7. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting, measuring, and/or monitoring americium, its metabolites, and other biomarkers of exposure and effect to americium. 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 americium into the human body can occur through ingestion, inhalation, or penetration through skin or via wounds. The quantities of americium within the body can be assessed from the use of bioassays, which include *in vivo* measurements and/or *in vitro* measurements. *In vivo* measurements can be obtained through techniques that directly quantify internally deposited americium (using, for example, a whole body counter). Conversely, *in vitro* measurements provide an estimate of internally deposited americium, utilizing techniques that measure americium in body fluids, feces, urine, or tissue obtain through an autopsy. Examples of these analytical techniques are given in NCRP Report No. 87 (1987) and are also listed in Table 7-1. The ultimate aim of making such measurements is to estimate intake and radiation dose. *In-vitro* measurements provide an assessment of intake and dose only when the data are interpolated using appropriate biokinetic models, taking account of pattern of exposure, chemical form, and other parameters.

7.1.1 Whole or Partial Body Measurements

In vivo measurement techniques are the most direct and widely used approach for assessing the content of many radioisotopes, including americium, within the body. The *in vivo* measurement of americium within the body is performed with various radiation detectors and associated electronic devices, which are

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

Sample matrix	Sample preparation	Analytical method	Detection limit[a]	Accuracy	Reference
Urine	None	Gamma-ray spectroscopy (phoswich detector)	0.08 nCi/ 200 cm^3	No data	Ide et al. 1985
Urine	Co-precipitation with oxalate	α-spectroscopy	0.08 pCi/ 80 cm^3	No data	Ide et al. 1985
Urine	None	Gamma-ray spectroscopy	0.04 pCi/cm^3	95% at 0.04 pCi/cm^3	Guilmette 1986
Urine	Sample wet ashed, treated with HNO_3 and H_2O_2	α-liquid scintillation	0.7 pCi/ 125 cm^3	95% at 0.01–1,000 nCi	Guilmette and Bay 1981
Urine	Sample wet ashed, purified by solvent extraction	Liquid scintillation	14 pCi/100 cm^3	96% at 20,000 dpm spike	Ham et al. 1977
Urine	Sample with ^{241}Am spike co-precipitated with $CaHPO_4$ then with oxalate, purification by diglycol succinate column	α-liquid scintillation	0.02 pCi/L	96% at 20 dpm spike	Hafez and Hafez 1992
Urine	Sample cleaned-up by co-precipitation, treated with HNO_3 and H_2O_2, wet ashed	Biphasic liquid scintillation	1 pCi/200 cm^3	84%	Bomben et al. 1994
Urine	Spiked sample clean-up by co-precipitation, purified by TRU-spec column and electro-deposition	α-spectroscopy	0.016 pCi/ 800 cm^3	95% at 0.1–100 pCi/ sample	Goldstein et al. 1997
Soft tissue	Sample wet ashed, spiked with ^{243}Am, purified by anion exchange, solvent extraction, and electrodeposition	α-spectroscopy	No data	98%	McInroy et al. 1985
Soft tissue	Spiked sample wet ashed, treated with HNO_3/H_2O_2, purified by A-CU column, anion exchange, TRU-spec column, and electro-deposition	α-spectroscopy	No data	53%	Qu et al. 1998
Soft tissue	Sample wet ashed, purified by solvent extraction	Liquid scintillation	1.3 pCi/ 100 cm^3	96% at 20,000 dpm spike	Ham et al. 1977

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

Sample matrix	Sample preparation	Analytical method	Detection limit[a]	Accuracy	Reference
Soft tissue	Sample wet ashed, purified by solvent extraction	α-liquid scintillation	0.7 pCi/g	99% at 3,000 dpm spike	Guilmette and Bay 1981
Bone	Sample wet ashed, purified by solvent extraction	α-liquid scintillation	0.7 pCi/g	99% at 3,000 dpm spike	Guilmette and Bay 1981
Bone	Sample wet ashed, spiked with ^{243}Am, and purified by anion exchange resin column, solvent extraction, and electrodeposition	α-spectroscopy	No data	98%	McInroy et al. 1985
Feces	Sample wet ashed, purified by solvent extraction	Liquid scintillation	13 pCi/g	91% at 20,000 dpm spike	Ham et al. 1977
Feces	Sample wet ashed, purified by solvent extraction	α-liquid scintillation	1.3 pCi/sample	96% at 3,000 dpm spike	Guilmette and Bay 1981
Feces	None	Phoswich detector	0.02–0.09 nCi/ 200g	No data	Kramer et al. 1989
Teeth	Sample dissolved in HNO_3, purified by TRU-spec column and electrode position	α-spectroscopy	2.7 fCi/sample	98%	Culot et al. 1997
Whole organs and tissues	Animal placed, backbone down, in lucite box, and positioned 33 cm from NaI(Tl) crystal; livers and other tissues were counted between two NaI(Tl) crystals	Gamma-ray spectroscopy	No data	No data	Lloyd et al. 1970

[a]1 Ci=3.7x10^{10} Bq=0.037 TBq or 1 Bq=2.7x10^{-11} Ci=27 pCi; 1 Ci=2.2x10^{12} dpm

TRU = transuranic

collectively known as whole body counters. These radiation detectors commonly utilize hyperpure germanium to detect the 59.5 keV gamma-ray that ^{241}Am promptly emits in 35.9% of its alpha decays to ^{237}Np (DOE 1979b, 2003a; Palmer et al. 1983).

Because the attenuation half thicknesses for the 59.5 keV gamma-ray are 3.5 cm for soft tissues and 1.3 cm for bone, ^{241}Am that has been deposited into specific organs or tissues, such as the lungs, liver, bones (e.g., skull or knee cap), or lymph nodes, can be detected and quantified using whole body or partial body counting techniques that appropriately account for attenuation by internal organs (Graham and Kirkman 1983; Palmer and Rhoads 1989; Palmer et al. 1983). Many configurations of the whole body counter have been utilized, ranging from the more common single-detector chest detectors to multiple-detector arrays (e.g., four HPGE detectors, two each of front and back over the lungs or abdomen) or linear whole body scanners that can be utilized to assess the regional distributions of ^{241}Am over the entire length of the body (Palmer et al. 1983; Toohey and Essling 1980). 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. Also, *in vitro* measurements of americium (see Section 7.1.2) are often used in conjunction with whole body counting when monitoring individuals working with americium.

Calibration of whole body counters is performed so that the operator can obtain a more accurate and unbiased estimate of internalized americium activity. The equipment calibration is achieved through the use of tissue-equivalent phantoms that are constructed to mimic the shape and density of the anatomical structure (e.g., the human torso), using tissue equivalent materials such as polystyrene or epoxides. In some phantoms, a human rib cage is added to account for the attenuation of gamma-rays by bone in the whole body counts (DOE 1979b). Americium standards are inserted or molded into the phantom at locations where this radionuclide is expected to accumulate, such as in the lung, liver, or bone. Comparisons of the activity obtained from the phantom to the known activity of the americium standards are used to determine the efficiency of the counting technique and, thus, provide the basis for calibrating the technique. Calibration of whole body counters can be further refined by obtaining actual anatomical measurements of the individual to be measured. For example, chest wall thickness measurements using ultrasound techniques are used to account for the variability in attenuation that result from individual differences in the chest wall thickness and improving the calibration of chest counts of americium (DOE 1979b). Another approach to refining the calibration of whole body counters is the comparison of external measurements to the actual americium content in organs and bone of cadavers (Palmer et al. 1985). These refinements in calibration phantoms can lead to more accurate and less biased assessments

of the total body or organ burden of americium. The calibration may include an assessment of the detection limit for the system or for the specific analytical protocol being used.

In assessing initial exposure, whole body counting techniques measure the amounts of americium that have been retained within organs or tissues. In cases of accidental ingestion, some of the americium may have been excreted in the urine or feces before exposure is assessed. In particular, soluble forms of americium are thought to be readily excreted through the urine. Long-term assessment of americium burden within an individual can be complicated by the mobilization of americium from the original site of deposition (e.g., the lung) to other sites within the body, such as the liver or bone (Fry 1976). This can lead to either overestimates or underestimates of the overall total body burden of americium, depending on the regions in which the americium counts are obtained relative to the shift in radionuclide distribution, and if local concentrations have been augmented by mobilization of americium from other tissues. Overestimates can also occur in cases where external contamination in the vicinity of a detector contributes to the collected spectrum. Showering immediately before monitoring to remove potential contamination should help reduce variability in temporal results and minimize the potential for obtaining false positive results. Additionally, the retention (biological half-life) of americium within the body can vary greatly between individuals (Fry 1976). Direct comparisons of americium body burdens and clearance rates between laboratories can be complicated by the differing whole body measurement techniques, calibration methods, and methods used to account for normal background radiation counts that are utilized within the different laboratories (DOE 1979b). These variations are largely resolved by performing periodic internal monitoring and adjusting the model parameters to account for the individual's actual distributed retention.

7.1.2 Assay of Excreta

In vitro analyses of americium are routinely performed in situations where *in vivo* analyses cannot be obtained, where *in vivo* measurements will not provide the information needed, or in support of an *in vivo* monitoring program. Urine is the preferred sample for *in vitro* analyses of americium, although other sample types, such as feces, tissue, bone, or blood, can also be used on a more limited basis. Urine provides for an analysis of soluble or transportable americium, fecal analysis can be used to measure gastrointestinal clearance of ingested material plus bile-related systemic clearance, and tissue is used to assess whole or regional body burdens of americium (Guilmette and Bay 1981; Ide 1986; Ide et al. 1985; McInroy et al. 1985).

There are a number of methods that have the selectivity, and/or sensitivity, to measure americium in biological matrices including spectrophotometry, fluorimetry, mass spectrometry (MS), and radioassays (Dacheux and Aupias 1998; Hafez and Hafez 1992; Poupard and Jouniaux 1990; Thouvenot et al. 1993). Of these methods, radioassays (e.g., gross alpha analysis, alpha spectroscopy, gamma-ray spectroscopy, liquid scintillation techniques) are preferred because of their ease of use, detection sensitivity, and rapidity of analysis (Alvarez and Navarro 1996; Dacheux and Aupiais 1997; Guilmette 1986). These methods typically involve a preliminary concentration step and wet/dry ashing of the sample that is often followed by an oxidation of the radionuclides in the sample residue. To remove the possible interferences of other elements and alpha-emitters, ion exchange, co-precipitation, and adsorption techniques are applied to the purified sample before alpha or liquid scintillation techniques are applied (see Table 7-1). Radioassays can also be applied to the measurement of americium in fecal samples, as well as tissue and bone samples obtained from autopsy, using methods that are similar to those described for urinalysis, except for some additional purification and extraction steps that are required to remove interfering materials such as iron (Guilmette and Bay 1981; Hafez and Hafez 1992; Ham et al. 1977; Qu et al. 1998).

Of the radioassays that are commonly used to quantify americium, α-spectroscopy is used when isotopic analyses of americium must be conducted (e.g., to obtain distinct results for ^{241}Am and ^{243}Am). ^{243}Am is often added as a tracer to estimate the recovery (efficiency of the radiochemical sample preparation method for removing americium from a biological matrix). The α-spectroscopy technique differentiates between the two americium isotopes based on the difference in the energies of the alpha particles that are emitted from ^{241}Am and ^{243}Am, and then quantifies the amounts present in the sample by considering the system's response to each, its detection efficiency, and the frequency with which the individual alpha particles are emitted. If ^{243}Am is to be analyzed in a sample, ^{241}Am can be used as a tracer. If a sample needs to be monitored for both ^{241}Am and ^{243}Am, the sample is split prior to adding the tracer and two analyses are performed (PNNL 2003). Mass spectrometric techniques, especially those using double focusing magnet spectrometers, are also capable of isotopic quantification of americium (Dacheux and Aupiais 1998; Poupard and Jouniaux 1990). These techniques are more rapid than the α-spectroscopy detection method, but the costs have been much higher. The cost of mass spectrometers, however, has decreased in recent years, making the cost of analyzing samples by mass spectrometry and α-spectroscopy more comparable. The breakeven point will depend on the sample throughput rate. Higher sensitivity can also be achieved with α-spectroscopy by resorting to long sampling times, sometimes referred to as time-averaging.

Accuracy and bias of *in vivo* and *in vitro* measurements of americium are determined through the use of standard, certified radioactive sources with known concentrations of americium. The primary source of certified americium standards is the National Institute of Standards and Technology (NIST). Secondary and tertiary level laboratories can also prepare, certify, and sell such sources, and the Health Physics Society is developing an accreditation program for providers who wish their products to be recognized as NIST-traceable (HPS 2004). Standard solutions are available for ^{241}Am (SRM 4322, 40 Bq/g [1.1 nCi/g]) and ^{243}Am (SRM 4332, 40 Bq/g [1.1 nCi/g]). Standard Reference Materials for human lung (SRM 4351) and human liver (SRM 4352) are also available from NIST.

7.2 ENVIRONMENTAL SAMPLES

There are two common approaches for measuring americium in the environment. Americium can either be measured directly in the field (*in situ*) using portable survey instruments or be quantified from samples that were procured from the field and returned to the laboratory.

7.2.1 Field Measurements of Americium

In situ measurement techniques are extremely useful for the rapid characterization of radionuclide contamination in the environment, such as surface soils, sediments, and vegetation, or when monitoring personnel for internal exposure from or external contamination with americium. Information regarding field measurement methods, minimum detectable concentrations, and soil-to-plant concentration factors is available for various radionuclides, including americium (MARSSIM 2000; NRC 1992, 1998b). The measurement of radionuclides in the environment is conducted with portable survey instruments that are equipped with α-scintillators or gamma-ray spectrometers. The use of gamma-ray spectrometers is preferred for measuring americium in the field, especially in the presence of plutonium isotopes. The reason is that the low-energy ^{241}Am gamma-ray photons are more penetrating than lower energy x-rays from ^{238,239}Pu for which it is a surrogate radionucide. This makes measurements less affected by surface type and texture and by the presence of vegetation and surrounding soil (Byrne and Komosa 1993). This provides the advantage for assessing the level of americium both on and below the surface (e.g., up to 3-cm depth in some soils). These gamma-ray spectrometers are equipped with either a thin phoswich type detector or a high purity germanium detector that is able to distinguish the 59.5 keV gamma-ray emitted from ^{241}Am from most environmental gamma-rays emitted from other radionuclides (Fong and Alvarez 1997). Another advantage of these spectrometers is the ability to discriminate the 59.5 keV

photons of ^{241}Am from the much lower energy photons emitted from ^{239}Pu and ^{240}Pu, which are usually associated with americium. Minimum detectable activities (MDAs) of 0.4 Bq/g (10 pCi/g) for ^{241}Am are routinely achieved, with MDAs as low as 0.04 Bq/g (1 pCi/g) obtained with longer counting times (~30 days).

One of the limitations of the portable field survey instruments in the measurement of americium is that their quantitative accuracy depends on how well the lateral and vertical distribution of americium in the soil compares with the calibration parameters used. These methods can provide a rapid assessment of americium levels on or below surfaces in a particular environment; however, laboratory-based analyses of samples procured from these environmental surfaces must be performed in order to ensure accurate quantification of americium (and other radionuclides). This is due, in part, to the strong self absorption of the 59.5 keV gamma-ray by environmental media, such as soil. Consequently, uncertainty in the depth distribution of americium and density of the environmental media may contribute to a >30% error in the field survey measurements. Refinements in calibration strategies are currently being developed to improve both the precision and the accuracy (10%) of gamma-ray spectroscopy measurements of americium within contaminated soils (Fong and Alvarez 1997).

7.2.2 Laboratory Analysis of Environmental Samples

Analytical methods for quantifying americium in environmental samples are summarized in Table 7-2. The methods that are commonly used in the analysis of americium based on activity are gross α analysis, α-spectroscopy, and gamma-ray spectroscopy. MS detection techniques are used to measure the mass of americium in environmental samples. The mass-activity conversion factor for ^{241}Am is 0.29 μCi/μg (11 kBq/μg) or 3.43 μg/μCi (0.091 μg/kBq) (Harvey et al. 1993).

The analysis of americium in air is based on the quantification of americium within particulates that become trapped on cellulose or glass fiber filters after a calibrated amount of air is pulled through the filters. The analysis for americium on a glass fiber filter is straight forward using gamma spectroscopy, but can be a rather complex procedure involving many solvent extraction and column purification steps, followed by electrodeposition and α-spectroscopy. The extensive purification is required to prevent impurities within the sample from absorbing or reducing the energy of emitted alpha particles, termed self-absorption. Alpha-emitting contaminants must also be removed (e.g., ^{238}Pu) from the samples to

Table 7-2. Analytical Methods for Determining Americium in Environmental Samples

Sample matrix	Sample preparation	Analytical method	Detection limit[a]	Accuracy	Reference
Air	Sample collection on cellulose filter, dry ashed, solvent extracted	Biphasic liquid scintillation	1 pCi	95%	Bomben et al. 1994
Air	Filter wet ashed in HNO_3/HF, purified with cation and anion exchange columns and electrodeposition	α-spectroscopy	No data	No data	Knab 1979
Air	Cellulose filter dry ashed, dissolved in HNO_3/HF, H_2O_2/$HClO_4$, purified with anion exchange, TRU-spec columns followed by electrodeposition.	α-spectroscopy	0.023 pCi/sample	102%	Goldstein et al. 1997
Water	Sample fusion with pyrosulfate, precipitated with barium sulfate	Scintillation counter	No data	99.5%	Sill and Williams 1969
Water	Wet ashed, purified by solvent extraction	Biphasic liquid scintillation	1 pCi/sample	95%	Bomben et al. 1994
Water	Treated with HNO_3/H_2O_2, HF/HCl, anion exchange, TRU-spec column, electrodeposition	α-spectroscopy	0.026 pCi/L	101%	Goldstein et al. 1997
Water	Solvent extracted	PERALS	0.007 pCi/L	104%	Dacheux and Aupiais 1998
Sea water	Co-precipitation with iron hydroxide, purified by anion exchange, co-precipitation with $BiPO_4$, cation exchange, electro-deposition	α-spectroscopy	No data	64–79%	Lovette et al. 1990
Sediments	Sample fusion with KF and pyrosulfate, co-precipitate with $BaSO_4$	Scintillation counter	No data	No data	Sill and Williams 1969
Sediments	Sample leached with HNO_3/HF, filtered, purified by KL-HDEHP resin columns, solvent extracted, and electro-deposition	α-spectroscopy	No data	95–99%	Guogang et al. 1998
Sediments	None	Gamma-ray spectroscopy	0.02–0.06 pCi/g	108–118%	Joshi 1989
Soil	Sample fusion with KF and pyrosulfate, co-precipitate with $BaSO_4$	Scintillation counter	No data	No data	Sill and Williams 1969

Table 7-2. Analytical Methods for Determining Americium in Environmental Samples

Sample matrix	Sample preparation	Analytical method	Detection limit[a]	Accuracy	Reference
Soil	Wet ash in HNO_3/HF, purified with cation and anion exchange columns, electrodeposition	α-spectroscopy	No data	No data	Knab 1979
Soil	Dry ash, digest in HNO_3/HCl, anion exchange, Ca-oxalate and Fe $(OH)_2$ coprecipitation, anion exchange, electro-deposition	α-spectroscopy	27 pCi/g	75–92%	Sanchez and Singleton 1996
Soil	Sample leached with HNO_3/HF, filtered, purified by KL-HDEHP resin columns, solvent extracted, and electro-deposition	α-spectroscopy	No data	95–99%	Guogang et al. 1998
Soil	None	Gamma-ray spectroscopy	0.02–0.06 pCi/g	108–118%	Joshi 1989
Vegetation (grasses)	Ashed, HNO_3/HF, precipitation with oxalate and La, anion exchange, solvent extraction	α-spectroscopy	0.011 pCi/g	No data	Bunzl and Kracke 1990
Vegetation	Ashed, digested with HNO_3-H_2O_2, oxalate and Fe precipitations, anion exchange, solvent extraction, electro-deposition	α-spectroscopy	0.3 fCi/g	73–109%	Cooper et al. 1993
Vegetation	Ashed, digested with HNO_3-HCl, anion exchange, Ca-oxalate and Fe precipitations, anion exchange, electro-deposition	α-spectroscopy	27 pCi/g	75–92%	Sanchez and Singleton 1996
Lichen, moss	Ashed, leached with HCl, Microthene-TNOA and KL-HDEHP column extractions, solvent extraction, electro-deposition	α-spectroscopy	0.9 fCi/g	No data	Jia et al. 1997

Table 7-2. Analytical Methods for Determining Americium in Environmental Samples

Sample matrix	Sample preparation	Analytical method	Detection limit[a]	Accuracy	Reference
Biota	Ashed, digested with HNO_3-H_2O_2, oxalate, and Fe precipitations, anion exchange, solvent extraction, electro-deposition	α-spectroscopy	0.3 fCi/g	98–100% 480% (shrimp)	Cooper et al. 1993

[a]1 Bq=2.7x10^{-11} Ci=27 pCi; 27 fCi=1 mBq

KL-HDEHP = 50% di(2-ethylhexyl) phosphoric acid, 60–100 mesh resin; PERALS = Photon/electron rejecting alpha liquid scintillation; TNOA = tri-*n*-octylamine; TRU = transuranic

prevent these materials from interfering with the α-spectroscopy measurements of ^{241}Am and ^{243}Am (ASTM 1997; Lovette et al. 1990). Initially, the filter media is dissolved with HNO_3 and H_2O_2, the residue is wet ashed with HNO_3 and then purified using anion exchange chromatography, the solvent is extracted with 50% bis-(2-ethylhexyl) phosphoric acid (HDEHP) in toluene, the sample is again passed through an anion exchange column, and then the sample is oxidized with HNO_3 and H_2O_2. ^{243}Am is commonly used as a surrogate for quantifying the chemical recovery of ^{241}Am during sample preparation, so quantification of ^{241}Am in a sample involves α-spectrometric analysis of both isotopes. Preparation of the purified filter sample for α-spectroscopy requires electrodeposition of the americium from a sulfate solution onto a stainless steel or platinum disc from which alpha counts are obtained during the α-spectroscopy analysis (DOE 1997b). The accuracy of this method of analysis for americium can vary between 85 and 102% and the MDA often ranges between 0.032 and 0.023 pCi/sample (1.2 and 0.85 mBq/sample) (Goldstein et al. 1997).

For the analysis of americium in water, there is a broad array of available sample preparation and detection methodologies (see Table 7-2). Many of the common and standardized analytical methodologies typically include the minimization of sample volume, purification through co-precipitation, anion exchange column chromatography, and solvent extraction techniques followed by radiochemical detection of americium in the purified sample. Gross alpha analysis or liquid scintillation are common detection techniques that are utilized to quantify americium in these methods. However, if lower detection sensitivity or isotopic determination is required, then α-spectroscopy is the preferred method to quantify ^{241}Am (Dacheux and Aupiais 1997; DOE 1997b; Goldstein et al. 1997; Harvey et al. 1993; Sill and Williams 1969). These detection methods can provide measurements of total americium activity within a sample, especially when appropriate steps have been taken to purify the sample of interfering materials or minimize the influence of other radionuclides on radiochemical activity (Dazhu et al. 1991). The presence of alpha emitting radionuclides in the sample can contribute to the alpha counts measured in radiochemical detection methods and, thus, affect the accuracy of the assay for determining the quantity of americium within a sample.

There are methods available to quantify the total mass of americium in environmental samples. Mass spectrometric methods provide total mass measurements of americium isotopes (Dacheux and Aupiais 1997, 1998; Halverson 1984; Harvey et al. 1993); however, these detection methods have not gained the same popularity as is found for the radiochemical detection methods. This may relate to the higher purchase price of an MS system, the increased knowledge required to operate the equipment, and the selection by EPA of α-spectroscopy for use in its standard analytical methods. Fluorimetric methods,

which are commonly used to determine the total mass of uranium and curium in environmental samples, have limited utility to quantify americium, due to the low quantum yield of fluorescence for americium (Thouvenot et al. 1993).

Several rapid analysis techniques involving gamma spectroscopy or spectrometry have been developed that require either no or minimal sample preparation that can, under optimized conditions, provide the required selectivity and sensitivity to quantify americium in environmental samples, such as soils and sediments (Byrne and Komosa 1993; Cutshall et al. 1983; Guilmette 1986; Joshi 1989). These techniques utilize either an intrinsic germanium detector or a phoswich-based cesium-sodium iodide low energy photon detector that detects the gamma-rays emitted from ^{241}Am in a neat (undiluted) or ashed environmental or biological sample. On average, these methods have a minimum significant measurable activity (MSMA) of approximately 1 pCi/sample (0.037 Bq/sample). To achieve this low MSMA, the counting efficiency of the detector must be standardized against the sample size and composition in order to assure the desired accuracy of the assay (Cutshall et al. 1983; Joshi 1989). Using a germanium detector with its vastly superior energy resolution facilitates the identification of multiple isotopes in the same sample without photopeak interference. It is the detector of choice for analyzing samples (and performing internal monitoring on individuals) by gamma spectroscopy. The disadvantages of using germanium are its greater purchase price and requirement to be cooled with liquid nitrogen or by electrocryogenic means whenever it is in use. One limitation of the phoswich assays is the need to know the isotopic composition of the sample since the x-rays that accompany the decay of other radionuclides may also be counted by the phoswich detector, which is typically calibrated with a wide energy window that focuses on the 59.5 keV photon, but also detects higher energy x-rays and Compton scattered photons.

Several methods have been described in the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM 2000) for the survey and investigation of sites contaminated with radioactive materials. At the high end of the survey instruments, costing over $1,000,000 in 1995, is an inductively coupled plasma-mass spectrometer (ICP-MS) with a laser added to the front end to vaporize small portions of a surface or a volumetric material to be analyzed (laser ablation), thereby avoiding physical sample collection. Prices in 2002 were a factor of two or three lower for an inductively coupled plasma double focusing magnet mass spectrometer capable of very accurate americium isotopic measurements.

The quantity of americium in soil, sediments, vegetation, and biota is determined using methods similar to those described above. For example, in a standardized method developed by DOE (1997b), soil samples are dissolved with a series of acid treatments (e.g., HNO_3, HF) and initially purified through co-

precipitation using calcium oxalate followed by co-precipitation with an Fe carrier. A final purification of the sample is achieved by passing the sample through a series of anion exchange columns (e.g., HNO_3, HCl, and NH_4SCN), followed by electrodeposition of the americium (chloride form) onto a platinum disc in preparation for α-spectroscopy analysis.

In another standardized method developed for the analysis of americium in soil (ASTM 1997), a different approach is taken towards purifying the dissolved soil sample that relies on a series of co-precipitations and solvent extractions to prepare the soil sample for α-spectroscopy analysis. After the soil has been dissolved, the sample is initially purified by co-precipitation with barium sulfate, followed by solvent extraction of the redissolved precipitate with 15% HDEHP in n-hexane. The extracted trivalent actinides and lanthanides are stripped from the organic phase using nitric acid containing sodium bromate. The subsequent solution containing the trivalent actinides and lanthanides is extracted again with 15% HDEHP in n-hexane to remove plutonium, thorium, and tetravalent curium. The aqueous phase is further purified through co-precipitation with a lanthanum carrier to isolate the rare earth fluorides followed by a treatment using silver nitrate and ammonium persulfate/ammonium fluoride to precipitate all remaining rare earth fluorides, except for hexavalent americium fluoride. The hexavalent americium is reduced back to the trivalent state using hydrogen peroxide and then reprecipitated with a neodymium carrier in preparation for α-spectroscopy analysis. Both the DOE and the American Society for Testing and Materials (ASTM) methods of analysis provide good precision (<6% standard derivation) with no statistically significant bias (at the 5% level) observed. Analysis of americium in sediments, vegetation, and biota can also be performed using variations of the abovementioned methods or other methods, as exemplified in Table 7-2.

The detection limits, accuracy, and precision of any analytical methodology, as well as the composition of the sample medium, are important parameters in determining the appropriateness of a method to quantify a specific analyte at the desired level of sensitivity within a particular matrix. The lower limit of detection (LLD) has been adopted to refer to the intrinsic detection capability of a measurement procedure (sampling through data reduction and reporting) to aid in determining which method is best suited for the required sample quantification (NRC 1984). Several factors influence the LLD, including background counting 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 LLDs between laboratories and for samples in the same laboratory, utilizing the same or similar measurement procedures, will vary.

The accuracy of a measurement technique in determining the quantity of a particular analyte in environmental samples is greatly dependent on the reliability of the calibrating technique. Thus, the availability of standard, certified radiation sources with known concentrations of americium are required in order to ensure the reliability of the calibration methods and the accuracy of americium measurements in environmental samples. The primary source of certified americium standards is the NIST. Standard solutions of ^{241}Am (SRM 4322, 40 Bq/g [1.1 nCi/g]) and ^{243}Am (SRM 4332, 40 Bq/g [1.1 nCi/g]) are available. Standard reference materials are also available from NIST and the International Atomic Energy Agency (IAEA) for a number of environmental matrices; for example, soils and sediments (Rocky Flats Soil [SRM 4353], river sediment [SRM 4350B], and Peruvian soil [SRM 4355] and sediments [IAEA 367, IAEA 135]).

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 americium 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 americium.

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 americium 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 quantification of americium, both total and isotopic, in environmental matrices (see Table 7-2).

Whether in the environment or in the human body, americium will undergo radioactive decay to form a series of radioactive nuclides that end in a stable isotope of lead (for ^{243}Am) or bismuth (for ^{241}Am) (see Chapter 4). The decay series proceeds slowly due to the long half-lives of some of the intermediate decay series isotopes. Therefore, more sensitive analytical methods for accurately measuring very low levels of these radionuclides would be useful. Practically speaking, since ^{239}Pu (for ^{243}Am) and ^{237}Np (for ^{241}Am) have such extremely long half-lives, 2.41×10^4 and 2.14×10^6 years, respectively, few decay products need to be considered since they would only begin to achieve measurable levels in the distant future.

7.3.2 Ongoing Studies

The Federal Research in Progress (FEDRIP 2004) database did not list any current studies involving developments in analytical techniques related to americium.