

An efficient method for γ -spectrometric determination of radium-226,228 via manganese fibers

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Abstract

Radium isotope activities are typically at such low levels in natural waters, especially in seawater, that their measurement requires preconcentration from very large samples. Many investigators accomplish this by passing large volumes (20 to 150 L) of seawater or groundwater through a cartridge loaded with MnO₂-impregnated acrylic fiber. We describe here a new approach for converting “Mn fiber” into a form suitable for measurement of long-lived ²²⁶Ra and ²²⁸Ra by γ -spectrometry. The fiber is packed into custom-made crucibles manufactured from stainless-steel sheets. The fiber is then ashed at 550°C resulting in a sample mass reduction of approximately 90%. The crucibles are subsequently folded to enclose the ash, pressed using a hydraulic press, and sealed on top with silicon caulking to prevent radon escape. This procedure has an advantage over similar techniques because there is no sample transfer needed, and it is very time efficient. Radium-228 is determined by counting photopeaks at 338 and 911 keV from its daughter ²²⁸Ac ($T_{1/2} = 6.1$ h). Radium-226 is determined either by its photopeak at 186 keV (clear from interferences from ²³⁵U as U is not extracted on Mn fiber from oxidizing waters) or by counting the more abundant photopeaks from the granddaughters ²¹⁴Bi and ²¹⁴Pb after a 3-week in-growth period. A recent International Atomic Energy Agency intercomparison study for radium determination in water as well as comparison to the traditional radon emanation method showed that this technique provided good results and is appropriate for radium measurements in natural waters.

There are four naturally occurring radium isotopes: ²²³Ra: $T_{1/2} = 11.4$ d, ²²⁴Ra: 3.6 d, ²²⁶Ra: 1600 y, and ²²⁸Ra: 5.8 y. Measurement of these isotopes in natural waters is of great interest in geochemistry as well as in radioprotection. For example, geochemists use isotopic ratios for calculations of various geochemical processes, like tracing submarine groundwater discharge or calculation of offshore and inshore water mixing coefficients (Moore et al. 1995; Moore 1996, 2000; Turekian et al. 1996; Charette et al. 2001; Kelly and Moran 2002; Burnett et al. 2002; Burnett and Dulaiova 2003).

Radium isotopes are typically at such low levels in natural waters, especially in seawater, that their measurement requires preconcentration from very large samples. Moore (1976) devel-

oped a method where radium is collected from 200 to 1000 L of seawater by passing the water through MnO₂-impregnated acrylic fiber. At near neutral pH and under controlled flow-rate, the fiber quantitatively adsorbs Ra, Pb, Th, Ac, and other elements. The fiber is subsequently processed for γ -spectrometry by leaching the MnO₂ off the fiber with mineral acids and coprecipitating radium as BaSO₄ (Moore 1984) or ashing the fiber and packing the ash into a vial for γ counting (Charette et al. 2001). Baskaran et al. (1993) used polypropylene fiber impregnated by MnO₂ because of its lower ²²⁸Ra blank activity and smaller residue after ashing. We describe here a method using MnO₂-impregnated acrylic fiber for preconcentration of radium and a modified approach for γ -spectrometry for the measurement of ²²⁶Ra and ²²⁸Ra using custom-made stainless steel crucible-counting vessels.

Materials and procedures

Fiber preparation and Ra preconcentration—The MnO₂-impregnated acrylic fiber is prepared by immersing the raw acrylic fiber for about 20 min in saturated KMnO₄ solution heated to 75°C. When the fiber turns jet black, it is removed from the bath and rinsed thoroughly (Moore 1976). Ra-free water, prepared by passing deionized water through previously prepared Mn fiber is used throughout the procedure. After a

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Acknowledgments

The authors wish to thank Christina Stringer for analyzing companion samples by the Rn-emanation technique, and W. S. Moore for his help with the collection and measurement techniques, the analysis of the Sicily samples, and his valuable comments. We also thank the staff of the Florida State University (FSU) Marine Laboratory and FSU Oceanography Machine Shop for their assistance. Financial support for this work came from the Biological and Chemical Oceanography Program, Office of Naval Research (Grant nr N00014-00-0175).

final rinse in Ra-free water, the fiber is stored damp in plastic bags until use. For applications, approximately 150 cm³ (~25 g dry weight) of fiber is packed into a cylindrical cartridge.

We have been using the fiber to measure radium isotope concentrations in groundwater and coastal seawater. The sample volumes usually range between 20 to 150 L depending on the expected activities. The water is either slowly (1 to 2 L min⁻¹) passed through the fiber without collection at a controlled flow-rate, or it is collected in containers and processed at a more convenient time. The flow-rate of water passing through the fiber has to be below 2 L min⁻¹ to achieve quantitative radium adsorption (Moore 1976; Moore et al. 1995). Kim et al. (2001) have checked for complete radium uptake by pumping 500 L of groundwater through two columns connected in series. No detectable radium was found on the downstream column, while significant radium was on the initial column, confirming quantitative adsorption.

In certain cases groundwater can be reducing, containing hydrogen sulfide or other reducing agents. In such cases the water can reduce and thus dissolve the manganese on the fiber, causing less than quantitative radium recoveries. In such cases we pump the water into an open container, and the sample is degassed and oxidized before processing.

In a different approach, one could pass water samples through Mn fiber using a high flow-rate to yield only the ratios of ²²³Ra, ²²⁴Ra, and ²²⁸Ra to ²²⁶Ra, and then the ²²³Ra, ²²⁴Ra, and ²²⁸Ra are quantified by a separate measurement of ²²⁶Ra using standard radon-emanation or some other convenient method. This later approach is preferred if the sampling time needs to be as short as possible. In a similar manner, if one desires to measure just the activity ratios of radium isotopes, the fiber could be either immersed in situ in the water to passively collect radium or towed through the water for times depending on the expected activities.

After exposing natural waters to the Mn fiber by whatever means, the fiber is flushed with Ra-free deionized water. This rinse is important to wash out any particulates and sea salts that can interfere with radon emanation during the measurement (Moore 2000; Sun and Torgersen 1998).

Short-lived radium isotopes measurement—After radium is extracted and Mn fiber is rinsed, the moisture of the fiber is adjusted to have a water-to-fiber weight ratio in a range from 0.7 to 2.5 (Kim et al. 2001; Sun and Torgersen 1998). This adjustment is easily performed by either hand squeezing or drying via compressed air. The short-lived isotopes ²²³Ra ($T_{1/2} = 11$ d) and ²²⁴Ra ($T_{1/2} = 3.6$ d) are then measured by a delayed coincidence counter system developed by Moore and Arnold (1996). The partially dried fiber is placed in a helium-circulation system in which the short-lived radon daughters of ²²³Ra and ²²⁴Ra (²¹⁹Rn and ²²⁰Rn) are swept into a scintillation detector, and a delayed coincidence circuit discriminates the α decays of the different radium daughters by the timing of the α -decay events. The system is calibrated using ²³²Th and ²²⁷Ac standards that are known to have their daughters in radioactive

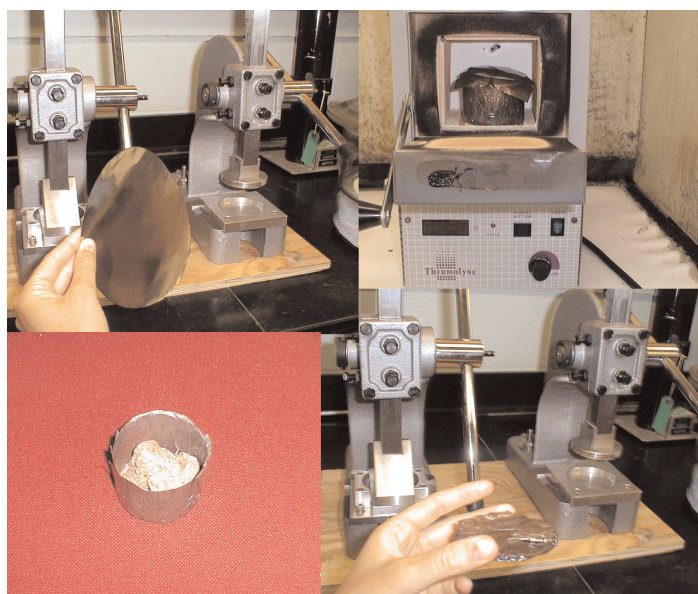


Fig. 1. The stainless-steel tool-wrap sheet is cut into a circle and a crucible is formed on a hand press. The Mn fiber is packed into the crucible and ashed at 550°C. The crucible is then folded, hydraulically pressed, and sealed with silicone sealant to create a ~3-mm thick counting vessel.

equilibrium and are adsorbed onto an MnO₂-coated fiber. Alternatively, one could measure ²²⁴Ra on the fiber by a method developed by Kim et al. (2001) that uses a commercially available radon-in-air monitor (RAD-7, DurrIDGE) to count ²²⁰Rn released from the fiber.

Long-lived radium isotopes counted by γ -spectrometry—When the short-lived radium measurements are completed, the fiber is processed for the measurement of long-lived ²²⁶Ra and ²²⁸Ra by γ -spectrometry. The sample is packed into a custom-made crucible (Fig. 1) that is fashioned from stainless-steel sheets in our laboratory. The crucible also serves as a counting vessel to eliminate any transfer steps. We needed to choose a material for the “crucible-counting vessel” that has low γ -ray attenuation, is easy to form, and withstands high temperatures for prolonged periods. We selected a stainless steel tool-wrap sheet Type 321 (MSC Industrial Supply), that has high titanium content, withstands temperatures up to 1000°C, and has a thickness of only 0.05 mm. To test its γ -ray absorption at the energies of interest for this study we used a high activity mixed γ source that we measured both directly positioned on the detector and then again after placing the stainless steel sheet between the source and the detector. Repetitive measurements showed that while there was a 15% attenuation of γ rays at 46 keV, the absorption was only 2% at 186 keV and less than 1% at the higher energies (295, 338, 352, 609, and 911 keV) that are most important for our application. We also measured the surface area of our germanium detector (19 cm²), and we prepared a die to press the crucibles at that exact diameter achieving the best possible measurement geometry.

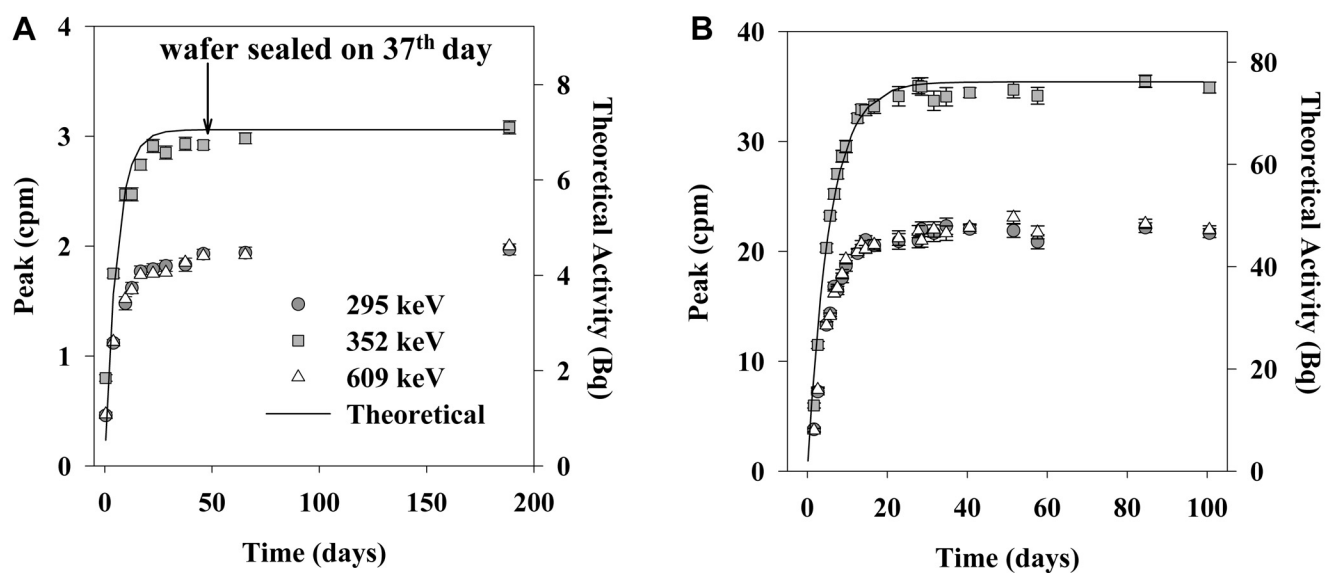


Fig. 2. Count rate data for a ^{226}Ra standard compared to theoretical in-growth. (A) Mn fiber was spiked with ^{226}Ra , ashed, folded, and measured at certain time intervals. After 37 d from preparation, the counting vessel was sealed with silicone sealant. This resulted in a 5% increase in the ^{222}Rn daughter activities most likely because of ^{222}Rn loss before sealing. (B) The Mn fiber was prepared in the same manner as above but sealed when prepared. Its activity followed the theoretical in-growth line precisely, demonstrating that there was no Rn escape.

We use these crucibles to ash the Mn fiber at 550°C for 6 h. During the ashing procedure the sample mass is reduced by approximately 90%. The stainless steel sheet has the advantage over materials like aluminum that it does not get brittle during this heating process. We allow a few hours cooling period after the ashing, otherwise the steel would lose its elasticity and crack easily. The crucibles are then folded to enclose the ash and pressed using 1 kg/cm^2 pressure with a hand press, creating an approximately 3-mm thick wafer (Fig. 1). This approach has the advantage that the sample is not transferred after ashing to a different measurement container. The sheet is folded in a way that there is no loss of the ash containing the radium, and there is apparently little or no radon escape from the pressed wafer. Prevention of radon escape is important because ^{222}Rn ($T_{1/2} = 3.8\text{ d}$) is the direct daughter of ^{226}Ra , and its short-lived daughters (^{214}Bi , ^{214}Pb) are used for ^{226}Ra determination.

We tested radon escape by preparing a fiber containing a known amount of ^{226}Ra , and we measured its activity from the time of preparation in short-time intervals. Without radon losses, the measurements should follow a theoretical in-growth line (Fig. 2A). Thirty-seven days after the preparation of the standard, we sealed the folded side of the vessel with silicon sealant. Shortly after that the measured activity increased by 5% implying that 5% of the radon had escaped from the vessel most likely because of ^{222}Rn loss before sealing. To ensure no radon escape, we now seal all wafers with the caulking material. The activity in-growth of another standard prepared in this manner shows that the in-growth follows the theoretical line (Fig. 2B).

Radium-228 is determined by counting its daughter ^{228}Ac ($T_{1/2} = 6.1\text{ h}$) that has photopeaks at energies 338 and 911 keV.

Radium-226 is determined either by its direct photopeak at 186 keV that should, in this case, be clear from interferences from ^{235}U (U is not extracted on Mn fiber from oxidizing waters) or by counting its granddaughters ^{214}Bi at 609 keV and ^{214}Pb , which have photopeaks at energies 295 and 351 keV. If one wants to measure ^{226}Ra via the 186 keV peak, the sample can be counted right away. Otherwise, approximately 3 weeks are needed to reach equilibrium between ^{226}Ra and its granddaughters. Counting ^{214}Bi and ^{214}Pb has the advantage over the 186 keV peak, in that they have lower backgrounds and significantly higher γ yields, both of which result in improved sensitivities and lower measurement errors.

Calibration—Blanks were prepared from the same amount of fiber as used for the sample collection, and these blanks were ashed and packed in the same way as described for the samples. Blanks were measured to obtain a background count rate value that was subtracted from every measurement.

The counting efficiencies of our γ -spectrometer were determined using NIST-traceable ^{226}Ra and ^{228}Ra standard solutions. As a part of efficiency calibration we had to be sure that the fiber extracts radium quantitatively and that radon does not escape from the counting vessel. To make these evaluations, we first packed standard-sized Mn fibers into stainless-steel crucibles and spiked with ^{133}Ba (15 Bq), ^{226}Ra (38 Bq), and ^{228}Ra (2.7 Bq). Pipetting directly onto the Mn fiber ensured that 100% of the activity stayed on the fiber. The fiber was then dried and ashed, and the crucible pressed into a counting wafer. A second set of two standards was prepared by passing 2 L of pH 7 spiked water (^{133}Ba , ^{226}Ra , ^{228}Ra) through the fibers. After passing the water through the fibers, we collected the

Table 1. Sample characteristics and results of the IAEA's intercomparison study of radium and uranium in natural waters

Sample Code IAEA	Cl ⁻ (mg/L)	Type*	Volume (kg)	IAEA reference value#		γ-spectrometric result†	
				²²⁶ Ra (Bq/kg)	²²⁸ Ra (Bq/kg)	²²⁶ Ra (Bq/kg)	²²⁸ Ra (Bq/kg)
421	760	S	0.999	0.055 ± 0.001	0.124 ± 0.002	0.05 ± 0.01	0.12 ± 0.05
422	760	S	0.486	0.568 ± 0.002	0.84 ± 0.02	0.52 ± 0.07	0.65 ± 0.12
424	930	N	2.015	0.054 ± 0.026	0.1 ± 0.1	0.081 ± 0.009	0.062 ± 0.056
425	1600	N	1.093	0.3 ± 0.1	0.5 ± 0.2	0.3 ± 0.1	0.5 ± 0.1
427	72300	N	0.594	65 ± 17	36 ± 4	71 ± 2	31.6 ± 0.4
431	52200	S	0.487	24.9 ± 0.4	4.14 ± 0.07	30.7 ± 0.5	4.14 ± 0.10

*S = synthetic sample; N = natural sample.

#The IAEA values of natural samples (N) represent consensus values ($n = 57$ [IAEA-424], $n = 49$ [425], and $n = 50$ [427]) calculated as robust mean and robust standard deviation (Muller 2000).

†The gamma spectrometric results for ²²⁶Ra represent mean values from ²¹⁴Pb (295, 352 keV) and ²¹⁴Bi (609 keV) peaks and the ²²⁸Ra results are averages of the two ²²⁸Ac (338, 911 keV) photopeaks. The listed uncertainties are based on the standard deviation of these averages.

effluent from two standards to see how efficiently the fibers extracted the radioisotopes. We did this by coprecipitating radium and barium isotopes from the effluent with BaSO₄. This precipitate was filtered, air-dried, and then measured by γ-spectrometry to evaluate whether any Ba or Ra remained. We did not find any statistically significant Ba or Ra activity in the precipitate from either standard. According to the γ-spectrometric measurements, these standards resulted in a chemical recovery for radium of at least 97%. We thus concluded that the radium and barium isotopes are quantitatively extracted from water by Mn fiber using these techniques.

Assessment and discussion

Blank measurements of Mn fibers prepared in the same manner as samples showed values indistinguishable from the normal detector backgrounds for the peaks of interest. We did not encounter any difficulties with high ²²⁸Ra blanks from the acrylic fiber as had been reported by Baskaran et al. (1993).

We validated our method by participating in a proficiency test organized by the Analytical Quality Control Services (AQCS) of the International Atomic Energy Agency (IAEA), called the "Interlaboratory Study on Determination of Radium and Uranium Radionuclides in Water." We received 6

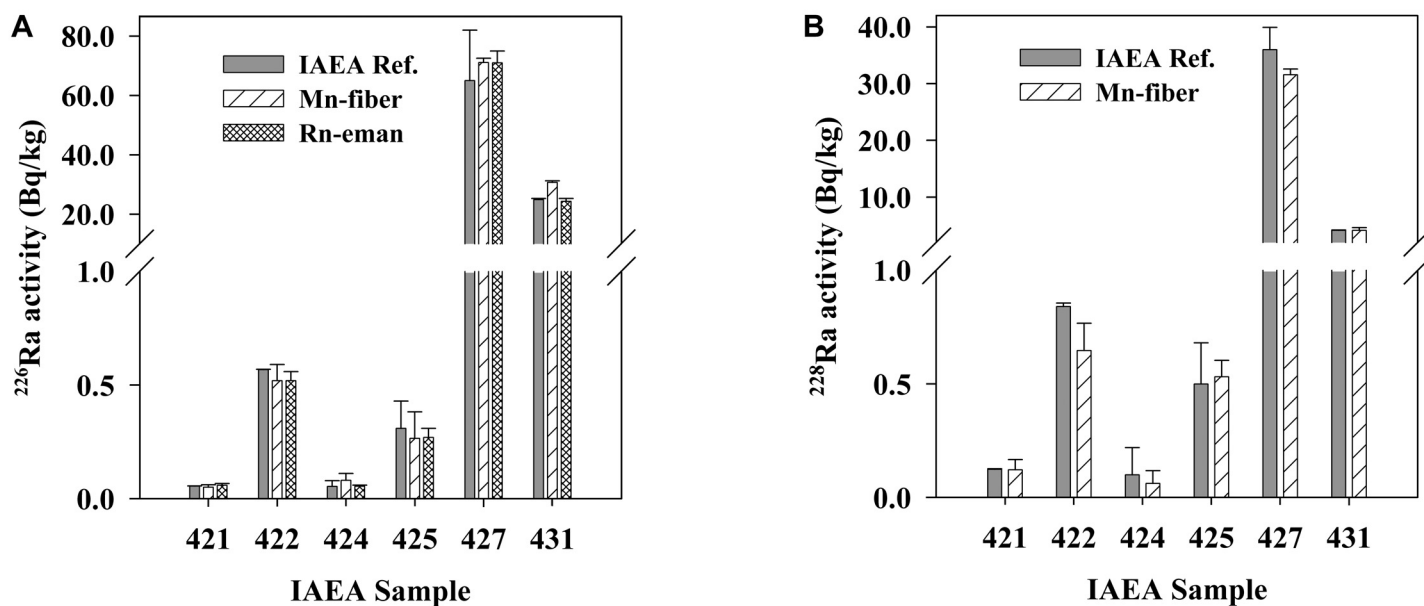


Fig. 3. Results of the 2003 IAEA intercomparison study of radium in waters. (A) Comparison of the IAEA reference values to our results of ²²⁶Ra measurements by γ-spectrometry using the average of 295, 352, and 609 keV photopeaks, and the radon emanation technique. (B) Comparison of the IAEA reference values to our results of ²²⁸Ra measurements using the average of the ²²⁸Ac photopeaks at 338 and 911 keV. Note the scale break on the activity axis of both plots. The IAEA values represent consensus values calculated as robust value of the average and robust standard deviation. The robust analysis is based on using the median instead of the mean to assure better stability against outliers (Muller 2000). Uncertainties shown for our analyses represent ± 1σ based on counting statistics.

acidified water samples (3 natural and 3 synthetic) from the IAEA in January 2003 (Table 1). For analysis, sample volumes were adjusted to 5 L with radium-free deionized water, which raised their pH to approximately 5. The samples were first measured for ^{226}Ra by standard Rn-emanation technique (Stringer and Burnett in press). Because Rn-emanation is a nondestructive method we could process the same samples for ^{226}Ra and ^{228}Ra determination using the MnO_2 -fiber method. We adjusted the acidity of the water samples to near neutral pH (6.5 to 8) and then passed each sample through an MnO_2 -fiber column. The fibers were ashed and sealed as described earlier, and we measured them after at least a 21-d holding period on a γ -spectrometry system.

We calculated ^{226}Ra results using an average calculated from the photopeaks of ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 keV) and ^{228}Ra using the mean results from the ^{228}Ac photopeaks at 338 and 911 keV (Fig. 3). The IAEA reference values of the natural samples had large standard deviations and were not appropriate for validation of our method. However, the synthetic sample reference values had standard deviations lower than 2%, and the agreement between our results and the IAEA reference values were very good. Our mean ^{226}Ra value relative to the IAEA reference value has a ratio of 1.05 ± 0.24 and for ^{228}Ra is 0.95 ± 0.09 . This comparison indicates that our results are not biased by a systematic error, and there is a good agreement between the reference values and our results both with low and high radium activities. The comparison of ^{226}Ra results measured using the Mn fiber method and by Rn emanation (Fig. 3A) also shows an excellent agreement.

Radium-226 was also measured by the 186 keV peak as well as the radon daughter peaks to demonstrate the improved sensitivity using the $^{214}\text{Pb} + ^{214}\text{Bi}$ peaks. Our results show that the measurement uncertainty from the counting statistics for the 186 keV peak is 3 to 5 times larger than that for the ^{214}Pb and ^{214}Bi peaks for comparable counting periods. The peak at 186 keV resulted in 1σ uncertainties that averaged 40%, while the others had uncertainties that averaged 10%. However, the 186 keV peak can be used if one wishes to measure the samples immediately after ashing, and the counting uncertainties can be reduced by longer acquisition times.

We used the MnO_2 -fiber method to measure radium activities in coastal ocean waters off the Florida State University Marine Laboratory (FSUML) and in Sicily, Italy, during recent experiments. At each location we collected measured amount of seawater (50 to 150 L) and passed it through MnO_2 fibers. After counting the short-lived radium isotopes, we processed the samples for γ -spectrometric measurement as described in this paper. To compare our results to a reference method we also collected parallel samples at both sites that were analyzed by another method. At the FSUML site, we collected 5-L grab samples for ^{226}Ra measurement by standard Rn-emanation technique (Mathieu et al. 1988). In the Sicily study, W. S. Moore (University of South Carolina) collected parallel Mn fiber samples that he analyzed for ^{226}Ra and ^{228}Ra by acid-

leaching the fibers and co-precipitating Ra with BaSO_4 before γ -spectrometry (Moore 1984). The average ratio of the method described here to the reference methods is 1.01 ± 0.3 .

We have shown that this technique provides good results, requires minimal operator time, and is simple to implement. It is appropriate for radium measurements in natural waters over a wide range in salinity and radium activity.

Comments and recommendations

While radium collection on Mn fiber is well known within the oceanographic community, it has also proven useful in analysis of radium isotopes in spring, lake, and river waters. We have also used the method successfully for radium analysis in public water supplies.

References

- Baskaran, M., D. J. Murphy, P. H. Santschi, J. C. Orr, and D. R. Schink. 1992. A method for rapid in situ extraction and laboratory determination of Th, Pb, and Ra isotopes from large volumes of seawater. *Deep-Sea Res. I.* 40:849-865.
- Burnett, W. C., and others. 2002. Assessing methodologies for measuring groundwater discharge to the ocean. *EOS* 83:117-123.
- , and H. Dulaiova. 2003. Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. *J. Environ. Radioactiv.* 69:21-35.
- Charette, M. A., K. O. Buesseler, and J. E. Andrews. 2001. Utility of radium isotopes for evaluating the input and transport of groundwater-derived nitrogen to a Cape Cod estuary. *Limnol. Oceanogr.* 46:465-470.
- Kelly, R. P., and S. B. Moran. 2002. Seasonal changes in groundwater input to a well-mixed estuary estimated using radium isotopes and implications for coastal nutrient budgets. *Limnol. Oceanogr.* 47:1796-1807.
- Kim, G., W. C. Burnett, H. Dulaiova, P. W. Swarzenski, and W. S. Moore. 2001. Measurement of ^{224}Ra and ^{226}Ra activities in natural waters using a radon-in-air monitor. *Environ. Sci. Technol.* 35:4680-4683.
- Mathieu, G., P. Biscayne, R. Lupton, and D. Hammond. 1988. System for measurements of ^{222}Rn at low levels in natural waters. *Health Physics* 55:989-992.
- Moore, W. S. 1976. Sampling ^{228}Ra in the deep ocean. *Deep-Sea Res. Oceanogr. Abstr.* 23:647-651.
- . 1984. Radium isotope measurements using germanium detectors. *Nucl. Instrum. Methods Phys. Res., Sect. A.* 223:407-411.
- , H. Astwood, and C. Lindstrom. 1995. Radium isotopes in coastal waters on the Amazon shelf. *Geochim. Cosmochim. Acta* 59:4285-4298.
- . 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. *Nature* 380:612-614.
- and R. Arnold. 1996. Measurement of ^{223}Ra and ^{224}Ra in coastal waters using delayed coincidence counter. *J. Geophys. Res.* 101(C1):1321-1329.

- . 2000. Determining coastal mixing rates using radium isotopes. *Cont. Shelf Res.* 20:1993-2007.
- Muller, J. W. 2000. Possible advantages of a robust evaluation of comparisons. *J. Res. Nat. Inst. Stand. Technol.* 105: 551-555.
- Sun, Y., and T. Torgersen. 1998. The effects of water content and Mn-fiber surface conditions on ^{224}Ra measurements by ^{220}Rn emanation. *Marine Chem.* 62:299-306.
- Stringer, C. E., and W. C. Burnett. In press. Sample bottle design improvements for radon emanation analysis of natural waters. *Health Phys.*
- Turekian, K. K., N. Tanaka, V. C. Turekian, T. Torgersen, and E. C. Deangelo. 1996. Transfer rates of dissolved tracers through estuaries based on ^{228}Ra : a study of Long Island Sound. *Cont. Shelf Res.* 16:863-873.

Submitted 5 April 2004

Revised 4 June 2004

Accepted 8 June 2004