A Practical Method for the Simultaneous Determination of $^{238}$Th, $^{226}$Ra, $^{210}$Pb and $^{210}$Po in Seawater*

Koh Harada† and Shizuo Tsunogai†

Abstract: A practical method has been developed for the simultaneous determination of $^{226}$Ra, $^{238}$Th, $^{210}$Pb and $^{210}$Po in seawater. In the method, the samples are spiked with $^{226}$Ra, $^{239}$Th, $^{210}$Pb and common lead to determine chemical yield. These nuclides are coprecipitated with calcium carbonate and ferric hydroxide from 20 to 50 l of seawater and separated from one another by using coprecipitation and ion exchange techniques. Counting sources of Ra and the other nuclides are prepared by electrodeposition onto silver discs. Their radioactivities are counted with an $\alpha$-spectrometer and a low background $\beta$-counter. This method gives a standard deviation of about 5% for replicate determination of $^{226}$Ra and the other nuclides.

1. Introduction

Natural radionuclides in seawater, such as $^{226}$Ra, $^{234}$Th, $^{210}$Pb and $^{210}$Po are useful tracers for studies in oceanography (Koczy, 1958; Bhat et al., 1969; Rama et al., 1961). These four nuclides in seawater, however, have not been measured simultaneously (Miyake and Sugimura, 1964; Broecker et al., 1967; Ku et al., 1970; Craig et al., 1973; Nozaki and Tsunogai, 1973a; Amine et al., 1974; Matsumoto, 1975; Minagawa and Tsunogai, 1980; etc.). As nearly the same volume of water is necessary for each individual determination, it seems worthwhile to determine $^{226}$Ra, $^{234}$Th, $^{210}$Pb and $^{210}$Po in the same seawater sample.

At present, $^{226}$Ra in seawater is usually determined by an indirect method based on the counting of $^{222}$Rn derived from the decay of $^{226}$Ra. This method, however, has several disadvantages including the necessity of frequent calibrations with a $^{226}$Ra standard, a varied extraction efficiency of $^{222}$Rn from sample to sample, and a relatively high background in the counting system.

There are some direct determination methods for $^{226}$Ra, in which $^{226}$Ra is purified by an ion exchange method, evaporated onto a platinum disc and counted with an $\alpha$-ray spectrometer (Sugimura and Tsubota, 1963; Nozaki, 1974) but the surface roughness of the counting source is likely to introduce counting errors. Koide and Bruand (1975) have also developed a direct determination method which involves coprecipitation of uranium series nuclides with aluminum phosphate followed by fuming nitric acid treatment and electrodeposition onto a platinum disc. This method, however, is rather tedious, corrosive and expensive.

We previously found that radium is electrodeposited onto a silver disc from a hydrochloric acid solution during the radiochemical determination of thorium. Based on this finding and previously established determination methods for $^{234}$Th, $^{210}$Pb and $^{210}$Po (Bhat et al., 1969; Matsumoto 1975; Nozaki and Tsunogai, 1973b) a practical method has been developed for the determination of $^{226}$Ra simultaneously with $^{234}$Th, $^{210}$Pb and $^{210}$Po in seawater.

2. Experimental

2.1. Apparatus

A silicon surface barrier detector (Ortec BR-25-450-100) attached to a 4096-channel pulse-height analyzer (Norland Model IT-5400), an anti-coincidence type 2$\pi$-gas flow counter (Aloka model LBC-451) and an atomic absorption spectrophotometer (Jarrel-Ash Model AA-8200) were used for the $\alpha$-spectrometry, the $\beta$-activity counting and the determination of lead, respectively.
The Simultaneous Determination of $^{224}$Th, $^{226}$Ra, $^{210}$Pb and $^{210}$Po in Seawater

2.2. Reagents

All reagents used were analytical grade except for sodium carbonate which was of foodadditive quality.

Lead carrier: 5.4 g of PbO was dissolved in 11 of 1 M nitric acid solution.

Iron carrier: 24 g of FeCl$_3$·6H$_2$O was dissolved in 11 of 1 M hydrochloric acid solution.

$^{228}$Ra tracer: Th(NO$_3$)$_4$·H$_2$O was dissolved in 7.5 M nitric acid solution. $^{228}$Ra was separated from this solution using an anion exchange column. A 20 dpm ml$^{-1}$ solution of $^{228}$Ra in 1 M nitric acid was prepared.

$^{230}$Th tracer: A 2 dpm ml$^{-1}$ solution of $^{230}$Th in 1 M hydrochloric acid was prepared. When we could not purchase the tracer, $^{230}$Th was extracted from deep-sea sediments (red clay).

$^{208}$Po tracer: A 2 dpm ml$^{-1}$ solution of $^{208}$Po in 1 M hydrochloric acid was prepared.

Mixed tracer solution: Prior to use, 5 ml each of the above five solutions were mixed. The mixed solution (25 ml) contained 25 mg each of Fe and Pb, 100 dpm of $^{228}$Ra, and 10 dpm of each $^{230}$Th and $^{208}$Po.

Ba carrier: 3.6 g of BaCl$_2$·H$_2$O was dissolved in 11 of 1 M hydrochloric acid solution.

Cation exchange column: BIO-RAD 50W-X12 resin (200-400 mesh) was used. The column was 120 mm in length and 6 mm in diameter. The resin was sufficiently conditioned and then finally washed with 200 ml of 1.6 M hydrochloric acid solution.

Anion exchange column: Dowex 1-X8 resin (100-200 mesh) was used. The column was 60 mm in length and 8 mm in diameter. The conditioned resin was finally washed with 50 ml of 7.5 M nitric acid solution or 10 M hydrochloric acid solution.

2.3. Recommended procedure

The recommended procedure is schematically shown in Fig. 1.

Immediately after sampling, transfer a 20-501 seawater sample to a thin polyethylene bag in a bucket. Acidify the sample with 200 ml of concentrated nitric acid. Add 25 ml of the mixed tracer solution and stir vigorously. After allowing it to stand for 6 hr or more, neutralize it with about 230 ml of 16 M ammonia water and add about 100 g of sodium carbonate (2.5 g per 11 of seawater) dissolved in water. Stir the solution vigorously and let it stand overnight.

Siphon off as much of the supernatant solution as possible by replacing the bucket with a smaller one. Transfer the precipitate to a 500 ml beaker and dissolve it with 200 ml of 7.5 M nitric acid including the portion used for washing the bag. Add 10 ml of the barium carrier solution to this solution. Then heat it on a hot plate to completely remove the carbon dioxide. Alkalize the solution to pH 8 with about 150 ml of 6 M ammonia water and separate the hydroxide precipitate by filtration. Acidify the filtrate with 5 ml of concentrated hydrochloric acid and store for $^{226}$Ra determination.

Dissolve the precipitate with about 50 ml of 0.5 M hydrochloric acid and transfer the solution to a 100 ml Teflon beaker with 1 ml of 20% hydroxylamine hydrochloride. Set afloat a silver disk (25 mm in diameter, 0.05 mm in thickness) coated on the upside with Teflon paste on the solution. Keep the temperature of the solution at 80-90°C for more than 3 hr with a hot plate, and polonium is spontaneously electroplated onto the silver disc. After washing the silver disc with a few ml of deionized water, count the α-activities emitted from its $^{210}$Po and $^{209}$Po.

Add 10 ml of 15% hydrogen peroxide to the remaining solution containing thorium and lead.
and heat the solution on a hot plate for more than 30 min. Filter the hydroxide precipitate made with about 5 ml of 6 M ammonia water, and combine the filtrate with the stored solution for $^{226}$Ra determination. Dissolve the precipitate with 10 ml of 6 M hydrochloric acid and evaporate the solution to dryness. Dissolve the residue again with 10 ml of 10 M hydrochloric acid and pass the solution through the anion exchange column. Elute thorium and lead with 50 ml of 10 M hydrochloric acid. Evaporate the eluate to dryness and dissolve the residue with 1 ml of 7.5 M nitric acid. Repeat this procedure three times and dissolve the residue with 20 ml of 7.5 M nitric acid. Pass the solution through the anion exchange column. Elute lead with 60 ml of 7.5 M nitric acid, including the washings and dilute effluent to exactly 100 ml. Take a 1 ml aliquot of the solution to determine the chemical yield of lead using an atomic absorption method. Add 5 ml of the $^{208}$Po tracer to the remaining solution. After more than 3 months, determine the activities of $^{208}$Po and $^{210}$Po produced from $^{210}$Pb during storage by the procedure described above and calculate the $^{210}$Pb content.

Thorium is eluted from the anion exchange column with 70 ml of 6 M hydrochloric acid. Evaporate the effluent to dryness. If a white residue is clearly observed, repeat the above anion exchange procedure. Dissolve the evaporation residue with a few drops of 6 M hydrochloric acid, and evaporate it to dryness again. Finally, dissolve it with 1 ml of 1 M hydrochloric acid and transfer to the electrodeposition cell (Fig. 4) with 15 ml of ethanol. Thorium isotopes are electroplated onto a silver disc at 100-200 mA and 15 V for 2 hr. After three days, count the $\beta$-activity of $^{234}$Pa in radioactive equilibrium with $^{234}$Th and the $\alpha$-activity of $^{210}$Th to obtain the chemical yield of thorium.

Dilute the solution reserved for $^{226}$Ra to about 800 ml with deionized water and add 15 ml of 25% sodium chromate. Neutralize the solution with 6 M ammonia water. Filter the barium chromate precipitate aged by heating, and dissolve it with 10 ml of 6 M hydrochloric acid and 200 ml of water. Repeat the precipitation procedure. Collect the precipitate on a Millipore HA (25 mm in diameter, pore size 0.45 $\mu$m) filter. After 20-30 days, dissolve the precipitate with 15 ml of 1.6 M hydrochloric acid, and pass it through the cation exchange column. After washing the column with 240 ml of 1.6 M hydrochloric acid solution at a rate of 0.6 ml min$^{-1}$, elute the radium with 50 ml of 8 M hydrochloric acid solution. Evaporate the eluate containing radium to dryness. After 6-14 days, radium in the evaporation residue is electroplated onto a silver disc using the same method as for thorium. Heat the silver disc under a weak flame and measure the $\beta$-activity emitted from $^{228}$Ac, a daughter of $^{228}$Ra, and the $\alpha$-activity of $^{226}$Ra.

3. Results and Discussion

3.1. Coprecipitation of $^{226}$Ra, $^{234}$Th, $^{210}$Pb and $^{210}$Po with carbonate and hydroxide from seawater

Matsumoto (1975) made a ferric hydroxide precipitate with 500 mg of iron for the coprecipitation of $^{234}$Th from 40-50 l seawater. This amount of iron, however, is so great that it interferes with the spontaneous electrodeposition of polonium. Nozaki and Tsunogai (1973b) obtained good results for the coprecipitation of lead and polonium with calcium carbonate. We have tried to coprecipitate thorium, radium, lead and polonium with calcium carbonate and a small amount of ferric hydroxide. The results are summarized in Table 1, where overall recoveries are given for thorium and polonium because they have been determined after all the analytical procedures were complete. The recovery of radium includes the effects of its coprecipitation with calcium carbonate and with barium chromate. The recovery of lead in calcium carbonate was determined using stable lead.

Radium, lead and polonium are always recovered with a high coprecipitation efficiency of more than 70%, showing no relation with the amount of iron carrier added. However, more than 10 mg of iron carrier is necessary for the coprecipitation of thorium.

3.2. The separation of radium from thorium, lead and polonium in the solution concentrated in calcium

The calcium carbonate and ferric hydroxide precipitates are dissolved in about 400 ml of 7.5 M nitric acid. As noted by Nozaki and Tsunogai (1973b), hydroxides of lead and polonium quantitatively precipitate from this solution at a pH of about 8.5. Some of the radium
Table 1. Effects of adding various amounts of Na$_2$CO$_3$ and Fe$^{3+}$ during the coprecipitation of Ra, Pb, Po and Th from seawater.

<table>
<thead>
<tr>
<th>Na$_2$CO$_3$ added (g)</th>
<th>Fe$^{3+}$ added (mg)</th>
<th>Ra$^a$ (%)</th>
<th>Pb (%)</th>
<th>Po$^b$ (%)</th>
<th>Th$^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>83.2</td>
<td>72.2</td>
<td>81.6</td>
<td>22.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(78.9-88.4)</td>
<td>(68.4-75.4)</td>
<td>(74.8-84.5)</td>
<td>(19.5-26.7)</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>81.3</td>
<td>75.7</td>
<td>87.4</td>
<td>70.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(79.4-83.5)</td>
<td>(71.3-80.5)</td>
<td>(74.8-98.4)</td>
<td>(68.9-74.2)</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>83.0</td>
<td>74.1</td>
<td>84.3</td>
<td>70.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(80.0-88.4)</td>
<td>(71.5-78.4)</td>
<td>(74.5-89.9)</td>
<td>(68.2-72.5)</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>79.1</td>
<td>81.3</td>
<td>n. d.</td>
<td>75.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(76.5-82.5)</td>
<td>(78.2-85.4)</td>
<td>(70.0-82.0)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ranges are shown in parentheses.

$^b$ Recovery of Ra includes the effects of its coprecipitation with CaCO$_3$ and Fe(OH)$_3$ and the effects with BaCrO$_4$.

$^c$ Recoveries of Po and Th include all the analytical procedures.

$^d$ Electroplating could not be performed because of interference with Fe$^{3+}$.

Fig. 2. Coprecipitation of $^{228}$Ra with BaCrO$_4$ from a solution containing calcium (20 g l$^{-1}$).

(about 20%), however, is also coprecipitated with them. Therefore, a reprecipitation procedure is necessary. In the recommended procedure, this procedure is carried out by preparing the hydroxide, containing thorium and lead, after the electrodeposition of polonium, and by adding the filtrate to the solution reserved for radium. As shown in Fig. 2 the separation of radium from the solution containing a large amount of calcium done quantitatively by coprecipitating with barium chromate which is comprised of 5 mg or more of barium.

3.3. Separation of radium from barium by the cation exchange technique

The electrodeposition of radium onto a silver disc is interfered with by the presence of barium and other alkaline earth metals, and thus these metals are first removed with a cation exchange column. We first examined ammonium formate as an eluting solution (Sugimura and Tsubota, 1963), however, we did not obtain good results because some solids were deposited on the silver disc after electrodeposition. Koide and Bruland (1975) used 1.65 M hydrochloric acid as an eluate in the presence of 2 mg of barium. We sought the best separation condition for a solution containing 10 mg of barium. Radium was completely separated from other alkaline earth metals when 1.6 M hydrochloric acid is eluted at a flow rate of 0.6 ml min$^{-1}$ as shown in Fig. 3, and then electroplated smoothly on a silver disc from the solution.

3.4. Preparation of the counting source for radium

To obtain a high resolution and good reproducibility in the $\alpha$-spectrometry of radium, the counting source must be thin and have a smooth surface. This condition is satisfied by the electrodeposition method. The electrodeposition cell used is shown in Fig. 4. It consists of a Teflon cylinder and a stainless jacket. Its anode is a coiled platinum wire (2 mm in diameter). A silver disc is set on the bottom of the stainless jacket which acts as a cathode. The solution in the cylinder is stirred with a magnetic stirrer.

To find the best settings for the electric current and voltage, 1 ml of 0.5 M hydrochloric acid containing $^{228}$Ra and 5 ml of ethanol were put into the planing cell. A few drops of 1 M hydrochloric acid or ethanol were then added to adjust the current at a given voltage. As shown in Fig. 5, the electroplating was examined under various conditions. The low
Fig. 3. Separation of Ra from Ba with a cation exchange column (BIO-RAD AG 50W-X12) using hydrochloric solution as eluent.

a: 1.6M hydrochloric acid solution is used as the eluent.

b: 1.6M hydrochloric acid solution is used as the eluent for the first 230 ml and 8M hydrochloric acid solution is used thereafter.

Fig. 4. Electroplating cell.

Fig. 5. Effects of electric current and voltage on the yield of Ra by electrodeposition.

Fig. 6. Effect of plating time on the electrodeposition yield of Ra on a silver disc.

3.5. Determination of the chemical yield of radium

To determine the chemical yield of $^{226}$Ra, $^{226}$Ra is added and its daughter $^{228}$Ac is counted. An aluminum absorber (12 mg cm$^{-2}$) perfectly absorbs $\beta$-rays from $^{226}$Ra and $\alpha$-rays from $^{228}$Ra. The counting source also contains some $\beta$-emitters having high energy such as $^{212}$Pb, $^{212}$Bi and $^{208}$Tl which are daughters of $^{226}$Ra and $^{214}$Pb and $^{214}$Bi which are produced from $^{222}$Rn. Their $\beta$-rays are apt to cause errors in the $^{226}$Ra determination. The recommended procedure minimizes these errors. After storing the barium chromate for about one month after the separation of radium from thorium, most of the initial
$^{224}$Ra has decayed out, and a few percent of $^{229}$Th and $^{224}$Ra (relative to $^{228}$Ra) are generated. The $^{228}$Th is separated again from radium using the ion exchange procedure. By allowing the effluent to stand for 6 days, the $\beta$-activities of the daughters of $^{224}$Ra amount to a nearly constant value of $1.6 \pm 0.3\%$ of the $^{228}$Ra activity (Nozaki, 1974). The errors from the daughter nuclides of $^{222}$Rn can be reduced to insignificant levels by igniting the silver disc and allowing it to stand for a few hours before the $\beta$-counting of $^{228}$Ac.

3.6. Reagent blank and precision

The reagent blanks were $0.04 \pm 0.02$ dpm (the error is one standard deviation calculated from five determinations) for $^{224}$Ra, $0.03 \pm 0.03$ dpm for $^{210}$Pb and $0.01 \pm 0.03$ dpm for $^{210}$Po. When we take a volume of seawater sample of more than 201, the reagent blanks constitute less than $1\%$ of the sample content for these nuclides. For $^{234}$Th, the reagent blank including a $\beta$-activity of $0.80 \pm 0.04$ dpm from short lived daughters of $^{228}$Ra was smaller than the amount of $^{234}$Th in 400 ml of seawater.

About $10\%$ of uranium in seawater was co-precipitated with calcium carbonate and ferric hydroxide. This uranium, however, was completely separated from the thorium fraction in the anion exchange column and, thus, the interference of $^{235}$U is practically negligible for the determination of $^{234}$Th when the separation of thorium from uranium is carried out within a week after sampling.

This method was applied to surface water in Funka bay. The $1\sigma$ values of counting errors were $7\%$ for $^{234}$Th counted for 2 hr, $5\%$ for $^{224}$Ra, $6\%$ for $^{210}$Po and $7\%$ for $^{210}$Pb for samples stored for 5 months, where the $\alpha$-activities of the latter three nuclides were counted for 48 hr. The standard deviations for five replicate determinations were within the counting errors as shown in Table 2.

### Acknowledgements

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### References


Nozaki, Y. and S. Tsunogai (1973a): Lead-210 in

### Table 2. Replicate determinations of $^{226}$Ra, $^{210}$Pb, $^{210}$Po and $^{234}$Th in about 401 of surface waters collected in Funka bay, Hokkaido, Japan in August 1978.

<table>
<thead>
<tr>
<th></th>
<th>$^{226}$Ra (dpm/100 l)</th>
<th>$^{210}$Pb (dpm/100 l)</th>
<th>$^{210}$Po (dpm/100 l)</th>
<th>$^{234}$Th (dpm/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>8.4 ± 0.3 b</td>
<td>10.3 ± 0.6 b</td>
<td>6.6 ± 0.3 b</td>
<td>2.02 ± 0.09 b</td>
</tr>
</tbody>
</table>

$^a$ 1σ value of the counting error.

$^b$ Standard deviation of five determinations.
海水中の$^{234}$Th, $^{226}$Ra, $^{210}$Pb, $^{210}$Poの実用的同時分析法

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要旨: 海水中の$^{226}$Raを$^{234}$Th, $^{210}$Pb, $^{210}$Poと同時に分析する実用的な方法を開発した。本法では、それぞれの化学的収率を、$^{226}$Ra, $^{238}$Th, $^{206}$Pbおよび、安定な鈉を用いて決定する。海水20〜50Lから、これらの核種を

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炭酸カルシウムと水酸化鉄中に捕集し、共沈法、イオン交換法を用いて相互に分離する。Ra, Th, Poの計測用溶液は、銅板上への蒸発によって調製する。放射能の計

測は、αスペクトロメーターおよび、低バックグラウン

Dß計測器によって行なう。本法により、いずれの核種についても5%以内の繰り返し精度で測定できる。