

A rapid field extraction method for determination of radon-222 in natural waters by liquid scintillation counting

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Abstract

A simple and robust method for determination of ^{222}Rn in natural waters is described. A 1.3-L water sample is collected in a plastic (PET) water bottle and shaken with 20 mL mineral oil scintillant for 4 minutes. Radon preferentially migrates to the mineral oil, and the ^{222}Rn activity is determined by counting ^{222}Rn and the short-lived daughter products ^{214}Po and ^{218}Po using an ultra-low-level LS counter via α/β separation technique. The PET method achieves a detection limit of $\sim 3 \text{ mBq L}^{-1}$, making it an ideal method for analysis of surface water and groundwater samples.

Introduction

Radon-222, a noble gas with half-life of 3.82 days, is frequently used in the study of hydrological and environmental problems. These include tracing groundwater input to streams (Ellins et al. 1990; Genereux et al. 1993; Cook et al. 2003), lakes (Corbett et al. 1997; Tuccimei et al. 2005), and coastal zones (Cable et al. 1996; Corbett et al. 2000; Schwartz 2003), as well as rates of river water infiltration to banks (Hoehn and von Gunten 1989) and sediment-water exchange (Martens et al. 1980). Furthermore, the heightened concern about radon in the environment, particularly the contribution of radon evasion from drinking water into indoor air within houses, has resulted in measurements of radon in domestic water supplies all around the world (Schonhofer 1989).

A variety of methods to measure radon in waters have been used since the 1960s, such as Lucas cell scintillation counting (Lucas 1964; Mathieu et al. 1988), liquid scintillation (Prichard and Gesell 1977; Schonhofer 1989; Salonen 1993; Herczeg et al. 1994), and γ counting (Shizuma et al. 1998), as well as a number of automated methods (Theodorsson 1996; Surbeck 1996). The Lucas cell method has the advantage of being portable, but suffers from low efficiency and is relatively time consuming (15- to 20-min extraction per sample). Most automated methods are good for monitoring at one site but not practical for regional field surveys. The automated meth-

ods described by Burnett et al. 2001 and Dulaiova et al. 2005 have proved popular recently, allowing analysis of ^{222}Rn in seawater with precisions of $\pm 5\%$ to 15% (Dulaiova et al. 2005). Low-level liquid scintillation, however, has been adopted as the method of choice because of its high efficiency (ability to measure low ^{222}Rn activities) and ease of analysis.

Liquid scintillation is now the most common technique used for measurement of ^{222}Rn concentrations in groundwater. It involves injection of the water sample into a vial containing some type of scintillant (toluene-based or mineral oil). The radon partitions preferentially into the toluene or mineral oil phase, and the α radiation is measured using a liquid scintillation counter. The detection level for this method (henceforth called the direct counting [DC] method), is $\sim 0.20 \text{ Bq L}^{-1}$ (based on 2 standard deviations above background and 100-min counting time).

The "typical" range in ^{222}Rn activity of surface water samples is 0.05 to 2 Bq L^{-1} , (a factor of 40), up to 2 orders of magnitude less than those found in groundwater. The lack of a convenient method of analysis of ^{222}Rn activity for surface waters has limited the application of ^{222}Rn in rivers and lakes.

A simple method for ^{222}Rn analysis of surface waters was originally developed by Noguchi (1964), who used liquid scintillation counting methodology similar to that used for groundwater analysis. His method involved concentrating radon from approximately 1 L surface water into a smaller quantity of mineral oil before measuring the α radiation in a liquid scintillation counter. Similar "surface water" methods were then described by Horiuchi and Murakami (1981) and Saito and Takata (1992). This article presents a refined and simplified method that builds on those original concepts. We also report the precision and limitations after extensive testing of the revised method.

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Fig. 1. Photo of the glass nozzle fitted to the PET bottle as used when displacing mineral oil to the scintillation vial.

The revised method is simple (using a minimum amount of readily available equipment and materials), quick (sampling time is 5 min for sampling and a 1- to 200-min counting time), and robust (the simplicity of the method minimizes errors introduced by different users). The results reported are those using a Quantulus liquid scintillation counter (LSC) (model no. 1220) commissioned in 1992. Newer counters have refined α/β separation capability and lower background values, allowing better precision and lower minimum detection levels. Results achievable using more modern counters are given later in the article.

Materials and procedures

Direct counting method—The DC technique involves adding 14 mL water to ~7 mL mineral oil cocktail (Perkin Elmer high-efficiency mineral oil scintillator, cat. no. 6NE9579) in a 24-mL low-diffusion, polyethylene (PE) scintillation vial (Packard, cat. no. 6000477). About 14 mL water is gently placed under the mineral oil layer via a plastic syringe, and the vial is sealed and then shaken for 30 s. The relative amount of water:mineral oil:air space is approximately 14:7:3. Radon-222 preferentially partitions into the mineral oil, and after 3 h, the counts derived from ^{222}Rn and its short-lived daughters, ^{214}Po and ^{218}Po , can be detected almost quantitatively. The three peaks are only partially resolved, but detection of β -emitting ^{214}Bi and ^{214}Pb nuclides are completely eliminated using the α/β separation facility of the LKB Wallac Quantulus LSC.

The precision and limit of detection for ^{222}Rn analyses is determined primarily by the figure of merit of the LSC (E^2/B), which is a function of efficiency, E , background count rate, B ,

and the total number of counts for each sample. Because the half-life of ^{222}Rn is relatively short (3.84 days), it is possible to count for extended periods of time only if there are relatively few samples to be analyzed. Samples are routinely analyzed until either 2000 decays are recorded or for a maximum of 200 min, whichever comes first. The limit of detection for samples using the DC method and 200-min count-time using the Quantulus LSC is 0.2 Bq L^{-1} (based on 2 standard deviations above background). The precision (1 SD) associated with analysis ranges from 20.0 ± 0.5 to $2.0 \pm 0.2 \text{ Bq L}^{-1}$ for a count-time of 200 min.

Because radon is only sparingly soluble in water ($0.01 \text{ mol kg}^{-1} \text{ bar}^{-1}$ at 20°C) (Lerman 1979), and because Henry's law partitioning coefficient favors transfer of radon to the air at concentrations in water $> 0.02 \text{ Bq/L}$, degassing of ^{222}Rn during sampling of water is always a potential problem. Although precautions to minimize gas losses during sampling are implicit, the ^{222}Rn concentration of water samples should be considered minimum concentrations, as some ^{222}Rn may inevitably be lost.

Enhanced concentration method—One method for concentrating radon is based on equilibrating water:scintillant:air (Nogushi 1964, Saito and Takata 1992) in a sealed container. Their methods use ~500 g of water weighed into a separating funnel into which is weighed ~30 g toluene and a scintillator (Permafluor 1; Packard). The mixture is shaken for about 5 min, and the extraction temperature is measured. The toluene, which is immiscible in water, is then displaced into a vial for counting. Counting commences 300 min after the toluene has been extracted so that secular equilibrium between the radon and short-lived daughters is established. The ^{222}Rn concentration of the sample water is then determined by back-calculating from the measured ^{222}Rn concentration in the toluene, allowing for the various volume ratios and solubilities of water:toluene:air. This method can be modified by transferring ~900 mL water directly into a 1-L Teflon-coated plastic separating funnel that has been fitted with a tap at the top and a tap with a capillary nozzle at the bottom (tapered end) of the funnel.

^{222}Rn Extraction using PET bottles—The method described here uses readily available 1.3 dm^3 polyethylene terephthalate (PET) soft drink bottles as a vessel for extraction of ^{222}Rn from the water (hereafter known as the PET method). The PET bottles are filled with sample water, ensuring minimal agitation of the sample. The bottles are then stored in an insulated container at a temperature close to 25°C until all samples are collected. A syringe is used to remove ~50 mL sample water from each bottle. Mineral oil (20 cm^3) is then added, the lid replaced, and the bottle shaken for 4 min, during which time the ^{222}Rn is preferentially transferred to the mineral oil. The bottle is allowed to stand for 1 min as the mineral oil and water separate. The lid of the plastic bottle is removed, and a glass nozzle is inserted in the bottle. The nozzle consists of 1 mm i.d. capillary tubing glass blown onto a B24 ground-glass cone that fits tightly into the bottle opening (Figure 1). The mineral oil is displaced into the vial

by squeezing the plastic bottle, carefully ensuring that no water is displaced into the vial.

The advantage of this method is that the only equipment required to be sent to the sampling sites is the glass nozzle, because the PET bottles are readily available at supermarkets. Also, either the collected samples can be transported back to the laboratory in drink bottles, or the ²²²Rn can be extracted into mineral oil in the field and the PET scintillation vial sent immediately to the laboratory from the field. Both of these options provide better temperature control during the extraction phase. Finally, because of the simplicity of the design, there is less potential for leaks than for previously described methods when transferring the mineral oil to the vial.

Assessment

To validate the PET method, several tests were undertaken to evaluate the importance of the following:

- loss of ²²²Rn during storage of sample in bottles;
- efficiency and reproducibility of extraction of ²²²Rn from the water to mineral oil as a function of time shaken; and
- sensitivity of analysis to temperature of extraction and salinity of water.

Most of the tests were made using groundwater collected from an artesian borehole near our laboratory (²²²Rn = 50 Bq L⁻¹). For some of the experiments, the bore water was diluted with ²²²Rn free water to make bulk quantities of water at lower known ²²²Rn concentrations. Results are reported as the ratio of ²²²Rn concentration measured using the PET method to that measured on the same sample using the DC method normalized to the weight of water used in the DC method. The relative efficiency of the surface water method, *E_{sw}*, is calculated by

$$E_{sw} = \frac{W_{gw}N_{sw}}{W_{sw}N_{gw}} \tag{1}$$

where *W_{sw}* and *W_{gw}* are the mass of water used for the surface water (1252 g) and groundwater (~14 g) methods, respectively. *N_{sw}* and *N_{gw}* are the net counts per min (cpm above background) for the PET and DC methods, respectively, for low-salinity water samples extracted at 22.5 °C.

E_{sw} = 1.00 means that the net count rate for water samples measured using the PET method is ~90 (= 1252 mL/14 mL) times that using the groundwater method. When estimating *E_{sw}*, we ignore differences in counting efficiency that would arise because of the different amounts of water and mineral oil in the vials when using the groundwater method (~7 mL of mineral oil and 14 mL of water) and the PET method (~20 mL of mineral oil and no water).

²²²Rn loss in different types of plastic bottles—The amount of ²²²Rn lost from the water via diffusion is dependent on the type of plastic bottle and lid, the area-to-volume ratio of the bottle, and the temperature at which the bottle is stored. Three readily available types of plastic bottles, 1.3-L PET (soft drink bottle), 2.5-L high-density polyethylene (as used for acid storage), and

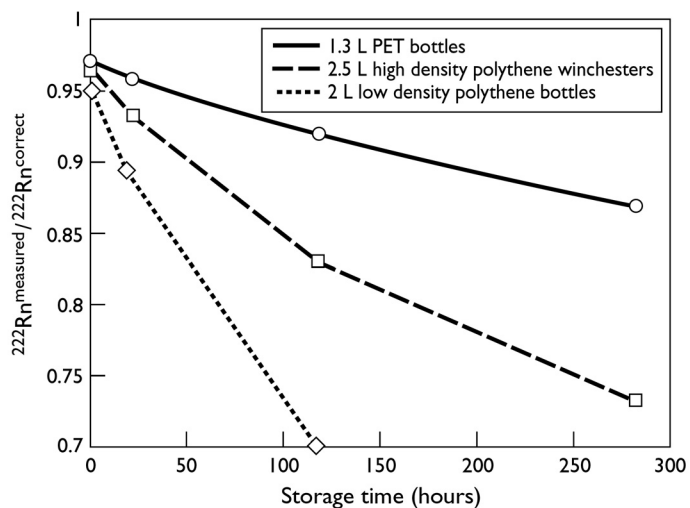


Fig. 2. Radon losses during storage for different types of plastic containers. (Note that ²²²Rn analyses for all vials have been corrected for decay.)

2-L low-density polyethylene (standard laboratory issue) were tested. Three or 4 samples of water were collected from the local groundwater bore in each of the 3 types of bottles to be tested. The ²²²Rn was extracted after storage times ranging from 0 to 428 hours. Groundwater from the bore was also collected directly into the Teflon separating funnel and measured using the direct counting method for comparison.

The measured ²²²Rn concentration for water that was stored in the three types of bottles and then transferred to glass separating funnels for extraction was always less than that when transferred directly to the Teflon separating funnel and also to that measured using the groundwater method (²²²Rn_{correct}). Between 3% and 5% of the ²²²Rn is lost for samples stored for 1 h (Figure 2). Most of this loss is the result of degassing during transfer (see below). Of the 3 types of plastic bottles tested, the 1.3-L PET bottles lost the least amount of ²²²Rn during storage, with only 1% lost after 20 h and 12% after 280 h. All of the following work uses 1.3-L PET bottles for storage and as a vessel for extracting ²²²Rn from the water to mineral oil.

Testing efficiency and consistency of extraction—One of the main factors that will increase the analysis uncertainty associated with the method described here is the variability in extraction efficiency associated with different operators and the time of shaking of the mineral oil with the water sample. The variability in efficiency for different shaking times was tested using shaking times between 1 and 10 min and settling time of 1 min, followed by transfer of the mineral oil into a vial for counting. A further 2 bottles were mechanically shaken end-over-end for a period of 120 min before settling and expelling the mineral oil. Following the results of this test, the shortest shaking time that achieved reasonable extraction efficiency (4 min) was chosen to test the variability in extraction efficiency by different operators.

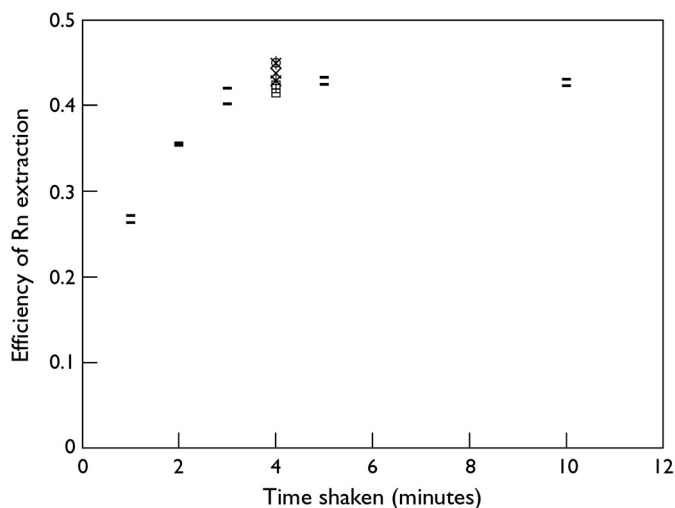


Fig. 3. Efficiency of extraction of radon from water collected in 1.3-L PET bottles and transferred to vial-sized mineral oil as a function of time shaken. Also shown is the variability resulting from different users of the method.

The maximum value for E_{sw} is ~ 0.43 , achieved after shaking the oil and water for 4 min (Figure 3). The efficiency after shaking the oil and water on an end-over-end shaker for 120 min (not shown) is the same as that after shaking by hand for 4, 5, or 10 min. A shaking time of 4 min was then chosen as routine for all subsequent analyses using the PET method in the following tests.

The extraction efficiency of the PET method is less than half that of DC, primarily owing to the larger ratio of mineral oil:water used in the DC method. However, the overall effect yields a much higher count rate (by a factor of nearly 40) because of the nearly 2 orders of magnitude greater volume used in the PET method. There is minimal variation in E_{sw} introduced by different users of the PET method ($E_{sw} = 0.429 \pm 0.011$) (Figure 3).

Extraction efficiency of ²²²Rn as a function of temperature and water salinity—Differences in temperature and salinity between calibration and unknown samples can cause systematic errors in ²²²Rn measured values due to decreased aqueous solubility of radon with increasing temperature and salinity. The variation in E_{sw} as a function of temperature of extraction was tested by extracting ²²²Rn from water samples equilibrated at temperatures ranging from 13 to 39 °C. This corresponds to solubility of radon in water ranging from 1.4×10^{-2} to 6×10^{-3} mol kg⁻¹ bar⁻¹ for temperatures of 13 and 39 °C, respectively (or a factor of ~ 2.3).

To test the effect of salinity, sodium chloride was added to groundwater samples to prepare 4 solutions (NaCl = 80, 16,500, 35,000, and 53,000 mg L⁻¹). The NaCl was dissolved completely by gently shaking the containers, and samples were collected for analysis using the PET and DC methods. We present the data as a ratio, $R_{(s,T)}$ of the ²²²Rn activity for each of the specified water salinity and temperature ($A_{(s,T)}$) relative

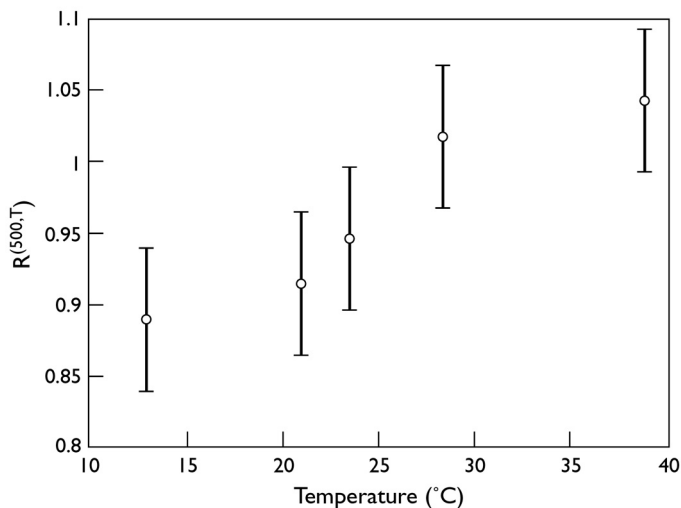


Fig. 4. $R_{(600,T)}$ vs. temperature of extraction for the PET method.

to the ²²²Rn concentration of the same water sample with no added salt and extracted at 25 °C using the DC method, $A_{(calib)}$.

$$R_{(s,T)} = \frac{A_{(s,T)}}{A_{(calib)}} \quad (2)$$

(S,T) refers to the salinity, S, of NaCl (mg/L) and temperature, T, (°C) of the water using the PET method.

For the PET method, $R_{(s,T)}$ increases as the temperature of extraction increases (Figure 4). The value is ~ 1.0 for the temperature at which the PET method was calibrated (25 °C) and is $\sim 10\%$ lower at the lowest test temperature (13 °C) and $\sim 5\%$ higher at the highest test temperature (~ 39 °C). It should, however, be considered that, although the temperature of the water and the mineral oil were kept at each of the nominated experimental temperatures during extraction, there will redistribution of ²²²Rn between the water and mineral oil phases in the vial for the DC method once in the counter (set at 13.5 °C).

There is no significant difference in the measured ²²²Rn activity for groundwater samples with NaCl concentrations up to 53 000 mg/L compared to that for samples with NaCl of ~ 80 mg/L when using both the DC and PET method (i.e., $R_{(s,T)} \sim 1.00 \pm 0.03$ for all NaCl solutions). Because the solubility of radon is only a function of ionic strength, these results would be independent of specific major anions or cation compositions of water sampled.

Discussion

The uncertainty associated with ²²²Rn analysis (excluding any errors induced during sampling) was measured using 200-min count times for 2 Quantulus LSCs, both having similar mechanisms for α/β separation (Figure 5). LSC 1, commissioned in 1992, is housed at the CSIRO Land and Water Laboratory in Adelaide and LSC 2, commissioned in 2002, is housed at the Isotope Hydrology Laboratory of the Chinese Academy of Science Institute Geology and Geo-

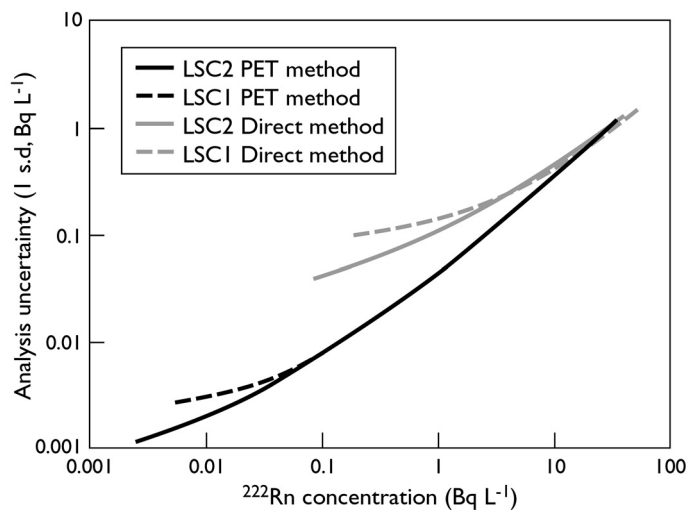


Fig. 5. Analytical uncertainties when using the PET and direct methods as a function of ^{222}Rn concentration for two Quantulus LSCs.

physics Institute. The uncertainty for LSC 1 is significantly greater than that for the newer counter. This may be the result of more sophisticated electronics or possibly lower background radioactivity at the Beijing site. For both counters, however, the uncertainty using the PET method is significantly less than that using the direct method when the ^{222}Rn concentration of the groundwater is less than 100 to 1000 mBq L^{-1} . Similarly, the limit of detection, based on 2 standard deviations above background, is as low as 3 mBq L^{-1} using the PET method. The limit of detection for the PET method is routinely less than 1/30th of that using the direct method of analysis (Figure 5).

Comments and recommendations

The PET method for analysis of ^{222}Rn concentrations in water samples is easy and robust. Although primarily designed for surface water, it can also be used when analyzing groundwater samples to reduce the counting time required to achieve similar precision to the more established DC methods. This is useful when a large number of samples are collected at any one time, as it minimizes the loss of ^{222}Rn while the samples are waiting for analysis. The precision achievable for this method using a state-of-the-art LSC and analyzing each sample for 200 min is 3% to 5% for samples with ^{222}Rn concentrations 1 to 30 Bq L^{-1} . The limit of detection is $\sim 3 \text{ mBq L}^{-1}$ based on 2 standard deviations above background.

Of the factors that limit the analytical precision, the PET method is most sensitive to the temperature at which the ^{222}Rn is extracted from the water to the mineral oil. For this reason, we suggest that samples be collected in the field and that extraction of the ^{222}Rn take place as soon as possible in an environment where there is some means of temperature control (such as that provided by motel accommodation or nearby laboratory).

References

- Burnett, W.C., G. Kim, and D. Lane-Smith. 2001. A continuous radon monitor for assessment of radon in coastal ocean waters. *J. Radioanalyt. Nucl. Chem.* 249:167-172.
- Cable, J.E., W.C. Burnett, J.P. Chanton, and G.L. Weatherly. 1996. Estimating groundwater discharge into the north-eastern Gulf of Mexico using radon-222. *Earth Plant. Sci. Lett.* 144:591-604.
- Cook, P.G., G. Favreau, J.C. Dighton, and S. Tickell. 2003. Determining natural groundwater influx into a tropical river using radon, chlorofluorocarbons and ionic environmental tracers. *J. Hydrol.* 277:74-88.
- Corbett, D.R., W.C. Burnett, P.H. Cable, and S.B. Clark. 1997. Radon tracing of groundwater input into Par Pond, Savannah River Site. *J. Hydrol.* 203:209-227.
- Corbett, D.R., K. Dillon, W.C. Burnett, and J.P. Chanton. 2000. Estimating groundwater contribution into Florida Bay via natural tracers, ^{222}Rn and CH_4 . *Limnol. Oceanogr.* 45: 1546-1557.
- Dulaiova, H., R. Peterson, W.C. Burnett, and D. Lane-Smith. 2005. A multi-detector continuous monitor for assessment of ^{222}Rn in the coastal ocean. *J. Radioanalyt. Nucl. Chem.* 263:361-365.
- Ellins, K.K., A. Roman-Mas, and R. Lee. 1990. Using ^{222}Rn to examine groundwater/surface water interaction in the Rio Grande de Manati, Puerto Rico. *J. Hydrol.* 115:319-341.
- Genereux, D.P., H.F. Hemond, and P.J. Mulholland. 1993. Use of radon-222 and calcium as tracers in a three-end-member model for streamflow generation in the West Fork of Walker Branch Watershed. *J. Hydrol.* 142:167-211.
- Herczeg, A.L., J.C. Dighton, M. L. Easterbrook, and E. Salomons. 1994. Radon-222 and Ra-226 measurements in Australian groundwaters using liquid scintillation counting. *Proc. Workshop on Radon and Radon Progeny Measurements in Environmental Samples*, Feb, 1994. Canberra, Australia, p. 53-57.
- Hoehn, E., and H.R. von Gunten. 1989. Radon in groundwater: a tool to assess infiltration from surface waters to aquifers. *Water Resource Res.* 25:1795.
- Horiuchi, K., and Y. Murakami. 1981. A new procedure for the determination of radium in water by extraction of radon and application of integral counting with a liquid scintillation counter. *Int. J. Appl. Radiat. Isotopes.* 32:291.
- Lerman, A. (1979) *Geochemical Processes*. New York: Wiley-Interscience, 481 p.
- Lucas, H.F. 1964. A fast and accurate survey technique for both radon-222 and radium-226. *In: The Natural Radiation Environment*. Chicago: The University of Chicago Press, p. 315-329.
- Martens, C.S., G.W. Kipphut, and J.V. Klump. 1980. Sediment-water chemical exchange in the coastal zone traced by in-situ radon-222 flux measurement. *Science* 208:285-288.
- Mathieu, G.G., P.E. Biscaye, R.A. Lupton, and D.E. Hammond,

1988. System for measurement of ^{222}Rn at low levels in natural waters. *Health Phys.* 55:989-992.
- Noguchi, M. 1964. New method of radon activity measurement with liquid scintillator. *Radioisotopes* 13:362-368.
- Prichard, H.M., and T.F. Gesell. 1977. Rapid measurements of ^{222}Rn concentrations in water with a commercial liquid scintillation counter. *Health Phys.* 33:577-581.
- Saito, M., and S. Takata, 1992. Improvements for measurement of ^{222}Rn in water. *Radioisotopes*, 41:391-396.
- Salonen, L. 1993. Measurement of low levels of radon-222 in water with different commercial liquid scintillation counters and pulse-shape analysis. *In: Liquid Scintillation Spectrometry*. J.E. Noakes, F. Schonhofer, and H.A. Polach, Eds. Proc. Int. Conf. on Advances in LSC, LSC 92, Vienna, Austria, Sep 14-18, 1992. Tucson, AZ: Radiocarbon, p. 361-373.
- Schonhofer, F. 1989. Determination of radon-222 and radium-226 in mineral water and drinking water: a survey in Austria. *Analyst* 114:1345-1347.
- Schwartz, M.C. 2003. Significant groundwater input to a coastal plain estuary: assessment from excess radon. *Est. Coastal Shelf Sci.* 56:31-42.
- Shizuma, K., S. Hamanaka, X. Q. Wen, K. Iwatani, and H. Hasai. 1998. A method for measuring accurate radon concentration in water by means of gamma-ray spectrometry. *Nucl. Instr. Meth. A* 410:309-313.
- Surbeck, H. 1996. A radon-in-water monitor based on fast gas transfer membranes. *Int. Conf. on Technologically Enhanced Natural Radioactivity (TENR) Caused by Non-uranium Mining*. Szczyrk, Poland.
- Theodorsson, P. 1996. A new method for automatic measurement of low-level radon in water. *Appl. Rad. Isotopes* 47:855-859.
- Tuccimei, P., R. Salvati, G. Capelli, M.C. Delitalia, and P. Primavera. 2004. Groundwater fluxes into a submerged sink-hole area, central Italy, using radon and water chemistry. *Applied Geochem.* 20:1831-1847.

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