7. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting, measuring, and/or monitoring radon and its progeny. The intent is not to provide an exhaustive list of analytical methods. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used for environmental samples are the methods approved by federal agencies and organizations 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 groups such as the Association of Official Analytical Chemists (AOAC), the American Public Health Association (APHA), the National Radon Safety Board (NRSB), and the National Radon Proficiency Program (NRPP), which is operated jointly by the National Environmental Health Association (NEHA) and the American Association of Radon Scientists and Technologists (AARST). Additionally, analytical methods are included that modify previously used methods to obtain lower detection limits and/or to improve accuracy and precision.

7.1 BIOLOGICAL MATERIALS

Table 7-1 lists various methods used to detect radon progeny in biological samples. Since the half-life of radon is short, its measurement in biological samples, such as serum, urine, blood, etc., is not practical. Measurements of the longer lived radon progeny ^{210}Pb and ^{210}Po in biological samples may be used as an indication of radon exposure; however, ingestion of these isotopes from food and drinking water or direct exposure from other environmental media are considered the primary sources of exposure for these isotopes. Therefore, while this chapter discusses the analysis of ^{210}Pb and ^{210}Po in biological media, their presence in the body arises from a variety of sources, not just direct inhalation of radon, and should not be considered unique biomarkers of radon exposure.

A method of estimating individual, chronic human exposure to natural waterborne radionuclides using *in vivo* skull measurements and *in vitro* urine measurements of ^{210}Pb and natural uranium (^{234,235,238}U) is described by Muikku et al. (2003). Four, high-purity broad energy Ge detectors, situated near the top and back of the head, measure the activity of the 186 keV ^{235}U and 46 keV ^{210}Pb gamma rays. Urine samples were analyzed with inductively coupled plasma mass spectrometry (ICP-MS) for uranium content (Muikku et al. 2003). A similar technique was used by Eisenbud et al. (1969), who concluded that *in vivo* skull measurements of ^{210}Pb allow cumulative exposure to radon daughters to be estimated in uranium miners. *In vivo* measurements of ^{210}Pb in the knee have also been reported (by measuring the 46 keV

Table 7-1. Analytical Methods for Determining Radon Progeny in Biological Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	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 total lead content in teeth	0.5 ppm	Anttila 1987
Urine, blood, hair, feces	Wet ash in HNO_3-$NaClO_4$, electrostatic precipitation	Alpha spectometry	0.1 pCi ($3.7x10^{-3}$ Bq)	Gotchy and Schiager 1969
Urine, blood, hair	Wet ashing with concentrated nitric acid and hydrogen peroxide, followed by drying and dissolution in hydrochloric acid solution	Alpha particle counting of ^{209}Po (4.866 MeV) and ^{210}Po (5.305 MeV) using silicon surface barrier detectors	1.1–1.5 mBq/L (24-hour counting time)	Al-Arifi et al. (2006)
Blood	Wet ash and plate on disk	Autoradio-graphy of alpha tracks, using nuclear emulsion	No data	Weissbuch et al. 1980
Bone	Wash with acetone, hydrogen peroxide and isopropanol followed by drying and homogenization to a grain size of 1–3 mm	Gamma ray spectrometry (46.5 keV ^{210}Pb) using HPGe detector	0.4–0.7 mBq per gram of sample	Johnston et al. 2005
Bone	Extract fat with anhydrous benzene; wet ash using nitric acid and perchloric acid	Alpha particle counting ^{210}Po using a ZnS(Ag) scintillation counter	No data	Blanchard et al. 1969
Bone	*In vivo*	Whole body gamma ray spectroscopy (46 keV ^{210}Pb)	No data	Eisenbud et al. 1969
Tissue	Immediate measurement of dissected tissue samples following inhalation exposure	Gamma ray activity using a NaI(Tl) scintillation counter	No data	Nussbaum and Hursh 1957
Tissue (Brain)	Homogenize tissue in trichloroacetic acid solution followed by centrifugation	Alpha particle counting of ^{210}Po and beta particle counting of ^{210}Bi	$1x10^{-5}$ Bq per gram tissue	Momčilović et al. 1999

HPGe = High purity germanium; PIXE = proton induced X-ray emission analysis

gamma ray); however, calibration for the skull is generally simpler than for the knee (Johnston et al. 2005).

Urine analysis and whole body counting have been used to measure levels of radon progeny in humans. It is generally known that ^{210}Pb is deposited primarily in bone with a relatively long biological half-life, which enables it to reach transient radioactive equilibrium conditions with its descendant, ^{210}Po (Clemente et al. 1984). The short half-lives of radon and the daughters, ^{218}Po through ^{214}Po, preclude their detection through normal bioassay techniques that typically require a day or more after the sample has been collected before counting can commence (Gotchy and Schiager 1969).

Al-Arifi et al. (2006) discussed an analytical method for measuring levels of ^{210}Po in samples of blood, urine, and hair for various populations using a high resolution alpha spectrometer. Although the main route of ^{210}Po intake by the human body is the ingestion of food, smoking, ingestion of drinking water, and inhalation of radon may also contribute to the body burden.

Radon exposure in humans is typically assessed by monitoring air levels indoors, outdoors, and under occupational settings as discussed in Section 7.2.

7.2 ENVIRONMENTAL SAMPLES

Most methods of measuring radon and its decay products in environmental samples are based on the detection of alpha particles emitted during the radioactive decay process, although some methods are based on the detection of emitted gamma rays. Detailed reviews of the measurement of radon and its progeny in environmental samples can be found in NCRP (1988), George (1988), and European Commission (1995). EPA issued updates regarding radon measurement techniques in 1992 and provided general guidelines for optimal measurement conditions, device placement, and documentation of results (EPA 1992a). EPA has also issued technical guidance for measuring radon concentrations in residences (EPA 1993b).

There are several generalizations about the measurement of radon that apply regardless of the specific measurement technique used. Radon concentrations in the same location may differ by a factor of 2 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, improvements in sampling methodology would be helpful. Since the accuracy and level of uncertainty of individual measurements are important, especially

when assessing the implications of elevated readings, the measurement uncertainty should be reported for each sample analysis result.

Air radon and radon progeny measurement devices fall broadly into two categories: passive devices and continuous monitor devices (AARST 2006). Passive radon monitors allow air to diffuse into a sensor chamber and do not require any power to operate. However, passive monitors only provide average concentrations for the entire sampling time period (usually at least 48 hours) and typically require laboratory analysis to determine radon concentrations. Continuous radon monitors (CRMs) measure radon gas and continuous working level monitors (CWMs) measure radon progeny. These continuous monitoring devices can record and review radon concentrations in time increments of ≤1 hour, but may require a power source. CRMs are commercially available to home inspectors or radon testing professionals. The principles by which radon detectors operate are described in the following paragraphs.

Activated charcoal adsorption devices are inexpensive, passive detectors used for monitoring radon in air samples. Commercially available devices are often sold at hardware or home improvement stores for estimating radon levels in households or buildings. A typical detector consists of a circular, 6–10 cm diameter container that is approximately 2.5 cm deep and filled with 25–100 g of activated charcoal (EPA 1992a). One side of the container is fitted with a screen that encloses the charcoal sample and allows air to diffuse in. The passive nature of these detectors allows for the continuous adsorption and desorption of radon, and the adsorbed radon undergoes radioactive decay during the measurement period. Following a brief exposure period (2–7 days), the charcoal detectors are returned to a laboratory and analyzed directly by counting gamma rays emitted by the radon decay products on the charcoal using a sodium iodide gamma detector. The detector may be used in conjunction with a multi-channel gamma spectrometer or with a single-channel analyzer with the window set to include the appropriate gamma energy window. The detector system and detector geometry must be the same used to derive the calibration factors for the device (EPA 1992a). Alternatively, the sample may be desorbed by an aromatic solvent (typically toluene or benzene) and analyzed using liquid scintillation counting using an appropriate fluor solution.

Indoor radon levels are also frequently measured using alpha track detection devices (EPA 1992a). The detector consists of a small piece of plastic or film enclosed in a container with a filter-covered opening or similar design to allow radon, but not its progeny, to enter. Some common materials used in this capacity for radon detection are the cellulose nitrate film (LR-115), the thermoset polymer plastic (CR-39), and the polycarbonate plastic (Makrofol) (European Commission 1995). Radon gas diffuses into the container and alpha particles emitted by the radon and its subsequently-produced progeny strike the detector and

produce submicroscopic damage tracks to the enclosed plastic material. Following the analysis period, the plastic detectors are placed in a caustic solution that accentuates the damage tracks so they can be counted using a microscope or an automated counting system. The number of tracks per unit area is correlated to the radon concentration in air, using a conversion factor derived from data generated at a laboratory. The number of tracks per unit of analyzed detector area produced per unit of time (minus the background) is proportional to the radon concentration. When compared to charcoal adsorption detectors, alpha track detectors have the advantage that they can be used for measurements over long time frames and thus, they measure true time-integrated average concentrations (EPA 1992a). Inexpensive alpha track radon detection kits are commercially available to the general public to estimate radon exposure in a dwelling. Unlike the activated charcoal test kits that have a brief exposure period, the alpha track monitors are typically used for 90 days to 1 year and provide a better estimate of the annual radon exposure.

Electret ion chamber (EC) radon detectors are passive detectors that use an electrostatically charged disk to collect ions formed in the chamber by radiation generated from radon and radon progeny (EPA 1992a). Radon diffuses into the chamber through filtered openings and ions that are generated continuously by the decay of radon, and its progeny are drawn to the surface of the electret, which subsequently reduces its surface voltage. The change of voltage measured by an electrostatic voltmeter is related to the average radon concentration based on the duration of the exposure period.

Flow through alpha scintillation cells (Lucas type cells) are frequently used to measure radon concentrations in air for field measurements and in occupational settings (NCRP 1988). The cell consists of a silver activated zinc sulfide (ZnS) phosphor screen that emits photons of visible light when impacted by alpha particles (Lucas 1957). Air is drawn continuously through the cell by an air pump and the cell is coupled to a photomultiplier tube for continuous analysis. The scintillations or flashes of light caused by the alpha particles from radon and its progeny, which strike the ZnS screen, are recorded by the photomultiplier tube. Using appropriate calibration and decay scheme factors, the radon gas concentration may be determined from the rate at which the pulses are recorded (European Commission 1995).

Personal and occupational exposure to radon is frequently assessed using personal dosimeters. An early personal radon dosimeter used in occupational settings by miners, called a radon film badge, was described by Geiger (1967). It consisted of a plastic holder, which encompassed a nuclear track film to detect emitted alpha particles. Radon gas diffused through the central opening of the badge and into the

film emulsion. The number of alpha particles was determined by counting the tracks in the processed film emulsion. Another example of a passive radon dosimeter based on alpha particle etched track detection used to assess personal exposure is described by Taheri et al. (2006). This particular dosimeter employs a polycarbonate detector and a porous fiberglass filter to collect the radon progeny, ^{218}Po and ^{214}Po. A thin aluminum foil is placed between the filter and the detector in order to attenuate the energy of the emitted alpha particles.

Retrospective radon detection methods using surface traps or volume traps provide a means of estimating long-term radon exposure at a building or residence. By determining the historical average concentration, the methodology provides an estimate of the indoor radon level to which a person was exposed over a period of time. For surface trap methods, the activity is measured at the surface of objects, such as glass, that were present in the location of interest during the exposure assessment period. The average radon concentration over several decades is related to the surface activity of the glass. This results from the radon progeny ^{210}Pb, which has a long half-life (22.26 years) and is found implanted within the glass (or other hard surface) due to the kinetic energy transferred by alpha decay to the radon progeny atoms plating out on the surface (Lagarde et al. 2002; Mahaffey et al. 1993; Samuelsson 1988; Steck and Field 1999). A field study conducted from 2005 to 2007 in 38 homes in Iowa occupied by either smokers or nonsmokers using surface trap CR-39 chip retrospective radon detectors indicated that radon progeny (^{214}Po and ^{218}Po) deposited on the surface of these detectors was effective for predicting the airborne radon progeny dose rate for individuals and estimating long-term exposure in nonsmoking environments. The operation of ceiling fans or fireplaces in monitoring areas adversely affected the measurements (Sun 2008).

Pressyanov et al. (2003) explored the use of compact disks as retrospective radon detectors. After exposure, a surface layer was removed and electrochemically etched marks were counted. The study results indicated that compact disks may be useful for retrospectively obtaining radon measurements for levels above 3 Bq/m^3 (0.08 pCi/L).

Radon volume trap detectors also provide a convenient method to estimate average radon concentrations in dwellings over several years in time (Oberstedt and Vanmarcke 1996). Sponge-like materials, such as mattresses and cushions, build-up ^{210}Pb, which reaches an equilibrium with the alpha emitter ^{210}Po, which is used to estimate the average radon concentration over the exposure period. Laboratory tests employing polyester foam samples to simulate mattress material of differing densities and rigidity were exposed to a radon source (Oberstedt and Vanmarcke 1996). Following the initial exposure period, the materials were

stored in a radon-free environment for at least one half-life of ^{210}Po (138 days). The ^{210}Po was separated from the polyester materials in a series of extraction steps and the activity was analyzed by alpha spectrometry. The results indicated that home dwelling materials, such as cushions and mattress material, could be used as an accurate and sensitive retrospective radon monitor. Wooden furniture material has also been tested as a volume trap; however, the natural varying background concentrations of ^{210}Po in different wood types make these materials a less attractive retrospective detection system.

A standard test method for the detection of radon in drinking water has been developed by the American Society for Testing and Materials (ASTM) based on scintillation counting of radon and its progeny (ASTM 1999). A sample of unaerated water is injected into a vial containing toluene or a scintillation cocktail mix and analyzed using a commercially available liquid scintillation spectrometer. This method has a reported detection limit of 0.040 Bq/L (1.1 pCi/L).

A method for measuring radon in soil gas that utilizes liquid scintillation counting for determining concentration is given by Wadach and Hess (1985). A description of this method may be found in Table 7-2. A detection system for continuous soil radon concentration measurements was developed using a continuous monitor RM-3. The system detects radon based on an airflow ionization chamber. Details are available in Fronka et al. (2008).

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 ^{226}Ra standard reference materials (SRM) is available from the National Institute of Standards and Technology (NIST) polyethylene-encapsulated ^{226}Ra/^{222}Rn emanation standards (PERE). These are used to produce an accurate concentration of ^{222}Rn in air, such as for calibrating passive radon detection systems. Ionization pulse chambers are often used for instrumental calibration and measurement systems in interlaboratory comparisons (NCRP 1988). NIST developed a ^{226}Ra-^{222}Rn generator for use as a transfer standard for radon-in-water measurement calibrations (Hutchinson et al. 1984, 1986). Modifications to this standard generator and its long-term performance have been evaluated and described using 4π-αβ liquid scintillation spectrometry of gravimetrically determined aliquants dispensed from the generator (Collé and Kishore 1997). Analytical methods for measuring radon in environmental samples are given in Table 7-2. To quantify the sensitivity of a particular analytical method, the lower limits of detection (LLD) are given when possible. The LLD is typically defined as the minimum activity that would result in a quantifiable signal on some analytical

Table 7-2. Analytical Methods for Determining Radon and Progeny in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Radon					
Air	Adsorb onto activated charcoal; 2–7 days	Gamma spectroscopy	No data	No data	Cohen and Nason 1986
Air	Adsorb onto activated charcoal followed by direct analysis; extract with toluene add 1–2 mL fluor	Gamma counting of 0.295 and 0.352 γ MeV lines of ^{214}Pb; liquid scinilation analysis of desorbed sample	No data	94% of true concentration	Prichard and Marlen 1983
Air	Scintillation cell method; allow air to enter detection chamber through millipore filter until equlibrated, or collect sample in bag (Mylar or Tedlar); transer to chamber as soon as possible	ZnS(Ag) scintillation/ photomultiplier tube	No data	No data	Crawford-Brown and Michel 1987
Air	Two-filter method: draw air into fixed length tube with entry and exit filters; monitor exit filter activity	ZnS(Ag) scintillation/ photomultiplier tube	No data	90%	Schery et al. 1980
Air	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 an alternating electric field	Solid state nuclear track detector Microscopic examination of damaged material	14 pCi/m^3 (0.519 Bq/m^3)	No data	NCRP 1988
Air	Adsorb onto compact disks; remove surface layer at 25 °C with aqueous 45% KOH and 40% methanol; apply electrochemical etching	Marks counted using video camera	No data	No data	Pressyanov et al. 2003
Air	Dissolve material in nitric acid followed by additional digestion in hydrochloric acid. Auto deposit polonium on a silver plate during drying with an infrared source	Volume trap detector using alpha spectrometer	54 pCi/L		Oberstedt and Vanmarcke 1996

Table 7-2. Analytical Methods for Determining Radon and Progeny in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Glass	Attach dosimetry-grade track registration material (CR-39 and LANTRAK®) to ordinary smooth glass without visible coatings or colorings that has been in an unobstructed location without strong air currents; leave in place for long periods (several weeks to a year)	Chemically etch the dosimeter, read ^{210}Po tracks manually with microscope, determine cumulative radon gas exposure as kym^{-1} (i.e., $kBq\text{-}ym^{-1}/Bqm^{-2}$)[a]	~0.3 kym^{-1}	NA	Steck et al. 2002
Soil	Dry in 55 °C oven for 24 hours; place 5 g 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
Soil	None	Track etch detector buried 30 cm deep	No data	No data	Rangarajan and Eapen 1987
Drinking Water	Draw an aliquot of unaerated water into a syringe and inject in a scintillation vial containing the liquid scintillation cocktail solution	ASTM Method D5072 (Scintillation counter)	0.04 Bq/L (1.1 pCi/L)	94–96%	ASTM 1999
Water	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^3)	90%	Crawford-Brown and Michel 1987

Table 7-2. Analytical Methods for Determining Radon and Progeny in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Water	Inject into glass vial containing liquid scintillation solution; shake vigorously	Liquid scintillation counter	10 pCi/L (370 Bq/m^3)	No data	Crawford-Brown and Michel 1987
Water	Direct measurement	Gamma ray spectroscopy	10 pCi/L for 1-L sample (370 Bq/m^3)	No data	Yang 1987
Air	CR-39 chip bathed in 6.25N sodium hydroxide at 75 °C oven for 6 hours	Alpha track density determined by microscopy	No data	No data	Sun 2008

[a]Unit of measure (kym^{-1}) equals radon gas exposure in kiloBecquerel-years per m^3 ($kBqym^{-3}$) divided by surface activity in Becquerels per m^2 (Bqm^{-2}).

TLD = thermoluminescent dosimeter

instrument that would yield a net count for which there is confidence at a predetermined level (usually the 95th percentile confidence limit) that activity is present (Harley and Pasternack 1982; NCRP 1988). In order to calculate the LLD, the measurement system characteristics, detection system efficiency, background count rate, sampling volume, and sampling period must be known.

The EPA Radiation and Indoor Environments National Laboratory (RIENL) provides radon measurement technical support for the radon monitoring proficiency testing programs in the United States (as supported by NIST) and for tribal, state, and local governments, federal agencies, and private industry (EPA 2011b). The National Environmental Health Association-National Radon Proficiency Program (NEHA-NRPP) operates a radon proficiency test (PT) and contractor certification program for those who want to become a Certified Radon Professional (NEHA-NRPP 2008). NIST has developed and provides precise radon emanation rate standards (currently, SRMs 4971, 4972, and 4973) for use in calibrating radon monitors. Since ^{222}Rn standards are required for home radon testing, NIST has worked to transfer the U.S. national standards (which are still based on the international standards produced by Marie Curie in 1912) to secondary calibration laboratories (NIST 2011).

7.3 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, 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 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 the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

7.3.1 Identification of Data Needs

Methods for Determining Biomarkers of Exposure and Effect.

Exposure. Methods are available to measure the presence of radon progeny in urine, blood, bone, teeth, and hair. However, these radon progeny detected in biological systems arise from ingestion of these progeny from food and drinking water as well as from the inhalation of radon. Therefore, these methods cannot be considered as specific biomarkers for radon inhalation.

Effect. 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 that 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.

7.3.2 Ongoing Studies

Researchers at the University of Iowa are involved in ongoing studies that include pooling results from Iowa and Missouri residential radon studies using glass-based detectors that are undergoing final calibration (field, personal communication) and pooling results from the residential radon studies that contributed to the results of Krewski et al. (2005, 2006; North American studies) and Darby et al. (2005, 2006; European studies).