Measurement of $^{224}$Ra and $^{226}$Ra Activities in Natural Waters Using a Radon-in-Air Monitor

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We report a simple new technique for measuring low-level radium isotopes ($^{224}$Ra and $^{226}$Ra) in natural waters. The radium present in natural waters is first preconcentrated onto MnO$_2$-coated acrylic fiber (Mn fiber) in a column mode. The radon produced from the adsorbed radium is then circulated through a closed air-loop connected to a commercial radon-in-air monitor. The monitor counts alpha decays of radon daughters (polonium isotopes) which are electrostatically collected onto a silicon semiconductor detector. Count data are collected in energy-specific windows, which eliminate interference and maintain very low backgrounds. Radium-$^{224}$ is measured immediately after sampling via $^{220}$Rn ($^{216}$Po), and $^{226}$Ra is measured via $^{222}$Rn ($^{218}$Po) after a few days of ingrowth of $^{222}$Rn. This technique is rapid, simple, and accurate for measurements of low-level $^{224}$Ra and $^{226}$Ra activities without requiring any wet chemistry. Rapid measurements of short-lived $^{222}$Rn and $^{226}$Ra, along with long-lived $^{222}$Ra, may thus be made in natural waters using a single portable system for environmental monitoring of radioactivity as well as tracing of various geochemical and geophysical processes. The technique could be especially useful for the on-site rapid determination of $^{224}$Ra which has recently been found to occur at elevated activities in some groundwater wells.

Introduction

The naturally occurring isotopes of radium ($^{223}$Ra, $^{224}$Ra, $^{226}$Ra, $^{228}$Ra) as well as $^{222}$Rn have been measured in natural waters for monitoring environmental radioactivity (1, 2) and for various geophysical studies including mixing and transport of different water masses and assessing submarine ground-water discharge (3–5). Recently, very high activities of $^{228}$Ra have been discovered in some groundwater wells in New Jersey and elsewhere (6, 7). This discovery has raised the concern that moderate-to-high levels of alpha-particle activity may exist in many drinking water supplies but have gone undetected because of the time delays which are typical between sampling and analysis. Because drinking water analysis protocols typically do not specify any holding period for gross alpha or beta activity determinations, there is a high likelihood that high alpha activity from $^{228}$Ra ($t_{1/2} = 3.66$ d) would be missed by routine monitoring protocols. Proper assessment requires a rapid and simple approach for analysis. Ideally, since time is of the essence, a field-based simple approach would be preferred. Unfortunately, the traditional techniques for measuring Ra isotopes, especially for short-lived $^{224}$Ra, are time-consuming and cumbersome (8–11).

Traditionally, Ra isotopes have been measured by counting alphas for $^{226}$Ra, $^{224}$Ra, and $^{222}$Ra and betas for $^{228}$Ra following tedious chemical separations and source preparations (8–10). Alternatively, Ra isotopes have been measured by gamma counting of appropriate daughter nuclides (11). However, energy discrimination of Ra isotopes by alpha and gamma spectrometry is not always straightforward due to interfering peaks generated by Ra isotopes and their short-lived daughters. Furthermore, gamma spectrometry is not very sensitive because of relatively low efficiencies and high backgrounds.

Another, much simpler, approach has been achieved by measuring Rn and its daughters by alpha scintillation counting following adsorption of Ra onto Mn fiber and transfer/circulation of Rn into a detection chamber. Rama et al. (12) developed this approach for $^{224}$Ra measurements, but the determination of low-level $^{220}$Rn was significantly interfered by $^{218}$Po generated from $^{222}$Rn during long counting periods. More recently, Moore and Arnold (13) developed a technique which provides simultaneous measurement of $^{224}$Ra and $^{226}$Ra using a delayed coincidence counter designed originally by Griffin et al. (14) for detection of radon isotopes. In this approach, signals from a detector are sent to a delayed coincidence circuit which discriminates decays of the $^{224}$Ra daughters, $^{218}$Po and $^{216}$Po, from decays of the $^{226}$Ra daughter, $^{215}$Po and $^{213}$Po. The detection efficiency (two alpha decays per Ra decay) is very high with this system, but one disadvantage is increased chance coincidence between $^{224}$Ra and $^{226}$Ra when the activity of one radium isotope is much higher than the other. In this study we have developed a technique for alpha counting of radon daughters using a commercial radon-in-air monitor which uses electrostatic attraction of positively charged radon daughters to a silicon semiconductor detector. Once precipitated onto the surface of the detector, $^{218}$Po + ions produce well-resolved alpha spectra allowing excellent energy resolution.

Experimental Section

General Strategy. This method is based on the principle of radioactive equilibria of Ra isotopes and their short-lived daughters and the different chemical characteristics of each daughter species (Figure 1). The Ra isotopes are first adsorbed onto Mn fiber by pumping water through a cartridge packed with the Mn-impregnated fiber. This process is quantitative for radium in natural waters at flow rates below about 2 L/min (15, 16). The water content of the Mn fiber is then adjusted to obtain constant recoil efficiency for Rn. The Ra daughters ($^{222}$Rn, $^{220}$Rn, and $^{219}$Rn) are circulated through an air-loop connected to (1) a desiccant column to remove any moisture that immobilizes the charged Po species; (2) an air filter to keep out particles and attached radon daughters; and (3) a radon-in-air monitor where Rn daughter isotopes ($^{218}$Po, $^{216}$Po, and $^{215}$Po) are electrostatically precipitated onto a semiconductor detector which produces alpha spectra thus allowing isotopic separation by energy discrimination (Figure 2). We use a RAD-7 (Durridge Co. Inc., 7 Railroad Ave., Suite 200, Tallahassee, Florida 32306; e-mail: wburnett@mailer.fsu.edu).
for extraction of Ra isotopes in natural waters. In the first approach, the flow rate of water through a Mn-fiber column is controlled to be lower than ~1.2 L/min which ensures quantitative adsorption of Ra (15). We have checked for complete radium uptake by pumping a large-volume sample through two-columns connected in series. No radium was found on the downstream column, while significant radium was on the initial column confirming quantitative adsorption on the first cartridge. In the alternative approach, water samples are passed through a Mn-fiber column using a high flow-rate to yield only the ratios of $^{224}$Ra to $^{226}$Ra, then the $^{224}$Ra was quantified by a separate measurement of $^{226}$Ra using a standard radon-emanation method (18). The later approach is preferred if the sampling time needs to be as short as possible and would also be more effective for anoxic waters when MnO$_2$ is partially reduced during preconcentration, causing loss of some Ra.

**Water Content of Mn Fiber.** The efficiency of Rn escape from Mn fiber to the air depends on the water content of Mn fiber (19). This is apparently due to a balance in the stopping effect of water on recoiling radon atoms. Too much moisture will significantly inhibit radon escape, while very dry conditions result in recoiling radon atoms becoming embedded in adjacent Mn fiber particles. We have tested the variation in the escape efficiency of Rn against the water content of Mn fiber by repetitive counting of one standard after several moisture adjustments (Figure 3). We prepared the $^{224}$Ra standard fiber for this experiment by repetitive rinsing of a 2-L, pH = 6 solution containing 1020 dpm $^{228}$Th (direct parent of $^{224}$Ra) through a single Mn fiber cartridge. Since thorium adsorbs to Mn fiber as well as radium, this standard will decay at the longer (1.91 y) half-life of $^{228}$Th. After six rinses of the standard solution, the fiber cartridge was drained until excess solution stopped flowing. We then gently squeezed the Mn fiber by hand to reduce the water content further, and the first RAD-7 measurement was taken. Each counting interval consisted of a 5-min cycle to allow equilibration between $^{222}$Rn and $^{224}$Ra activities in natural waters.

**Preconcentration of Radium.** The Ra isotopes are extracted by passing 20–200 L (more or less may be used depending upon the expected activities) of water through a plastic column (5 cm diameter, and 20 cm length) filled with Mn fiber (~60 g-wet). This can be done conveniently in the field by pumping the water directly through the cartridge—no “sample” needs to be collected but a volume measurement is necessary. The Mn fiber is prepared by impregnating acrylic fiber with MnO$_2$ following the method described by Moore (17) and Reid et al. (15). We used two different approaches...
We observed that the highest efficiency of Rn loss from the fiber occurred for weight ratios of water-to-fiber between 0.7 and 2.5, similar to that reported by Sun and Torgersen (19). They claimed that even at optimal moisture conditions 220Rn is not completely released from the Mn-fiber although the very high efficiencies observed on delayed coincidence counters (13) suggest that the removal must be very high. We find that we can maintain nearly the same water content (wt. ratio ~2) for all standards and samples by firmly hand-squeezing the Mn fiber. This ensures that we are near the high (wt) end of the counting plateau so any additional drying will have little consequence. The firm hand-squeezing approach also eliminates the need for bulky equipment in the field. Our observations thus suggest that as long as the weight ratio is between about 0.7–2.5, the escape efficiency of Rn from Mn fiber is reproducible.

**Determination of 226Ra.** Since radioactive equilibrium is achieved between 222Rn and 224Ra in about 5 min, the measurement of 226Ra via 220Rn can be done immediately after sampling. After the moisture on the Mn-fiber is reduced to the proper range, the column is connected to the system (Figure 2), and 220Rn is circulated via an air loop, and 214Po events are monitored using the RAD-7. To test the effect of airflow rate on the detection efficiency of 220Rn, we set the flow rate to 1.3, and 1 L/min using an external air pump (the internal pump of the RAD-7 may be set to generate a fixed flow rate of 1 L/min). We observed no significant difference in the count rates using the same source at these various flow rates. Thus, one may conveniently use the internal air pump of the RAD-7 for determination of 226Ra. As mentioned earlier, it is important to remove any moisture which comes off the Mn fiber before the air circulates into the RAD-7 chamber. To minimize 220Rn decay in air before it reaches the radon chamber (volume ~ 700 mL) of the RAD-7, we used a small Drierite column (2 cm diameter, 20 cm length). To allow equilibration of 220Rn and 226Ra, we run the system for 5 min before initiating counting. In general, we program the RAD-7 to integrate 220Rn count data every hour to check the influence of any external factors (i.e., moisture effects) during the total count time. Total counts are integrated when the full time cycle is completed (in general, 4–5 hours).

**Determination of 222Ra.** To measure 222Ra using this system, we placed Mn fiber in a column which was then sealed to allow ingrowth of 222Rn for several days in a manner similar to the approach used by Butts et al. (20). Before the column is sealed, any Rn in the Mn fiber is expelled to reset the ingrowth time. We maintained a slightly negative pressure inside a thick plastic or glass column (by pumping air out) to minimize any escape of Rn from the column during the ingrowth period. For measurements of 222Rn via 222Rn, the circulation rate of air is not an important factor due to the long half-life of 222Rn. To allow equilibration of 222Rn and 214Po, the system is allowed to run for 15 min before data are collected. In general, about 1–2 h count times are used for each sample, but this is highly dependent upon the 222Ra activities and the sample volume passed through the fiber. The alpha spectrum clearly discriminates 214Po (6.0 MeV) from the other radon daughters, and if there is any interference from 212Bi (6.08 MeV), the RAD-7 corrects for this by simultaneously counting 214Po (8.78 MeV), the direct daughter of 212Bi.

**Applications to 222Ra and 228Th Measurements.** In principle, measurements of 222Ra can be made simultaneously with 222Rn by counting 214Po as shown in Figure 4. However, we have found that natural activities of 222Ra are typically too low to be detected easily with this system. We were able to obtain a clear 214Po peak for a 1000-L groundwater sample, but such large samples are not often practical. However, if one should encounter higher levels of 222Ra, it can be measured easily with this system in a manner similar to the

**FIGURE 4.** A spectrum showing Po peaks produced by the alpha detector located in the RAD-7. If any 220Rn alpha happens by chance to reach the detector, they will have passed through an indeterminate air thickness en route. The pulses will thus be distributed across the spectrum at lower apparent energies than its theoretical value (~6.2 MeV). Very few such events occur, and any effect on the lower energy 218Po peak is further lessened because of the rapid decay of 218Po during 220Rn ingrowth.

226Ra measurement. Our testing for the large-volume sample shows that it is helpful if any Rn in the column is first eliminated, and 214Po peaks in the detector are allowed to decay away before 226Ra measurements are initiated. Since the half-life of 220Rn (daughter of 222Ra) is very short (3.9 s), the air circulation rate is an important factor (we estimate that approximately 7 L air/min with an external pump would be sufficient). In addition, one should open the air loop for 220Rn counting in order to minimize ingrowth of 218Po in the chamber from 222Rn.

Although thorium isotopes tend to be very low in natural waters, thorium, as well as radium, will be adsorbed onto Mn fibers. If the measurement of 228Th (parent of 224Ra) is desired using this system, it can be measured via the same 224Ra method described here after they reach radioactive equilibrium (~20 days) and any excess 224Ra has decayed away.

**Results and Discussion**

To obtain the detection efficiency of 226Ra, 224Ra, and 222Ra, we prepared a mixed standard solution containing known activities of 226Ra, 232U/228Th/224Ra, and 227Ac/223Ra. The solution was added to 1 L of deionized water, and a few drops of NH₄OH were added to adjust the pH to ~8, close to that of seawater. The solution was passed through a Mn-fiber column by gravity flow and repeated three times to avoid any loss of Th, Ac, and Ra isotopes. After the water content was adjusted in a manner similar to that used for the samples (firmly hand-squeezed), the detection efficiencies of the system were determined for each isotope.

The purity of 226Ra determined via 220Rn, 218Po counting was confirmed using a counting-time series from a large-volume groundwater sample. As shown in Figure 5a, the slope of the excess 224Ra decay curve matches precisely the theoretical decay constant of 224Ra (λ₂₂₄ Ra = 0.00793 h⁻¹). In addition, we monitored the ingrowth of 222Rn, 218Po from 226Ra in a column (Figure 5b). The slope of the ingrowth curve matches exactly the theoretical 222Rn ingrowth curve (λ₂₂₂Rn = 0.00755 h⁻¹), confirming that no escape of 222Rn occurred during ingrowth.

To validate our technique against a documented methodology, we processed several large volume groundwater and seawater samples through Mn fibers. These samples were measured by the RAD-7 system first, and the fibers from the groundwater and standard samples were then sent to the USGS (St. Petersburg, FL) and the seawater samples to the University of South Carolina (Columbia, SC) where delayed
off FSU Marine Laboratory on August 15, 2000. Seawater samples were collected around the K-tower, Gulf of Mexico, to monitor the uncertainties are based on 1-

decay are measured by the delayed coincidence counter. The efficiency is especially low for 222Rn due to rapid decay of 222Rn in the air stream, which must pass through the Mn-fiber, a Drierite column, and an air filter. However, the technique described here has the advantage of energy discrimination of each Ra isotope using alpha spectrometry. In addition, the equipment is less expensive than a delayed coincidence system and is completely portable allowing field measurements. The system can also be used for precise measurements of 222Rn in air and water. Since the RAD-7 can determine 222Rn in water using a water–air gas equilibrator (21), our system allows one to determine Rn as well as Ra isotopes using a single portable radon-in-air monitor for environmental monitoring of radioactivity as well as for various geophysical studies.

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Literature Cited


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TABLE 1. Intercomparison of 224Ra (Disintegrations per Minutes) Results Measured by the Delayed Coincidence Counter (13) versus Radon-in-Air Monitor (This Study) for Deep-Well Waters and Offshore Seawaters

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Coincidence Counter</th>
<th>Radon Monitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSU deep well A</td>
<td>19.52 ± 3.08</td>
<td>17.26 ± 0.42</td>
</tr>
<tr>
<td>FSU deep well B</td>
<td>7.80 ± 0.13</td>
<td>6.65 ± 0.37</td>
</tr>
<tr>
<td>FSU deep well C</td>
<td>6.44 ± 0.45</td>
<td>6.96 ± 0.33</td>
</tr>
<tr>
<td>Seawater (5 m)</td>
<td>4.94 ± 0.25</td>
<td>5.51 ± 0.41</td>
</tr>
<tr>
<td>Seawater (10 m)</td>
<td>5.41 ± 0.27</td>
<td>5.24 ± 0.39</td>
</tr>
<tr>
<td>Seawater (19 m)</td>
<td>7.12 ± 0.36</td>
<td>6.73 ± 0.43</td>
</tr>
<tr>
<td>FSU standard</td>
<td>200.16 ± 0.06</td>
<td>200</td>
</tr>
</tbody>
</table>

* The uncertainties for the delayed coincidence counter are based on standard deviations of multiple measurements, and for the radon monitor the uncertainties are based on 1-σ counting statistics. The seawater samples were collected around the K-tower, Gulf of Mexico, off FSU Marine Laboratory on August 15, 2000.