7. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting, measuring, and/or monitoring cesium, its metabolites, and other biomarkers of exposure and effect to cesium. 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) and the American Public Health Association (APHA). 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

Entry of cesium and its radioisotopes into the human body occurs by ingestion, inhalation, or penetration through skin (IAEA 1988; NCRP 1977, 1985). The amounts of cesium in the body can be assessed by bioassay *(in vivo* and *in vitro)* measurements. *In vivo* measurements are made with whole-body counters. *In vivo* measurement techniques are commonly used to measure body burdens of cesium radioisotopes, but can not be used to measure the body content of the stable isotope of cesium. *In vitro* measurements provide an indirect estimate of internally deposited cesium (both the stable and radioactive isotopes), by techniques that measure cesium in body fluids, feces, or other human samples (Gautier 1983). Examples of these analytical techniques are given in NCRP Report No. 87 (1987) and are also listed in Table 7-1 for stable cesium and Table 7-2 for radioactive cesium.

7.1.1 *In Vivo* Cesium Measurements

In vivo measurement techniques are the most direct and widely used approach for assessing the burden of cesium radioisotopes in the body. The *in vivo* measurement of these radioisotopes within the body is performed with various radiation detectors and associated electronic devices that are collectively known as whole-body counters. These radiation detectors usually employ sodium iodide (NaI), hyperpure germanium, or organic liquid scintillation detectors to measure the 605 (98%) and 796 keV (85%) gamma

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Urine	Sample dried, ashed, and irradiated	INAA	$1x10^{-5}$ µg/g	No data	Oughton and Day 1993
Soft tissue	Sample ashed and then concentrated by precipitation with AMP, extracted with sodium phenylboron	Flame photometry	0.005 µg/g	96–99%	Feldman and Rains 1964
Feces	Sample dried, ashed, and irradiated	INAA	$1x10^{-5}$ µg/g	No data	Oughton and Day 1993

AMP = ammonium molybdophosphate; INAA = instrument neutron activated analysis

Table 7-2. Analytical Methods for Determining Radiocesium in Biological Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Urine	Sample is acidified and concentrated on a KCFC column	γ-spectrometry with NaI detector	6 pCi/L	98%	Boni 1966
Urine	Sample transferred to Marinelli beaker and counted	γ-spectrometry with NaI detector	100 pCi/L	98%	Gautier 1983
Urine	Sample transferred to Marinelli beaker and counted	γ-spectrometry with NaI(Tl) detector	2 pCi/L	No data	Cahill and Wheeler 1968
Soft tissue	Sample wet-ashed	γ-spectrometry	No data	No data	Baratta et al. 1969
Soft tissue	Sample directly counted in detector	γ-spectrometry	5 pCi/g	No data	Rabon and Johnson 1973
Soft tissue	Sample digested in acid, oxidized with $HClO_4$, concentrated by precipitated with AMP, purified by resin column, precipitated with hexachloroplatinic acid	β-counter	0.1 pCi/g	40–85%	Nevissi 1992
Feces	Sample directly counted in detector	γ-spectrometry with NaI detector	0.14 nCi/L	No data	Lipsztein et al. 1991
Human milk	Sample directly counted in detector	γ-spectrometry with NaI detector	0.001 pCi/L	No data	Risica et al. 1994

KCFC = potassium cobalt ferrocyanide

rays from the decay of ^{134}Cs, and 662 keV (89.9%) gamma rays that are emitted from the decay of ^{137}Cs (Palmer et al. 1976). ^{134}Cs and ^{137}Cs distribute uniformly in muscle and soft tissue of the body. The photons emitted by ^{134}Cs and ^{137}Cs are easily detected and quantitated using whole-body counting techniques (NCRP 1987; Palmer et al. 1976; Sun et al. 1997). Many configurations of the whole-body counter and scanning methods have been utilized, ranging from unshielded single-crystal field detectors to shielded, multi-detector scanning detectors (IAEA 1962, 1970, 1972, 1976, 1985; NCRP 1987; Palmer et al. 1976). Where appropriate, shielding of the room that houses the whole-body counter and/or the detector is often used to increase the detection sensitivity of the equipment by minimizing background radiation. Additionally, care must be exercised to ensure that external contamination with radioactive cesium or other gamma-emitting radioisotopes are not present on the clothing or skin of the individual to be scanned. *In vitro* measurements of cesium (see Section 7.1.2) are used in conjunction with whole-body counting when monitoring individuals working with cesium, especially in conjunction with the assessment of individuals who have experienced accidental exposures to cesium (Bhat et al. 1973).

Whole-body counters are calibrated using tissue-equivalent phantoms. These phantoms are constructed to mimic the shape and density of the anatomical structure using tissue-equivalent materials such as water-filled canisters or masonite (Barnaby and Smith 1971; Bhat et al. 1973; Sun et al. 1997). For example, the bottle mannequin absorber (BOMAB) consists of a series of water-filled polyethylene canisters constructed into seated or reclined human forms (Sun et al. 1997). Cesium standards are measured either as point sources along the phantom or dissolved within the water-filled canisters. Comparisons of the actual counts obtained from the phantom to the known activity of the cesium standards are used to determine the efficiency of the counting technique and, thus, to provide the basis for calibrating the counting system.

Assessment of short- and long-term retention of cesium radioisotopes takes into account the turnover rate for cesium within the human body. Although the physical half-life of ^{137}Cs is 30 years, the biological and effective half-life of cesium inside the body is approximately 110 days (NCRP 1987; Rundo and Newton 1964). This relatively high turnover rate for cesium in the body is due to the high solubility of cesium in body fluids that allows for the rapid uptake (e.g., absorption of ingested cesium through the gut) and elimination of cesium into and from the body (e.g., excreted through urine) (NCRP 1987). For acute and chronic exposures to cesium, the estimates of cesium retention are determined from direct, whole-body measurements. Models for cesium in the human body have been developed for estimating the short- and long-term retention of cesium based on whole-body measurement techniques (ICRP 1979, 1989, 1993; NCRP 1987; Sun et al. 1997).

7.1.2 *In Vitro* Cesium Measurements

In vitro analyses of cesium are routinely performed in support of an *in vivo* monitoring program or in situations where direct *in vivo* measurements can not be obtained. Urinalysis is the preferred sample for *in vitro* analyses of cesium, although other sample types, such as feces, tissue, bone, or blood, can also be analyzed. Urinalysis is an optimum method for assessing the clearance of soluble cesium. Fecal analysis is used to assess the clearance of ingested, insoluble cesium (Baratta et al. 1969; Gautier 1983; Ide and McInroy 1975; NCRP 1987).

The *in vitro* analysis of the stable isotope of cesium, ^{133}Cs, in human samples (e.g., urine, tissue, feces) is performed by a number of methods that have the selectivity and sensitivity to measure cesium in biological matrices. These methods include spectrophotometry, instrumental neutron activation analysis (INAA), and inductively coupled plasma mass spectrometry (ICP-MS) (Dreizen et al. 1970; Iyengar and Woittiez 1988; Paschal et al. 1996). Of these methods, the INAA and ICP-MS methods offer the greatest detection sensitivity and are the preferred method of analysis for cesium in human samples (Iyengar and Woittiez 1988).

For the *in vitro* analysis of the cesium radioisotopes ^{134}Cs and ^{137}Cs in human samples, a number of analytical methods can be used to measure the cesium radioisotopes directly in the samples without requiring an extensive sample preparation procedure. In the radiochemical analysis of cesium in urine, a 24-hour urine collection (approximately 2 L) is obtained, followed by the transfer of a 1 L aliquot to a Marinelli beaker for counting in a gamma-ray spectrometer (Gautier 1983). This simple procedure offers high recoveries of cesium (98%) and the minimum detection sensitivity (100 pCi/L) that is required to evaluate individuals for exposures to radioactive cesium (Gautier 1983). Similar methods are also used for the analysis of cesium radioisotopes in tissues, feces, and blood (Table 7-1). Mass spectrometry techniques have also been employed to measure cesium radioisotopes in human samples.

Accuracy of *in vivo* and *in vitro* measurements of cesium is determined through the use of standard, certified solutions or radioactive sources with known concentrations or activities of cesium. National Institute of Standards and Technology (NIST) traceable standards for ^{133}Cs can be obtained through a number of commercial sources. The primary source of certified cesium radioisotope standards is the NIST. Gamma-ray point sources for ^{137}Cs (standard reference material [SRM] 4200, 60,000 Bq [1.6 μCi]

and SRM 4207, 300,000 Bq [8 μCi]) and standard solutions of ^{137}Cs (SRM 4233, 600,000 Bq/g [16 μCi/g]) are available from NIST.

7.2 ENVIRONMENTAL SAMPLES

Two common approaches are available for measuring cesium radioisotopes in the environment. Cesium radioisotopes can either be measured directly in the field (*in situ*) using portable survey instruments, or samples can be procured from the field and returned to the laboratory for quantitation of cesium. However, quantitation of the stable cesium isotope in environmental samples is generally conducted in the laboratory.

7.2.1 Field Measurements of Cesium

In situ measurement techniques are useful for the rapid characterization of radionuclide contamination in the environment, such as soils, sediments, and vegetation, and for monitoring personnel for exposure to radionuclides. The measurement of gamma ray-emitting radionuclides such as ^{134}Cs and ^{137}Cs in the environment is conducted with portable survey instruments such as Gieger-Mueller detectors, sodium iodide scintillation detectors, and gamma-ray spectrometers. The use of gamma-spectrometers in field survey equipment is preferred for measuring cesium in the field because of its energy selectivity and detection sensitivity. The relatively high energy and penetrance of the gamma ray that is emitted during the decay of ^{134}Cs and ^{137}Cs provide an advantage for assessing the level of cesium. These gamma-ray spectrometers are equipped with a high purity germanium detector that is able to separate the 602, 662, and 796 keV gamma rays emitted from ^{134}Cs and ^{137}Cs from the gamma rays emitted from other radionuclides; for example, ^{40}K (USNRC 1997). Minimum detectable activities (MDAs) of 0.005 Bq/g for ^{137}Cs are routinely achieved using p-type germanium gamma spectrometers with 10-minute counting times (USNRC 1997). Computational methods have been derived to aid in determining the concentrations and distributions of ^{134}Cs and ^{137}Cs in different soil types and depths (Fülöp and Ragan 1997; Hillmann et al. 1996; USNRC 1997). The concentrations and distributions of ^{134}Cs and ^{137}Cs that have been derived from the computational analysis of the survey data are often verified by laboratory-based analyses of soil samples procured from the survey area.

7.2.2 Laboratory Analysis of Environmental Samples

Analytical methods for measuring cesium and cesium radioisotopes in environmental samples (e.g. air, water, soil, and biota) are summarized in Tables 7-3 (^{133}Cs) and 7-4 (^{134}Cs, ^{137}Cs). The methods that are commonly used in the analysis of ^{133}Cs are based on instrumental analytical techniques such as spectrophotometry, instrumental neutron activation analysis, and mass spectrometry. The analysis of ^{134}Cs and ^{137}Cs can be determined either as total mass or total activity, depending on the analytical technique that is used. Typically, radiochemical methods of analysis employing gamma spectrometry techniques are used to quantitate ^{134}Cs and ^{137}Cs in environmental samples. However, spectrophotometric and mass spectrometry techniques have been used to determine the total mass of ^{134}Cs and ^{137}Cs in samples. Using the specific activity of ^{137}Cs (89 μCi/μg), it can be deduced that a sample with activity of 1 μCi of ^{137}Cs contains roughly 0.011 μg of ^{137}Cs.

The analysis of cesium in air is based on the measurement of cesium in aerosols or particles that become trapped on cellulose or glass fiber filters after a measured amount of air is pulled through the filters. For the analysis for ^{133}Cs, the filter is solvent extracted and the extracted metals are analyzed by INAA (Gone et al. 2000). Analysis of ^{134}Cs and ^{137}Cs can be performed directly from the filter, or by following some sample preparation (e.g., ashing or solvent extraction), using gamma spectrometry (Kanapilly et al. 1983; Kolb 1971; Krieger et al. 1976).

For the analysis of cesium in water, a broad array of sample preparation and detection methodologies are available (see Tables 7-3 and 7-4). Different standardized methods that can directly measure cesium or its radioactive isotopes within a water sample using INAA or radiochemical techniques with minimal sample preparation and good detection sensitivities (10–20 pCi/L), precision (4–9%), and bias (-5–1%) (ASTM 1999; EPA 1980). Other methods are available that preconcentrate cesium from natural or potable waters when interfering impurities are present or the activity of the cesium radioisotopes are too low (<30 pCi/L) for quantitation by gamma spectrometry (APHA 1998; Frigieri et al. 1980). This preconcentration of cesium can be achieved either through precipitation with molybdate compounds, for example, or through chromatographic techniques using columns packed with resins that specifically bind cesium (EPA 1980; Frigieri et al. 1980; Gaur 1996; Petrow and Levine 1967).

The quantity of cesium and its radioisotopes in soil, sediments, vegetation, and biota is determined using detection methods similar to those described above (Tables 7-3 and 7-4). Analysis of the stable cesium isotope by INAA and ICP-MS requires either digesting the sample in acid or ashing the sample before

Table 7-3. Analytical Methods for Determining Cesium in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Water	Sample is purified by passage through Dowex 50-X8 resin, concentrated with NCFC column	Electrothermal-AA	1 µg/L	99% at 10–100 µg/L	Frigieri et al. 1980
River water	Sample concentrated by precipitation with AMP, purified by extraction with sodium tetraphenylboron	Flame photometry	0.010 µg/L	94.5%	Feldman and Rains 1964
River water	Sample is purified by passage through Dowex 50-X8 resin, concentrated with NCFC column	Electrothermal-AA	1 µg/L	99% at 10–100 µg/L	Frigieri et al. 1980
Lake water	Filtered samples were irradiated	INAA	0.010 µg/L	90%	Hakonson and Whicker 1975
Sea water	Sample was precipitated with sodium tetraphenyl-borate, and the precipitate was neutron irradiated	INAA	0.008 µg/L	92%	Taskaev 1987
Sea water	Sample precipitated with AMP, purified by extraction with sodium tetraphenyl-boron	Flame photometry	0.010 µg/L	94.5%	Feldman and Rains 1964
Mineral and thermal waters	Direct aspiration of sample into graphite furnace	Graphite furnace-AA	0.00185 µg/L	92.3–100.9%	Bermejo-Barrera et al. 1989
Groundwater	Sample purified by ultracentrifugation	ICP-MS	0.010 µg/L	No data	Probst et al. 1995
Groundwater	Sample purified by ultracentrifugation	ICP-AES	0.010 µg/L	No data	Probst et al. 1995
Soil	Sample was pre-ashed, digested with acid	Electrothermal-AA	0.09 mg/g	80–85%	Anderson et al. 1996
Soil	Sample was dried, ground, and irradiated	INAA	0.003 ng/g	No data	Oughton and Day 1993
Soil	Sample digested with acid	ICP-MS	0.011 µg/g	95%	Robb et al. 1995
Sediment	Sample was dried and irradiated	INAA	0.010 µg/g	90%	Hakonson and Whicker 1975
Silicate rock	Sample digested in HF/H_2SO_4	Graphite furnace-AA	0.05 µg/L	76%	Grobenski et al. 1983

Table 7-3. Analytical Methods for Determining Cesium in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Vegetation	Sample ashed and irradiated	INAA	$1x10^{-5}$ µg/g	No data	Oughton and Day 1993
Vegetation	Sample prepared by microwave digestion	ICP-MS	$2x10^{-5}$ µg/g	95–105%	Dombovári et al. 2000

AA = atomic absorption; AMP = ammonium molybdophosphate; ICP-AES = inductively coupled plasma-atomic emission spectrometry; ICP-MS = inductively coupled plasma-mass spectrometry; INAA = instrumental neutron activation analysis; NCFC = ammonium hexacyanocobalt ferrate

Table 7-4. Analytical Methods for Determining Radiocesium in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air (occup-ational)	Sample filter was solvent extracted	Scintillation counter with NaI detector	No data	95%	Kanapilly et al. 1983
Air (ambient)	Sample filter digested in acid, cesium precipitated with chloroplatinate	γ-spectrometry with Ge/Li detector	0.01 fCi/m^3	80%	Krieger et al. 1976
Drinking water	Direct count of sample	γ-spectrometry with Ge/Li detector	10 pCi/L	No data	EPA 1980
Drinking water	Direct count of sample	γ-spectrometry with Ge detector	<2 pCi/L	92–100%	APHA 1998
Fresh water	Sample concentrated with Dowex 1x8/KCFC mixed ion exchange column	γ-spectrometry with NaI detector	3 pCi/L	99%	Boni 1966
River water	Sample precipitated with AMP, concentrated with Dowex-50 cation exchange column	Scintillation counter with NaI detector	<7 fCi/L	99%	Kahn et al. 1957
River water	Sample concentrated on Dowex 50W-X8 column	γ-spectrometry with Ge(Li) detector	2 pCi/L (50 L sample)	97%	Luetzelschwab 1976
Lake water	Sample concentrated on ACFC column	γ-spectrometry with NaI(Tl) detector	No data	97%	Eyman and Kevern 1975
Water and waste water	Direct count of sample	γ-spectrometry with Ge/Li detector	<2 pCi/L	92–100% at 2–94 pCi/L	ASTM 1999
Sea water	Sample purified by passage through chelating resin, concentrated with KCFC ion exchange column	γ-spectrometry with NaI detector	0.07 pCi/L	98%	Boni 1966
Soil	Sample dried and crushed	γ-spectrometry with Ge(Li) detector	0.05 pCi/g	No data	Arnalds et al. 1989
Soil	Sample mixed with 5% Ag and compressed into disc	GDMS	0.2 pg/g	No data	Betti et al. 1996
Sediment	Sample extracted with acid, concentrated by precipitation with AMP, solvent extracted with sodium tetraphenylboron	γ-spectrometry with Ge(Li) detector	No data	96%	Eyman and Kevern 1975

Table 7-4. Analytical Methods for Determining Radiocesium in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Biota	Sample ashed, oxidized with $HClO_4$, concentrated by precipitation with AMP, puriifed by resin column, precipitated with hexa-chloroplatinic acid	β-counter	0.1 pCi/g	No data	Nevissi 1992

ACFC = ammonium hexacyanocobalt ferrate; AMP=ammonium molybdophosphate; ICP-MS = inductively coupled plasma-mass spectrometry; KCFC = potassium cobalt ferrocyanide; GDMS = glow discharge mass spectrometry

analysis. In some cases where interfering compounds or materials may be present, additional sample concentration or purification may be required. For the radioisotopes of cesium, direct detection of ^{134}Cs and ^{137}Cs within the neat sample can be performed using gamma spectrometry detection methods.

The detection limits, accuracy, and precision of any analytical methodology are important parameters in determining the appropriateness of a method to quantitate a specific analyte at the desired level of sensitivity within a particular matrix. The MDA refers to the intrinsic detection capability of a measurement procedure (sampling through data reduction and reporting) (USNRC 1984). Several factors influence the MDA, including background count rates, size or concentration of sample, detector sensitivity, recovery of desired analyte during sample isolation and purification, level of interfering contaminants, and particularly, counting time. Because of these variables, the MDAs may vary between laboratories using the same or similar measurement procedures.

The accuracy of a measurement technique in determining the quantity of a particular analyte in environmental samples is dependent on the reliability of the calibrating technique. Thus, the availability of standard, certified radiation sources with known concentrations of cesium and its radioisotopes is required in order to insure the reliability of the calibration methods and accuracy of cesium measurements in environmental samples. NIST traceable standards for ^{133}Cs can be obtained through a number of commercial sources. The primary source of certified cesium radioisotope standards is the NIST. Gamma-ray point sources for ^{137}Cs (SRM 4200, 60,000 Bq [1.6 μCi] and SRM 4207, 300,000 Bq [8 μCi]) and standard solutions of ^{137}Cs (SRM 4233, 600,000 Bq/g [16 μCi/g]) are available from NIST. SRMs are also available containing the stable (SRM 1944 [sediment], SRM 2710 and 2711 [soil]) and radioactive isotopes of cesium (SRM 4350 [sediment] and SRM 4357 [sediment]).

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 cesium 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 cesium.

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. Analytical methods with satisfactory sensitivity and precision are available to determine the levels of cesium and its radioisotopes in human tissues and body fluids.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Analytical methods with the required sensitivity and accuracy are available for measuring cesium, both total and isotopic, in environmental matrices (Tables 7-2 and 7-4). Knowledge of the levels of cesium in various environmental media, along with appropriate modeling (see Chapters 4 and 6), can be used to evaluate potential human exposures through inhalation and ingestion pathways.

Whether in the environment or in the human body, cesium radioisotopes will undergo radioactive decay to nonradioactive isotopes (see Chapter 4). Current analytical methods, such as mass spectrometry, have the necessary resolution and sensitivity to detect and quantitate these decay products.

7.3.2 Ongoing Studies

Current research trends in the quantitation of cesium and its radioisotopes are focused on improving the selectivity and detection sensitivity of cesium in biological and environmental samples. Mass spectrometry approaches, such as double focusing sector field inductively coupled mass spectrometry or time-of-flight selected ion monitoring systems, are being developed further to provide the required selectivity and sensitivity to rapidly measure cesium in the presence of other trace metals in complex environmental samples. Cesium-selective electrodes are being developed into a highly-selective, rapid detection technique for measuring cesium in environmental samples and waste streams. Current efforts are focused on the development of electrode membranes that contain cesium binding agents, such as crown ether derivatives. New cesium-selective resins, for example lanthanum-based resins or montmorillonite clays, are being developed and tested for selectivity and recovery of cesium.

The database of federal research programs in progress (FEDRIP 2002) indicates several current projects that may fill some existing data gaps and add to the current database of knowledge. W.H. Aberth from Antek Incorporated, located in Palo Alto, California is attempting to increase the sensitivity to which cesium can be analyzed in human tissue through the use of a cluster ion gun in liquid dynamic secondary ion mass spectrometry (SIMS).