

## 6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring radon in environmental media and in biological samples. The intent is not to provide an exhaustive list of analytical methods that could be used to detect and quantify radon. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used to detect radon in environmental samples are the methods approved by federal agencies such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Other methods presented in this chapter are those that are approved by a trade association such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that refine previously used methods to obtain lower detection limits and/or to improve accuracy and precision.

### 6.1 BIOLOGICAL MATERIALS

Urine analysis and whole body counting are most frequently performed to monitor exposure to radon. Tooth enamel and bone are also used as indicators of radon exposure. The longer-lived radioactive isotopes, lead-210 and polonium-210, are generally used as a means of estimating exposure to the short-lived radon-222 decay products. It is generally known that lead-210 is deposited primarily in bone with a relatively long biological half-life, which enables it to reach transient radioactive equilibrium conditions with its descendant, polonium-210 (Clemente et al. 1984). The short half-lives of radon and the daughters, polonium-218 through polonium-214, preclude their detection through normal bioassay techniques which typically require a day or more after the sample has been collected before counting can commence (Gotchy and Schiager 1969).

Direct measurements of emerging gamma rays typically use the gamma rays from lead-210 and rely on decays occurring in lung or bone tissues. This method utilizes a system of either sodium iodide or germanium detectors placed over the body in a well-shielded room (Crawford-Brown and Michel 1987). For past exposures, the lead-210 and polonium-210 concentrations in the urine are determined by counting the number of decays on a sodium iodide system or by use of liquid scintillation.

Applying these concentrations to estimate the exposure an individual might have received introduces large uncertainties. Pharmacokinetic metabolic models are used to detail the movement of the radionuclides within the organs and tissues of the body (EPA 1988a; ICRP 1978). Several additional models are described in BEIR IV (1988). The uncertainties involved make it unlikely that these approaches can yield estimates of exposure to within better than a factor of four to five, particularly when values specific to individuals (rather than populations) are required (Crawford-Brown and Michel 1987). Analytical methods for determining radon in biological samples are given in

## 6. ANALYTICAL METHODS

Table 6-1. These methods provide indirect measurements of radon; i.e., the activity emitted from radon and radon progeny is detected and quantified.

### 6.2 ENVIRONMENTAL SAMPLES

Radon has been recognized as a health hazard for many years, primarily for uranium miners. Recently, unusually high radon concentrations have been found in several areas of the country, particularly Northeast Pennsylvania. This has prompted nationwide concern and interest in the measurement of radon.

To aid in the effort in standardizing procedures for making accurate and reproducible measurements and to ensure consistency, the EPA has issued two reports recommending measurement techniques and strategies. The 1986 report, "Interim Radon and Radon Decay Product Measurement Protocols," provides procedures for measuring radon-222 concentrations with continuous monitors, charcoal canisters, alpha-track detectors and grab techniques (EPA 1986). The second report, "Interim Protocols for Screening and Follow-up Radon and Radon Decay Product Measurements" (EPA 1987a), outlines the recommendations for making reliable, cost effective radon measurements in homes (Ronca-Battista et al. 1988).

There are several generalizations about the measurement of radon which apply regardless of the specific measurement technique used. Radon concentrations in the same location may differ by a factor of two over a period of 1 hour. Also, the concentration in one room of a building may be significantly different than the concentration in an adjoining room. Therefore, the absolute accuracy of a single measurement is not critical, but improvements in sampling methodology would be helpful. Since radon concentrations vary substantially from day to day, single grab-type measurements are generally not very useful, except as a means of identifying a potential problem area, and indicating a need for more sophisticated testing.

An initial screening for radon can be made with activated charcoal. After a potential problem is identified, more accurate measurements can be made using additional techniques.

There are three main methods of determining the air concentration of radon: an instantaneous measurement, or grab sample, a continuous readout monitor which continually registers the concentration, and a time averaged concentration where the sample is obtained over a relatively long period of time and yields a single, average concentration for an extended time period from a few days to a week or more.

Several techniques to measure air concentrations are outlined by Breslin (1980). Most of the techniques for measuring radon use the fact that both radon-222 and the short-lived daughters are alpha-emitting nuclides. The sample is collected and taken back to the laboratory for "alpha-counting" or an alpha-detector is taken to the field for on-site measurement. There are

## 6. ANALYTICAL METHODS

TABLE 6-1. Analytical Methods for Determining Radon in Biological Materials

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
Tooth	Clean and dry tooth; dry overnight and grind to fine powder; separate enamel from dentin and compress into pellets; coat with titanium nitride	PIXE for PB-210 content	No data	0.5 ppm	Anttila 1987
Urine	Wet ash in HNO <sub>3</sub> -NClO <sub>4</sub> , electrostatic precipitation	Alpha spectrometry	0.1 pCi (3.7x10 <sup>-3</sup> Bq)	85%	Gotchy and Schiager 1969
Blood	Wet ash	Alpha spectrometry	0.1 pCi (3.7x10 <sup>-3</sup> Bq)	85%	Gotchy and Schiager 1969
Blood	Wet ash and plate on disk	Autoradiography of tracks, using nuclear emulsion	No data	No data	Weissbuch et al. 1980
Bone	Extract fat with anhydrous benzene; wet ash	Scintillation counter	No data	No data	Blanchard et al. 1969
Bone	<u>In vivo</u>	Whole body counting gamma spectroscopy	No data	No data	Eisenbud et al. 1969
Tissue	Place in tared test tube	Scintillation counter	No data	No data	Nussbaum and Hursh 1957

PIXE = proton induced X-ray emission analysis

## 6. ANALYTICAL METHODS

several ways to measure alpha decay. A scintillation flask is one of the oldest and most commonly used methods. The flask is equipped with valves which are lined with a phosphor (silver-activated zinc sulfide) and emit light flashes when bombarded with alpha particles. Other methods draw the air through a filter (or filters) for a variety of time intervals and then count the number of alpha-decays occurring on the filter. EPA (1986) and NCRP (1988) reports provide more in-depth discussions of these methods.

EPA (1986) outlines the most common procedures for making measurements and describes conditions that should exist at the time of the measurement. The simplest, least expensive method of radon measurement is with charcoaladsorption. One side of the container is fitted with a screen to keep the charcoal in and allow the radon to diffuse into the charcoal. The adsorbed radon subsequently decays, depositing decay products in the charcoal. After exposure for 3 to 7 days the canister is sealed and sent to the laboratory where the charcoal is placed directly into a gamma detector.

For continuous monitoring of an indoor environment, a common method is the scintillation cell method. The monitor pumps air into a scintillation cell after passing it through a particulate filter that removes dust and radon decay products. As the radon in the cell decays, the decay products plate out on the interior surface of the scintillation cell. The alpha particles emitted by radon and radon daughters strike the coating on the inside of the cell causing scintillations to occur. These scintillations are detected by a photomultiplier tube in the detector and an electrical signal is generated.

Another widely used method is solid state nuclear track detection. In the case of radon, an alpha track detector is used. It consists of a small piece of plastic enclosed in a container with a filter-covered opening. Alpha particles in the air strike the plastic and produce submicroscopic damage tracks. At the end of the measurement period the plastic is placed in a caustic solution that accentuates the damage tracks. The tracks are then counted using a microscope or automated counting system.

Radon daughter aerosols may also be measured by using electrets. These are uniformly charged surfaces which provide a collection medium with a builtin electrostatic force to attract the aerosols, therefore avoiding use of a pump (Khan and Phillips 1984). Deposition is quantified with an alpha counter.

There are two primary methods for measuring radon in aqueous samples, the radon bubbler/alpha scintillation cell method and the liquid scintillation counting method. There are problems associated with sample collection for the radon bubbler/alpha scintillation method. One problem is that the sample in the field must be collected in a glass bubbler flask that must then be transported to the lab. Due to transport and handling problems, sample results may be compromised. Therefore, the liquid scintillation counting method is more commonly used. A description of the liquid scintillation counting method is given in Table 6-2. The greatest analytical uncertainty of

## 6. ANALYTICAL METHODS

TABLE 6-2. Analytical Methods for Determining Radon in Environmental Samples

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
<u>Air</u>					
Radon					
	Adsorb onto activated charcoal, 2 to 7 days	Gamma spectroscopy	1.3 pCi/m <sup>3</sup> (0.048 Bq/m <sup>3</sup> )	No data	Cohen and Nason 1986
	Adsorb onto activated charcoal; extract with toluene; gently shake	Liquid scintillation	0.21-0.37 pCi/m <sup>3</sup> (0.007-0.014 Bq/m <sup>3</sup> )	0.094 of true concentration	Prichard and Marlen 1983
	<u>Scintillation Cell</u> Allow air to enter detection chamber through millipore filter until equilibrated, or collect sample in bag (Mylar or Tedlar), transfer to chamber ASAP	ZnS(Ag) scintillation/photomultiplier tube	0.1 pCi/m <sup>3</sup> (0.004 Bq/m <sup>3</sup> )	No data	Crawford-Brown and Michel 1987
	Diffuse through filter into detector housing; collections with electret	TLD chip	89 pCi/m <sup>3</sup> (3.30 Bq/m <sup>3</sup> )	0.95-1.08 of true concentration	Maiello and Harley 1987
	<u>Two-Filter Method</u> Draw air into fixed length tube with entry and exit filters; monitor exit filter activity	ZnS(Ag) scintillation/photomultiplier tube	0.011 pCi/m <sup>3</sup> ( $<0.001$ Bq/m <sup>3</sup> )	90%	Schery et al. 1980

## 6. ANALYTICAL METHODS

TABLE 6-2 (Continued)

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
<u>Solid State Nuclear Track Detector</u>					
	Diffuse through a filter into a cup containing alpha track material (cellulose nitrate film) for up to 1 year; etch in acidic or basic solution operated upon by an alternating electric field	Microscopic examination of damaged material	14 pCi/m <sup>3</sup> (0.519 Bq/m <sup>3</sup> )	No data	NCRP 1988
Radon progeny					
	Draw air through filter for a sampling time of 5 to 10 minutes	Gross alpha counting	1.1 pCi/m <sup>3</sup> (0.041 Bq/m <sup>3</sup> )	No data	NCRP 1988
	Draw air through filter at a known flow rate for specified time (10 m to 1 hr)	Alpha spectrometry	1.1 pCi/m <sup>3</sup> (0.041 Bq/m <sup>3</sup> )	70%	NCRP 1988
	Charge surface electrostatically to attract aerosols	Alpha spectrometry	1.1 pCi/m <sup>3</sup> (0.041 Bq/m <sup>3</sup> )	70%	NCRP 1988
<u>Soil</u>					
	Dry in 55°C oven for 24 hours; place 5 grams in 20 ml borosilicate glass scintillation. Cover with 10 ml distilled water; allow soil to become wet; add 5 ml high-efficiency mineral oil; allow to age 30 days	Scintillation counter	No data	No data	Rangarajan and Eapen 1987; Wadach and Hess 1985

## 6. ANALYTICAL METHODS

TABLE 6-2 (Continued)

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
	None	Track etch detector buried 30 cm deep	No data	No data	Rangarajan and Eapen 1987
<u>Water</u>					
Radon					
	Pass carrier gas through samples in a bubbler flask to purge out dissolved radon; transfer radon to evacuated scintillation cell	Scintillation counter	1.4 pCi/L (52 Bq/m <sup>3</sup> )	90%	Crawford-Brown and Michel 1987
	Inject into glass vial containing liquid scintillation solution; shake vigorously	Liquid scintillation counter	10 pCi/L (370 Bq/m <sup>3</sup> )	No data	Crawford-Brown and Michel 1987
	Direct measurement	Gamma ray spectroscopy	10 pCi/L for 1 L sample (370 Bq/m <sup>3</sup> )	No data	Yang 1987

TLD = Thermoluminescent Dosimeter

## 6. ANALYTICAL METHODS

these methods is due to sampling. Since radon is a gas, care must be taken to prevent its escape from the sample (Crawford-Brown and Michel 1987). A discussion of measurement techniques in water may be found in the report by Crawford-Brown and Michel (1987).

There has been little attempt to standardize a method for measuring radon in soil. However, a method which utilizes liquid scintillation counting for determining concentration is given by Wadach and Hess (1985). A description of this method may be found in Table 6-2.

The accuracy of any measurement will depend upon the calibration of the instrument used. The calibration of an instrument determines its response to a known amount or concentration of radioactivity. This allows a correlation to be made between the instrument reading and the actual amount or concentration present. A range of activities of radium-226 standard reference materials (SRM) is available from the U.S. Department of Commerce, National Bureau of Standards (NBS) as solutions for calibrating detection systems. Also, an elevated radon atmosphere may be produced in a chamber, and samples drawn and measured in systems previously calibrated by radon emanation from an NBS radium-226 SRM. Other radon detectors may then be filled from or exposed in the chamber and standardized based on this "secondary" standard (NCRP 1988). Analytical methods for measuring radon in environmental samples are given in Table 6-2. These methods provide indirect measurements of radon; i.e., the activity emitted from radon and radon progeny is detected and quantified.

### 6.3 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of radon is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of radon.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met would reduce or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

#### 6.3.1 Identification of Data Needs

Methods for Determining Biomarkers of Exposure and Effect. Methods are available to measure the presence of radon progeny in urine, blood, bone, teeth, and hair. However, the accuracy and the sample detection limits for

## 6. ANALYTICAL METHODS

the majority of these methods are unknown and should be determined so that exposure to radon may be quantified. In addition, measurement of radon gas in expired air should be possible by methods such as gas chromatography. However, descriptions of any such methods have not been found in the literature.

The frequency of abnormalities in sputum cytology has been utilized as a possible early indicator of radiation damage to lung tissue (Band et al. 1980; Brandom et al. 1978; Saccomanno et al. 1974). The accuracy and precision of this measurement is not known.

**Methods for Determining Parent Compounds and Degradation Products in Environmental Media.** Analytical methods are available which allow for the quantification of radon in air, water, and soil. However, methods for the measurement of radon concentrations in soil-gas are limited. The ability to accurately measure soil-gas is needed to provide a better understanding of the emanation rate of radon gas from soil.

### 6.3.2 On-going Studies

Although several analytical methods for measuring and determining radon and radon progeny from environmental media or biological tissues exist, several on-going studies have been identified in the Federal Radon Activities Inventory. There are a number of animal studies underway. Occupationally exposed individuals are continually monitored in order to obtain more accurate models and better measurement techniques.

R. Cole (National Institute for Standards and Technology (NIST)) is currently upgrading the primary radon measurement system which constitutes the national radon measurement standard. D.R. Fisher (Pacific Northwest Laboratories) is attempting to develop analytical methods which will aid in calculating microdosimetry within the tracheobronchial epithelium after inhalation of radon and radon progeny. Also, R.S. Caswell (NIST) is working on a related investigation but with cells at risk in other parts of the lung and adjacent areas.

J.R. Duray (Chem Nuclear Geotech, formerly United Nuclear Corporation Geotech) is testing instruments and devices in order to develop accurate and reliable measurements of annual indoor and outdoor levels of radon and radon daughters. I. Pomerantz (EPA) is investigating analytical techniques to measure certain radionuclides, which would aid in monitoring radon levels in drinking water; whereas K. Fox (EPA) is working on radon removal techniques for community water supplies in New Hampshire. Another area of concern is the development of analytical methods for measuring radon in buildings. C. Arnolts (Department of Housing and Urban Development) is investigating techniques builders can use to identify the presence of radon in a given building, and T. Peake (EPA) is working on methodology which would identify areas with a high potential for radon exposure. M. Ronca-Battista (EPA)

## 6. ANALYTICAL METHODS

reports the steps that are being taken to revise EPA radon measurement protocols and includes a new method for measuring indoor radon and radon progeny concentrations.