>
<td>150.66 ± 5.67</td>
<td>150.39 ± 9.99</td>
<td>22.95 ± 2.03</td>
<td>N.D</td>
</tr>
</tbody>
</table>
The detection of these very low activities was made possible because we used the low background facility available at the laboratory and counting time were exceeding 3 days analyses. Results for both $^{226}$Ra and $^{228}$Ra activity concentrations determined by $\alpha$-spectrometry were then compared with those obtained for the same nuclide by $\gamma$-ray spectrometry, as shown in Table 2.

Two ground water samples from different regions (Banha and Bilbies) were analyzed to determine Ra concentrations as shown in Table 2. Despite their low counting statistics, the data with very low counting rates did not rejected because these counts were obtained during long counting sessions (5 days). The mean radioactivity level of both $^{226}$Ra and $^{228}$Ra in water samples collected from Banha and Belbeis were 18.36 ± 1.08 pCi, 6.48 ± 0.68 pCi and 21.06 ± 2.16 pCi, 17.01 ± 2.57 pCi respectively. Dyck and Jonasson in 1986 study the geochemistry of radium in the environment depending on the environmental distribution of radium varies depending on its origin. Nevertheless, according to Dyck and Jonasson, the processes affecting distribution can be referring to the following main (oversimplified) equations [10].

$$\sigma \text{Ra}^{2+} + \text{Ba}^{2+} + \text{Ca} + \text{Cl} \rightarrow \text{Ca}^{2+} + \text{Ra}^{2+} - \text{Cl} - \text{Ba}$$

Adsorption,

$$x\text{Ca}^{2+} + (1-x) \text{Ra}^{2+} + \text{MCO}_3^- \rightarrow \text{Ca}_x\text{Ra}_{1-x}\text{CO}_3^- + \text{M}^{2+}$$

Co-precipitation,

$$\text{Ra}^{2+} + \text{SO}_4^{2-} \rightarrow \text{RaSO}_4$$

Surface reaction,

$$\text{Ra}^{2+} + 2\text{Cl}^- \rightarrow \text{RaCl}_2$$

Soluble Species... etc.

Also, the physical and chemical characteristics of water mostly affected the radioactivity level of the radium in groundwater rather than the concentration of the parent naturally occurring nuclides in host rocks [11]. So, physical characteristics and major element compositions were determined (chemical contents, conductivities and different chemical compositions) as shown in Table 3 taking into consideration the effect of physical and chemical properties of the samples such as TDS, pH, soluble species, sulphate and bicarbonate. As shown in Table 3, the chemical composition of water in the first sample is Ca-Mg-HCO-type water, whereas the second one is Ca-Mg-Cl-type depending on the geological area and its composition [12].

Table 4 represents the comparison of the minimum detectable activity and efficiency obtained using the gamma spectrometry with other techniques [13] such as LSC and alpha spectroscopy for the determination of $^{226}$Ra and $^{228}$Ra. However, this method is the first trial and in the near future, more development will considered

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Banha ground water (a)</th>
<th>Belbeis ground water (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical yield fraction (Y) %</td>
<td>90 ± 0.5</td>
<td>88 ± 20</td>
</tr>
<tr>
<td>Ingrowth factor (D)</td>
<td>Ra-226 0.99</td>
<td>Ra-228 1</td>
</tr>
<tr>
<td>Activity calculated Bq/L</td>
<td>Ra-226 609.3 keV 0.70 ± 0.05</td>
<td>Ra-228 351.9 keV 0.271 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>Ra-226 338.3 keV 0.66 ± 0.03</td>
<td>Ra-228 911.2 keV 0.62 ± 0.12</td>
</tr>
<tr>
<td>Mean activity calculated Bq/L</td>
<td>Ra-226 609.3 keV 0.68 ± 0.04</td>
<td>Ra-228 351.9 keV 0.78 ± 0.08</td>
</tr>
<tr>
<td>Activity in pCi/L</td>
<td>Ra-226 18.36 ± 1.08</td>
<td>Ra-228 21.06 ± 2.16</td>
</tr>
</tbody>
</table>

Table 3. Physical characteristics and major elements composition in the groundwater under this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Cond. (µS)</th>
<th>TDS</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banha</td>
<td>8.1</td>
<td>467</td>
<td>400</td>
<td>41.7</td>
<td>5.70</td>
<td>24.9</td>
<td>38.8</td>
<td>44.3</td>
<td>45.20</td>
<td>220.4</td>
</tr>
<tr>
<td>Belbeis</td>
<td>7.7</td>
<td>400</td>
<td>370</td>
<td>56.1</td>
<td>5</td>
<td>14.2</td>
<td>41.1</td>
<td>80</td>
<td>56.20</td>
<td>69.80</td>
</tr>
</tbody>
</table>

*Uncertainties are around 10% for Cl and SO₂, and around 5% for other cations.*
Table 4. Minimum detectable activity and counting efficiency for alpha particle 226Ra using LSC, Alpha spectrometry and gamma spectrometry.

<table>
<thead>
<tr>
<th></th>
<th>CPM background</th>
<th>226Ra counting efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSC</td>
<td>0.1 - 1.0</td>
<td>95%</td>
</tr>
<tr>
<td>Alpha spectrometry</td>
<td>0.003 - 0.01</td>
<td>20%</td>
</tr>
<tr>
<td>Gamma spectrometry</td>
<td>0.096</td>
<td>70% - 90%</td>
</tr>
</tbody>
</table>

...to optimize the measuring conditions.

4. Conclusion

Calibration of the gamma spectrometric method for 228Ra measurement via the 228Ac daughter, and development of a digestion procedure for radium sources prepared by BaSO4 co-precipitation to enable alpha spectrometric measurement of the 228Ra daughter, 228Th, were undertaken. This work is aimed to the validation of the methodology currently applied in our laboratory for the determination of 226Ra and 228Ra in environmental samples by γ-spectrometry. The methodology presented in this paper has been checked by means of its application to different water samples in which the 226Ra and 228Ra activity concentrations had been previously determine by validated α-ray spectrometry procedure. This comparison was carried out through the application of both 226Ra and 228Ra methodologies (γ and α) to a total of 4 water samples (2 spiked and 2 references).

REFERENCES


