

**METHODS, OCCURRENCE AND MONITORING
DOCUMENT FOR RADON IN DRINKING WATER**

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1. INTRODUCTION

1.1 Purpose of This Document

This Methods, Occurrence, and Monitoring (MOM) Document has been developed by EPA in support of the rulemaking process for radon in drinking water. The Agency is proposing a Maximum Contaminant Level Goal (MCLG) and National Primary Drinking Water Regulations (NPDWR) for radon-222 in public water supplies (EPA, 1999a). The purposes of this document are:

- Identification of available analytical methods for monitoring radon in groundwater sources and in drinking water,
- Discussion of the patterns of occurrence of radon in groundwater and drinking water, and
- Explanation of alternative monitoring schemes for assuring compliance with the proposed rule.

1.2 Statutory Requirements

The 1996 Amendments to the Safe Drinking Water Act (PL 104-182) establish a new charter for public water systems, states, tribes, and EPA to protect the safety of drinking water supplies. Among other mandates, Congress amended Section 1412 to direct EPA to take the following actions regarding radon in drinking water.

Withdraw the 1991 Proposed Regulation for Radon

Congress specified that EPA should withdraw the drinking water standards proposed for radon in 1991.

Arrange for a National Academy of Sciences Risk Assessment.

The amendments in § 1412(b)(13)(B) require EPA to arrange for the National Academy of Sciences (NAS) to conduct an independent risk assessment for radon in drinking water and an assessment of the health risk reduction benefits from various mitigation measures to reduce radon in indoor air.

Set an MCLG, MCL, and BAT for Radon-222

Congress specified in § 1412 (b)(3)(C) that EPA should propose a new MCLG and NPDWR (an MCL, BAT, and monitoring, reporting, and public notification requirements) for radon-222 by August, 1999. EPA is also required to finalize the regulation by August, 2000. As a preliminary step, EPA was required to publish a radon health risk reduction and cost analysis

(HRRCA) for possible radon MCLs for public comment by February, 1999. This analysis must consider seven topics: (1) health risk reduction benefits that come directly from controlling radon; (2) health risk reduction benefits likely to come from reductions in contaminants that occur with radon; (3) costs, (4) incremental costs and benefits associated with each MCL considered; (5) effects on the general population and on groups within the general population likely to be at greater risk; (6) any increased health risk that may occur as the result of compliance; and (7) other relevant factors, including the quality and extent of the information, the uncertainties in the analysis, and factors with respect to the degree and nature of the risk.

Set an Alternative MCL (AMCL) and Develop Multimedia Mitigation (MMM) Program Guidelines

The amendments in § 1412(b)(13)(F) introduce two new elements into the radon in drinking water rule: (1) an Alternative Maximum Contaminant Level (AMCL) and (2) radon multimedia mitigation (MMM) programs. If the MCL established for radon in drinking water is more stringent than necessary to reduce the contribution to radon in indoor air from drinking water to a concentration that is equivalent to the national average concentration of radon in outdoor air, EPA is required to simultaneously establish an AMCL. The AMCL would be the standard that would result in a contribution of radon from drinking water to radon levels in indoor air equivalent to the national average concentration of radon in outdoor air. If an AMCL is established, EPA is to publish guidelines for state multimedia mitigation (MMM) programs to reduce radon levels in indoor air. Section V describes what a state or public water system must have in their multimedia mitigation program.

Evaluate Multimedia Mitigation Programs Every Five Years

Once the MMM programs are established, EPA must re-evaluate them no less than every five years. [§1412(b)(13)] EPA may withdraw approval of programs that are not expected to meet the requirement of achieving equal or greater risk reduction.

Develop Monitoring Requirements and Characterize Contaminant Occurrence

Under every SDWA rule, EPA is required to develop monitoring requirements to assure compliance with the rule. Water systems are responsible for conducting monitoring of drinking water to ensure that it meets all drinking water standards. To do this, water systems and states use analytical methods developed by government agencies, universities, and other organizations.

EPA is responsible for evaluating analytical methods developed for drinking water and approves those methods that it determines meet Agency requirements. Laboratories analyzing drinking water compliance samples must be certified by the EPA or the state. Chapter 2 of this document reviews the available analytical methods for radon in drinking water and their performance and costs.

EPA must also characterize the sources of drinking water contaminants, their fate and transport properties, and how they relate to potential exposures. Available data related to the occurrence of contaminants must be evaluated, and the patterns of occurrence across different regions of the country, different types of water systems (community and non-community) and in water systems of different sizes, must also be evaluated in order to develop a national picture of the distribution of contaminants. The degree to which the occurrence of the contaminant is correlated with that of other contaminants must also be evaluated. Chapters 3 through 7 of this document address these issues.

Whether addressing a regulated or unregulated contaminants, EPA establishes requirements as to how often water systems must monitor for the presence of the subject contaminant. Water systems serving larger populations generally must conduct more monitoring (temporally and spatially) because there is a greater potential human health impact of any violation, and because of the physical extent of larger water systems (e.g., miles of pipeline carrying water). Small water systems can receive variances or exemptions from monitoring in limited circumstances. In addition, under certain conditions, a state may have the option to modify monitoring requirements on an interim or a permanent basis for regulated contaminants, with a few exceptions. Chapter 8 of this document discusses monitoring strategies for determining compliance with the proposed rule.

2. ANALYTICAL METHODS

2.1 Introduction

This chapter addresses the analytical methods that may be applicable to the measurement of radon in drinking water samples. It does *not* recommend a specific method for radon analyses, but rather, identifies possible candidate techniques and evaluates the extent to which the performance of those techniques has been demonstrated

As part of its overall responsibility for regulating the nation's drinking water supplies, in 1991 EPA proposed regulations on various radionuclides under 40 CFR Parts 141 and 142 (July 18, 1991, FR 56 [138]: 33050-33127). Although eventually withdrawn, part of that proposal addressed the regulation of radon (^{222}Rn or radon-222). Among other topics, the proposal discussed methods for the analysis of radon in drinking water.

As EPA prepares to propose new regulations for radon in drinking water, the Agency has reviewed and updated the information on the analytical techniques that appeared in the 1991 proposal (EPA 1991). Specifically, in 1998, at EPA's direction, SAIC reviewed the information in the 1991 proposal and also conducted an electronic literature search to identify additional analytical techniques that might be used to measure the concentration of radon in drinking water. The focus of the 1998 effort was to determine if new monitoring techniques had become available since the 1991 proposal. The techniques identified by that search were further evaluated to determine their performance capabilities and possible costs. The remainder of this chapter addresses the following aspects of the techniques:

- Inventory of methods
- Performance capabilities of the methods
- Skill requirements
- Practical availability of methods
- Anticipated unit costs
- Practical performance and analytical uncertainties
- Degree to which each method meets EPA's regulatory needs

This last section summarizes the results of the review of the analytical techniques relative to EPA's need for a method for a nationwide compliance monitoring program. The focus of this section is on techniques for the analysis of radon in drinking water, and as such, does not attempt to review information relevant to the analysis of other environmental matrices

2.1 Inventory of Methods

The 1991 EPA proposal focused on two techniques for the analysis of radon in drinking water. liquid scintillation counting and the Lucas cell. The 1991 discussion of these techniques is summarized in Sections 2.1.1 and 2.1.2, below.

Five newer techniques, or combinations of techniques, were identified in an electronic search of the open literature. Because EPA had reviewed older analytical techniques prior to proposing the radionuclides rule in 1991, the search was constrained to identify publications that have appeared since 1990, in an effort to identify newer techniques that may not have been considered in conjunction with the 1991 proposed rule on radionuclides. The discussion of the five newer techniques is presented in Sections 2.3.1 to 2.3.5.

2.1.1 Liquid Scintillation Counting

Radon is an alpha-emitting radionuclide and is just one of 14 radionuclides in what is known as the "uranium series," the term used to describe the chain of 15 elements that begins with ^{238}U and ends with ^{206}Pb , a stable (non-radioactive) element. ^{222}Rn is the seventh element in the series, created as a decay product of ^{226}Ra . Radon undergoes radioactive decay itself, forming ^{218}Po through the loss of an alpha particle. Polonium decays through the emission of a beta particle to form ^{214}Pb . The portion of the decay series from radon onward is illustrated in the Exhibit 2-1, and includes the manner of the decay (alpha or beta particle) and the half-life of each element.

Exhibit 2-1. Radon Decay Series

Element	Decay Emission	Half-life
^{222}Rn	alpha	3.8 days
^{218}Po	alpha	3 minutes
^{214}Pb	beta	27 minutes
^{214}Bi	beta	20 minutes
^{214}Po	alpha	1.6×10^{-4} seconds
^{210}Pb	beta	22.3 years
^{210}Bi	beta	5 days
^{210}Po	alpha	138 days
^{206}Pb	beta	stable

Radon's alpha particle emissions can be used as the basis for measuring radon in a variety of environmental media. The principal technique for radon analysis considered by EPA in the 1991 proposal was liquid scintillation counting.

Scintillation counting refers to the measurement of the light emitted when an alpha particle from the sample strikes some form of scintillating material. The two most common forms of scintillators are the scintillation disk, which is a planchet or metal disk coated with zinc sulfide, and a liquid scintillation fluid or an organic phosphor. The light emitted from the scintillator strikes the surface of a photomultiplier tube that is placed next to the sample in a light-proof container, releasing electrons from the photocathode in the tube at levels proportional to the intensity of the emitted light. The electrical pulses that result are counted to determine the number of disintegrations per minute (dpm) that occur, which can be related to the concentration of a given radionuclide.

In liquid scintillation counting, a volume of sample is mixed with the organic phosphor contained in a mineral oil solution or "cocktail" in a glass container which is then placed in the instrument, where it is held against the photomultiplier for counting.

As noted in the 1991 proposal, radon can be measured through a direct, low-volume liquid scintillation technique in which approximately 10 ml of water is added to a vial with the scintillation cocktail, mixed, and placed in a liquid scintillation counter. The sample can be left in the counter for periods ranging from several minutes to several hours, depending on the level of radon in the sample.

The energy of the alpha particles released by radioactive decay is characteristic of the radionuclide. In the case of liquid scintillation counting techniques, the counting apparatus can be configured to measure the scintillations in narrow energy ranges across the emission spectrum. In the case of radon analyses the counter can be set to look in the portion of the energy spectrum that represents the alpha particles emitted by ^{222}Rn and as well as ^{218}Po and ^{214}Po , the next two alpha-emitting daughters in the series. Given the short half-lives of these two daughters, their alpha particle emissions can be measured along with that of the radon itself in less than an hour of counting time. From a practical standpoint, the emissions of three alpha particles can be measured and related back to one radon atom, thereby amplifying the signal from that single radon atom's decay.

It is important to distinguish between an analytical technique and a specific analytical method. Liquid scintillation counting is a technique. EPA's 1991 proposal stated that the Agency planned to establish a specific analytical method, EPA Method 913, based on the liquid scintillation technique.

2.1.2 The Lucas Cell Technique

The second technique that EPA considered in the 1991 proposal involved the Lucas cell, a specially constructed 100- to 125-ml metal cup coated on the inside with zinc sulfide (a scintillator) and fitted with a transparent window. The Lucas cell replaces the scintillation disk or planchet in the counting instrument. The analysis of radon in a water sample is accomplished by purging a volume of the sample with radon-free helium or "aged" air (air in which the radon has already decayed). The purge gas removes the dissolved radon from the sample and carries it into a Lucas cell that has been evacuated of any air. After an equilibration period of three to four hours, the Lucas cell is placed in the counter and the scintillations resulting from the alpha particles striking the zinc sulfide are counted through the transparent window.

The Lucas cell technique is a modification of other scintillation counting techniques and was considered by EPA because it can permit the measurement of lower levels of radon than in the liquid scintillation technique. However, the Agency noted that the method is more difficult to use than the liquid scintillation method, in particular, requiring specialized glassware and greater skill on the part of the analyst. It was the Agency's intent to include procedures for the Lucas cell technique in Method 913, as an adjunct to the liquid scintillation procedures.

2.2 Major Analytical Methods

2.2.1 Liquid Scintillation Counting and Lucas Cell Methods

Subsequent to the 1991 proposal, EPA published a report on its method validation efforts in fiscal year 1992 (Pia and Hahn 1992). That report described the results of collaborative studies for the analysis of radon in drinking water and provided performance data on both the direct low-volume liquid scintillation technique and the Lucas cell technique that the Agency planned to incorporate into Method 913.

The 1992 study evaluated both the liquid scintillation technique and the Lucas cell technique for the analysis of performance evaluation samples spiked with radon at levels of 111 and 153 picoCuries per liter (pCi/L).¹ The 1992 study also investigated two means of spiking the samples. The first sample was spiked with radium (²²⁶Ra), which produces radon as a decay product. The second sample was produced using a "radon generator" in which ²²⁶Ra was bound to a strong cation exchange resin. The decay of the radium released radon into the water, while the remaining radium was still bound to the resin and therefore not present in dissolved form in

¹ The Curie is a measure of a quantity of radioactive material. Specifically, a Curie is defined as the quantity of a radioactive nuclide which produces 3.7×10^{10} atomic disintegrations per second. The prefix "pico" stands for one trillionth (10^{-12}), thus, a picoCurie would be 3.7×10^{-2} atomic disintegrations per second.

the sample. The data from the 1992 study are summarized Exhibit 2-2, for both techniques, both radon concentrations, and both sources of radon.

Exhibit 2-2. Summary of EPA 1992 Collaborative Study Data

Technique ¹	Spike Conc. (pCi/L)	Mean Conc. Found (pCi/L)	Mean Recovery (%)	Precision within Lab (pCi/L)	Reproducibility (pCi/L)	% Bias
LSC Ra	111	112	101	9	12	0.7
LCS Rn ¹	111	112	101	14	24	1.1
LC Ra	111	114	102	9	12	2.3
LC Rn	111	127	114	16	23	14.5
LCS Ra	153	156	102	10	18	2.3
LSC Rn	153	154	101	17	28	0.9
LC Ra	153	158	103	10	16	3.4
LC Rn	153	174	114	17	28	13.7

¹ LSC Ra = Liquid scintillation counting of samples spiked with ²²⁶Ra

LSC Rn = Liquid scintillation counting of samples spiked with radon generator

LC Ra = Lucas cell counting of samples spiked with ²²⁶Ra

LC Rn = Lucas cell counting of samples spiked with radon generator

Another important aspect of the EPA 1992 collaborative study were the findings with regard to sampling, sample containers, and sample handling. EPA conducted single-laboratory studies that were designed to evaluate factors related to sampling methods for proficiency testing of radon laboratories. Such performance evaluation (PE) samples have been used as an important aspect of EPA's certification program for laboratories performing analyses under the Safe Drinking Water Act monitoring programs. The 1992 report describes studies of four sample collection techniques (displacement, immersion, catch, and grab sampling). EPA also evaluated the effectiveness of two types of scintillation vial cap materials (polypropylene and PTFE-lined caps) at maintaining the integrity of the samples. The effects of headspace or bubbles in the sample containers were also evaluated.

The analysis of sampling techniques found that the four techniques were statistically equivalent, in that no systematic error was introduced into the results by any of the four techniques. The report stated that displacement sampling and immersion sampling were the most conservative sampling approaches, requiring only that the flow of water from which the sample is collected not be aerated or turbulent.

With regard to the vial cap materials, EPA found that as much as 10-15% of the radon in the sample may be lost by its sorption into the polypropylene cap itself. The loss appeared to

occur within the first four hours after the sample was collected. Caps equipped with PTFE liners did not show this loss of radon over time.

As with volatile organic constituents, radon in water samples may be lost into the headspace of the sample container. Although careful sampling techniques should result in the sample container being filled to the top and sealed with no headspace, changes in sample temperature will affect the solubility of *all* gases dissolved in the sample, including air and radon. As the temperature of the sample in the sealed container increases, the solubility of all gases will decrease and they may come out of solution, forming bubbles at the top of the container. It is not uncommon to observe air bubbles in a container that form as a result of such a temperature increase. Given the typical levels of radon in water, it is highly unlikely that a visible bubble of pure radon would form. However, the concentration of air is much higher and if radon is present in the sample, then the radon can partition into the headspace created by a bubble of air and the radon in the headspace would be lost from the sample when the container is opened.

EPA compared the radon concentrations measured in samples containing six air bubble volumes ranging from 0 - 5 ml in 63-ml sample bottles. The results of this study indicate that for bubbles up to 0.25 ml in volume, there was no significant loss of radon from solution. At a bubble volume of 0.5 ml, the loss of radon was 12%, with even larger losses for larger bubbles. Based on the solubility of air at 20°C and 24°C, EPA concluded that the headspace resulting from the formation of air bubbles as the sample warmed did not present a problem with respect to the loss of radon from the sample.

In the 1992 report, Pia and Hahn noted that there was a relatively large positive bias for the Lucas cell technique when using the radon generator approach (13.7 and 14.5% for the 111 pCi/L and 153 pCi/L sample, respectively). They attributed this bias to problems with transferring the radon standard supplied by EPA and calibration of the instrument in the Lucas cell procedure. They indicated that the systematic error could be addressed by standardizing the technique used to transfer the sample and the radon standard, and that this issue would be addressed in EPA Method 913.

2.2.2 Standard Method 7500: Radon Liquid Scintillation Counting

This method is published in *Standard Methods for the Examination of Water and Wastewater*, (APHA 1996). The method is specific for ^{222}Rn in drinking water supplies from groundwater and surface water sources. This method grew out of EPA efforts in connection with the 1991 radionuclides proposal. In that proposed rule, EPA discussed the development of EPA Method 913, a liquid scintillation technique for radon analysis. Subsequent to the 1991 radionuclides proposal, EPA submitted the draft procedure to APHA and it was published in *Standard Methods* as SM 7500-Rn. Having been published by a consensus organization (APHA), there was no need for EPA to pursue the promulgation of a separate EPA method.

In Standard Method 7500-Rn, the radon is partitioned selectively into a mineral-oil scintillation cocktail that is immiscible with the water sample. The sample is held in the dark for three hours. This "dark adaptation" serves two purposes. First, exposure to light can cause the cocktail to scintillate and this period in the dark allows this light-induced scintillation to dissipate before sample analysis, thereby reducing the background count. Secondly, the decay of the radon creates a number of short-lived daughter products. Compared to the half-lives of its daughter products, the half-life of radon is relatively long, 3.8 days (see the table in Section 2.1). Thus, during this equilibration period, the alpha emissions due to the daughter products ^{218}Po and ^{214}Po become equal to that of the radon itself and the signal from the radon is essentially amplified by a factor of three. After the equilibration period, the alpha particle emissions from the sample are counted in a liquid scintillation counter using a region or window of the energy spectrum optimal for the alpha particles from the three radionuclides. The results are reported in units of pCi/L. The diffusion of radon is affected by temperature and pressure. Therefore, it is important to allow the samples to equilibrate to room temperature before processing.

The precision of the method is affected by the background signal in the counting window used for analysis. A procedure is provided for selection of the analytical window to minimize the background contribution to the measurement. An important aspect of SM 7500-Rn is that it does *not* include any mention of the Lucas cell technique that EPA had planned to include in EPA Method 913.

The performance data in SM 7500-Rn shown in Exhibit 2-3 were incorporated from the 1992 EPA collaborative study cited earlier, which included 36 participants. However, the EPA 1992 study data were incorporated without differentiation between the liquid scintillation counting and Lucas cell techniques, even though, as previously noted, SM 7500-Rn does not even mention the use of the Lucas cell.

Exhibit 2-3. Standard Method 7500-Rn Performance Data

Sample Conc. pCi/L	Accuracy %	Repeatability pCi/L	Reproducibility pCi/L	Bias %
111	101 - 102	9	12	0.7 - 2.3
153	102 - 103	10	16 - 18	2.3 - 3.4

The significance of the inclusion of the Lucas cell data is probably not great. As can be seen by comparing the data above with that in Exhibit 2-2, the accuracy data reported by EPA differ only by one percent between the two techniques. At each sample concentration, the reported precision within a laboratory (repeatability in the table above) is the same for both techniques and differs by only 1 pCi/L between the two radon activity levels. The most notable differences are in the reproducibility figures, where the lower value in the 16 - 18 pCi/L range, and the higher value in the 2.3 - 3.4% bias range both come from the Lucas cell technique.

SM 7500-Rn incorporates other important information from the EPA studies as well. For example, the method specifies the use of glass sample containers or glass scintillation vials with PTFE- or foil-lined caps, avoiding the problems associated with the loss of radon into the polymer caps. The method describes the sample collection and employs the immersion procedure, although the method does not use that term by name.

2.3 Other Radon Measurement Techniques

As noted in Section 2.1, EPA's literature search identified several other recently developed radon measurement techniques, which are discussed in turn in the following sections

2.3.1 Delay-Coincidence Liquid Scintillation Counting System

The literature search performed in 1998 identified a report of an automated liquid scintillation counting system for determination of ^{222}Rn in ground water (Theodorsson 1996). The focus of the report was on the use of radon activity levels for earthquake prediction in Iceland. The report describes an automated radon detection system intended for mostly unattended operation

The technique involves a two-part system which includes a prototype assembly for transferring radon (^{222}Rn) from water to toluene and a single phototube liquid scintillation counter. The radon in the toluene is detected by liquid scintillation counting, using a method known as delayed coincidence counting. Delayed coincidence counting takes advantage of the fact that the next four daughter products of radon all have short half-lives. As shown in Exhibit 2-1, the half-lives of ^{218}Po , ^{214}Po , and ^{214}Bi are all under 30 minutes, and the half-life of ^{214}Po is only 0.16 milliseconds. The delayed coincidence counter is programmed to respond to the beta particle decay of an atom of ^{214}Bi . Upon detecting that beta particle from ^{214}Bi , the system waits about 5 microseconds and then opens an electronic "gate" to the detector channel that corresponds to the energy of the alpha particle decay of ^{214}Po and holds that gate open for about 1 millisecond. The result is that the background count measured by the detector is greatly reduced because the detector is only looking for ^{214}Po scintillations in the very narrow time interval immediately after the beta particle decay of ^{214}Bi . The detection efficiency for the delayed coincidence counting of ^{214}Po is about 95%.

Most of the other aspects of the technique are modifications of those used in liquid scintillation counting and the Lucas cell techniques. For example, the transfer of the radon from the water sample by purging is employed in the Lucas cell, though in this case, the final reservoir is an organic liquid not unlike that used in liquid scintillation counting.

This technique is designed to permit the use of a much larger water sample than any of the previously described techniques. The use of a larger sample compensates for the fact that the percentage of radon transferred from the water to the toluene is only about 40%. In addition, delayed coincidence counting essentially ignores the alpha decay of the parent radon and ^{218}Po ,

thereby reducing the technique's sensitivity by a factor of three. Theodorsson anticipates this concern, arguing that although the ability to count multiple pulses for each disintegration of a radon atom is generally considered to increase the sensitivity and accuracy of measurements, that assumption is in error because the pulses are *"not statistically independent."* He states that the delayed coincidence counting

"hardly effects [sic] the resulting accuracy and sensitivity, compared to counting in a broad alpha-beta window, although the latter may give a pulse rate almost five times higher."

Unfortunately, Theodorsson does not present any performance data to substantiate this statement.

At the time of the report, the author had only constructed a prototype system that was designed for primarily unattended operation in the field. This technique may be attractive for various types of low-level environmental radon measurements since it is relatively simple, very sensitive, and well protected from disturbances. However, no multiple laboratory data describing such performance characteristics as sensitivity are provided in the article. Thus, it is not possible to evaluate this technique more fully.

2.3.2 Activated Charcoal Passive Radon Collector

A technique that measures ^{222}Rn in river water using an activated charcoal passive radon collector has been described by Yoneda, et al (1994). Unlike other radon methods that require the collection of a discrete water sample, the passive radon collector is immersed in the river by means of a string.

The radon collector used in this study consists of a sealed polyethylene bag containing a thin layer of activated charcoal. As water passes through the collector, the radon is adsorbed onto the charcoal and retained there. After a suitable period of immersion in the water of interest, the bag is removed and sealed in an air-tight plastic container and allowed to stand overnight until secular equilibrium among the decay products was achieved. The radon on the charcoal is determined by gamma-ray spectral analysis of its ^{214}Pb and ^{214}Bi daughter products.

The author describes experiments that evaluated the performance of the passive collector, including an evaluation of bag thickness, amount of charcoal used in the collector, immersion time and, most importantly, the use of dry and wet charcoal. This method claims to have the advantage of simplicity, low cost, and the ability to measure the average radon activity in flowing water over a specified period of time.

The author reported that:

- The mean amount of ^{222}Rn adsorbed by the collector was about reached a maximum when the quantity of charcoal reached 20 grams. and that the quantity of radon did not

appear to be proportional to the amount of charcoal in the collector. Also, the charcoal should be fully spread out in a single layer within the bag.

- The thickness of the polyethylene bag did have an impact on the final results (a thin film collects more ^{222}Rn), but it was noted that when wet charcoal was used, the effectiveness of the polyethylene film decreases. The general recommendation was that a relatively thick polyethylene film, 0.005 cm, be used because it is stronger and less likely to tear.
- Collectors containing dry charcoal collected more ^{222}Rn than those containing wet charcoal. However, given the difficulty in keeping the charcoal dry during the immersion phase, it was concluded that, in order for efficient quantitative measurement of radon, wet charcoal should be used in the collectors. A revised radon absorption equation was developed to indicate the amount of ^{222}Rn collected in the wet charcoal collector.

The principal advantage of this method is that a discrete sample is not required, as the passive collector is immersed directly in the body of water. This method does not measure radon directly, rather it measures the decay of the daughter ions. An equation is given that allows the user to quantify the total ^{222}Rn absorbed by fully wet-activated charcoal sealed in a polyethylene bag in water.

The study report includes data for a variety of tests of the collection device. While some tests were conducted at lower radon levels, the majority of the performance data were generated from waters containing greater than 100 Bq/L of ^{222}Rn (>2700 pCi/L). Thus, it is not clear how well the method would perform at the levels of interest to EPA. The available performance data described in the article are limited to a single laboratory.

Because of the way that the monitoring is conducted, e.g., immersing the collector in the water body and monitoring the average radon concentration over a long time period (6-10 days), it may not be a particularly useful technique for monitoring compliance with a Maximum Contaminant Level (MCL). Low radon levels over a portion of the monitoring period could mask higher levels that would violate the MCL. However, if performance data were available for radon levels near the likely MCL (300 pCi/L), this technique might be useful as a screening method. If used as a screening method, long-term sample results that averaged over the MCL could be expected to violate the MCL if a grab sample were analyzed using a method such as Standard Method 7500-Rn, so no additional testing would be needed. In contrast, long-term sample results below the MCL would still require confirmation using another technique on a grab sample. However, such screening might not be cost-effective.

In addition, the need to leave the collector in a container of running water for 6-10 days imposes some practical limitations in comparison to other methods that employ some a sample

collected over a short period (e.g, a few minutes). The adsorption coefficient of radon from water onto the charcoal can be defined as:

$$\text{adsorption coefficient (k)} = \frac{\text{Bq radon per gram of charcoal}}{\text{Bq radon per mL of water}}$$

where Bq, the Becquerel, is the SI unit of radioactivity corresponding to 1 disintegration per second (approximately 27 picoCuries). It may be possible that the adsorption coefficient reaches a constant during the exposure period of the collector. However, the study does not provide sufficient data to determine if that is the case. If the adsorption coefficient is not found to constant, it would be necessary to determine the total volume of water passing over the collector during that 6-10 day period. In some monitoring situations, such measurements would likely be more difficult than the measurement of the radon itself.

No collaborative data were available for this method.

2.3.3 Degassing Lucas Cell

A paper by Mullin and Wanty (1991) compares the use of a "degassing Lucas cell" (DLC) technique with liquid scintillation counting. This paper describes the degassing Lucas cell technique in general terms, noting that a paper by Reimer in the same volume of the USGS Bulletin provides greater detail. The paper by Reimer was not reviewed directly, as the comparisons conducted by Mullin and Wanty provided more useful information.

As noted in Section 2.2, the Lucas cell technique is a well-established method for the analysis of radionuclides in water, including radon. In the degassing Lucas cell technique, a water sample is agitated in a closed vessel to extract the radon. The air in the headspace of the vessel is sampled with a gas-tight syringe and injected into a Lucas cell for counting. The principal advantage of this technique is that the results can be obtained in the field, at each site, which was the apparent reason for developing the technique.

The primary disadvantage of this method is that unless the sample is analyzed immediately, the radon level can be biased low by radon diffusing out of the syringe containing the air sample. Increased lag time from sampling to analysis via the DLC leads to greater uncertainty and usually lower radon measurements, both of which were attributed to loss of radon from the syringes in which the samples were stored. The loss of radon through radioactive decay during the lag time between sample collection and measurement was accounted for by using an exponential formula that corrects for the decay of the radon in the sample. However, that correction factor does account for the diffusion losses of radon from the syringe.

In addition, as written, this method does not expressly include the three-hour equilibrium period, in an effort to speed the use of the technique for field measurements. The lack of the

equilibration period presents concerns as well. In particular, ^{218}Po , one of the short-lived progeny of ^{222}Rn , closely approaches secular equilibrium with ^{222}Rn in about 10 minutes, and may not be accounted for adequately in the calibration scheme. Finally, because the DLC analyses is performed at a time when the net alpha activity of ^{218}Po is rapidly building, large errors in apparent radon levels may result.

The authors of the study concluded that the liquid scintillation technique was more accurate than the degassing Lucas cell technique, but that the degassing Lucas cell may have utility for reconnaissance sampling, where the results can be used to design sampling schemes for use of the more accurate liquid scintillation technique. However, field measurements may not be an important factor relative to SDWA compliance monitoring for radon.

2.3.4 Electret Ionization Chamber System

Several articles were found that discuss the use of an electret system for the measurement of radon (Tai-Pow 1992, Sabol et al. 1995). Additional information was provided to EPA by the US manufacturer of the electret device, Rad Elec Inc., of Frederick, MD.

An electret is a device which has been treated to hold a stable electrostatic-field potential (initially 700 to 750 volts). In the case of these two studies, the electret is made of a wafer of Teflon that is housed in a chamber made of electrically-conducting plastic. The device is called an electret passive environment radon monitor (E-PERM) by the manufacturer of the device.

The decay products from the radon gas enter the chamber through the filtered inlet at the top and the alpha particles striking the electret discharge the static charge on the electret. The surface charge of the electret is measured before and after exposure by using a specially designed voltage reader. This electric field sensor can detect small changes on the electret. The electret is designed to handle exposures of two to seven days at levels of 0.04 to 1.85 Bq/L (1 to 50 pCi/L) of radon in air.

Electret ionization chambers are simple, portable, and easy to use. They are also well-suited for field measurements, since more than one measurement can be made from the same electret. Drawbacks to this simple and relatively inexpensive method include poor reproducibility at lower radon levels, uncertainty in the use of manufacturer-suggested gamma correction factors, and limited reusability. The electret device lacks specificity for radon. The surface charge of the electret will change with exposure to gamma radiation from within the sample chamber or from an external gamma source. It will also change in response to the alpha decay of other volatile radionuclides that enter the chamber headspace from the water.

When measuring radon concentrations in air, the gamma radiation can be subtracted through the use of voltage-dependent correction factors, resulting in improved accuracy. In the studies cited above, the end results showed that a higher concentration of radon in water may result in elevated airborne radon concentration in the surrounding areas, including increased radon

activity in buildings served by a hot spring water. For routine waterborne radon monitoring, including use in field conditions, the technique based on electret ion chamber technology may sometimes be a suitable choice.

In a 1990, a survey of laboratories conducting radon analyses in drinking water was performed by Wade Miller Associates, under contract to EPA. The goals of that study were to identify the types of certification programs that exist for radon analyses in drinking water, to identify laboratories capable of performing the analyses, and to determine the daily analysis capacity of each identified laboratory. Of 45 commercial and state laboratories contacted in 1990, only one listed the electret method.

Recent information provided by the US manufacturer included cited three additional studies that were not directly reviewed by SAIC. These include the following papers and presentations:

- Kotrappa, P and Jester, W A., "Electret Ion Chamber Radon Monitors Measure Dissolved ^{222}Rn in Water," *Health Physics*, 64. 397-405 (1993)
- Colle, R. Kotrappa, P., and Hutchinson, J.M.R., "Calibration of Electret-Based Integral Radon Monitors Using NIST Polyethylene-Encapsulated $^{226}\text{Ra}/^{222}\text{Rn}$ Emanation (PERE) Standards," *Journal of Research of National Institute of Standards and Technology*, 100: 629-639 (1995).
- Budd, G, and Bentley, C , "Operational Evaluation of the EIC Method for Determining Radon In Water Concentrations," 1993 International Radon Conference, Hosted by AARST

Those studies provide precision and bias data on the electret technique over a wide range of concentrations. According to the manufacturer, the electret technique has recently been certified by the States of Maine and New Hampshire for monitoring radon in water.

As summarized by the manufacturer, the precision of the electret technique ranged from 4 to 10% across all three of the studies. The bias of the technique was estimated by the manufacturer to be from -17% to +1% in these three studies, following the application of a correction factor of 1.15 to the initial sample results. Prior to the use of this correction factor, the bias ranged from -27% to -9% across these three studies. SAIC contacted the manufacturer and obtained information on the ranges of radon concentrations that were used in these studies.

According to the manufacturer, the Kotrappa and Jester study examined five radon activity levels, ranging from a low of about 220 pCi/L to a high of 73,200 pCi/L, and found no significant change in precision and bias across the range. The Colle *et al.* study examined only one radon level of 10 Bq/g, which equates to approximately 270,000 pCi/L. The Budd and Bentley study examined a variety of activity levels, ranging from about 350 pCi/L to 46,000

pCi/L. The first and third studies included at least some activities near the levels of interest to EPA

The correction factor recommended by the manufacturer is intended to relate the electret results to those expected by the liquid scintillation counting method, although the manufacturer points out that the liquid scintillation method may not be *"accurate with traceability to NIST"*

As is the case for the activated charcoal collector method described in Section 2.3.2, the electret method requires a long exposure of the detector to the sample. The range of exposure times in the papers reviewed by SAIC is 2-7 days. However, unlike the charcoal collector technique, the electret is exposed to a discrete sample container in a sealed vessel. Thus, although the measurement may take up to 7 days to complete, the results represent the concentration of radon in the discrete water sample.

Although the manufacturer's literature indicates that electret technique performed well in a 1994 US Department of Energy (DOE) "intercomparison" study, those data appear to be for the measurement of radon in air. No collaborative data for water samples have been identified.

2.4 Performance Capabilities of the Methods

The performance capabilities of these methods for the analysis of radon were difficult to evaluate in a consistent manner, in part, because many of the methods were developed in university settings for purposes other than those envisioned by EPA, i.e, not for compliance monitoring. Wherever possible, SAIC has reviewed the information on the sensitivity (detection limit) and precision of these methods. The selectivity of the procedures for ^{222}Rn is generally excellent and consistent across most of the methods. This is because most of the methods measure the alpha particle decay of ^{222}Rn and/or its daughter products, and these particles are released at discrete alpha energies. In the case of ^{222}Rn , the energy of the alpha particle is 5.49 MeV. The exception is the electret method described by Tai-Pow *et al.*, which measures the change in the electrical potential of the circuit containing the electret. This technique is less selective for radon than the other techniques, in that it will respond to both gamma radiation and other volatile radionuclides in the water sample.

As noted earlier, most of the methods lack data from collaborative studies. The two exceptions are the liquid scintillation method (SM 7500-Rn) and the Lucas Cell method. Both of these methods were evaluated as part of the 1992 EPA collaborative study. The accuracy, reproducibility, repeatability, and bias data for Standard Method 7500-Rn and for the Lucas Cell method are shown in Section 2.3, above.

As noted above, the performance capabilities of some of the other techniques have not been demonstrated for relatively low activities of ^{222}Rn . Several of the techniques were described as having poorer performance at low radon activities. A number of the papers did not present data on the sensitivity of the techniques, and in those cases no attempts were made to estimate the

sensitivities. Rather, the radon levels at which performance was demonstrated were noted in the discussion.

Based on the information provided by the manufacturer, the performance of the electret method has also been relatively well-characteristics. While the summary information suggests that the bias is greater than that reported for Standard Method 7500-Rn, even the -17% figure is not so severe as to rule out this procedure, since methods for some organic analytes can be shown to have similar bias. However, as noted earlier, no collaborative study data on water samples were identified.

2.5 Skill Requirements

The two major techniques employed in most of these methods are liquid scintillation and Lucas cell counting. Neither of these techniques is technically difficult. Liquid scintillation counting has been used in medical laboratories and environmental research laboratories for over 30 years. The skills required are primarily the ability to remove an aliquot of the sample from the original vial and adding an aliquot of the scintillation cocktail, sealing the vial, and placing it into the counter. The counting process is highly automated and the equipment runs unattended for days, if needed.

The Lucas cell methods described in the papers considered for this report requires somewhat more manual skill. As noted in the 1991 proposed rule, EPA expects that this technique would require greater efforts to train technicians than the liquid scintillation technique. The Lucas cell technique requires that the counting cell be evacuated to about 10 mTorr pressure. Then, a series of stopcocks or valves must be manipulated to transfer the radon that is purged from the sample into the counting cell. Potential problems with the analysis, such as a high background level of radon that can develop over the course of the day, or aspirating water into the counting cell, can be minimized by a well-trained analyst. However, as EPA concluded in 1991, the Lucas cell technique is not expected to form the sole basis of a compliance monitoring program for radon in drinking water.

The electret method is relatively simple to perform. The water sample (<150mL) is transferred to a larger, leak-tight container housing the electret device. The radon escapes from the water into the air in the container. The electrical potential (voltage) of the electret must be measured before and after the analysis, using a specially designed sensor.

Overall, although the requirements vary across the techniques, the skills required to measure radon using the techniques described here are generally comparable to those required used to perform gas chromatographic or atomic absorption analyses, methods that EPA has identified for use in quantifying common organic and inorganic contaminants in water samples.

In discussions between EPA and the water utility industry, concerns have been expressed about the difficulties in collecting samples and the skills that may be required to do so in a

reproducible fashion. As noted in Section 7.0, the ability to generate useful analytical results for radon is dependent in an important way on the sample collection process. The 1992 EPA collaborative study evaluated four sample collection techniques and found them all equally good at providing equivalent results. The State of California has developed a sampling protocol for radon in water that employs one of the four techniques evaluated by EPA, namely the immersion technique. SAIC has reviewed a copy of that protocol that was provided to EPA (Jensen, 1997)

As described in the California protocol, the well is purged for 15 minutes to ensure that a representative sample is collected. Purging simply means that the water is withdrawn from the well for this period of time. After purging, a length of flexible plastic tubing is attached to the spigot, tap, or other connection, and the free end of the tubing is placed at the bottom of a small bucket. The water is allowed to fill the bucket, slowly, until the bucket overflows. The bucket is emptied and refilled at least once.

Once the bucket has refilled, a glass sample container of an appropriate size is opened and slowly immersed into the bucket in an upright position. Once the bottle has been placed on the bottom of the bucket, the tubing is placed into the bottle to ensure that the bottle is flushed with fresh water. After the bottle has been flushed, the tubing is removed while the bottle is still on the bottom of the bucket. The cap is placed back on the bottle while the bottle is still in the bucket, and the bottle is tightly sealed. As noted in the California protocol, the choice of the sample container is dependent on the laboratory that will perform the analysis, and will be a function of the liquid scintillation counter that is employed. If bottles are supplied by the laboratory, there is no question of what container to employ.

Once the sealed sample bottle is removed from the bucket, it is inverted and checked for bubbles that would indicate headspace. If there are no bubbles, the outside of the sealed bottle is wiped dry and cap is sealed in place with electrical tape, wrapped clockwise. After the sample bottle is sealed, a second (duplicate) sample is collected in the same fashion from the same bucket. The date *and time* of the sample collection is recorded for each sample.

As described above, the sample collection procedures are not particularly labor-intensive. Most of the time is spent allowing the water to overflow the bucket. Likewise, there are no significant manual skills required. Personnel who can manage to slowly fill a 1-liter glass bottle to collect a sample for analysis of semivolatile organics, or fill a 40-mL VOA vial without headspace, can certainly collect samples for radon, using the method described above.

2.6 Practical Availability of the Methods

In order to determine the practical availability of the methods, SAIC considered two major factors. First, the availability of the major instrumentation was reviewed. Secondly, several laboratories performing drinking water analyses were contacted to determine their capabilities to perform radon analyses.

The major instrumentation required for Standard Method 7500-Rn is a liquid scintillation counter. Automated counters capable of what that method terms "automatic spectral analysis" are available from at least a dozen suppliers. The Lucas cell apparatus is the same as has been used for radium analyses for many years. The electret system is used for the measurement of radon in air as well as in water. Information provided by the manufacturer of the electret system suggests that there are more than 600 users in the US, of whom, the manufacturer estimates, 10% measure radon in water.

In order to evaluate the availability of laboratory capacity to perform radon analyses, in early 1998 SAIC contacted the drinking water certification authorities in the states of California, Maryland, and Pennsylvania. These states were chosen based on SAIC's knowledge of radon problems associated with the "Reading Prong" that stretches through parts of Pennsylvania and Maryland, and the overall status of California's laboratory certification program. A total of eight commercial laboratories were contacted during this initial survey. Each laboratory was advised that SAIC was simply collecting information on the availability and relative costs of radon analyses for drinking water. SAIC was limited in its ability to perform a broader survey, since an upper limit of nine was placed on the survey, in order to abide by the Federal information collection regulations.

Six of the eight laboratories that were contacted in the initial survey perform radon analyses. All the laboratories were certified in one or more states to perform radiochemical analyses, though it was unclear if the certifications were specifically for radon or the more general radiochemical analysis category.

When asked what specific methods were used, the laboratories responded with either the technique (liquid scintillation counting) or a specific method citation. EPA Method 913 was cited by two of the six laboratories. As noted earlier, this method is the precursor to the current Standard Method 7500-Rn. EPA Method "EERF Appendix B" was cited by another laboratory. The remaining three laboratories indicated that they performed liquid scintillation analyses and could accommodate requests for methods employing that technique.

When asked about capacity, the laboratories indicated that they perform between 100 and 12,000 analyses per year. The latter figure came from a laboratory that is currently involved in a large ground water monitoring project in the western US. The next largest estimate was 300 samples per year. However, SAIC expects that like any other type of environmental analysis, given a regulatory driver to perform the analysis, the laboratory capacity would develop quickly.

The 1992 EPA collaborative study on radon analysis (Pia and Hahn, 1992) included 51 laboratories with the capability to perform liquid scintillation analyses. This suggests that there already exists a substantial capacity for these analyses. Further, the liquid scintillation apparatus is used for other radiochemical analyses, including tritium. Information from EPA regarding the performance evaluation program for tritium analyses suggests that there are approximately 100-200 laboratories with the necessary equipment. Much of the capacity for tritium analyses could also be used for radon (EPA 1997). As of September 1997, 136 of 171 participating laboratories

achieved acceptable results for tritium. Both the total number of participants and the number achieving acceptable results vary from study to study, but these data indicate that there is already a substantial capability for liquid scintillation analysis nationwide

Recent information provided by the manufacturer of the electret indicate that the States of Maine and New Hampshire are certifying laboratories for drinking water analysis using the electret method. Several months after the initial laboratory survey, based on information from the manufacturer, SAIC contacted a laboratory in New Hampshire that uses the electret method and obtained information on the analysis price for water samples. The laboratory charges \$30 per sample for drinking water analyses. They have been certified for drinking water analyses using the electret method in New Hampshire for at least three years and in Maine for one year. They have a current capacity of at least 40 samples per week (2000 per year), and indicated that they could easily increase that capacity to meet demand.

The availability of laboratories is also dependent on laboratory certification efforts in the individual states with regulatory authority for their drinking water programs. A major component of many of these certification programs is continued participation by the laboratory in the current EPA Water Supply (WS) performance evaluation (PE) program. Efforts are underway at EPA that will lead to the privatization of all of EPA's PE programs, including the WS studies. Those efforts will affect laboratory certifications for all analytes regulated under the SDWA, including radiochemicals such as radon. Any delays in implementing a private PE program will affect not only radon, but the certification status of laboratories for all regulated analytes.

Because of the issue involved with safe handling of radiochemical standards, there will likely be fewer laboratories seeking certification for radon than for other non-radiochemical parameters. However, there is no fundamental regulatory reason that a radon laboratory in one state cannot receive certification in another state. Even for more commonly performed analyses, there are numerous commercial laboratories that are certified in multiple states. Given the regulatory requirement for radon analyses, one can expect that those laboratories with the capability for radon analysis will pursue certifications in as many states as practical.

The National Environmental Laboratory Accreditation Conference (NELAC) is also evaluating the issues surrounding privatization of the SDWA PE program through its proficiency testing committee. NELAC serves as a national standard-setting body for environmental laboratory accreditation, and includes members from both state and Federal regulatory and non-regulatory programs.

The short holding time for radon, 4 days in Method 7500-Rn, presents a concern relative to the practical availability as well. The 4-day holding time was also the focus of a number of comments that EPA received in response to the 1991 proposed rule. Many commenters stated that if a local laboratory is not available, the only alternative would be to send the samples by overnight delivery to a laboratory elsewhere. Again, this situation is not unique to the analysis of radon. Several large commercial laboratories already account for a sizable share of the market for

SDWA analyses for non-radon parameters, including organics, for which the holding times are often 7 days. Given that a day would be required for shipping the samples, only three days would remain for the laboratory to perform the radon analysis (the day on which the sample is collected being "day zero"). Some commenters argued that for a large commercial laboratory serving the water utilities, this short holding time will make it difficult if not impossible to perform the necessary analyses within the holding time. However, through common-sense scheduling efforts between the utility and the laboratory, such as not collecting samples on Thursdays and Fridays, the holding time issue should be able to be accommodated with relative ease. At worst, some laboratories may choose to offer analytical services over the weekend, perhaps at an increased cost.

For the vast majority of other analytes for which EPA has established formal holding times in its various regulatory programs, the holding times are specified in "days." This is typically understood to mean "calendar days" with the day of sample collection being "day zero." Because of the relatively short half-life of radon, the holding time is expected to be proposed as 4 days, beginning at the time of collection. SAIC strongly urges EPA to publish this holding time as "96 hours" instead of just "4 days," in an effort to reinforce how the holding time is to be calculated.

2.7 Anticipated Unit Costs

As part of its 1991 proposal, EPA conducted a limited survey of laboratories providing radon analyses. Four laboratories provided price information to EPA regarding the analysis of a single SDWA compliance monitoring sample, employing liquid scintillation counting as the analytical technique. The data from the 1991 survey are in Exhibit 2-4.

As part of the 1998 review of analytical methods for radon, SAIC contacted nine laboratories that perform radiochemical analyses. Of those nine, seven perform radon analyses. The prices from the those seven laboratories are shown in Exhibit 2-5. None of the laboratories contacted were among those contacted by EPA in 1991, but to avoid any confusion, the arbitrary numbers assigned to each laboratory begin where the 1991 numbers left off.

There was no clear correlation between the estimated price and the method cited by the laboratory. One of the laboratories that provided an estimate of \$40 per sample is certified by the States of Maine and New Hampshire to perform radon analyses of drinking water using the E-PERM electret device. The other laboratory that quoted a price of \$40 employs liquid scintillation counting. The 1998 range of prices brackets those collected by EPA in 1991.

Exhibit 2-4. 1991 Radon Cost Survey Data

Arbitrary Lab Number	Cost Estimate	Descriptive Statistics	
1	\$30	Mean	\$49.80

2	\$44	Median	\$47.00
3	\$50	Std. Dev.	\$18.80
4	\$75	Range	\$45
		Minimum	\$30
		Maximum	\$75

Exhibit 2-5. 1998 Radon Cost Survey Data

Arbitrary Lab Number	Cost Estimate	Descriptive Statistics	
5	\$75	Mean	\$54.29
6	\$50	Median	\$50.00
7	\$40	Std. Dev	\$15.12
8	\$75	Range	\$35.00
9	\$45	Minimum	\$40.00
10	\$55	Maximum	\$75.00
11	\$40	NA	NA

As noted above, one possible response to concerns about the effect of the short holding time on laboratory capacity would be for some laboratories to offer analyses over the weekend. The increased cost of such services would likely be due to increased labor costs, particularly if overtime were paid to the analysts. Assuming a 1.5 multiplier for overtime (e.g., "time and a half"), the unit cost might rise to the range of \$60 to \$112 per sample, but only for those utilities that could not arrange to sample at more convenient times.

2.8 Practical Performance and Analytical Uncertainties

The available information on the performance of the various methods is greatest for the liquid scintillation procedure, SM 7500-Rn, and the Lucas Cell technique. The data from the 1992 EPA collaborative study cited earlier indicate excellent precision and accuracy for liquid scintillation. The Lucas Cell technique yielded slightly less accurate and less precise results, but still within the realm of performance that EPA has accepted for the measurement of other contaminants. Performance data for the electret method are incomplete, with no clear evidence of a collaborative study in drinking water.

As with many environmental measurements, an overall evaluation of the effectiveness of a monitoring method must also consider the practical aspects of collecting a representative sample. The analysis of radon presents two specific challenges. First, like many organic contaminants,

radon is volatile, and some radon will come out of solution in a sample if exposed to the atmosphere for long periods. Secondly, being a radioisotope, ^{222}Rn undergoes radioactive decay.

The volatility of radon can be addressed in a fashion similar to that for the organic chemicals, namely careful sample collection techniques that minimize the disturbance of the sample, and the use of containers that can be sealed tightly

The conclusions of the 1992 collaborative study indicate that while all four sample collection techniques examined in that study (displacement, immersion, catch, and grab sampling) can provide equivalent results, displacement and immersion sampling are the preferred approaches. Both can be accomplished with little or no specific expertise. Displacement sampling involves attaching a filling tube attached to the water source, inserting the other end into the sample container, and allowing the water to fill the container with no aeration until the container overflows. The filling tube is withdrawn while still running, so that water constantly overflows the container. The container is then quickly sealed with an appropriate cap (e.g., PTFE-lined).

Immersion sampling is somewhat similar, in that a sample container is placed in the bottom of a large container. The filling tube is then inserted into the sample container which is then filled to overflowing with the water to be sampled. The sample container is removed from the larger container with forceps and sealed. The use of immersion sampling further reduces the chances of leaving headspace in the sample container, by allowing the filling tube to be withdrawn while the sample container is still submerged in the larger container. However, as noted in the 1992 study report, there was little difference between the results from both sampling techniques. The sampling procedure developed by California that was described earlier in this document is an immersion technique. The losses of radon due to sorption on cap liners and in air bubbles that occur during transportation and storage appear to be minimal for this technique.

The radioactive decay of ^{222}Rn presents some concerns because the half-life of this isotope is approximately 3.82 days. However, even with this relatively short half life, it is both possible and practical to calculate the concentration of ^{222}Rn at the time of sampling with a high degree of accuracy. Depending on the regulatory action level (MCL or other level) that is specified, the sensitivity of the liquid scintillation method should be sufficient to be used for compliance monitoring even if the sample is held for several days. Method 7500-Rn currently specifies a 4-day holding time. For this analyte, sampling documentation *must* include the time of sample collection, as well as the date. However, this documentation requirement does not present any practical difficulty for this technique.

2.9 Degree To Which Each Method Meets EPA's Regulatory Needs

Of the six techniques for the measurement of radon that were evaluated in this report, only two appear to meet all of EPA's needs relative to compliance monitoring. SM 7500-Rn and the

Lucas Cell technique can achieve reasonable standards for precision and accuracy, are readily available, and have been subjected to collaborative testing.

The four other techniques lack collaborative testing data, which is a significant problem in establishing methods for a nationwide compliance monitoring program such as the SDWA. Of those four other techniques, the electret technique shows greatest promise, and should collaborative data indicating acceptable performance in water matrices become available in the future, EPA may wish to consider this technique at a later date.

The other three techniques, the delayed coincidence liquid scintillation counting system, the activated charcoal passive collector technique, and the degassing Lucas cell technique may have some utility in screening samples or in field measurements. The activated charcoal procedure requires a lengthy exposure to running water and provides an average radon concentration over the entire sampling period. The extent to which such time-averaged measurements might be employed in SDWA compliance monitoring is a policy decision that goes beyond the scope of this evaluation.

In summary, the results of this most recent review of possible analytical techniques for radon in drinking water has reached the same conclusions as that of the 1991 EPA proposal. The liquid scintillation counting technique (SM 7500-Rn) is most able to support a SDWA compliance monitoring program, supported by the possible use of the Lucas cell technique.

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3. SOURCES OF RADON IN GROUNDWATER

3.1 Natural Sources of Radon Groundwater Contamination

Radon is produced in rock, soil and water by the decay of naturally occurring radioactive elements in minerals. This process transfers radon into air- or water-filled soil pore spaces by alpha recoil or diffusion. Radon is then transported by air or water until it decays to its progeny or reaches the atmosphere.

Radon is a member of the "uranium series" of radionuclides all the members of which are derived from the decay of uranium-238. Each radioactive isotope spontaneously decays to emit a radioactive particle, radiant energy, and forms "progeny" isotopes. This process continues until a stable isotope of lead is formed. Radon has three naturally-occurring isotopes, radon-222 (Rn-222), radon-220 and radon-219. Of the three radon isotopes, Rn-222 is the only one of environmental concern, because the other isotopes have much shorter half-lives which limit their potential for causing human radiation exposure. Radon-222 decays into Polonium-218 with a half-life of approximately 3.82 days by alpha emission. The uranium decay series is shown in Exhibit 3-1.

EXHIBIT 3-1 Uranium Decay Series (Including Rn-222)

SOURCE		PRODUCTS	HALF-LIFE
Uranium 238	→	Thallium 234 + α	4.46 X 10 ⁹ years
Thallium 234	→	Palladium 234 + β	24.1 days
Palladium 234	→	Uranium 234 + β	1.17 minutes
Uranium 234	→	Thorium 230 + α	2.45 x 10 ⁵ years
Thorium 230	→	Radium 226 + α	7.5 x 10 ⁴ years
Radium 226	→	Radon 222 + α	1622 years
Radon 222	→	Polonium 218 + α	3.825 days
Polonium 218	→	Lead 214 + α	3.11 minutes
Lead 214	→	Bismuth 214 + β	26.8 minutes
Bismuth 214	→	Polonium 214 + α	19.9 minutes
Polonium 214	→	Lead 210 + β	1.6 x 10 ⁻⁴ minutes
Lead 210	→	Bismuth 210 + β	22.3 years
Bismuth 210	→	Polonium 210 + β	5.01 days
Polonium 210	→	Lead 206 + α	138.4 days
Lead 206			Stable

3.1.1 Release and Transport Properties of Radon and Radium

On a microscopic scale, the release of radon into groundwater water is directly related both to the concentration of radium in the host soil or rock, which determines the amount of radon generated, and to the emissivity of the mineral (which determines the fraction of the generated radon that is released from the particle in which it is generated). The physical condition of the rock (particle size, pore structure) plays a large role in determining emissivity. Because of the importance of these physical factors in determining radon release, there is often no strong correlation between radium levels in rocks or soils and radon levels in adjacent groundwater. The dominant radon route of release into interstitial water is diffusion along microcrystalline fractures in the rock. However, in most cases (i.e., cases in which the percolation velocity is greater than 10^{-5} cm/sec), the mass transport of radon in groundwater water is governed more by advection than this diffusion (Hess, et al. 1985).

Radium-226 is the immediate radiologic precursor of radon-222. Radium can be released to groundwater by three routes: the dissolution of aquifer solids; by direct recoil across the liquid-solid boundary during its formation by radioactive decay of its parent, and by desorption. In contrast to radon, radium has very low solubility in water and very low mobility in groundwater. Also, radium does not exist as a gas, and vapor phase transport is therefore not important. Thus, as discussed below the transport patterns of radium generally do not greatly affect the transport of radon and radium concentrations in groundwater can be a poor predictor of radon levels.

3.1.2 Factors Affecting Distribution of Radon in Groundwater

The levels of radon in groundwater in specific areas or types of systems are affected by a number of factors. Geologic regime and geological parameters are strongly associated with radon levels in groundwater. A number of studies have examined the correlations among radon levels in groundwater and the occurrence of other elements, aquifer lithology, and the depth to the groundwater. Analysis has suggested, that for a defined geographic area, relative radon levels can be inferred from the dominant aquifer lithology and implied activity levels of the parent isotopes. Loomis (1985) has identified six geologic and hydrologic variables that together can be used to predict radon activity in groundwater at a regional level. Each variable, except meteorology, tends to be strongly correlated with lithology type.

- *Uranium-radium geochemistry.* As noted above aquifer minerals with high uranium or radium content may exhibit a relatively high rate of radon release.
- *Physical properties of source rocks.* The escape of radon from rocks into water varies according to the rock's grain size, degree of weathering, microfractures, and the distribution of radon's parent nuclides within the rock's mineral grains. Generally, the smaller the grain size and more pervasive the fracturing and weathering, the greater the amount of radon that escapes.

- *Dissolved radium.* The relationship between dissolved radium in the water and radon in water is inconclusive; several studies indicate there is little to no correlation in the co-occurrence of these two nuclides.
- *Aquifer properties.* The transfer of radon from rocks to the aquifer is largely determined by the flow characteristics of water through the aquifer. The transfer of radon from rocks to water is enhanced when the rocks are relatively permeable, weathered, and fractured and flow rates are relatively high. Given radon's relatively short half-life, groundwater flow must be relatively rapid for radon to reach water supply wells before it decays.
- *Meteorologic factors.* Some studies have indicated that radon levels co-vary positively with precipitation. Moreover, there is some evidence that radon emanation from the rocks and soils is related to barometric pressure. Several studies that have looked for a relationship between radon in water and meteorologic factors have found none.
- *Well and water system design and use.* Several studies have reported that radon levels in water are inversely proportional to a groundwater system's number of customers and yield. Reasons for this consistently-seen relationship are not clear, although it may be that wells serving smaller numbers of customers may draw from less productive granitic aquifers with higher levels of radon precursor elements.

The aquifers with the highest radon concentration have a lithology profile that is dominated by granite and granite alluvia. These rocks tend to have higher levels of uranium and a physical structure that facilitates the release of radon into adjacent water. Radon levels are also often elevated near volcanic ash layers. Lower radon levels are found in basalts and sand aquifers. This relationship between lithology and radon concentration is illustrated by the regional differences in radon levels in groundwater between the southern Mississippi valley (a predominance of basalts and sand results in low radon levels) and Appalachian uplands (a predominance of granite results in high radon levels).

3.1.3 Large-Scale Geographic Patterns of Radon Occurrence in Groundwater

As noted above, groundwater radon levels in the United States have been found to be the highest in New England and the Appalachian uplands of the middle Atlantic and southeastern states. There are also isolated areas in the Rocky Mountains, California, Texas, and the upper Midwest where radon levels in groundwater tend to be higher than the U.S. average. The lowest groundwater radon levels tend to be found in the Mississippi valley, lower Midwest, and plains states. However, even in areas with generally very high or low levels of radon in groundwater, local differences in geology strongly affect observed radon levels (e.g., not all groundwater radon levels in New England are high; not all radon levels in the Gulf Coast region are low). For example, the presence of faults and shear zones in a geographic area characterized by low radon levels can produce localized areas of high radon levels (Gunderson, et al. 1992). It was found that radon levels in groundwater were correlated with measured radioactivity of rocks and soils in

the area, the prevalence of rock types known to produce radon in the area, and the area's soil permeability. The general pattern of groundwater radon occurrence across the US is shown in Exhibit 3-2. Data related to geographical patterns of radon occurrence are discussed in more detail in Chapter 5. The potential for radon to co-occur with other pollutants is discussed in Chapter 7.

3.2 Anthropogenic Sources of Radon Contamination in Groundwater

Radon in the environment is derived primarily from natural sources. Because of its short half life, there are relatively few anthropogenic sources of groundwater radon contamination. The most common manmade sources of radon groundwater contamination are wastes from phosphate or uranium mining or milling operations and from thorium or radium processing. These sources can result in high groundwater levels in very limited areas if, for instance, homes are located on soil contaminated with such wastes or tailings, or if a contaminated aquifer is used as a source of potable water (EPA 1999a). Otherwise, significant groundwater transport of radon is limited by its short half-life.

3.3 Distribution System Sources

3.3.1 Radon Sources in Distribution Systems

Radon levels in distribution systems are usually lower in distribution systems than in source water because radioactive decay and water treatments involving storage, aeration, or carbon filtration act to reduce radon levels. As will be discussed in more detail in Section 5.2, this is not always the case, however. In a number of systems in Iowa, for example, radon levels in finished water samples were found to be substantially higher than those from the wells supplying the systems. Detailed studies have shown elevated levels of radium in pipe scale in these systems. The decay of the radium increases radon levels over and above those already present in the influent water. The greater the length of old, scaled pipe through which the water passes, the greater the radon levels. The extent to which this is a general phenomenon is not known, but it suggests that care should be taken in estimating radon exposures on the basis of wellhead or point-entry-samples where iron-manganese scaling is likely to be a problem.

3.3.2 Radon Sources in Households

Except to the extent that pipe scale in residences sequesters radium, there are no radon sources that increase the levels of radon after water enters the household. Radon is released to indoor air during domestic water use, however, as discussed in Section 4.3.

3.4 Non-Water Supply Sources of Radon Exposures

It has been estimated that only between 1 to 3% of the total residential radon exposures results from radon in public water supplies (NRC 1998). The most important source of radon exposure (accounting for approximately 95 percent of exposures) is indoor air contaminated by radon released from rocks and soils and infiltrating into basements and living spaces. Other sources of radon exposures include ambient (outdoor) air, fuel gas, and construction material (primarily gypsum board).

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4. FATE AND TRANSPORT

4.1 Physical and Chemical Properties of Radon and Progeny

Radon, atomic number 86, is a “noble” and chemically inert gas. It does not react with other elements in the environment. Radon is soluble in water, but also very volatile. It has a high Henry’s Law Constant ($>10^{-3} \text{ m}^3/\text{l}$), indicating a high potential to volatilize from water solution. Its melting point is -71°C and its boiling point is -61.8°C . Its solubility in water is $230 \text{ cm}^3/\text{liter}$ at 20°C . Radon is adsorbed by activated carbon, and therefore presumably to some extent to other organic matter, although radon partitioning to organic matter in the environment has not been extensively studied.

As noted in Chapter 3, radon-222 has a half-life of 3.82 days. Radon’s progeny radionuclides (primarily isotopes of lead, polonium, and bismuth) unlike radon, are not gases, and are less soluble in water than radon. When radon undergoes radioactive decay in water, the resultant nuclides tend to precipitate out onto suspended particulates or other surfaces. Similarly, radon progeny in air “plate out” onto airborne particles, and the bulk of radon-related radiation exposures through the inhalation pathway are often due to the deposition of progeny-bearing particulates in the respiratory tract.

4.2 Relationship of Fate and Transport Properties to Human Exposures and Intake

Radon’s chemical and physical properties, particularly its radioactive half-life and volatility, greatly effect its behavior in the environment, and human exposures from domestic water use.

Because of its short radioactive half-life, the distance over which radon can move in groundwater is severely limited. In just under four days, the activity of radon will be reduced about 50 percent, and it will be reduced another 50 percent in the following four days, etc. In an aquifer where typical horizontal flow velocities are on the order of 10-100 cm/day, this limits the distance over which radon can be transported and still cause significant exposure to a few meters or less. In bedrock aquifers, where water flow may be primarily through fractures, this distance might be larger. As noted in Section 4.1, when radon decays in water, the resulting progeny are much less soluble and mobile, and do not result in appreciable exposures.

Another consequence of radon’s short half-life is that radon levels are reduced when water is stored for any appreciable time prior to use. Thus, water systems which use storage devices such as water towers, tanks or reservoirs, are already reducing radon levels in water. The amount of reduction achieved depends on the average residence time in the storage device, and whether the storage vessel is open to the atmosphere (see below).

When radon is released to surface water, its high volatility results in rapid release to the atmosphere. Radon levels in surface water bodies are almost always below measurable levels.

(NAS, 1998). Systems that store water in contact with the atmosphere therefore achieve radon reduction both through radioactive decay and volatilization.

4.3. Exposures to Radon in Indoor Air After Release During Domestic Water Use

When water is heated or agitated during domestic use, radon is rapidly released to the air. NAS (1998) estimates that between 80 and 100 percent of the radon in tap water remains in solution to be ingested if the water is consumed immediately and is not heated. Between 60 and 80 percent of dissolved radon is released from water from showers, sinks, and washing machines. If water is heated to boiling (e.g., during cooking), essentially all of the radon is driven off.

The radon level in indoor air resulting from domestic water use is often estimated using a transfer factor (TF) approach. This transfer factor is defined as the average increase in long-term radon in air (pCi/L_a) due to a long-term increase of one pCi/L_w radon in water. The value of the transfer factor depends on three factors:

- Patterns of household water use (amount, timing, duration, agitation, and temperature);
- Volume and air exchange rate of the room in which the water is being used; and
- Volume and air exchange rate of the entire house.

Measured Transfer factors in typical American houses generally fall between 1:1,000 and 1:100,000, with the mean being between 1:10,000 and 1:15,000. That is, the domestic water supply entering a house on average needs to have a radon level of approximately 10,000 pCi/l to increase the average indoor air level by 1.0 pCi/l . This value is estimated based on modeling studies, validated by some of the measurements described above.

More refined models are available for predicting radon levels as a function of water usage and building design parameters (e.g., "the three-compartment model"). Generally, it has been found that, while these models provide additional insights into short-term peak exposures in specific areas of the home (for, example, in the shower), they provide little improvement in the quality of long-term estimates of inhalation exposures compared to the simpler transfer factor approach.

4.4 Relationship of Fate and Transport Properties to Radon Behavior in Treatment and Distribution Systems

As noted above, radon undergoes spontaneous radioactive decay during storage and residence in distribution systems. Thus, radon levels in distribution systems and at the point of use are usually lower than in the source water (but see below). In addition, radon's chemical and physical properties mean that some technologies that are used to remove other contaminants also

result in reduced levels of radon. These properties have also been used to design treatment technologies specifically for removing radon from domestic water. Because radon is an inert gas, processes which involve chemical treatment of water (e.g., chlorination, iron/manganese sequestration, chemical coagulation) do not effect radon levels unless they cause it to volatilize or be removed bound to solids.

4.4.1 Aeration Technologies

Aeration technologies make use of radon's volatility to reduce radon levels in treated water. In the *Proposed Rule*, (EPA 1999), high-performance aeration has been selected as the Best Available Technology (BAT) for radon removal. The specific technologies which have been identified include packed-tower aeration, multi-stage bubble aeration, and shallow tray aeration. In addition, there are other aeration technologies that can also cost-effectively achieve radon reduction in commercial-scale use. All the technologies identified above are capable, under defined operating conditions, of achieving at least 99.9 percent radon removal from influent water. Capital and operating costs can be lower if lower removal efficiencies are required (EPA 1999b).

A significant proportion of community groundwater systems already employ aeration technologies to remove odors or organic chemicals, or as an adjunct iron/manganese removal. EPA estimates (1999b) that between approximately 16 and 24 percent of groundwater systems serving 1,000 or more customers currently employ some form of aeration treatment. A smaller proportion of smaller systems also employ aeration technologies. EPA estimates that these existing technologies are likely to achieve a 90 percent reduction in radon levels in the majority of cases.

4.4.2 Granular Activated Carbon Treatment

As noted above, radon also can be adsorbed onto granular activated carbon (GAC). EPA has indicated (1999b) that GAC technologies, while not BAT for most systems, may be appropriate for some very small systems where the capital costs of aeration technologies are prohibitive. Both point-of-entry (POE) and point-of-use (POU) GAC technologies can achieve up to 99 percent radon removal under certain conditions. However, the amount of carbon and contact time required to achieve high radon removal efficiencies are considerably greater than those required to achieve efficient removal of organic chemicals. Thus, at a minimum, changes in operating conditions would be required to adapt existing GAC systems (which EPA estimates to be present at about two percent of all small and very small systems) to address radon contamination.

4.4.3 Radon Release from Pipe Scale

As discussed in Section 3.3, there is evidence that radon can be released from pipe scale pipes in distribution systems. The best information regarding this phenomenon comes from

studies of radon distributions in groundwater systems from Iowa. Information was provided concerning raw and finished water radon analyses from 150 water systems across the state, from systems of different sizes (Kelley and Mehrhoff, 1993). The geometric mean radon level in the raw data samples was 284 pCi/l. As expected, the geometric mean value of water radon levels from the finished water was lower, at 176 pCi/l. However, the ratio of the radon levels in the finished water to the raw water varied considerably. In a substantial proportion of the cases (Exhibit 4-1), the radon level in the finished water exceeded that from the raw water, by up to six-fold.

Exhibit 4-1. Ratios of Finished/Raw Radon Levels in 150 Iowa Water Systems

Ratio Finished/Raw Radon Levels	Number of Systems
Less than 1.0	107
1.0-1.5	29
1.5-2.0	6
2-5	7
>5	1

Radon levels that were higher in finished water than in raw water occurred with varying frequency across the types of geological formations. When water was drawn from alluvial aquifers, finished water levels increased over the wellhead levels only five percent of the time (3/60 systems). In contrast, this phenomenon was seen in 41 percent (9/22) of the wells finished in Cambrian/ Ordovician and 40 percent (2/5) of wells finished in Cambrian/ Precambrian units.

Although no specific geochemical data were provided for the systems where the increases in radon occurred after entry into the systems, the basis for this phenomenon has been previously described in studies of several of the systems included in the Iowa data (Field et al. 1994, Fisher et al. 1998). The increases in radon in the distribution system appear to occur as a result of the accumulation of iron pipe scale in the distribution systems. The scale sequesters radium, and the resultant buildup of radium results in the releases of radon into the water as it passes through the system. The ultimate outcome may be in-system radon levels that substantially exceed the levels seen in the aquifers from which the water is drawn.

There is little evidence concerning the frequency or severity of this phenomenon outside of Iowa, although there is no reason to think it would not occur wherever the geochemical conditions are similar. There would be a lower likelihood of scaling and radon buildup in systems drawing from alluvial aquifers, and more potential for problems whenever iron levels are high and pH levels low in the producing aquifer. Systems treating water to reduce iron and manganese might expect that radon levels would also be reduced in distribution systems.

4.5 References

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