

Comparison of measurement methods for radium-226 on manganese-fiber

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Abstract

Acrylic fibers impregnated with MnO_2 (Mn-fiber) have become a valuable tool for concentrating dissolved radium for oceanographic applications. With four naturally-occurring radium isotopes (^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra) of vastly different half-lives (3.6 days to 1600 years), radium can be a powerful tool for tracing terrestrial water discharges into the ocean and studying coastal mixing processes. Several techniques have been outlined in the literature describing the measurement of ^{226}Ra on Mn-fiber via its gaseous daughter, ^{222}Rn . We present a proven, air-tight cartridge design that allows one to use these measurement techniques. We then review the procedures for three radon-based nondestructive measurement techniques for ^{226}Ra on Mn-fiber (via RAD7, RaDeCC, and Rn emanation line systems) and perform an intercomparison among them, using the standard technique of γ -spectrometry as a reference. We find that all methods statistically agree in terms of measured activity. The Rn emanation line and the RaDeCC systems (both based on Lucas cell counting) provide the lowest measurement uncertainties and minimum detectable activities (MDAs) for a given counting time. The RAD7 technique, on the other hand, offers the advantage of being an automated system, thus requiring minimal user interaction. The standard γ -spectrometry technique, while more time-consuming and sample destructive, has the advantage of providing a simultaneous measurement for ^{228}Ra .

Introduction

One of the great advancements in the field of marine environmental radioactivity was the introduction of MnO_2 -impregnated acrylic fiber (Mn-fiber). Mn-fibers were first introduced in the early 1970s (Moore and Reid 1973). This material is known to quantitatively adsorb dissolved radium isotopes, thus concentrating them to allow for more accurate measurements. Although other metals are also adsorbed onto Mn-fiber (e.g., Ba, Ca, Pb, Hg, Cu, Zn, Co, Cd, Th, Ac, Pu, Am; see Moore 1976; Mann et al. 1984), radium has most often been the intended target for environmental studies using Mn-fibers. Four naturally-occurring radium isotopes exist (^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra), and their large range in half-lives (11.4 days, 3.6 days, 1600 years, and 5.7 years, respectively) allows

researchers to adopt them as useful tracers for many different oceanographic processes of varying temporal scales.

W.S. Moore pioneered the use of the long-lived radium isotopes (^{226}Ra and ^{228}Ra) for open-ocean studies after the introduction of Mn-fibers. For example, Moore (1976) demonstrated the sampling protocol of ^{228}Ra in the deep ocean to examine thermohaline circulation and the benthic input of ^{228}Ra into bottom waters. He later mapped the North Atlantic basin for ^{226}Ra and ^{228}Ra in surface and deep waters (Moore et al. 1985). In a study along the southeastern US continental shelf, Moore (1996) extended the use of radium isotopes (namely ^{226}Ra) to quantify submarine groundwater discharge (SGD) inputs along the continental shelf. That study inspired many researchers to examine the role of SGD as an input mechanism of dissolved substances to coastal waters and today stands as one of the most prominent of early SGD studies.

After the adaptation of a preexisting delayed coincidence counting system (Griffin et al. 1963) to measure the short-lived radium isotopes (^{223}Ra and ^{224}Ra), termed the Radium Delayed Coincidence Counter (RaDeCC) (Moore and Arnold 1996), the applications of these isotopes to oceanographic studies expanded substantially. By using all four isotopes in the coastal environment, radium can act as a tracer to determine river plume mixing rates (Krest et al. 1999; Moore 2000a; Peterson et al. 2008a), apparent water mass ages and/or residence times

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Acknowledgments

Guebuem Kim and Hannelore Waska (Seoul National University) supplied the sample set used for the intercomparison of the different methods presented here. Dave Oliff in the FSU Oceanography Instrument Shop provided valuable assistance in the cartridge design and construction. Two anonymous reviewers provided insightful comments. This work was funded by National Science Foundation Collaborative Research Grant OCE04-51386 to W.C.B.

(Moore 2000b; Dulaiova and Burnett 2008), and saline SGD fluxes (Hwang et al. 2005; Kim et al. 2005; Mulligan and Charette 2006; Peterson et al. 2008b). Radium is a useful tracer of terrestrial waters (both surface and groundwater) because it is supplied by radioactive ingrowth from its particle-reactive thorium parents contained in sediments and subsequently desorbs in the presence of high ionic strengths (Li and Chan 1979; Martin and Akber 1999; Nozaki et al. 2001).

Whereas Mn-fibers containing short-lived radium isotopes are relatively simple to measure via the RaDeCC system, the analysis of the long-lived ^{226}Ra and ^{228}Ra is far more time consuming. The traditional measurement protocol for long-lived isotopes on Mn-fiber involves γ -spectrometric counting techniques (Moore 1984; Dulaiova and Burnett 2004), but other options exist, especially for ^{226}Ra . Most of these other counting methods indirectly analyze ^{226}Ra via its gaseous daughter, ^{222}Rn (half-life of 3.8 days). We evaluate three of these techniques using measurements based on (1) a radon-in-air monitor (RAD7 produced by DurrIDGE Co.; Kim et al. 2001); (2) the RaDeCC delayed coincidence counting system (Moore and Arnold 1996; Waska et al. 2008); and (3) a radon emanation line that sparges and traps radon followed by counting in a Lucas cell (Key et al. 1979). Other possible techniques exist for ^{226}Ra measurement from Mn-fiber, but these require further wet chemistry procedures to extract the radium from the fiber for later quantification by either liquid scintillation counting or γ/α -spectrometry (Sill 1987; Moon et al. 2003). We focus here on the non-destructive counting techniques directly from the Mn-fiber.

The techniques described here rely on the concept of radioactive ingrowth of ^{222}Rn and its emanation from the fiber. A Mn-fiber containing ^{226}Ra , when sealed in an air-tight container for a known amount of time, will eventually produce ^{222}Rn in the air space at an activity directly proportional to the ^{226}Ra on the fiber. One can then measure the ^{222}Rn activity in this air space and use the ingrowth time to calculate the activity of ^{226}Ra on the fiber. By calibrating each method with known amounts of ^{226}Ra on Mn-fiber, we can determine the efficiency of each approach.

The objectives of this article are thus to assemble the protocols for each of these radon ingrowth-based methods and use a common set of samples to compare the techniques among themselves and to a standard γ -spectrometry method. It is important to note that we use the methods as they appear in the literature and as the measurement systems are commonly used. Further enhancements to the methods are possible and are suggested later. We consider the following measurement figures of merit: operator interaction, measurement time, efficiency, uncertainty, MDA, and associated costs (which are rarely reported in the original method publications). The ultimate goal here is to provide the necessary information to determine the most appropriate method based on one's needs and resources.

Materials and procedures

Cartridge design—One of the most important aspects of measuring ^{226}Ra via ^{222}Rn is the design of an air-tight cartridge that

can mount directly to all the different measurement systems. The following design (Fig. 1) has proven to be reliable throughout the course of our experiments. This cartridge is based on the style of those supplied with the RaDeCC system (Moore and Arnold 1996) but is adapted to allow air-tight sealing.

The foundation of our cartridge is a 15-cm-long section of 1.25-inch clear PVC pipe (Fig. 1A, #4; e.g., US Plastic Corp. item 34105). The advantage of the clear pipe is that one can visually observe the Mn-fiber inside to ensure that it is well-fluffed (Sun and Torgersen 1998; Moore 2007). On one end of the pipe, we glue a 1.25-inch PVC end cap (Fig. 1A, #5). On the other end, we glue the base of a 1.25-inch PVC Schedule 80 union (Fig. 1A, #3; e.g., Spears Manufacturing Co. item 897-012). This union consists of two separate slip couplings, which are connected with an o-ring seal and held together by a screw lock (Fig. 1B). The cartridge must provide open access to the Mn-fiber, but also must remain airtight when sealed. A PVC union with o-ring meets these needs. Into the other end of the union, we glue a 1.25-inch PVC plug (Fig. 1A, #2). The ends of the cap and plug are each tapped with threaded holes to allow barbed brass ball valves to screw in with Teflon tape (Fig. 1A, #1;

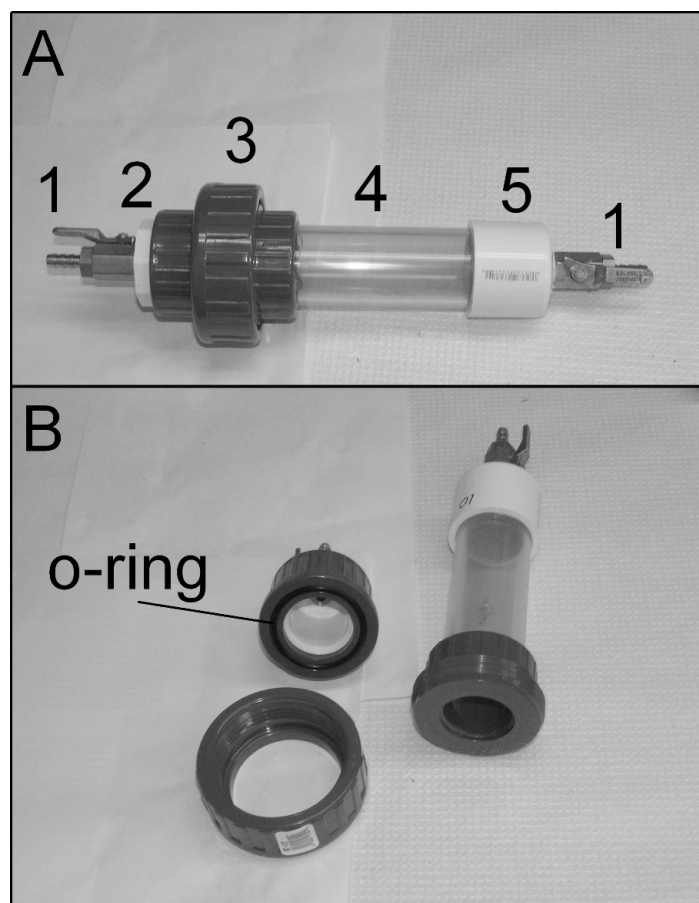


Fig. 1. Picture of the cartridge design fully assembled (A). The specific parts are the brass valves (1), the PVC plug (2), the union with o-ring (3), the clear PVC pipe (4), and the end cap (5). Also included is a picture of the open cartridge, showing the different parts of the union (B).

e.g., MSC Direct item 09881608). These ball valves allow the cartridge to be mounted directly to a measurement device via tubing without the risk of losing any ^{222}Rn during a transfer. To keep the apparatus airtight, we have found that brass ball valves are better suited than those made from plastic. The supplies required to build a cartridge cost less than \$40 USD.

Because the Mn-fiber held inside a cartridge will be producing radon gas over time, we recommend testing to ensure each cartridge is indeed airtight. For evaluation, we created positive pressure inside each cartridge with compressed gas, sealed the valves, and submerged the cartridge under water. If no bubbles are visible, that is a strong indication that the cartridge was successfully constructed.

Standard preparation—We planned to calibrate each method to a series of Mn-fiber standards spanning a range of ^{226}Ra activities that would more than cover the range anticipated from 100-L samples of natural ocean waters. We started with a NIST-traceable primary standard with an activity of 2285 dpm/mL in 1M HNO_3 . From this, we conducted a series of dilution (with Ra-free water) to produce five 1-L standards containing a range of activities from 5 dpm to the full strength of the standard. Each solution was adjusted to pH ~ 8 , and then passed (gravity-fed) through prerinsed Mn-fibers three times for quantitative extraction (Dimova et al. 2008).

Before each standard (and sample) run for the methods examined here, the Mn-fiber was moistened with Ra-free water, inserted into a cartridge, sparged with compressed air (~ 2 min), and sealed inside the cartridge by closing the valves. The sparging serves to adjust the fiber moisture content and also remove any background ^{222}Rn that may be sealed in the cartridge from the air. Proper humidity of the fiber is important to ensure optimum emanation of radon from the fiber (Sun and Torgersen 1998). The time of sealing is recorded for later calculation of the ingrowth time.

RAD7 method—The RAD7 is a radon-in-air monitor containing an internal air pump and an α semiconductor detector that employs energy discrimination to count the daughters of ^{222}Rn and ^{220}Rn . This tool has been widely used recently in groundwater discharge studies, as ^{222}Rn is a useful tracer of groundwater flow (Burnett et al. 2001). The RAD7 is a fully automated and portable radon detector, capable of running continuously for days. An important requirement of this system is that the airstream supplied to the unit remains dry (humidity $< 10\%$).

We connect the Mn-fiber cartridge in a closed air loop with the RAD7 and a tube of desiccant. Using two 2-way valves, we also plumb in a bypass loop that can isolate the cartridge. Because the premise is to distribute the ^{222}Rn that has ingrown inside the cartridge throughout the air loop, the volume of the air loop is a vital part of the calibration and must be held constant for each successive measurement (Lee and Kim 2006).

The method of using the RAD7 to measure ^{226}Ra on Mn-fiber was first introduced by Kim et al. (2001), but the measurement protocol used here is based on that presented by

Dimova et al. (2007). Before each measurement, it is important to know the effective background of the ^{222}Rn in the air loop, which acts as the carrier gas. To measure this, we connect the tubing system with the bypass valves set to isolate the cartridge. We run the RAD7 to measure the background ^{222}Rn count rate for roughly 90 min and later subtract this value from the sample count rate. We then switch the bypass valves to introduce the cartridge to the air loop, open the brass valves on the cartridge, and turn the RAD7 pump to “on” for 25 min to fully distribute the ^{222}Rn throughout the system. The RAD7 does not count at this time. Once this pumping period is complete, we isolate the cartridge with the bypass loop and start a RAD7 run for 15 h. We find that a 15-h counting time is a convenient overnight counting period and is usually sufficient to provide reasonable counting statistics, but this can be altered according to a user’s needs.

We take the background-corrected RAD7 window A count rate (cpm) as the effective instrument response for the calibration. This window represents the counts that are due to the decays of ^{218}Po , the direct daughter of ^{222}Rn . The RAD7 has a different window (C) that counts decays from radon’s great-granddaughter ^{214}Po (after 3 h for equilibration), but for simplicity in this application, we only use the window A count rate. The calibration curve for one RAD7 (Fig. 2) indicates a linear response of the system to increasing ^{226}Ra activity on the Mn-fiber, with an efficiency of about 0.1 cpm/dpm (or 10%). For this and all of these examined methods, we calibrate to only the four lower standards, excluding the highest standard to achieve a calibration within the typical range of environmental samples. The system efficiency is not only related

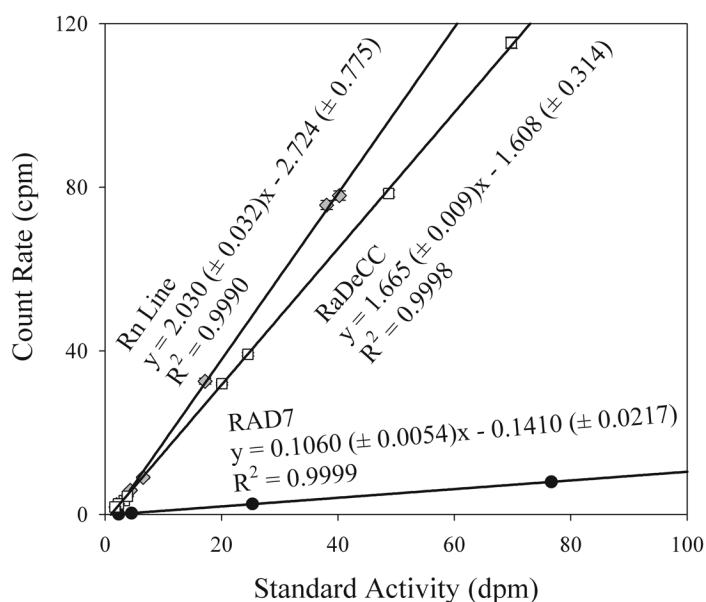


Fig. 2. Sample calibration curves for the Rn emanation line, RaDeCC system, and RAD7 system. Slopes provide a measure of efficiency (cpm/dpm). These represent one example of several units of these systems used for this work.

to the counting efficiency of the RAD7 itself, but is also dependent on the specific geometry/volume of the system. One could use window C of the RAD7 to increase the system efficiency and measurement precision, as there would be two measured counts (^{218}Po and ^{214}Po) for each decay of ^{222}Rn . However, this would require a 3-h equilibration time before beginning the counting.

Radon emanation line (Lucas cell) method—The detection device used with a radon extraction line was first proposed by Henry Lucas (1957) when he invented a radon scintillation cell, later termed the Lucas cell. The cell is an air-tight chamber (ours have a volume of $\sim 125\text{ cm}^3$) with inner walls coated with silver-activated zinc sulfide, which emits photons when struck by α decay particles. Key et al. (1979) later described a system by which radon can be extracted from water samples, concentrated on a trap held at liquid nitrogen temperatures (or dry ice when used with a charcoal trap), and later transferred to a Lucas cell for measurement by a photo multiplier tube (PMT) and a timer/scaler. Later enhancements were made by several authors to enable precise measurements of ^{222}Rn , and thus its parent ^{226}Ra (Butts et al. 1988; Mathieu et al. 1988).

Butts et al. (1988) were the first to suggest measuring ^{222}Rn directly from Mn-fibers with this system, and provided the method by which we measure ^{226}Ra bound on Mn-fiber via the Rn emanation line. Before measurement, the radon emanation line is purged with compressed helium while the background of the Lucas cell is counted (60 min). Then the cartridge is placed inline, the He flow is diverted through the cartridge, and the ingrown ^{222}Rn is flushed to the liquid nitrogen trap for 90 min. Afterward, the cartridge is again bypassed, the trap is heated, and the concentrated ^{222}Rn is transferred to an evacuated Lucas cell via a stream of helium. The cell is held for 3 h to allow the ^{222}Rn daughters to grow into equilibrium, and then counted for 60 min. By allowing full ingrowth of the short-lived α -producing daughters of ^{222}Rn , one can maximize the counting efficiency because there will be three photons produced by each decay of ^{222}Rn (the ^{222}Rn decay itself and one each from subsequent ^{218}Po and ^{214}Po decays). Thus, the ideal counting efficiency of this system would be 3 cpm/dpm.

Figure 2 illustrates a calibration curve for one port on our emanation line. The calibration shows a linear system response to increasing ^{226}Ra activity on the fiber, with an overall efficiency of about 2 cpm/dpm (or 200%). This is the highest efficiency of the three methods examined here.

RaDeCC coincidence counting system method—Waska et al. (2008) recently introduced the following method of using the RaDeCC system to measure ^{226}Ra . This system consists of a closed air loop between a cartridge, an air pump, and a large Lucas cell. The cell is coupled with a PMT and an electronic system that can discriminate decays of different radon isotopes based on the timing of subsequent decays. The RaDeCC system was adopted principally to measure ^{224}Ra (via ^{220}Rn decay to ^{216}Po) as well as ^{223}Ra (via ^{219}Rn decay to ^{215}Po) on Mn-fiber (Moore and Arnold 1996).

The routinely used RaDeCC short-lived radium protocol calls for purging the system with ambient air before a measurement. For ^{226}Ra measurements, however, this should be avoided, as it unnecessarily introduces ^{222}Rn from air into the system. Instead, we simply fill the air loop with He and plug the cartridge inline. The brass valves on the cartridge are opened, and the air pump is run for 25 min, circulating the ^{222}Rn -rich air inside the cartridge throughout the system. At the completion of the pumping, the brass valves are closed to prevent addition of ingrown ^{222}Rn from the Mn-fiber, and the system is left to equilibrate for 3 h. During this time, the short-lived polonium daughters of ^{222}Rn are growing into equilibrium inside the Lucas cell, but also the other isotopes of radon (^{220}Rn and ^{219}Rn) are decaying away. After 3 h, we start a measurement with the RaDeCC software and take the total count rate to be the system response to the ^{222}Rn in the air loop after 3–4 h of counting time.

As with the radon emanation line, the Lucas cell will emit three photons for each ^{222}Rn decay, so a perfect system would have an efficiency of 3 cpm/dpm. The calibration of a representative system (Fig. 2) shows lower values, as a result of counting efficiency and the dilution effect of the ^{222}Rn through the air loop, but the calibration curve is linear throughout the intended range of activities, with an efficiency around 1.6 cpm/dpm (or 160%).

γ -Spectrometry method— ^{226}Ra and ^{228}Ra on Mn-fibers are conventionally measured by γ -spectrometry. We follow the procedure established by Dulaiova and Burnett (2004) where Mn-fibers are ashed (at 550°C for 8 h) in special stainless steel crucibles that are later pressed into a specific geometry for our planar γ -spectrometer. This technique avoids the potential loss of MnO_2 ash during a transfer from one container to another. Once a fiber is ashed and the crucible pressed, the disc must be sealed with epoxy to prevent ^{222}Rn escape and held for ~ 21 days to allow all daughters to grow into equilibrium before a sample can be measured. Of all the techniques summarized here, this is the only destructive method, as the Mn-fiber is not usable after the ashing procedure. Other techniques of measuring the long-lived radium isotopes by γ -spectrometry include ashing followed by a transfer to another counting vessel or by acid-leaching the Mn-fiber and barium sulfate precipitation of the radium, followed by transfer to a counting vessel (Moore 1984).

The γ -spectrometer used in this study is an Ortec IG detector with a relative efficiency of 20%. We have calibrated the system for ^{226}Ra by preparing Mn-fibers from several aqueous IAEA radium standards using the combination of three ^{226}Ra daughter peaks: ^{214}Pb (at 295.1 and 351.9 keV) and ^{214}Bi (at 609.3 keV). The average efficiency of all three peaks is very low at 0.025 cpm/dpm. Based on these efficiencies, our detector typically requires ~ 48 h of counting time for each sample to achieve a reasonable uncertainty (<5 – 10%). This technique will serve as the standard method of measurement for comparison among the other techniques reviewed here, but note that larger

γ -spectrometers and those with lower backgrounds can produce results with lower uncertainties in shorter counting times.

Assessment

We used a series of seawater samples for a comparison of the previously presented methods that are reviewed above. In doing so, we have not enhanced any of the techniques as they are originally presented so as to not bias our results. The sample set consists of eight samples collected from 80 L seawater each as a water column profile from the Sea of Japan. We measured each sample twice according to each of the ^{222}Rn ingrowth methods, and once by γ -spectrometry (Fig. 3). The samples indicate a rise in ^{226}Ra activity from the surface to 1000 m, then the activity remains nearly constant to 3500 m. Considering that the error bars in Fig. 3 represent 1- σ measurement uncertainties, no statistical differences exist among measurements for any particular sample. The overall narrow range in activities among the sample set tends to magnify the differences between measured values, i.e., correlation coefficients would likely be higher had there been more variation in the activity range of the sample set.

Based on the measurement parameters associated with the sample set, we have summarized the important topics to consider when comparing methods (Table 1). In terms of user interaction, we use the same amount of ingrowth times for all radon-based methods (4 days). The preparation/holding time (for polonium daughter ingrowth) parameter indicates that the RAD7 method, being much more automated, requires less user time than the RaDeCC and the Rn line methods. The RAD7 only requires a 15 min holding time (versus 3 h for the Rn emanation line and RaDeCC techniques) because it only counts radon's daughter ^{218}Po instead of both ^{218}Po and ^{214}Po . The γ -spectrometric method here incorporates the recommended 21-day ingrowth time. The Rn line method (and to a lesser extent, the RaDeCC method) requires much less counting time than do the RAD7 and γ -spectrometry systems because of their higher efficiencies. Even considering their longer counting times, the RAD7 and γ -spectrometric methods still produce larger measurement uncertainties than do the Rn line and RaDeCC methods.

Table 1. Average preparation times and measurement parameters associated with the sample set.

	RAD7	Rn Line	RaDeCC	γ -Spectrometer
Rn ingrowth time, days ^a	4	4	4	21
Preparation/holding time, h ^b	2	4	3.5	8
Counting time, h	15	1	4	48
Total time per sample, h ^c	17	5	7.5	56
Efficiency, cpm/dpm ^d	0.100	2.000	1.500	0.025
Uncertainty, % ^e	10.3	3.9	2.5	12.4

^aTime from fiber sealing until a measurement begins.

^bTime necessary to prepare the sample and to allow the polonium daughters to equilibrate.

^cSum of preparation/holding time and counting time.

^dAverage of our units used to make the reported measurements.

^eAverage from all sample set measurements.

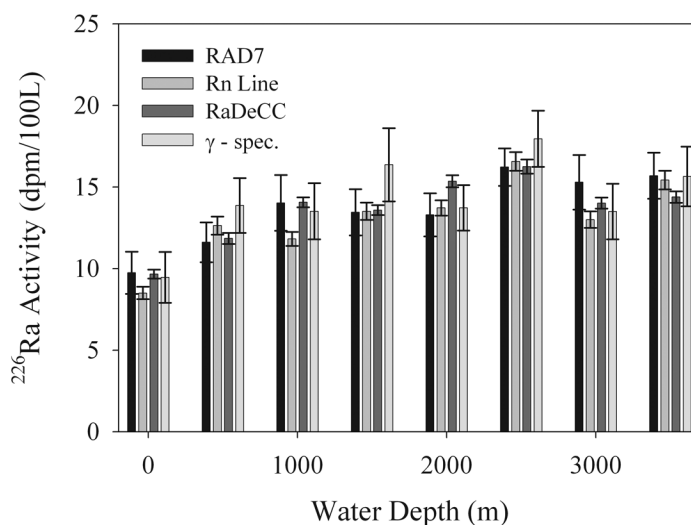


Fig. 3. Sample set ^{226}Ra results based on each measurement technique. The RAD7, Rn line, and RaDeCC results represent the average of two separate measurements. The error bars (+ and -) represent the average 1- σ measurement uncertainties based on counting statistics.

It should be noted that we are using low-level environmental samples (<0.15 dpm/L ^{226}Ra) for these comparisons.

We use the equation derived by Currie (1968) to determine the MDA values, based on a blank measurement and the respective efficiencies (Table 1). Figure 4 plots the theoretical MDA of each method with increasing counting time. To attain an MDA of 3 dpm/100 L, the Rn line and RaDeCC methods require much less counting time than do the other methods. Figure 4 also plots the calculated relative uncertainty for each measurement method with increasing counting time. To achieve a relative measurement uncertainty of <10%, the Rn line and RaDeCC methods again require the least amount of counting time. An important consideration here is that Ge γ detectors with much higher efficiencies and lower backgrounds than ours are available (for a much higher price). Both of these factors would help to substantially lower the counting time required to attain these measurement results.

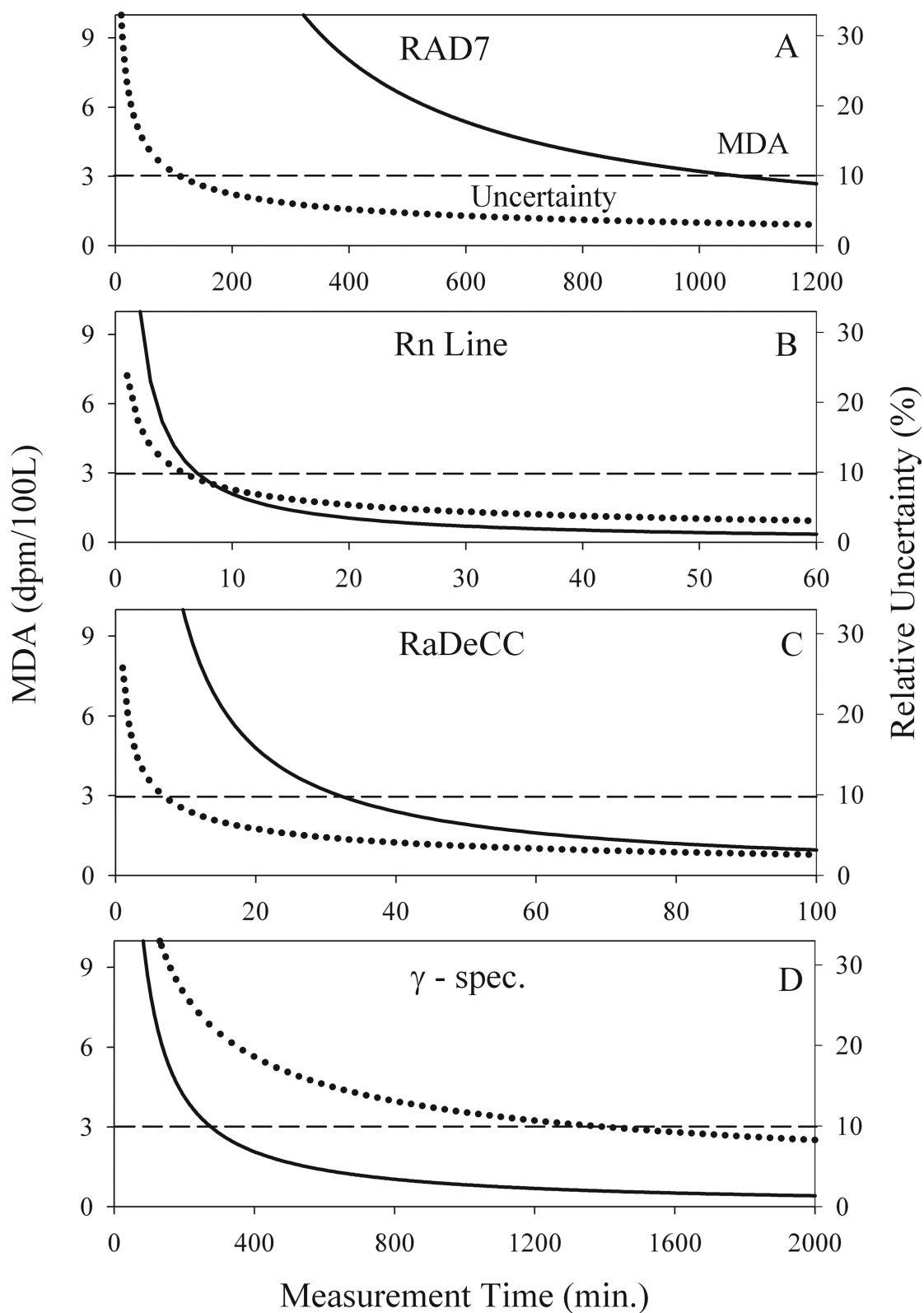


Fig. 4. Minimum detectable activity (solid line) and relative uncertainty (dotted line) plots for each measurement system showing their dependence on the counting time. The horizontal dashed lines indicate an MDA of 3 dpm/100 L and a relative uncertainty of 10%, and thus the corresponding measurement time needed by each system to attain that level of precision. The uncertainty calculations are based on a fiber containing a total activity of 10 dpm ^{226}Ra (10 dpm/100 L activity and 100-L volume).

Discussion

One flexible parameter of the methods considered here is the sparging time necessary to transfer the ²²²Rn that has ingrown inside the cartridge to the measurement system. This parameter is incorporated into the preparation/holding time category listed in Table 1. The initial choices for the methods (25 min for RAD7 and RaDeCC; 90 min for Rn emanation line) were based on previously established methods for these measurement systems. We used our highest activity standard to evaluate each of these systems for shorter sparging times (Fig. 5), anticipating lower efficiencies at lower sparging times. For the RAD7 and RaDeCC systems, the sparge time must be sufficiently long to achieve even distribution of the ²²²Rn throughout the air loop, and based on Fig. 5, that time could be shortened somewhat. For the Rn emanation line, the sparging is required to quantitatively transfer the ²²²Rn from the cartridge to the trap. Figure 5 shows that this could be shortened to about 15 min, significantly shortening the preparation/holding time for the Rn emanation line in Table 1 to just over 3 h.

We highlight some important advantages and disadvantages of each method under different practical scenarios in Table 2. During routine, day-to-day ²²⁶Ra measurements in the laboratory, we believe that the RAD7 method offers the user the most benefit. As that system is automated and can run unattended, one can start the measurement at one's convenience and leave it counting as long is necessary to achieve the desired uncertainty level. The Rn emanation line and RaDeCC require more user interaction and cannot be left unattended for long periods. Although the γ -spectrometric method is also automated and requires little user interaction, its extended counting time is not desirable for high-volume throughput.

If a user wants to take a measurement system into the field or to sea, other considerations become important. With all its required lead shielding, taking a γ -spectrometry system to the

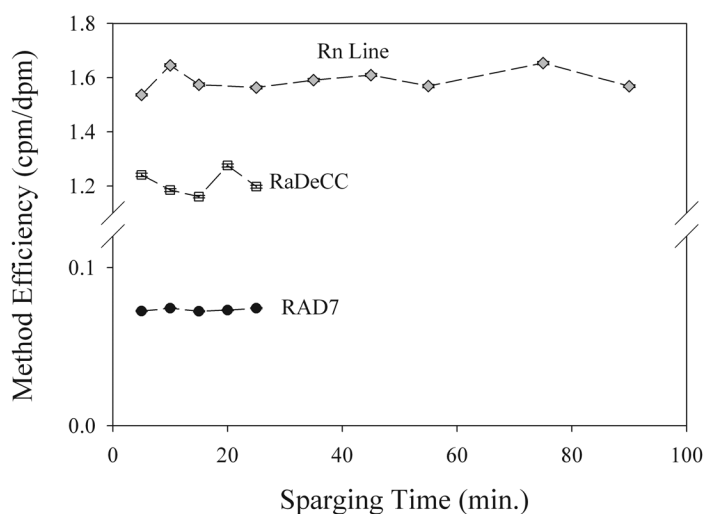


Fig. 5. Results of the sparging time analysis and the corresponding system efficiencies based on the associated sparging time.

field is possible but requires considerable effort. In addition to moving heavy shielding, one must prepare for sufficient liquid nitrogen (LN₂) or other required detector cooling system as well as move and reassemble sensitive electronic systems. Nevertheless, researchers use γ -spectrometer systems in the field to measure other tracers (e.g., see review in Rutgers van der Leoff et al. 2006 for ²³⁴Th methods). Although the Rn emanation line is portable and various researchers have used this system in the field for decades (see Broecker and Peng 1982), transporting this type of system is not ideal for a number of reasons. First, the maze of air lines is vulnerable during shipment and can be easily compromised and thus cause a leak. Also, many extra parts are needed for extraction lines such as a vacuum pump, compressed helium, Lucas cells, photomultiplier tubes, and liquid nitrogen (or dry ice for the cold trap). The RAD7, being completely self-contained, is the most portable

Table 2. Characteristics (positive and negative) associated with each measurement technique under a variety of scenarios.

	RAD7	Rn Line	RaDeCC	γ -Spectrometer
Routine laboratory measurements	Automated; limited user interaction required	Requires user attention, must start in morning	Limited user interaction needed, must start in morning	Very little user interaction needed
Taking the system to field/sea	Very portable, few extra supplies needed	Must have compressed He, LN ₂ , or dry ice; portable with difficulty	Need compressed gas, but allows other Ra isotope measurement	Need LN ₂ or other cooling system, very heavy Pb shielding
Limited equipment budget	Relatively inexpensive	Relatively inexpensive, but assembly required	Moderately expensive	Very expensive
Many samples/short time available	1 per day per unit	Several per day per unit	1 per day per unit	1 per unit every 1–2 days
Low activities	Long counting time required	Very short counting time required	Short counting time required	Very long counting time required
²²⁸ Ra	Only possible after long delay	Not possible	Only possible after long delay	Same measurement

system, only requiring a set of tubing to connect it to a drying column and the Mn-fiber cartridge. However, the RaDeCC system can be set up in a field laboratory or on board a ship, thus offering a system readily available to measure other radium isotopes. When possible, we believe that this system offers the greatest advantage for field excursions.

One can also consider the scenario of operating under a limited equipment budget and setting up a laboratory capable of measuring ^{226}Ra . Using rough estimates and recognizing that γ -spectrometer prices can range over a wide scale, we estimate that with about the same funds needed to buy a middle-range γ -spectrometer, one could purchase about 10 RAD7s, 10 ports of a Rn emanation line with counters and Lucas cells, or six RaDeCC counters. The Rn emanation line requires a substantial amount of assembly, but nonetheless, many more counting facilities of each system could be purchased for the price of one modern γ -spectrometry system (Table 2).

To further develop this comparison, we examine Table 1 for the total time required to measure a sample with each method. In the time required to count a sample by our γ -spectrometer to <10% uncertainty (24 h; Fig. 4), a single operator could also measure one sample by RAD7, one sample by RaDeCC, or two samples with a single port on the Rn emanation line. The total time required for a Rn emanation line measurement is 5 h, but most of this time (3 h) consists of holding the Lucas cell to allow for radioactive equilibration, so an operator can start another run on the Rn emanation line during this period. Considering the number of units of each system that one could purchase for the price of a single γ -spectrometer, it would be feasible for an operator to measure six samples by RaDeCC, 10 samples by RAD7, or 20 samples by Rn emanation line in the time it takes to count a single sample by γ -spectrometry and without any loss in precision. Therefore, we believe that the Rn emanation line is the most beneficial technique when dealing with a large number of samples or a limited time to count them (Table 2).

Based on the results from Fig. 4, we believe that the Rn emanation line also offers the most benefit when counting low-activity samples (Table 2). Both the RAD7 and γ -spectrometer techniques require counting times of hours to achieve an MDA <3 dpm/100 L. The Rn emanation line, owing to its higher efficiency and lower Lucas cell background compared to the RaDeCC, requires the shortest counting time to achieve this MDA. On the other hand, if a user also wants to measure ^{228}Ra , the γ -spectrometric method is the only option that can concomitantly measure this other long-lived radium isotope (Table 2).

Comments and recommendations

The sample set presented in Fig. 3 was measured according to previously published methods (summarized above), and the resulting measurement figures of merit were determined based on these established protocols. However, some advancements

to the protocols can be made to improve the counting statistics for each system. For example, while collecting the radium samples in the field, simply passing more water through the Mn-fiber will yield more activity on the fiber, thus enhancing the associated counting statistics and lowering the MDA. Counting for a longer period will help decrease the measurement uncertainty and MDA level (Fig. 4) of each system compared here. One could also preconcentrate the ^{222}Rn before counting it, as is done on the Rn emanation line with the cold trap. Such an improvement could work with the RAD7 and RaDeCC systems to improve their efficiencies. Also, if one were to allow ^{214}Po ingrowth, which is done in the other methods, the RAD7 system efficiency would be nearly doubled, providing lower measurement uncertainties than those reported here for similar counting times.

We believe that the field of oceanography will benefit from this comparison regarding various options of measuring ^{226}Ra on Mn-fiber. Some researchers do not have access to γ -/ α -spectrometry systems to analyze for ^{226}Ra , but could use any of these ^{222}Rn ingrowth methods instead. Some researchers only use ^{224}Ra and ^{223}Ra in their studies, but the latter is often subject to large measurement uncertainties because of its relatively low natural abundance. When available, ^{226}Ra is a much better long-lived analog to ^{224}Ra than ^{223}Ra .

Perhaps the main benefit of this comparison is that researchers will be aware of the benefits that are afforded from each of these systems. Several previous studies could have benefited from the information presented here. For example, during a research cruise along the South Atlantic Bight, Moore (1996) measured more than 70 Mn-fiber samples for ^{226}Ra via γ -spectrometry to examine submarine groundwater inputs to the region. Using one or two detectors, these analyses likely required a time frame of several months to complete. However, an investigation of similar magnitude could be undertaken with several RAD7s on board the ship (or RaDeCC systems to also allow for ^{224}Ra and ^{223}Ra measurements), and the samples could be measured within days of their collection. With a much shorter delay between sample collection and measurement, researchers could alter the sampling scheme based on the more rapidly obtained results. One can imagine that there would be several benefits to making ^{226}Ra measurements during the cruise instead of much later. For example, results obtained from these rapid measurements could lead investigators to revisit a particular site of interest or study a new site revealed by sample trends.

We recommend the cartridge design presented here for measuring ^{226}Ra because it has proven to be effective at remaining air-tight throughout various holding times. In addition, the thick-walled PVC prevents ^{222}Rn diffusional losses out of the cartridge. If any such losses should occur, we feel that they are minimal and inherently considered in our calibration procedures. With the cartridge described here, other researchers can adopt this design without fear of leakage.

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Submitted 22 July 2008

Revised 12 December 2008

Accepted 6 February 2009