

6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring plutonium 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 plutonium. 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 plutonium in environmental samples are the methods approved by federal agencies such as EPA. Other methods presented in this chapter are those that are approved trade associations, 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.

The accurate and reliable determination of plutonium in biological and environmental samples is important because of the potential impact of this element on public health. Analytical methods used to measure plutonium in biological and environmental media are highly refined compared to other transuranics.

Analytical methods used to quantify plutonium in biological and environmental samples are listed in Tables 6-1 and 6-2. Emphasis has been placed on well-established methods approved by EPA, the American Public Health Association, and in accordance with accepted standards of the American Society for Testing and Materials (ASTM). Reviews of analytical methods for measuring plutonium concentrations are provided by Brouns (1980), Bernhardt (1976), Metz and Waterbury (1962), and Singh and Wrenn (1988).

General environmental survey instruments (e.g., alpha particle meters) are available, but they are not specific for plutonium. The predominant analytical method for measuring plutonium present at or near background concentrations in both biological and environmental media requires radiochemical separation and purification in conjunction with a quantitative measurement technique (e.g., alpha spectrometry, liquid scintillation, or mass spectrometry).

6.1 BIOLOGICAL MATERIALS

The procedures that have been developed for the determination of small quantities of plutonium in biological as well as in environmental samples include the following steps:

- Release of plutonium from the sample's matrix into solution and the addition of plutonium tracers;

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

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
Biological soft tissues	Wet ash; filter; extract; electrodeposit on platinum disk	α spectrometry ²³⁸ Pu, ^{239/240} Pu	no data	no data	Singh and Wrenn 1988
Urine	Evaporate; wet ash; filter; extract, electrodeposit on platinum disk	α spectrometry ²³⁸ Pu, ^{239/240} Pu	no data	no data	Singh and Wrenn 1988
Fecal matter	Wet ash; filter; extract; electrodeposit on platinum disk	α spectrometry ²³⁸ Pu, ^{239/240} Pu	no data	no data	Singh and Wrenn 1988
Bones	Dry ash; reduce valence state; extract; electrodeposit on platinum disk	α spectrometry ²³⁸ Pu, ^{239/240} Pu	no data	no data	Singh and Wrenn 1988
Milk	Dry ash; extract; reduce valence state; coprecipitate with lanthanum fluoride	α spectrometry	no data	no data	EPA 1984
Plant	Dissolve starch; filter; wet ash; extract; electrodeposit on platinum disk	α spectrometry ²³⁸ Pu, ^{239/240} Pu	0.0027 pCi (0.1x10 ⁻⁴ Bq)	no data	Bunzl and Kracke 1987

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

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
Air	Extract; filter; coprecipitate with cerium fluorides; electrodeposit on platinum disk	α spectrometry (solid state detector) (tentative Method 605)	0.08x10 ⁻⁶ pCi/m ³ (2x 10 ⁻⁶ Bq/m ³)	±10%	APHA 1977
Air	Dry ash; filter; extract; reduce valence; coprecipitate with lanthanum fluoride	α spectrometry	no data	no data	EPA 1984
Soil	Digest; filter; extract; electrodeposit on platinum disk	α spectrometry ²³⁸ Pu, ^{239/240} Pu	no data	no data	Singh and Wrenn 1988
Soil, Water	Ash soil or evaporate water samples; reduce valence; extract; wet ash; coprecipitate with lanthanum fluoride	α spectrometry ²³⁸ Pu, ^{239/240} Pu	no data	no data	EPA 1984
Water	Filter; extract; coprecipitate with lanthanum fluoride	α particle counter (either proportional or scintillation detectors) (EPA Method 907.0)	no data	15%	EPA 1980

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- Concentration by precipitation with a nonisotopic carrier or by solvent extraction;
- Purification by precipitation, liquid extraction, or ion exchange chromatography; and
- Determination of the plutonium content of the sample by alpha-particle counting or other techniques (Brouns 1980).

Two common methods for releasing plutonium from the sample's matrix into solution are acid extraction and acid dissolution. Samples are wet, or dry, ashed prior to solubilization. Leaching the sample with a mixture of acids (e.g., nitric acid and hydrochloric acid) has the advantage of easily handling large sample volumes, but with the potential disadvantage of leaving plutonium compounds in the residue. The acid dissolution procedure includes the addition of excess hydrofluoric acid (HF) to the above mixture of acids and results in dissolution of much, if not all, of the sample matrix. Refractory plutonium compounds (e.g., PuO_2) are more likely to be dissolved upon addition of HF. However, dissolution of interfering elements, such as iron, phosphorous, and other rare earths (e.g., alpha-particle emitters), is also increased in acid dissolution. A third example of a dissolution method is fusion. It is less routinely used, however, because it is relatively labor intensive. Fusions with pyrosulfate, or a combination potassium fluoride and pyrosulfate fusion, can insure complete dissolution of the sample matrix. The potassium fluoride fusion dissolves the siliceous material in the sample, whereas the pyrosulfate fusion dissolves the nonsiliceous matrix materials, especially the refractory plutonium dioxides (Bernhardt 1976).

Plutonium solutions that contain: (1) other alpha-particle emitters (e.g., americium and neptunium), (2) large amounts of fission products (e.g., cesium), or interfering amounts of other substances such as iron, calcium, uranium, and phosphorous need to undergo additional chemical separation procedures. Nonisotopic carriers, such as lanthanum fluoride (LaF_3) and zirconium phenylphosphate ($\text{ZrC}_6\text{H}_6\text{PO}_4$), are used to selectively precipitate the rare earths. Solvent extraction and ion exchange separation methods are preferred methods because of better separations. In addition, they do not involve the addition of nonvolatile substances resulting in an easier preparation of the co-precipitation source used for alpha-particle counting.

These extraction techniques can be made very efficient and selective by adjusting the oxidation state of the plutonium and other sample constituents. Common extraction methods specific for plutonium use 2-thenoyltrifluoroacetone (TTA), tetrapropylammonium trinitrate in isopropylacetone or triisooctylamine, cupferron in chloroform, tributylphosphphate, and tri-octylphosphine dioxide. Anion exchange

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methods with either nitric or hydrochloric acid solutions are commonly used. Cation exchange column methods are less frequently used (Brouns 1980).

Alpha-particle counting is the most commonly used method for determining plutonium concentrations at low levels in biological samples, as well as in process waste streams, and in soil, water, and air filter samples (Brouns 1980). This method does not distinguish between the different alpha-particle emitters of plutonium (plutonium-236, plutonium-238, plutonium-239, plutonium-240, plutonium-242), nor does it detect plutonium-241, a beta-particle emitter.

Prior to measurement, the separated and purified plutonium must be incorporated into a source to produce a low mass, uniformly distributed deposit on a highly polished metal surface. Two techniques that are commonly used are: (1) electrodeposition, and (2) co-precipitation with a carrier. Electrodeposition is currently used in a minority of laboratories to prepare a thin, uniform, and reproducible source. The alpha-particle emitting isotopes of plutonium are electrodeposited on a polished stainless steel, or platinum disk. In the co-precipitation technique, a small amount of a carrier (e.g., LaF₃) is used to coprecipitate the separated and purified plutonium from solution. The precipitate is then prepared for counting by either filtration or by evaporation of a slurry of the precipitate onto a stainless steel disk or planchet (ASTM 1982; 1987). Recent methods use a glass fiber filter which can be used as the source for alpha counting techniques. It has been suggested that low yields result from electrodeposition due to the presence of traces of interfering elements (e.g., iron) (Bernhardt 1976).

Alpha spectrometry is the single most widely used method for measuring concentrations of plutonium-238, or a mixture of plutonium-239 and plutonium-240. However, the energy of the alpha particles emitted from plutonium-239 and plutonium-240 are too close to be resolved by alpha spectrometry. The two remaining alpha-particle emitters among the plutonium isotopes, plutonium-236 and plutonium-242, are normally not found in environmentally significant quantities, and are not common constituents of nuclear fuels or waste waters. Therefore, they can be used as tracers to aid in the analysis of other isotopes. In this calibration procedure, a known quantity of a tracer is added to the sample being analyzed in order to determine the yield. This is the percentage of the total amount of plutonium in the sample that is actually measured in the electrodeposited amount after the separation, purification, and preparation of the source (ASTM 1987; Brouns 1980).

The most critical step in the analysis of biological samples is complete dissolution of the sample to assure solubilization of all plutonium compounds. Biological samples are generally dissolved by wet ashing or a combination of wet and dry ashing. High temperatures (700%

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to 1,000°C) during ashing should be avoided in order to prevent the formation of an insoluble form of plutonium dioxide (Nielsen and Beasley 1980; Sill 1975). Plutonium that has been distributed to urine, blood, or soft tissue as a result of metabolic processes is usually in a readily soluble form. Lung tissue, feces, and excised tissue from wound sites will likely contain insoluble forms of plutonium and will require treatment with HF and repeated ashings to effect solubilization. Tissues, feces, and vegetation require repeated treatment with a mixture of concentrated nitric acid (HNO_3), perchloric acid (HClO_4), and sulphuric acid (H_2SO_4) in order to oxidize the large amount of organic materials in these samples. If an insoluble residue remains after repeated ashings, then fusion of the residue with gram quantities of an inorganic flux (e.g., sodium carbonate, sodium pyrosulfate) can be used to effect solution. Known amounts of a plutonium isotope are commonly added subsequent to the dissolution step so that the percentage of plutonium recovered after separation and purification (i.e., the yield) may be determined. This added plutonium must be in the same chemical form as the plutonium in the sample or the yield estimates will not reflect the percentage of plutonium recovered from the dissolved sample (Bernhardt 1976; Nielsen and Beasley 1980).

Methods used for concentrating plutonium in a sample by a carrier are often specific to one oxidation state of the plutonium. For example, the classical bismuth phosphate-lanthanum fluoride method of concentrating plutonium from urine samples is specific to plutonium in the tri- and tetravalent states and will leave plutonium(VI) in solution. The fate of the various oxidation states of plutonium in man is not well understood and analysis procedures must insure reduction or oxidation of plutonium into appropriate oxidation states. Liver and kidney samples may contain metals (e.g., iron) which may greatly reduce chemical yields during the final electrodeposition step (Bernhardt 1976).

Sensitive methods for analysis of plutonium in urine are particularly important for estimating occupational plutonium body burdens. Routinely available instrumentation, such as the alpha spectrometer, can readily detect these low concentrations. More sensitive methods are commonly required for urine samples in order to assess chronic exposures to plutonium. These low detection limits were first achieved in the past by nuclear emulsion track counting (see Table 6-1). In this method, the electrodeposited sample is exposed to nuclear track film, subsequent to the isolation of plutonium. The alpha particle emitting isotopes of plutonium will leave tracks on the film which are counted to quantify the amount of plutonium. Nuclear emulsion track counting has been used in the past to measure plutonium concentrations in the urine of workers at a nuclear reactor plant (Nielsen and Beasley 1980). A type of scintillation counting has been used to measure plutonium-239 and americium-241 in animal tissues (NCRP 1985).

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6.2 ENVIRONMENTAL SAMPLES

Common analytical methods used to measure plutonium in environmental samples are listed in Table 6-2. The separation and extraction methods used to prepare biological samples for plutonium analysis are commonly used for environmental samples.

Large volumes of air particulate samples (e.g., 10,000 m³) should be collected in order to obtain detectable amounts of plutonium. Fiberglass filters may have trace amounts of metals which decrease the yield when electroplating is used to prepare the sample source for alpha spectrometry (Bernhardt 1976).

Field survey instruments for measuring photons of americium-241 in surface soils and on airborne particulates are available (e.g., Field Instrument for Detecting Low Energy Radiation: FIDLER) with a minimum detection limit of approximately twice the magnitude of a background level of plutonium-239 (1-2x10³ pCi/m²; 37-74 Bq/m²). The FIDLER uses a sodium iodide or calcium fluoride crystal and photon-height discrimination in order to detect the 17 KeV X-rays emitted from the progeny of plutonium, or the 60 KeV gamma photons of americium-241. These instruments are useful for identifying areas of contamination, but cannot be used to accurately predict the concentration of plutonium in surface soils (Bernhardt 1976). This instrument has been used in aerial surveys of large area sources, such as the Nevada Test Site.

Since soil-adsorbed plutonium contamination exists as discrete particles of various sizes, analysis of larger soil volumes (25 to 100 grams) is recommended (Bernhardt 1976). Commonly, soil samples with high amounts of carbonate are difficult to analyze. More rapid, efficient, and economical procedures are being developed to sequentially analyze a number of radioactive actinides (Hindman 1986).

An EPA-approved procedure for the analysis of plutonium in water is listed in Table 6-2. In addition, the following ASTM standard methods relate to the measurement of plutonium in water: D 3648, D 3084, D 3972, and D 1943 (ASTM 1981, 1982a, 1982b, 1987). Recent work has focused on more rapid analytical methods in order to routinely monitor plutonium levels in waste process streams at nuclear facilities. For example, Edelson et al. (1986) have investigated the applications of inductively coupled plasma-atomic emission spectrometry (ICP-EAS) to routinely analyze water samples.

Alpha counting and alpha spectrometry are the two most common analytical methods for measuring plutonium concentrations in environmental samples. Other measurement techniques available are liquid scintillation, mass spectrometry, and gamma spectrometry.

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Liquid-scintillation counting is a less common method used to measure plutonium concentrations from the various alpha-particle emitters among the isotopes of plutonium. Although liquid scintillation counting avoids the interferences from iron and other metals seen with electrodeposition, this method generally has higher detection limits than obtained with alpha spectrometry. In addition, the composition of the scintillation solution must be carefully controlled to prevent polymerization, deposition, or precipitation of the plutonium (NCRP 1985).

Mass spectrometry is used by some research laboratories to determine the concentration of each plutonium isotope, including the naturally-occurring plutonium-244. Mass spectrometry determines the number of atoms of a given mass number and, therefore, can measure the concentration of all of the plutonium isotopes, not only the alpha-particle emitters as in alpha spectrometry. Mass spectrometry is several orders of magnitude more sensitive than alpha spectrometry in determining the quantities of plutonium isotopes with long half-lives, which also tend to be the heavier isotopes. However, plutonium-238 is most accurately determined by alpha spectrometry (Bernhardt 1976) because of its relatively short half-life and the potential interferences from traces of uranium-238.

Quantities of plutonium-241, a beta-particle emitter, can be quantified from: (1) assumed isotopic abundance ratios, (2) estimated in-growth of its progeny americium-241 by gamma spectrometry, or by (3) mass spectrometry (Bernhardt 1976). Americium-241 is produced from the beta decay of plutonium-241 and, therefore, can be used to indirectly measure the concentration of plutonium-241 (Metz and Waterbury 1962). Direct determination of plutonium-241 by measurement of its low energy beta-particle decay has been reported using liquid scintillation analysis (Martin 1986).

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 plutonium is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of plutonium.

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

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the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.3.1 Identification of Data Needs

Methods for Determining Biomarkers of Exposure and Effect. There are methods available for measuring the isotopes of plutonium in biological samples. The measurement of plutonium in the urine is considered a biomarker of exposure to plutonium. Methods are available to detect plutonium in the urine. However, no information was available concerning the reliability of these methods for determining plutonium levels in the urine. In the studies that reported these methods of analyses, neither the sample detection limit nor the accuracy of the method was reported. Therefore, more information is needed to define a detection limit and to determine the accuracy of the method used to analyze plutonium in the urine. On-going studies continue to refine these procedures. Additional studies would be helpful to determine the migration of plutonium in the body over time.

No biomarkers have been linked to plutonium health effects in humans. Further testing to identify any potential biomarkers of effect should be conducted; if biomarkers are identified, testing will then be needed to determine what analytical methods will detect these biomarkers with the greatest degree of accuracy.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Environmental media are analyzed to identify contaminated areas and to determine if contaminant levels constitute a concern for human health. The detection of plutonium in air, water, and soil is of concern due to the potential for human exposure. There are many steps involved in the analysis of plutonium in environmental media. Reliable and accurate methods are available to detect plutonium in air. However, no detection limit or degree of accuracy was reported for the methods used to determine plutonium in soil and water. Attempts to improve these methods should be focused on separation techniques, increasing yields, and increasing the measurement efficiency.

6.3.2 On-going Studies

The Environmental Research Laboratory of the U.S. Department of Energy located in New York is conducting studies to refine analytical methods for the measurement of plutonium in biological and environmental media. Lawrence Livermore National Laboratory in California is currently refining techniques for the measurement of plutonium in biological samples. On-going studies of the solution chemistry of plutonium are currently being undertaken at Brookhaven Laboratory in New York and by researchers in Japan (Aoyagi et al. 1987).

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Individuals occupationally exposed to plutonium in the past are continually monitored in programs across the country. For example, whole body counting studies are currently conducted at Los Alamos National Laboratory in New Mexico. Animal studies conducted at the Lawrence Berkeley Laboratory, University of California, Berkeley, by P. Durbin are evaluating the behavior and movement of plutonium inhaled into the lungs. Models used to estimate body burden based on urinary excretion data and other biological measurements of plutonium (Leggett and Eckerman 1987) are under continual revision.