

6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring radium 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 radium. 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 radium 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

The presence of radium in biological materials or environmental samples is generally determined by virtue of its radioactivity. Except in the laboratory where radium compounds have been isolated and determined for a certain purpose, determination of radium compounds in biological and environmental samples is relatively rare. As a Group IIA alkaline earth element, radium is similar in its chemical behavior to other members of that group, especially its nearest neighbor, barium. For example, radium tends to precipitate as the sulfate, which is the basis for its isolation for chemical analysis by coprecipitation with barium sulfate. Furthermore, radium associates with calcium in living systems and accumulates in bone. The determination of radium compounds or specific isotopes is usually accomplished by a separation procedure, followed by quantitative analysis of total radium based on its radioactivity.

Radium is determined in both biological and environmental samples by the emission of ionizing radiation from its radioisotopes (alpha-emitting radium-223, radium-224, and radium-226, as well as beta-emitting radium-228) and from its daughter products. Gamma-ray spectrometry of the gamma rays emitted by decay products of radium can also be used to measure radium. One of the most important examples is the measurement of gamma rays emitted by ^{214}Bi (Davis et al. 1987). Intermediate loss of radon gas in the decay chain can be troublesome in this kind of measurement. One method of radium measurement in bone collects the radioactive radon-222 gas product of the decay of radium-226, and its radioactivity is measured and extrapolated back to the concentration of radium-226 (Walton et al. 1959).

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A method has been developed to measure the rate of elimination of radon in exhaled breath (Stehney et al. 1955). Based on the assumption that 70% of the radon from fixed body radium is exhaled, this test can be used to calculate approximate levels of the body burden of radium. Some analytical methods for the determination of radium in biological materials are given in Table 6-1. It is important to note that the major contributions of these studies are descriptions of sample preparation techniques rather than advances in alpha or gamma spectrometry.

6.2 ENVIRONMENTAL SAMPLES

Because small amounts of radium radionuclides in environmental samples may be regarded as hazardous, it is usually necessary to detect very small quantities of radium which may require processing large quantities of sample (Quinby-Hunt et al. 1986). This introduces possibilities for contamination and sample loss. Specifically, in the case of water samples, sorption of the radionuclide to container walls and to suspended matter may be important sources of error.

Significant concentrations of contaminant radium may be submicromolar. Therefore, radiochemical separations are commonly employed that make use of a carrier, a nonradioactive element with chemical properties similar to those of radium. For radium, barium is the element of choice, and radium is coprecipitated from solution with barium sulfate, BaSO_4 . Correction for losses in the precipitation procedure may be made by adding a tracer consisting of an isotope of radium not expected in the sample and noting its recovery at the end of the analytical procedure. The isotope radium-223 can be used for this purpose.

Radium is commonly determined in environmental samples by the emission of alpha particles from the radium-226 radioisotope. Beta-emitting radium-228 can also be measured. Measurement of the radioactive radon-222 gas product of the decay of radium-226 can be used to give the concentration of radium-226. Gamma-ray spectroscopy of daughter radioisotopes such as ^{214}Bi can also be used to determine radium.

Because of the low penetrating power of alpha particles, special counters are required to assay alpha activity. These include gas-filled counters (thin window or internal, proportional counters), scintillation counters, and semiconductor detectors. In addition, a very thin sample is required to prevent the sample itself from absorbing alpha particles.

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

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit ^a	Accuracy ^a	Reference
Fish, whole, skin, bone	Skin, bone, flesh separated, bones ashed, dissolved, coprecipitated with barium sulfate	Alpha spectrometry	<0.8 pCi/g (0.03 Bq/g)	No data	Swanson 1983
Vole skeletal bones	Flesh separated from bones, bones ashed, dissolved, radium coprecipitated with barium sulfate	Alpha spectrometry	No data	98 ± 10%	Burns et al. 1987
Biological samples (fish tissue)	Freeze dry, grind, seal in counting vials to ensure equilibrium with daughter nuclides	Gamma spectrometry	0.14-0.27 pCi/g ^b (5-10 mBq/g)	No data	Joshi 1987
Human, whole body	Count total activity with a whole body counter	Gamma spectrometry	No data	No data	Toohey et al. 1983
Plant tissue	Collection of plant material, ashing	Gamma spectrometry	No data	No data	Teixeira and Franco 1986
Plant shoots	Collection of plant material, ashing	Gamma spectrometry	No data	No data	D'Souza and Mistry 1970
Human skeletal bones	Bone ashed, dissolved in hot, dilute hydrochloric acid, filtered. (Radon emanation is measured)	Gamma spectrometry	No data	No data	Walton et al. 1959
Dog urine, feces	Urine and feces each sealed in cans, frozen for one month, then counted	Gamma spectrometry	No data	No data	Lloyd et al. 1983

^aMost studies presented in this table were generally chosen because they present information on sample preparation rather than on advances in alpha or gamma spectrometry.

^bBased on dry mass.

< = less than; pCi = picocurie; g = gram; mBq = milliBecquerel.

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A promising method has been developed for measuring radium-226 concentrations in water samples of one liter size (Whittaker 1986). All nongaseous alpha-emitting radionuclides are coprecipitated with barium sulfate and iron hydroxide, followed by counting alpha emissions from the precipitate. A count at 3 hours followed by one at 7 days is used to measure radium-226.

Some analytical methods for the determination of radium in environmental samples are given in Table 6-2.

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 radium is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (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 radium.

The following categories of 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 known, would reduce or eliminate the uncertainties of human health assessment. Each data need discussion highlights the availability, or absence, of the relevant exposure information. A statement that reflects the importance of identified data needs is also included. In the future, these 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. As discussed above, the presence of radium in biological materials is usually determined by virtue of its radioactivity. Methods available for the determination of radioactivity in biological materials include alpha spectroscopy and gamma spectrometry, which is more convenient, but generally less sensitive, than alpha spectroscopy (Joshi 1987). It would be useful to have additional data on the sensitivity and accuracy of the methods that are currently in use.

Effects specifically associated with radium exposure have not been identified. The development of methods for detecting biomarkers of radium's effects would be useful.

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

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
Soils	Samples collected to 0.3 m with a coring tool	No data	No data	No data	ASTM 1988a
Soils	Samples collected from soil, reduced to small, homogeneous sample	Gamma spectrometry suggested ^a	No data	No data	ASTM 1988b
Water	Precipitate with barium sulfate and iron hydroxide	Alpha counting	No data	94.2%	Whittaker 1986
Water	Precipitate with barium sulfate and lead sulfate	Alpha counting	No data	94.9-99.4%	APHA 1985a
Water	Precipitate with barium sulfate, redissolve, evolve radon	Alpha counting of radon daughter	0.03 pCi	97.1-98.0%	APHA 1985b
Water (for Radium-228)	Precipitate with barium sulfate and lead sulfate, separate actinium-228	Beta counting of actinium-228	No data	94.2%	APHA 1985c
Water	Precipitate with barium sulfate and lead sulfate	Alpha counting of radium isotopes	1 pCi/L	No data	ASTM 1988c
Water, soils, sediments	Collection of radium by resin	Gamma spectrometry	0.5 pCi/L Ra-226	100 ± 2%	Lucas 1987
Water, soils, sediments	Collection of water samples	Gamma spectrometry	No data	No data	Davis et al. 1987
Water ^b	Samples collected from soil reduced homogeneous sample	Alpha and beta counting	<3 pCi/L	85 ± 24%	EPA 1986a
Water	Precipitate with barium sulfate and lead sulfate	Alpha counting of radium isotopes	No data	No data	EPA 1986b

^aThis is a sample processing and homogenization technique with which various analysis methods can be used.

^bMethod for gross alpha and beta activity, which may be indicative of radium content.

m = meter; pCi = picocurie; L = liter; Ra = Radium; < = less than.

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Methods for Determining Parent Compounds and Degradation Products in Environmental Media. It would be useful to have data on the sensitivity and accuracy of methods that are currently used to determine radium in environmental media. In addition, continued development of sensitive and accurate methods and instrumentation that would minimize problems with background and contamination would be useful in determining radium levels in environmental media. It would also be useful to develop portable, compact instruments to conduct field analyses with optimum sensitivity and accuracy.

6.3.2 On-going Studies

Refinements continue to be made in detecting radioactivity from radium isotopes and their daughter products. These developments include better, more sensitive detectors and more efficient data handling systems. Substantial improvements may be anticipated in the area of high resolution gamma spectroscopy. Research is underway to improve sample preparation and separation to give more sensitive analysis and better speciation. Because of the demands of cleanup programs including Superfund II, the Formerly Utilized Sites Remedial Action Program, and the Uranium Mill Tailings Remedial Action Program, research is underway to increase sample output and to decrease time and costs per sample (Donivan et al. 1987).