6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring uranium 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 uranium. 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 uranium in environmental samples are the methods approved by federal agencies such as EPA, DOE, 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 lower detection limits, and/or to improve accuracy and precision.

Most of the equipment and analytical methods described in this chapter for field measurements and, to a lesser extent, laboratory sample analysis are summarized in the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM 1997). It is anticipated that its companion manual, the Draft Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) manual, will robustly describe relevant analytical equipment and methods, and be available for public comment in 2000.

6.1 BIOLOGICAL MATERIALS

Uranium can enter the human body through inhalation, ingestion, or penetration through the skin. Measurement of the quantities of uranium in the body can be performed by two primary methods, *in vivo* measurements and *in vitro* measurements. These types of measurements are called bioassays. *In vivo* techniques measure the quantities of internally deposited uranium directly using a whole body counter while *in vitro* techniques permit estimation of internally deposited uranium by analysis of body fluids, excreta, or (in rare instances) tissues obtained through biopsy or postmortem tissue sectioning (NCRP 1987) (USUTR 1999). Some of these analytical methods are summarized in Table 6-1.

6.1.1 Internal Uranium Measurements

In vivo or direct measurements of uranium in the body are made with radiation detector systems and associated electronics called whole body counters that measure radiation as it leaves the body from internally deposited uranium. *In vivo* assays are the most direct method of quantifying internally deposited

radioactive materials. However, not all radionuclides emit radiations than may be detected outside the body (^{234}U and ^{238}U, for example) (NCRP 1978). The most commonly used detectors for uranium *in vivo* counting are sodium iodide, phoswich (NaI and CsI sandwich), and hyperpure germanium which measure the gamma rays emitted during uranium decay (DOE 1988). Since the gamma radiations emitted from uranium and a number of its progeny are the same as those emitted by uranium in the environment, shielded rooms are normally used to house the uranium internal monitoring equipment to ensure that background radiation is as low as possible (DOE 1999; Parrington et al. 1996) . Although whole body counters may be made in many configurations, a chest counter is usually used for inhaled uranium. *In vivo* analysis is widely used throughout the nuclear industry, both commercial and government, for quantifying levels of insoluble uranium in the body. *In vitro* analysis (see Section 6.1.2) is often used in conjunction with whole body counting for monitoring workers handling uranium (DOE 1988).

In vivo counting systems are calibrated using tissue-equivalent phantoms. These phantoms have shapes similar to the human torso and are made of polystyrene or other tissue equivalent material. Standard uranium sources of known activity are inserted into the phantom at locations where uranium would be expected to accumulate in a human body (DOE 1988). Relationships are determined between the uranium activity measured by the detection system and the known activity in the phantom (DOE 1988; HPS 1996).

There are limitations associated with *in vivo* counting uranium measurements. First, soluble uranium is readily excreted, with fractions retained for varying periods in the bone and kidney, so detectability depends on factors such as intake quantity, chemical and physical form, biodistribution fraction, time since intake, background uranium contribution, analysis time, and detection system efficiency. Second, only the ^{235}U isotope can be detected using the sodium iodide or hyperpure germanium detectors, since ^{234}U and ^{238}U decay does not result in emission of gamma rays, which are required for detection by sodium iodide and hyperpure germanium detectors (NCRP 1987). In such cases, indirect *in vitro* methods can be used for measuring uranium in urine or feces (DOE 1988; HPS 1996). Analytical equipment and procedures vary widely among laboratories and often require individual-specific input (NCRP 1987). The Minimum Testing Level (MTL) of 0.81 nCi ^{235}U (lung) has been established as a performance level to which laboratories are expected to adhere for *in vivo* detection (HPS 1996).

6.1.2 *In Vivo* and *In Vitro* Uranium Measurements

In vitro uranium analyses are routinely performed in support of a personnel monitoring program, or in cases where the size of an operation does not justify the cost of whole body counter facilities. These analyses are usually done on urine samples, but other types of body materials may also be used (e.g., feces or blood).

Urinalysis is effective for analysis of transportable or soluble uranium. A fraction of insoluble uranium also appears in the urine (DOE 1988).

The excretion of uranium in fecal material results primarily from intakes by ingestion, and includes uranium swallowed after inhalation. Usually, uranium will appear in feces within hours after intake thus providing a rapid means of determining whether an intake has occurred. Fecal analysis requires prechemistry preparation that includes ashing of the sample, cleaning by co-precipitation, and solvent extraction followed by electrodeposition. Alpha spectroscopy is then performed (Singh and Wrenn 1988). Urinalysis is typically favored over both fecal and blood analysis because it is generally more sensitive and less costly, and because fecal analysis provides no uptake or retention information and blood analyses is invasive.

Several methods that do not require chemical separation are available for measuring uranium in urine (in units of total mass or total activity). These methods include spectrophotometric (total mass), fluorometric (total mass), kinetic phosphorescence analysis (KPA) (total mass), and gross alpha (total activity) analyses (Wessman 1984). The most widely used methods for routine uranium analysis are α-spectrometry and liquid scintillation spectrometry. These methods utilize the natural radioactivity of uranium and are sensitive and require little sample preparation. Photometric techniques such as fluorometry and phosphorometry are less widely used, but kinetic phosphorescence analysis is becoming more widely used. Measurements of total uranium do not provide the relative isotopic abundance of the uranium isotopes, but this may only be important when converting between activity and mass when the isotopic ratios are uncertain.

If quantification of an individual uranium isotope is needed (e.g., ^{234}U, ^{235}U, or ^{238}U), the most commonly used methods require chemical separation followed by α-spectrometry, or chemical separation and electrodeposition followed by α-spectrometry (see Table 6-1). Mass spectrometric methods have emerged as sensitive, reliable techniques for determining uranium isotopes at low concentrations. Inductively coupled plasma-mass spectrometry (ICP-MS) requires sample preparation, but is rapid and is becoming less expensive (Twiss et al. 1994).

Uranium may also be measured in fecal material using the same methods identified above for urinalyses, except that this matrix requires extensive preparation. For α-spectroscopy, this includes ashing of the sample, cleaning by co-precipitation, and solvent extraction followed by electrodeposition and α-spectroscopy (Singh and Wren 1988). In the other methods, electrodeposition is replaced with an equipment-specific step, such as direct injection for ICP-MS and mixing with a scintillation cocktail for liquid scintillation.

Table 6-1

Table 6-1. Analytical Methods for Determining Uranium in Biological Samples

Sample matrix	Sample preparation	Analytical method	Detection limit	Accuracy	Reference
Urine	Enrichment on an anion exchange column, solvent extraction	α-Counting (total uranium)	Not given	92% at 0.9 dpm spike	Hinton 1983
	Spiked urine wet ashed; sample clean-up by coprecipitation, solvent extraction and electro-deposition	α-Spectrometry (total uranium)	0.02 dpm/L for ^{238}U [a]	78%	Singh and Wrenn 1988
	Sample treated with HCl and H_2O_2, clean-up on anion exchange resin column	Spectrophotometric (total uranium)	5 µg/L	87% at 11 µg/L	Kressin 1984
	Sample wet ashed, enrichment on anion exchange column, purification by solvent extraction	Fluorometric (total uranium)	0.1 µg/L	75% at 0.1–100 µg/L	Dupzyk and Dupzyk 1979
	Sample digestion with $K_2S_2O_8$ and dissolution in water	Laser-induced fluorometry (total uranium)	1 µg/L	86% at 7 µg/L	Hinton and White 1981
	Wet-ashed; solubilized	KPA	~0.050 µg/L	90–110	Birkenfeld et al. 1995
	Acid digestion, purification by coprecipitation and column chromatography	NAA (isotopic quantification)	<6 µg/L	80% at 2 µg added uranium	Pleskach 1985
	Sample with ^{232}U spike wet ashed, clean-up by anion exchange chromatography	Isotope dilution-MS (isotopic quantification)	5 pg (10^{-6} µg) uranium (total chemical blank)	No data	Kelly et al. 1987
	Acidification; dilution	ICP-MS	3 ng/L	No data	Karpas et al. 1996
Soft tissue	Spiked tissues wet ashed; clean-up by coprecipitation, solvent extraction and electrodeposition	α-Spectrometry (total uranium)	0.03 µg/ sample	85–92%	Singh and Wrenn 1988

Table 6-1. Analytical Methods for Determining Uranium in Biological Samples (continued)

Sample matrix	Sample preparation	Analytical method	Detection limit	Accuracy	Reference
Soft tissue	Spiked sample wet digested; purification by anion exchange; loaded into a single ion-exchange bead as a point source for MS	Isotope dilution-MS (isotopic quantification)	<5 pg/L	77%	Kelley and Fassett 1983
Bones	Spiked sample dry ashed; clean-up by coprecipitation, solvent extraction and electrodeposition	α-Spectrometry (isotopic quantification)	0.03 µg/ sample	60–93%	Singh and Wrenn 1988; Singh et al. 1984
Bone ash	Spiked sample wet ashed; clean-up by solvent extraction and electrodeposition	α-Spectrometry (isotopic quantification)	0.4 µg/kg for ^{238}U	>95%	Fisenne et al. 1980
Feces	Spiked sample dry and wet ashed; clean-up by coprecipitation, solvent extraction and electrodeposition	α-Spectrometry (isotopic quantification)	0.03 µg/ sample	58%	Singh and Wrenn 1988
	Sampled dried; wet-ashed; homogenization; dissolution in acid	ICP-MS	3 ng/g	No data	Twiss et al. 1994
Lung, liver, kidney, thyroid, bone	Sample wet or dry ashed, irradiation	^{3}He neutron analyzer	0.04 ng/ sample	No data	Gonzales et al. 1988

[a] This detection limit was reported by Melgard 1988.

ICP = inductively coupled plasma spectrometry; KPA = kinetic phosphorescence analysis; MS = mass spectrometry; NAA = neutron activation analysis

The MTL for ^{234}U, ^{235}U, and ^{238}U using α-spectroscopy is 0.54 pCi/L in urine. An acceptable minimum detection activity of 20 µg/L of urine has also been established for natural uranium based on mass determination (HPS Standard N13.30 1996). Determining the accuracy and precision of the quantification methods for biological materials by either *in vivo* or *in vitro* methodologies requires that standard, certified sources with known concentrations of appropriate radionuclides be available for calibrations. The primary source of certified standards is the National Institute of Standards and Technology (NIST) (Inn 1987). An aqueous solution of uranium containing 10 mg/mL (SRM 3164) standard stock solution is available, as are solutions of ^{232}U (1.1 nCi/g [40 Bq/g]) (SRM 4324) and ^{238}U, "natural uranium," (6.7 nCi/g [250 Bq/g]) (SRM 4321B) (NIST 1995). Standard Reference Materials of human lung (SRM 4351) and human liver (SRM 4352) are also available from NIST.

6.2 ENVIRONMENTAL SAMPLES

Two types of methods are commonly used for measurement of uranium in environmental samples. The first are field surveys using portable survey instruments, and the second is analysis of samples procured in the field that are returned to the laboratory for quantification.

6.2.1 Field Measurements of Uranium

Uranium measurements in the field are typically qualitative in nature in that the instruments simply respond to alpha emissions, regardless of their isotopic origin. However, the levels can be measured quantitatively if key parameters are known, such as relative abundances of all alpha-emitting isotopes present, the thickness of the layer being assessed, and the detection efficiency of the instrument for the type of surface being assessed. Measurements in the past have typically been made using a portable, hand-held alpha scintillation detector (e.g. ZnS) equipped with a count rate meter, which detects alpha radiation while discriminating against beta-emitters in the same area. However, the need for low detection limits in radiological remediation efforts has found a more suitable and sensitive instrument in the large-area gas-flow proportional counter. These instruments can be carried by an individual or attached to a holder for maintaining a selected surface-to-detector distance. The latter method can be integrated into a system which moves along a surface at a predetermined velocity recording spatially-related real-time data for later graphical imaging of absolute surface activity distributions (DOE 1988). These surveys can also be performed on people whose skin or clothing is contaminated. Survey instruments can provide a quick

estimate or a measure of the level of activity that might be present. However, more accurate measurement of uranium activity may require that samples be taken for laboratory analyses. Under normal usage, the lowest level of uranium that can be reliably detected using an alpha scintillation survey meter is 200–500 disintegrations per minute/100 cm^2 (0.09–0.23 nCi/100 cm^2) (DOE 1988); however, detection of levels several time lower is practical with gas flow proportional counters, especially when used in the integrate mode. Detection capability varies with the type of detector used, the active area of the probe, the electronics, etc.

Several limitations are associated with the measurement of uranium by portable survey instruments. First, the uranium must be present on the surface of the material being surveyed. Since uranium decays by emission of α particles, which travel only short distances in materials, any uranium that is imbedded in the surface being surveyed will be partially or completely masked . Secondly, when performing surveys, it must be possible to place the detector very close to the surface being surveyed (i.e., approximately one-quarter of an inch) (DOE 1988, 1994), and uneven surfaces that are unintentionally touched can tear the detector window, disabling the instrument. Additional information is available in MARSSIM (1997) on the use and usefulness of field survey instruments.

6.2.2 Laboratory Analysis of Environmental Samples

Analytical methods for measuring uranium in environmental samples are summarized in Table 6-2. The available methods can be divided into two groups: chemical methods to determine the total mass of uranium in a sample, and radiological methods to determine amounts of individual isotopes. Environmental media that have been tested for uranium include air filters, swipes, biota, water, soil, and others; a full range of laboratory analysis methods has been used to quantify the total uranium or its individual isotopes. The equipment and methods tend to improve over time. The radiological analysis methods primarily use high resolution α-spectroscopy, although gamma spectroscopy is usable with great care. The chemical methods which are often used include spectrophotometry, fluorometry, and kinetic phosphorescence, with the recent addition of various mass spectrometer applications (ICP-MS, AES-MS, and accelerator-MS). If conversions between mass and activity are to be made accurately, prior knowledge of the relative abundance of the various uranium isotopes must be available or measured radiologically. A few media-specific methods which have been used successfully for measuring uranium concentrations in environmental samples are described below. The current trend, however, is away from prescriptive methods and toward

Table 6-2. Analytical Methods for Determining Uranium in Environmental Samples

Sample matrix	Sample preparation	Analytical method	Sample detection limit	Accuracy	Reference
Air	Air particulate collection on glass fiber filter; digestion in HNO_3	ICP-MS (total uranium)	0.1 µg/L in final solution	No data	Boomer and Powell 1987
Air	Spiked air particulate dry and wet ashed; dissolution; coprecipitation with iron hydroxide and Ca oxalate, purification by solvent extraction and electrodeposition onto platinum	α-Spectrometry (isotope quantification)	0.02 dpm/L[b] for ^{238}U in solution	No data	Singh and Wrenn 1988
Air	Sample collection on cellulose filters; ashing; extraction with triisooctylamine; purification by anion exchange chromatography and coprecipitation.	α-Spectroscopy	0.015 pCi	No data	EPA 1984b
Air	Collection on cellulose filters	INAA	0.03 µg per filter	No data	Querol et al. 1997
Rainwater	Coprecipitation with iron hydroxide, radiochemical, ion-exchange and solvent extractive purification, and electrodeposition on steel	α-Spectrometry (isotope quantification)	0.02 dpm/Lfor ^{238}U in solution[a]	68%	Jiang et al. 1986
Drinking water	Direct analysis or concentration by co-precipitation and solvent extraction; fusion	Fluorometry (total uranium)	<20 µg/L (direct); 0.1 µg/L (cleaned)	104% (cleaned)	Krieger and Whittaker 1980 (EPA Method 908.1)
Drinking water	Concentrated by co-precipitation; separation; clean-up by ion-exchange	Gross α-counting (total uranium)	1 pCi/L	92.6%	Krieger and Whittaker 1980 (EPA Method 908.0)

Table 6-2. Analytical Methods for Determining Uranium in Environmental Samples (continued)

Sample matrix	Sample preparation	Analytical method	Sample detection limit	Accuracy	Reference
Drinking water	Sample chelation in EDTA; addition of Fluron	Laser-induced fluorometry	0.08 µg/L	100% at 1 µg/L	Velten and Jacobs 1984 (EPA Method 908.2)
Natural waters	Sample concentration by cation-exchange resin, separation by ion-exchange resin and complexation with Arsenazo III	Spectrophotometry (total uranium)	0.1 µg/L	80%	Paunescu 1986
Water	Sample fusion with NaF and LiF	Fluorometry (total uranium)	5 µg/L	117.5% at 6.3 µg/L	ASTM 1986 (ASTM Method D2907-83)
Water	Coprecipitation with iron hydroxide; purification by ion-exchange chromatography and electrodeposition	α-Spectrometry (isotope quantification)	0.02 dpm/L	97.7–108% at 0.028–0.044 Bq/L	ASTM 1986 (EPA Method D3972-82)
Water	Solvent extraction; coprecipitation with $BaSO_4$; dissolution in $HClO_4$; reprecipitation with TiF_3; filtration	α-Spectrometry (isotope quantification)	0.02 dpm/L[b] for ^{238}U	No data	Stewart et al. 1988
Water	Preconcentration by complexation with oxine and adsorption on activated carbon	NAA (total uranium)	3 µg/L	>80%	Holzbecher and Ryan 1980
Water	Preconcentration by ion-exchange chromatography; purification by ion-exchange and solvent extraction	NAA (^{235}U and ^{238}U)	No data	No data	Gladney et al. 1983
Water	Extraction by ion-exchange; dissolution in low oxygen solvent; irradiation	Delayed neutron analysis (total uranium)	0.4 µg/L	No data	Zielinski and McKown 1984

Table 6-2. Analytical Methods for Determining Uranium in Environmental Samples (continued)

Sample matrix	Sample preparation	Analytical method	Sample detection limit	Accuracy	Reference
Water	Wet-ashed; reaction with complexant	Pulsed-laser phosphorimetry	0.05 ppb	103 (average)	ASTM 1994 (Method 5174-91)
Water (uranyl nitrate)	Solvent extraction	Fluorescence spectroscopy	6.1-10.5 ppm	No data	ASTM 1994 (Method D4763-88)
Groundwater	Separaration on resin; automated	FI-ICP-MS (isotope quantification)	0.3 ng/L for ^{238}U	±1.8%	Aldstadt et al. 1996
Groundwater	Separation and concentration on two HPLC columns; complexation with Arsenazo III	Spectrophotometry (total uranium)	1–2 µg/L	No data	Kerr et al. 1988
Water and wastes	Acid digestion; filtration (dissolved); acid digestion (total recoverable)	ICP-MS (total uranium)	0.1 µg/L	105–110%	Long and Martin 1991 (EPA Method 200.8)
Seawater	Uranium enriched by chelation with APDC in the presence of Fe^{+2}, complexation with APDC followed by adsorption on activated carbon	X-ray fluorescence (total uranium)	0.56–0.64 µg/L	No data	Nagj et al. 1986
Seawater	Oxine addition	Cathodic stripping voltametry (total uranium)	0.02–0.2 nM	No data	Van den Berg and Nimmo 1987
Sediment	Sediment dried and well-mixed; dissolution in HCl-$HClO_4$-HF; purification by coprecipitation, ion exchange and electrodeposition	α-Spectrometry (isotope quantification)	No data	No data	Anderson and Fleer 1982
Soil	Soil leached with HCl-HNO_3-HF; purification by ion-exchange, and solvent extraction, and electrodeposition	α-Spectrometry (isotope quantification)	No data	No data	Golchert et al. 1980

Table 6-2. Analytical Methods for Determining Uranium in Environmental Samples (continued)

Sample matrix	Sample preparation	Analytical method	Sample detection limit	Accuracy	Reference
Soil	Dissolution in HCl-HNO_3-HF; purification by coprecipitation, solvent extraction and electrodeposition	α-Spectrometry (isotope quantification)	0.03 µg/sample	67%	Singh and Wrenn 1988
Soil, sediment, and biota	Ashing; fusion with KF and $K_2S_2O_7$; purification by extraction with triisooctylamine, anion exchange chromatography and coprecipitation.	α-Spectroscopy	No data	No data	EPA 1984b
Soil, sediment, and biota	Ashing; extraction into triisooctylamine, strip from triisooctylamine with HNO_3 and coprecipitation with lanthanum.	gross α-Spectroscopy or α-Spectroscopy	No data	No data	EPA 1984b
Minerals	Dissolution in HNO_3-HF-$HClO_4$; purification by solvent extraction	Laser fluorometry (total uranium)	No data	No data	Veselsky et al. 1988
Low level radioactive waste	Dissolution; purification by coprecipitation, ion-exchange and electrodeposition	α-Spectrometry (isotope quantification)	0.03 dpm	No data	Wessman 1984
Building materials and lichen	Wet ashing with HNO_3-H_2O-HF; purification by coprecipitation, solvent extraction and electrodeposition	α-Spectrometry (isotope quantification)	0.03 µg/sample	54–73%	Singh and Wrenn 1988
Vegetation	Sample dried and homogenized; dry and wet ashing	ICP-MS (total uranium)	0.1 µg/L in final solution	No data	Boomer and Powell 1987
Vegetation	Sample dried and homogenized; wet ashing and purification by solvent extraction	Laser fluorometry (total uranium)	0.05 mg/kg in plant ash	No data	Harms et al. 1981
Process water	Dilution and filtration water	Laser fluorometry (total soluble uranium)	0.01 µg/L[b]	No data	Hinton and White 1981

Table 6-2. Analytical Methods for Determining Uranium in Environmental Samples (continued)

Sample matrix	Sample preparation	Analytical method	Sample detection limit	Accuracy	Reference
Process water	Direct analysis	Ion chromatography spectrophotometric detection (U^{+6})	0.04 mg/L	No data	Byerley et al. 1988
Field survey	None	Scintillation detector and count rate meter	200–500 dpm/ 100 cm^2 (scintillation detector)	No data	ANSI 1978 (ANSI Standard N323)

[a] This detection limit was reported by Melgard 1988.
[b] This detection limit was reported by Wessman 1984.

APDC = ammonium pyrrolidine dithiocarbamate; Bq = Bequerel and 1 pCi = 0.37 Bq; dpm = disintegration per minute and 1 pCi = 2.22 dpm; EDTA = ethylenediaminetetraacetic acid; FI = flow injection; HPLC=high performance liquid chromatography; ICP = inductively coupled plasma spectrometry; INAA = instrumental neutron activation and analysis; MS = mass spectrometry; NAA = neutron activation analysis; nM = nanomole or 10^{-9} of a mol

performance-based methods which enable the user to optimize their available analytical tools. A cornerstone of this method is the development of Data Quality Objectives and the use of Data Quality Assessment to ensure that the selected method is properly developed and the results are of the appropriate quality (DOE 1997; EPA 1994b, 1996).

DOE's method for analyzing environmental materials is based on a method of Welford et al. (1960) and involves preparing triplicate air, water, and soils samples by concentrating or isolating uranium from the media prior to separation in an anion exchange column, followed by fluorometric analysis (DOE 1997).

In one analytical method for air filters, the air filters are ashed, silica content is volatilized with hydrogen fluoride, uranium is extracted with triisooctylamine, purified by anion exchange chromatography and co-precipitated with lanthanum as fluoride. The precipitated uranium is collected by filtration, dried, and α-spectroscopy is performed (EPA 1984b). The activities of ^{234}U, ^{235}U, and ^{238}U are determined based on the number of counts that appear in the α energy region unique to each isotope. This method is used by the EPA National Air and Radiation Environmental Laboratory for measurement of uranium in air as part of the Environmental Radiation Ambient Monitoring System (see Chapter 5).

Singh and Wrenn (1988) describe a method for uranium isotopic analysis of air filters. Air filters are ashed, redissolved, and co-precipitated with iron hydroxide and calcium oxalate. The uranium is further purified by solvent extraction and electrodeposition. An alpha spectroscopy detection level of 0.02 dpm/L for ^{238}U in solution was reported (Singh and Wrenn 1988).

Considerable work has been done to develop methods for analysis of uranium in water. In 1980, the EPA published standardized procedures for measurement of radioactivity in drinking water which included uranium analysis by both radiochemical and fluorometric methods (Krieger and Whittaker 1980), and more recently developed an ICP-MS method. An example of each is provided below.

The radiochemical method quantifies gross α activity utilizing either a gas flow proportional counter or a scintillation detection system following chemical separation. In the EPA radiochemical method, the uranium is co-precipitated with ferric hydroxide, purified through anion exchange chromatography, and converted to a nitrate salt. The residue is transferred to a stainless steel planchet, dried, flamed, and counted for α particle activity (Krieger and Whittaker 1980).

For the fluorometric method, uranium is concentrated by co-precipitation with aluminum phosphate, dissolved in diluted nitric acid containing magnesium nitrate as a salting agent, and the co-precipitated uranium is extracted into ethyl acetate and dried. The uranium is dissolved in nitric acid, sodium fluoride flux is added, and the samples fused over a heat source (EPA 1980).

The ICP-MS method was developed for measuring total uranium in water and wastes. The sample preparation is minimal—filtration for dissolved uranium, acid digestion for total recoverable uranium. Recovery is quantitative (near 100%) for a variety of aqueous and solid matrices and detection limits are low, 0.1 μg/L for aqueous samples and 0.05 mg/kg for solid samples (Long and Martin 1991).

The EPA developed two methods for the radiochemical analysis of uranium in soils, vegetation, ores, and biota, using the equipment described above. The first is a fusion method in which the sample is ashed, the silica volatilized, the sample fused with potassium fluoride and pyrosulphate, a ^{236}U tracer is added, and the uranium extracted with triisooctylamine, purified on an anion exchange column, coprecipitated with lanthanum, filtered, and prepared in a planchet. Individual uranium isotopes are separately quantified by high resolution alpha spectroscopy and the sample concentration calculated using the ^{236}U yield. The second is a nonfusion method in which the sample is ashed, the silica volatilized, a ^{236}U tracer added, and the uranium extracted with triisooctylamine, stripped with nitric acid, co-precipitated with lanthanum, transferred to a planchet, and analyzed in the same way by high resolution α-spectroscopy (EPA 1984).

The detection capability of any measurement process is an important performance characteristics, along with precision and accuracy. The Lower Limit of Detection (LLD) has been adopted to refer to the intrinsic detection capability of the measurement process (sampling through data reduction and reporting) (USNRC 1984). Factors that influence the LLD include background count rate, sensitivity of detector, and, particularly, the length of time a sample and background are counted. Because of these variables, LLDs between laboratories, employing the same or similar chemical separation procedures, will vary. Additional examples of the techniques for quantification of uranium (as described above) are available, as well as examples of less frequently used techniques. These are identified in Table 6-3.

Determining the accuracy of the analytical methods for environmental samples and for calibrating radiation instrumentation requires that standard, certified radioactive sources with known concentrations of uranium,

Table 6-3. Additional Analytical Methods for Determining Uranium in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Rocks, minerals, nuclear fission products, biological material	Solvent extraction as MHFA complex; optional purification by back-extraction	Spectro-photometric	0.0062 mg/L (with back-extraction)	99–103	Abassi 1989
Ore leachates	Separation as arsenazo III complex	Flow injection; spectro-photometric	6.6 µg/L	No data	Perez et al. 1990
Aqueous solutions	Complexation with o-hydroxy-propiophenone isonicotinoyl-hydrazone	Spectro-photometric	No data	No data	Ramachandraiah et al. 1993
Natural waters	Co-precipitation with $Fe(OH)_3$; selective separation by precipitation; determined as dibenzoyl methane complex	Laser fluorometry	5 ppb	No data	Eral 1989
Rocks, minerals, nuclear fission products and biological material	Solvent extraction as MHFA complex; optional purification by back-extraction	Atomic absorption spectrometry	<0.08 mg/L	No data	Abassi 1989
Phosphate rock and phosphoric acid	Wet digestion; separation by extraction with trioctylphosphine oxide; destruction of complex prior to analysis	Argon plasma emission spectrometry	No data	98–100	Woodis et al. 1980
Uranium tailings (U_3O_8)	Wet digestion; solvent extraction	ICP-OES	No data	101	Feeney et al. 1983
Phosphate rock	Wet digestion; extraction with trioctylphosphine oxide; back-extraction with stripping solution	dc argon ICP	<1 ppm	99–106	Norman et al. 1983
Ground, mine waters	Direct analysis	ICP	low ppm	No data	Greene et al. 1985
Coal ash	Acid digestion; separation with s-thenoyltrifluoric acetone; back-extraction	ICP	29 µg/L	98	Kamata et al. 1987
Seawater	Separation on chelate fiber	ICP-OES	5 µg/L	No data	Chang et al. 1990

Table 6-3. Additional Analytical Methods for Determining Uranium in Environmental Samples (continued)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Apatite minerals	Extraction with 3-phenyl-4-benzoyl-s-isoxazolone	ICP-AES	0.02 mg/L	No data	Fujino et al. 1994
Natural waters	Extraction with s-thenoyltrifluoric acetone and tri-n-butyl phosphate	Stripping voltametry	10^{-10} mol/dm^3	≈90	Mlakar and Branica 1989
Groundwater, soil	Separation as propyl gallate complex	Stripping voltametry	subnanomolar	No data	Wang et al. 1994
Surface soils	*in situ*	Gamma spectrometry	0.1 Bq/g	No data	Miller et al. 1994
Ceramic and plastic semiconductor packaging material	None	NAA with fission track counting	0.02 ppb	No data	Riley 1982
River sediments	None	Instrumental NAA	No data	≈70 (certified materials)	Labrecque et al. 1986
Air samples	Sample collection on filters	Instrumental NAA	2 ng/sample	95	Landsberger and Wu 1993
Sediment, pore water	Dilution	ICP-MS	40 pg/mL	99	Toole et al. 1991
Soil	None	Proton induced fluorescent X-rays	No data	No data	Lazo et al. 1991
		Isotope dilution MS			Wessman 1984
Biological and environmental samples	Complexation with phosphoric acid	Laser phosphorimetry	Sensitivity 10^{-12} g	No data	Bushaw 1984

AES = atomic emission spectrometry; Bq = Bequerel; ICP = inductively coupled plasma (spectrometry); MHFA = N-p-methoxyphenyl-2-furylacrylohydroxamic acid; MS = mass spectrometry; NAA = neutron activation analysis; OES = optical emission spectrometry

or other appropriate radionuclides, be available for use. The primary source of such certified standards is NIST (Inn 1987). An aqueous solution of uranium containing 10 mg/mL (SRM 3164) standard stock solution is available, as are solutions of ^{232}U (1.1 nCi/g [40 Bq/g]) (SRM 4324) and ^{238}U, "natural uranium" (6.7 nCi/g [250 Bq/g]) (SRM 4321B) (NIST 1995). Standard Reference Materials of human lung (SRM 4351) and human liver (SRM 4352) are also available from NIST.

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 uranium 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 uranium.

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 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. Analytical methods with satisfactory sensitivity and precision are available to determine the levels of uranium in human tissues and body fluids. However, improved methods are needed to assess the biological effects of uranium in tissues.

Uranium is in essentially all food, water, and air, so everyone is exposed to some levels. In a study reported by NIOSH (Thun et al. 1981, 1985), enhanced levels of β_2-microglobulin levels were observed in the urine of uranium workers. It was postulated that enhanced excretion of β_2-microglobulin might be used as an indication of uranium exposure; however, Thun et al. (1981, 1985) were unable to establish a dose response correlation between level of exposure and excretion of the β_2-microglobulin. Limson-Zamora et al. (1996) identified changes in several potential biomarkers of effect following exposure to uranium, in which each

individual biomarker could be affected by a range of chemicals, but the results suggested that it may be possible to identify a series of biomarkers whose combined responses could serve as a single uranium-specific biomarker of effect. Development of new or combination biomarkers for high uranium exposures would be useful.

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

Whether in the environment or in the human body, uranium will undergo radioactive decay to form a series of radioactive nuclides that end in a stable isotope of lead (see Chapter 3). Examples of these include radioactive isotopes of the elements thorium, radium, radon, polonium, and lead. Analytical methods with the required sensitivity and accuracy are also available for quantification of these elements in the environment where large sample are normally available (EPA 1980, 1984), but not necessarily for the levels from the decay of uranium in the body. More sensitive analytical methods are needed for accurately measuring very low levels of these radionuclides.

6.3.2 Ongoing Studies

The Federal Research in Progress (FEDRIP) database lists ongoing studies investigating new methods for detection and speciation of uranium (FEDRIP 1999). These are shown in Table 6-4.

Table 6-4. Ongoing Studies on Analytical Methods for Uranium

Investigator	Affiliation	Subject	Sponsor
Wang J	New Mexico State University, Dept of Chemistry and Biochemistry Las Cruces, NM	Development of *in situ* microsensor for the measurement of chromium and uranium in groundwater at DOE sites.	DOE
Blancett, A	Aiken SC	Fiber optic sensor for measurement of uranium in solution.	DOE
Hainfeld JF	Brookhaven National Laboratory Upton, NY	Site specific labels for biomolecules: electron microscopy and X-rays.	DOE
Lieser KH	Technische Hochschule Darmstadt, Germany	In-line measurement of U, Pu, and Np in process currents using energy-dispersive X-ray fluorescence analysis.	National Ministry for Research and Technology Bonn, Germany
John A	Los Alamos Nat Lab, Los Alamos NM	P-electron spectroscopy of transuranics.	DOE
Metzger R	Radiation Safety Engineering, Chandler, AZ	A portable gamma spectrometer with a high resolution cdte array detector	DOD, Defense Special Weapons Agency

DOE = Department of Energy; DOD = Department of Defense

Source: FEDRIP 1999