Determination of Radium Concentrations in Hot-Spring Waters with Cation Exchange Resin

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Abstract

Experimental conditions are discussed for a new analytical method for determining $^{226}$Ra and $^{228}$Ra concentrations in hot-spring waters. The method is aimed to be applicable to the field works. The acidity of the sample water is adjusted to 0.1 M HCl and Ra isotopes are collected by the cation exchange resin in a successive ion exchange procedures of batch operations: the second ion exchange procedure is applied to the same sampled water after the removal of the resin in the first procedure. The concentration of Ra isotopes in the sample water can be estimated from the amount of Ra isotopes recovered in the two operations by calculation. The amounts of $^{226}$Ra and $^{228}$Ra on the resin are obtained by a $\gamma$-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 present estimation method is applicable to 5 l of hot-spring waters having $^{226}$Ra concentrations of larger than 10 mBq/l, and may be applicable to the ordinary underground waters of less than 1 mBq/l by using 50 l of sample water.

Key words: radium concentration, hot-spring water, cation exchange resin, field work, gamma-ray spectrometry
要旨

温泉中の$^{226}\text{Ra}$および$^{228}\text{Ra}$を定量する新しい方法を開発するための実験条件を検討した。本方法は野外調査時に応用することを目的としている。試料水の酸濃度を0.1 M HCl 調整した温泉水試料に対し、陽イオン交換樹脂をパッチ法で用い、回収操作を2回連続して行うことにより回収量を求め、計算によりラジウム濃度を求めることができる。樹脂に回収された$^{226}\text{Ra}$と$^{228}\text{Ra}$の量は、ガンマ線スペクトロメトリーにより$^{226}\text{Ra}$と$^{228}\text{Ra}$と放射平衡になった$^{214}\text{Pb}$の511 keVのガンマ線と$^{228}\text{Ac}$の911 keVのガンマ線を測定することにより求められる。この方法により、$^{228}\text{Ra}$として10 mBq/l以上含む温泉水試料では5 L、1 mBq/l以下の濃度の地下水試料では50 Lを対象にすればラジウムの定量が可能である。

キーワード：ラジウム、温泉、陽イオン交換樹脂、野外調査、ガンマ線スペクトロメトリー

1. Introduction

Several techniques have been reported in the literature on the determination of the concentrations of $^{226}\text{Ra}$ in thermal spring waters or natural waters, including the coprecipitation with BaSO$_4$ or with PbSO$_4$, followed by $\alpha$-ray spectrometry, $\gamma$-ray spectrometry and liquid scintillation spectrometry (Sato et al., 1975; Honma and Murakami, 1977; Horiuchi and Murakami, 1978; Environment Agency of Japan, 1978; Horiuchi et al., 1979; Horiuchi, 1981; Moron et al., 1986; Yamamoto et al., 1989; Hancock and Martin, 1991; Burnett and Tai, 1992; Yamamoto et al., 1994). “Guide to the analysis of mineral spring waters” appeared in J. Soc. Eng. Mineral Springs, Jpn, issued in 1978 recommends the procedure of the coprecipitation of $^{226}\text{Ra}$ with BaSO$_4$, followed by the measurement of $^{222}\text{Rn}$ in equilibrium with $^{226}\text{Ra}$ by a liquid scintillation spectrometer (Environment Agency of Japan, 1978).

However, Ba reagents frequently contain small but significant amounts of $^{226}\text{Ra}$ of several fractions of 1 Bq/g. As the amount of $^{226}\text{Ra}$ impurity in BaCl$_2$·2H$_2$O reagents from 3 major makers in Japan was found to be in the range of 20–100 mBq/g, several tens mBq of $^{226}\text{Ra}$ might be mixed by the coprecipitation with several tens mg of Ba. Yamamoto et al (1989) who found the amount of $^{226}\text{Ra}$ impurity in Ba reagents ranged 100–400 mBq/g proposed the procedure to eliminate $^{228}\text{Ra}$ impurity from Ba compounds by cation exchange separation using CyDTA (cyclohexanediaminetetraacetic acid) as eluant. An $\alpha$-ray spectrometry was applied for $^{226}\text{Ra}$ separated from the coprecipitating Ba compounds thus purified. These observations show that the separation procedure including coprecipitation of Ra with Ba compounds is generally not preferable in the determination of a minute amount of $^{226}\text{Ra}$ of less than 1 mBq/l in the water sample. Furthermore, most of these methods have difficulties in applying them to the field works because of their tedious chemical procedures which need the transportation of a large amount of sample water to the laboratory for the isolation of $^{226}\text{Ra}$ by a series of chemical procedures.

The experimental conditions of a new easy field work method for the isolation and measurement of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ in thermal spring waters or underground waters are studied. This method consists of two procedures : (1) collection of Ra isotopes by cation exchange resin for the isolation, and (2) the determination of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ by $\gamma$-ray spectrometry.
2. **Experimentals**

Most of the present studies on experimental conditions for chemical procedures with cation exchange resin were made by use of Ba instead of Ra, mainly because the amount of the waste water containing $^{226}$Ra should be in minimum size. Barium was determined by the atomic absorption spectrometry.

### 2.1 Collection

Collection rate of Ba on resin was investigated with the solution of 3 and 30 ppm concentrations. The acidity of the solution was adjusted to 0.1 M HCl and cation exchange resin of Dowex 50W-X8, #20-50, in H-form, was employed. The amount of water volume was set to be 5 l or 50 l.

Collection rate was observed with the 3 methods described below:

- **Method (1):** A 30 g of resin was put into a 5 l of the solution directly and the solution was stirred for 15 min.
- **Method (2):** A 30 g of resin was put into a 50 l of the solution directly and the solution was stirred for 15 min.
- **Method (3):** A 30 g of resin was placed within a plastic tube. A 50 l of the solution was circulated for 15 min through the tube at a flow rate of 6 l/min with the aid of a portable pump.

The collection rates vs the operating time is given in Fig. 1. Figure 1 indicates that the Method (1) is effective in case where the amount of the water sample is as small as 5 l, while the Method (3) is favorable for the water samples of a larger amount than 50 l.

### 2.2 Estimation of Ra concentration in sample water

The time required for the ion exchange equilibrium between a large volume of sample water and a small amount of resin will be longer than 1 hour. However, a short time as possible is usually required for the operation in the field work. Assuming that the temperature and chemical properties of the large volume of sample water may not change

![Fraction Recovered vs Time](image-url)

*Fig. 1 Recovery curve of Ba by cation exchange resin.*

- **•**: Method (1)
- **△**: Method (2)
- **○**: Method (3)
significantly after a shot-time collection operation, the Ra content in the water samples can be estimated by the amount of Ra recovered by the two successive ion exchange procedures operated in the fixed time from the same water sample by using the following equations:

\[
C_1 = C_0 \cdot \alpha \\
C_2 = (C_0 - C_1) \cdot \alpha \\
\Rightarrow \alpha = 1 - \frac{C_2}{C_1} \\
\Rightarrow C_0 = \frac{C_1}{1 - \frac{C_2}{C_1}}
\]

where \( C_0 \) : Total quantity of Ra in the initial water sample, which can be converted into the concentration by the volume of sampled water.

\( C_1 \) : Quantity recovered from the initial sample water by the 1st operation.

\( C_2 \) : Quantity recovered by the 2nd operation from the remaining water sample after removal of the resin used in the 1st operation.

\( \alpha \) : Collection efficiency in the fixed operation time for the water sample. The collection efficiency is assumed to be the same for the two successive operations. The operation time was set to the 15 min for the present estimation.

### 2.3 Interference of coexisting ions

Calcium and Fe are one of the major constituents usually existing in the natural waters. Though some thermal spring waters contain Ca more than 500 ppm, most of the concentrations of 2,350 thermal spring waters from 30 localities in Japan are reported to be less than 100 ppm (Hirakawa et al., 1977). Frequency distribution of concentrations of Ca and Fe are shown in Fig. 2.

![Fig. 2 Frequency distribution of concentration of Ca and Fe ion in Japanese thermal waters. (after Hirakawa et al., 1977).](image)
Interference of the coexisting ions to the present method was studied with the 0.1 M HCl solutions of 30 ppm Ba by mixing a following range of Ca and Fe ions with the solution: the concentrations of Ca were adjusted to 250, 500, 750, 1,000 and 1,250 ppm, and those of Fe were adjusted to 300, 650, 950 and 1,600 ppm. The calculated concentrations \( C_C \) estimated from \( C_1 \) and \( C_2 \) by eq. (4) are compared with the known initial concentration \( C_0 \) in Fig. 3. As the \( C_C \)'s for different Ca and Fe concentrations are approximately equal to the initial \( C_0 \) within their concentration range up respectively to 1,250 and 650 ppm, the interference of coexisting ion to the present method of estimation can be ignored as far as the samples are the ordinary natural waters.

2.4 Collection of Ra isotopes

The phosphorite from Florida, U.S.A., was used throughout the following studies. This phosphorite containing 3 Bq/g of \(^{226}\)Ra was dissolved in 6 M HCl to prepare the stock solution of \(^{226}\)Ra. Initially, the U impurity was eliminated from the stock solution with UTEVA Resin, an extraction chromatograph material supplied by Eichrom Industries, Inc., U.S.A., because the 186 keV \( \gamma \)-ray from \(^{235}\)U interferes the 186 keV spectral line from \(^{226}\)Ra. An aliquot of the \(^{226}\)Ra solution thus refined was poured into a vessel, in which a 30 g of cation exchange resin (Dowex 50W-X8, #100-200, in H-form) had been placed in advance in order to obtain the initial quantity of \(^{226}\)Ra (\( C_0 \)). The acidity of another aliquot was adjusted to 0.1 M HCl and the volume of the solution was adjusted to 5 l. After the solution and a 30 g of cation exchange resin were mixed, the mixture was stirred for 15 min. The resin that collected \(^{226}\)Ra was taken out from the solution to measure \( C_1 \) in eq. (1). The second collection procedure was applied to the remaining solution after the removal of the resin in the first operation and the resin was taken out to measure \( C_2 \) in eq. (2). Each recovered resin was dried and packed into containers for \( \gamma \)-ray measurement and were stored for one month in order that \(^{222}\)Rn attained to be in radioactive equilibrium with \(^{226}\)Ra. Radioactivities of \(^{226}\)Ra and \(^{214}\)Pb in equilibrium with \(^{222}\)Rn were determined by \( \gamma \)-ray spectrometry.
2.5 Gamma-ray spectrometry

Gamma-ray intensities were measured with an HPGe semiconductor detector. The counting efficiency for γ-rays in the present detector was estimated by the efficiency curve constructed by using the relative counting efficiencies for the plural γ-rays from a single nuclide such as 132Eu, 60Co and 138La, together with the normalizing point at the 1,460 keV γ-ray from 40K in the chemical reagent of KCl. The logarithmic relationship between the relative counting efficiency and the γ-ray energy was made to fit to the quadratic function by the method of least squares and was normalized at 1,460 keV. Radioactivities of 226Ra, 214Pb, 214Bi and 228Ac were determined respectively by the 186 keV, the 351 keV, the 609 keV and the 911 keV γ-rays.

2.5.1 The use of the 351 keV γ-ray from 214Pb equilibrated with 226Ra

Though the 186 keV γ-ray from 226Ra itself can be used for the determination of 226Ra, the branching ratio of the 186 keV γ-ray is only 3.6%. On the other hand, as that of the 351 keV γ-ray from 214Pb is 37.6%, the indirect detection of 226Ra by the 351 keV γ-ray from 214Pb in equilibrium with 226Ra is more effective than the direct use of the 186 keV γ-ray from 226Ra. If U coexists in the sample water, the 185.7 keV γ-ray from 235U may interfere the determination of the 186.2 keV γ-ray from 226Ra. U should be removed before the ion exchange procedure of 226Ra as described before in [24]. In addition, as the correction factors due to absorption and self-absorption of the higher energy γ-rays are smaller, the use of the 351 keV from 214Pb is preferable for the spectrometry.

2.5.2 Escape of 222Rn from the sample container

Measurement of 214Pb and 214Bi for 226Ra was made to confirm whether 222Rn is completely in a radioactive equilibrium with 226Ra in the container.

Ion exchange resins by which 226Ra was collected were packed into containers made of 3 different materials: polypropylene, glass and steel.

The establishment of the equilibrium of 222Rn with 226Ra in the sample container is checked by the activity ratio of 214Pb to 226Ra and 214Bi to 226Ra. The measured activity ratios for 3 different containers are given in Table 1.

(1) Container of polypropylene (65 mmφ, 15 mmH): The activity ratio has showed to be about 0.75, indicating that one fourth of the equilibrated 222Rn escapes through the material (polypropylene) of the container wall of 1.0 mm thick.

<table>
<thead>
<tr>
<th>Container</th>
<th>226Ra (186keV)</th>
<th>214Pb (351keV)</th>
<th>214Bi (609keV)</th>
<th>214Pb/226Ra</th>
<th>214Bi/226Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>1.22±0.33</td>
<td>-</td>
<td>0.89±0.04</td>
<td>-</td>
<td>0.73±0.20</td>
</tr>
<tr>
<td></td>
<td>2.12±0.33</td>
<td>-</td>
<td>1.63±0.33</td>
<td>-</td>
<td>0.77±0.12</td>
</tr>
<tr>
<td>Glass culture dish</td>
<td>1.39±0.12</td>
<td>-</td>
<td>0.52±0.02</td>
<td>-</td>
<td>0.37±0.04</td>
</tr>
<tr>
<td></td>
<td>0.79±0.10</td>
<td>-</td>
<td>0.06±0.01</td>
<td>-</td>
<td>0.08±0.02</td>
</tr>
<tr>
<td>Steel (Tin can)</td>
<td>0.89±0.31</td>
<td>0.98±0.05</td>
<td>0.88±0.05</td>
<td>1.10±0.39</td>
<td>0.99±0.35</td>
</tr>
<tr>
<td></td>
<td>5.21±0.54</td>
<td>5.00±0.10</td>
<td>4.38±0.10</td>
<td>0.96±0.10</td>
<td>0.84±0.09</td>
</tr>
<tr>
<td></td>
<td>3.60±0.53</td>
<td>3.08±0.08</td>
<td>2.72±0.09</td>
<td>0.84±0.13</td>
<td>0.76±0.11</td>
</tr>
<tr>
<td></td>
<td>0.87±0.29</td>
<td>1.00±0.05</td>
<td>0.93±0.05</td>
<td>1.15±0.39</td>
<td>1.07±0.36</td>
</tr>
</tbody>
</table>
(2) Container of glass (70 mmφ, 16 mmH): This container is a pair of glass culture dish having the wall of 2.0 mm thick and it was sealed with silicone. Different and small activity ratios are observed. Major part of the $^{222}\text{Rn}$ formed from $^{226}\text{Ra}$ can easily escape through the possible cavity between the wall and the sealing material or through the sealing material itself.

(3) Container of steel (60 mmφ, 10 mmH): This container is a tin can having a thin wall of 0.25 mm thick. The activity ratios indicate that $^{222}\text{Rn}$ exists in radioactive equilibrium with $^{226}\text{Ra}$. As this type of can is available commercially, the use of tin cans is useful for the routine measurement.

### 3. Results and discussion

#### 3.1 Ra concentrations of some hot-spring waters

Eleven hot-spring water samples from Tamagawa, Masutomi, Sarugajo, Arima, Onogawa, Misasa and Hijiori hot-springs were used for the experiment. Radium was separated by Method (1) in [2.1] for the hot-spring waters of 5–10 l and by Method (3) for the well water of 50 l. Results are given in Table 2. Concentration of the well water in Table 2 was deduced from the 609 keV γ-ray from $^{214}\text{Bi}$, because the 351 keV γ-ray from $^{214}\text{Pb}$ was not determined due to the larger Compton background than the 609 keV from $^{214}\text{Bi}$. While $C_1$ in eq. (1) was obtained for all of the sample, $C_2$ was not always obtained, because the collection efficiency is so large that $C_2$ was not detected. In this case, $\alpha$ was assumed to be unity in the estimation of the concentration. Different collection efficiencies ($\alpha$) were observed for different water sources which may due to the different properties of respective sample waters. The concentrations of $^{226}\text{Ra}$ deduced from the 186 keV spectral line were observed significantly larger than those of $^{214}\text{Pb}$, because the 186 keV spectral line was possibly overlapped with the 186 keV

<table>
<thead>
<tr>
<th>Sample water</th>
<th>$^{226}\text{Ra}$ ($^{214}\text{Pb}$)</th>
<th>$^{226}\text{Ra}$ ($^{228}\text{Ac}$)</th>
<th>$\alpha$</th>
<th>$^{226}\text{Ra}$ reported</th>
<th>$^{228}\text{Ra}$/$^{226}\text{Ra}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tamagawa</td>
<td>60±8</td>
<td>1120±110</td>
<td>0.89±0.06</td>
<td>55–270 (Yokoyama, 1955)</td>
<td>18±3</td>
</tr>
<tr>
<td>Masutomi 1</td>
<td>9±2</td>
<td>--</td>
<td>--</td>
<td>160–300 (Horiuchi and)</td>
<td>--</td>
</tr>
<tr>
<td>Masutomi 2</td>
<td>46±5</td>
<td>56±10</td>
<td>0.90±0.02</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Masutomi 3</td>
<td>980±80</td>
<td>2140±130</td>
<td>0.27±0.03</td>
<td>37±5 (Yamamoto et al., 1994)</td>
<td>2.2±0.2</td>
</tr>
<tr>
<td>Sarugajo</td>
<td>38±3</td>
<td>--</td>
<td>--</td>
<td>6–110 (Sato et al., 1975)</td>
<td>--</td>
</tr>
<tr>
<td>Arima 1</td>
<td>186±13</td>
<td>64±26</td>
<td>0.58±0.03</td>
<td>37–7750 (Yokoyama, 1955)</td>
<td>0.34±0.14</td>
</tr>
<tr>
<td>Arima 2</td>
<td>63±9</td>
<td>46±13</td>
<td>0.46±0.06</td>
<td>--</td>
<td>0.73±0.23</td>
</tr>
<tr>
<td>Onogawa 1</td>
<td>322±33</td>
<td>495±60</td>
<td>0.32±0.03</td>
<td>--</td>
<td>1.5±0.2</td>
</tr>
<tr>
<td>Onogawa 2</td>
<td>257±14</td>
<td>533±40</td>
<td>0.59±0.03</td>
<td>--</td>
<td>2.1±0.2</td>
</tr>
<tr>
<td>Misasa</td>
<td>50±2</td>
<td>106±5</td>
<td>--</td>
<td>37–550 (Yokoyama, 1955)</td>
<td>2.1±0.1</td>
</tr>
<tr>
<td>Hijiori</td>
<td>12±2</td>
<td>30±3</td>
<td>--</td>
<td>--</td>
<td>2.5±0.5</td>
</tr>
<tr>
<td>Well water (*)</td>
<td>0.64±0.15</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

(*) Well water from Meiji University, Kawasaki
γ-ray from $^{235}$U coexisting in the sample waters. The concentrations of $^{214}$Pb and $^{228}$Ac represent those of $^{226}$Ra and $^{228}$Ra, respectively. The concentrations estimated presently are in the same order of magnitude as the reported values. Different activity ratios of $^{226}$Ra/$^{228}$Ra were observed in the various water samples from different water source.

Though different collection efficiency ($\alpha$) was obtained in different combination of the volume for sample water and the mesh-size for collecting resin for the sample of Masutomi and Onogawa as shown in Table 3, the two estimated Ra concentrations agreed well with each other, indicating that the present estimation method is effective even when different collection efficiency is obtained for any experimental condition of isolation.

### 3.2 Application to field works

The Ra concentrations estimated in an in-situ separation were compared with those determined by the separation method carried out in the laboratory for the same water samples transported. The Method (3) described in [2.1] was applied to 50 l water samples from Onogawa and Hijiori hot-springs. The good agreement between two data (lab. and field) shown in Table 4 suggests that the present field work analytical method is applicable enough.

#### Acknowledgements

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### Table 3 Ra concentrations obtained in different experimental conditions

<table>
<thead>
<tr>
<th>Volume (l)</th>
<th>Resin (mesh)</th>
<th>$^{226}$Ra ($^{214}$Pb)</th>
<th>$^{226}$Ra ($^{228}$Ac)</th>
<th>$^{226}$Ra/$^{228}$Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Masutomi 3-1</td>
<td>10</td>
<td>20-50</td>
<td>980±80</td>
<td>2410±130</td>
</tr>
<tr>
<td>Masutomi 3-2</td>
<td>5</td>
<td>100-200</td>
<td>1026±23</td>
<td>2673±63</td>
</tr>
<tr>
<td>Onogawa 1-1</td>
<td>10</td>
<td>20-50</td>
<td>322±33</td>
<td>495±60</td>
</tr>
<tr>
<td>Onogawa 1-2</td>
<td>5</td>
<td>100-200</td>
<td>267±8</td>
<td>469±17</td>
</tr>
</tbody>
</table>

### Table 4 Ra concentrations obtained in the field work and in the laboratory work

<table>
<thead>
<tr>
<th></th>
<th>$^{226}$Ra ($^{214}$Pb)</th>
<th>$^{228}$Ra ($^{228}$Ac)</th>
<th>$^{226}$Ra/$^{228}$Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onogawa 2 (lab.)</td>
<td>257±14</td>
<td>507±24</td>
<td>2.0±0.1</td>
</tr>
<tr>
<td>Onogawa 2 (field)</td>
<td>257±23</td>
<td>533±40</td>
<td>2.1±0.2</td>
</tr>
<tr>
<td>Hijiori (lab.)</td>
<td>10±2</td>
<td>32±3</td>
<td>3.2±0.7</td>
</tr>
<tr>
<td>Hijiori (field)</td>
<td>12±2</td>
<td>30±3</td>
<td>2.5±0.5</td>
</tr>
</tbody>
</table>
References


