6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods available for detecting and/or measuring and monitoring thorium 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 thorium. 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 thorium in environmental samples are the methods approved by federal agencies such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Other methods presented in this chapter are those that are approved by a trade association such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that refine previously used methods to obtain lower detection limits, and/or to improve accuracy and precision.

6.1 BIOLOGICAL MATERIALS

Some of the methods commonly used for the determination of thorium in biological materials are given in Table 6-1. The calorimetric methods are not capable of isotope-specific determination of thorium isotopes. Alpha spectrometric and neutron activation analysis are useful in the quantification of isotope-specific thorium and thorium-232, respectively, and have better sensitivities than calorimetric methods. Alpha spectrometry is the commonly used isotope-specific analysis for the determination of thorium-232 and the thorium-230 derived from the decay of uranium-238 (Wrenn et al. 1981). Standard reference materials (SRMs) containing thorium in human liver (SRM-4352) and human lung (SRM-4351) necessary for the determination of absolute recovery in a given sample are available from the National Institute of Standards and Technology (Inn 1987).

In vitro monitoring methods for the analysis of thorium in urine, feces, hair, and nails have been used to show that none of these biological media is a good indicator of thorium uptake, and hence thorium exposure in the human. In vivo monitoring with large NaI detectors are probably good methods for determining thorium lung burdens. In one method, thoron (radon-220) is determined in exhaled air as a measure of thorium lung burden. The exhaled air is passed to a delay chamber where the positively-charged decay products of thoron (e.g., polonium-216 and lead 212) are collected electrostatically and the collection electrode is measured in an alpha scintillation counter. The method has the required sensitivity to be used as an indicator of thorium uptake. However, because of lack of information regarding the thoron escape rate from the thorium particles in the lungs, the method is not accurate for indicating lung uptake of thorium (Davis 1985). Several authors have measured the levels of exhaled thoron or its decay products in human breath (Keane and Brewster 1983; Mayya et al. 1986).

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

Sample Matrix	Sample Preparation	Analytical Method	Detection	Accuracy[a] Limit	Reference
Soft tissues (lung, lymph nodes, liver, kidney, spleen, heart, gonads, thyroid, and muscle)	Tissue spiked with Th-229 wet ashed with acid mixtures, coprecipitated with Fe-hydroxide, cleaned up by complexation and electrodeposited.	alpha-spectrometry	0.005 pCi/kg	59-68%	Singh et al. 1979; Singh and Wrenn 1988
Bones	Bones spiked with tracer dry ashed, Th coprecipitated with Fe-hydroxide, cleaned up by complexation and solvent extracted and electrodeposited.	alpha-spectrometry	0.005 pCi/kg	62-73%	Singh et al. 1979; Singh and Wrenn 1988
Blood, urine, ashed bone	Samples wet ashed, dried in quartz ampules, sealed and irradiated in a reactor. ^{233}Pa in the cooled irradiated sample was cleaned up by multiple column chromatography, and solvent extracted and evaporated on counting planchettes.	NAA, gamma-counting	<0.2 pg/mL	60% at 0.045 µg	Picer and Strohal 1968
Urine and feces	Tracer-spiked sample wet ashed, Th coprecipitated with Fe-hydroxide, cleaned up by complexation, and solvent extracted and electrodeposited.	alpha-spectrometry	Not reported	56-66%	Singh and Wrenn 1988
Urine	Acidified sample precipitated with NH_4OH, irradiated with thermal neutron, reprecipitated with La-hydroxide and precipitate dissolved in acid.	NAA, gamma-counting	<1 ng/L	Not reported	Twitty and Boback 1970
	Precipitated Th with La-fluoride, clean-up by complexation and solvent extraction, develop color as thorium-morin complex.	Colorimetrically	0.095 µg/ 500 mL	Not reported	Perkins and Kalkwarf 1956

TABLE 6-1 (Continued)

Sample Matrix	Sample Preparation	Analytical Method	Detection	Accuracy[a] Limit	Reference
Bones	Dry ash bone, dissolve ash in acid, clean-up by solvent extraction and ion-exchange method, develop color with Arsenzazo III.	Colorimetrically	Not reported	96-99%	Petrow and Strehlow 1967
Bone marrow	Paraffin-embedded tissue, deparaffinized and stained.	Energy dispersive x-ray	Not reported	Not reported	Bowen et al. 1980

[a]Where accuracy value is not available, the recovery data are given.

NAA = neutron activation analysis.

6. ANALYTICAL METHODS

6.2 ENVIRONMENTAL SAMPLES

Some of the commonly used methods for the determination of thorium in environmental samples are shown in Table 6-2. Standard reference materials (SRMs) for thorium in river and freshwater lake sediment (SRM-4350B and SRM-4354), soils (SRM-4355 and SRM-4353), coal (SRM-1632), and fly ash (SRM 1633) are available from the National Institute of Standards and Technology (formerly National Bureau of Standards) (Inn 1987; Ondov et al. 1975). Neither calorimetric nor atomic absorption/emission methods are suitable for the determination of thorium-specific isotopes; these methods are also not sensitive enough for the quantification of trace amounts of thorium, e.g., in seawater. The filtration of particulate phases by inert polypropylene fiber filter and adsorption of solution phase thorium onto $Mn0_2$-coated fiber or preconcentration of thorium on XAD-2 resin by adsorption of thorium-Xylenol Orange complexes and quantitation by alpha spectrometry or neutron activation analysis are two of the better methods for the quantification of low levels of thorium in water (Hirose 1988; Huh and Bacon 1985; Livingston and Cochran 1987). The isotope dilution-mass spectrometric method provides the most accurate and sensitive thorium quantification (Arden and Gale 1974) but is rarely used because of the specialized nature and the cost of the analytical technique. The beta counting of thorium deposited on counting discs is useful for the determination of thorium-234 derived from uranium-238 (Velten and Jacobs 1982). The direct gamma radiation counting with a Ge planer detector has been used for the quantification of thorium-228 in grass samples (Joshi 1987). The recoveries of thorium from soil and sediment samples are usually poor (Singh and Wrenn 1988) and special attention should be given to sample treatment during their analysis.

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 thorium 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 thorium.

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.

TABLE 6-2. Analytical Methods for Determining Thorium in Environmental Materials

Sample Matrix	Sample Preparation	Analytical Method	Detection Limit	Accuracy[a]	Reference
Air	Particulate matter collected on filter wet ashed, fused with LiF and H_2SO_4, interference eliminated by complexation and fluorescence developed in buffered solution with 3,4,7-trihydroxyflavanone.	Fluorescence	0.03 μg	Not reported	Sill and Willis 1962; Filer 1970
	Particulate matter collected on filter wet ashed, fused with $K_2S_2O_7$, coprecipitate Th with $PbSO_4$, dissolve in DTPA, clean-up by complexation, extract Th in aqueous oxalic acid and electrodeposit Th.	α-Counting	5 fCi/m^3	96%	Percival and Martin 1974
	Filter spiked with tracer, dry and wet ashed, coprecipitated Fe-hydroxide, cleaned by complexation and extraction and electrodeposited.	α-Spectrometry	0.01 pCi	Not reported	Singh and Wrenn 1988
Water	Sample wet ashed, coprecipitated with Fe-hydroxide, cleaned up by complexation and solvent extracted and electrodeposited.	α-Spectrometry	Not reported	60%	Singh and Wrenn 1988
	Direct aspiration.	AAS	Not reported	Not reported	APHA/AWWA/WPCF 1985
	Dissolve particulate matter in sample by filtrate and acid treatment, combine filtrate and dissolved particulate matter, precipitate Th with Ca-oxalate, develop color with Thorin.	Colorimetrically	<1 ng/g	Not reported	ASTM 1986
Ocean water	Particulate matter filtered by polypropylene fiber filter cartridge and soluble phase collected on MnO_2 impregnated absorber. Each cartridge dried and dissolved in acid, Th purified by anion exchange resin.	α-Spectrometry	<0.2 fCi/L for Th-230	Not reported	Livingston and Cochran 1987

TABLE 6-2 (Continued)

Sample Matrix	Sample Preparation	Analytical Method	Detection Limit	Accuracy[a]	Reference
Drinking water	Thorium coprecipitated from acidified sample with $Fe(OH)_3$, clean-up Th by selective solvent extraction, coprecipitated with $Al(OH)_3$ and develop color by Arsenazo III reagent. After color development, coprecipitate Th with LaF_3.	Colorimetric (for Th-232) α and β Counting (for Th-230 and Th-234) (EPA method 910)	Not reported	98%	Velten and Jacobs 1982
Soil, sediment, ashed vegetation or food and air particulate	Sample dissolved in a mixture of acids, cleaned by anion-exchange resin, electrodeposited on silver disc.	α-Spectrometry	Not reported	Not reported	Golchert et al. 1980
Soil	Sample dissolved in a mixture of acids, Th coprecipitated with Ce-fluoride, cleaned up by solvent extraction and oxalate formation, and solution wet ashed and fused with $NaHSO_4$.	α-Spectrometry	Not reported	95%	Bernabee 1983
Soil	Soil dissolved with acid mixtures, coprecipitated with Fe-hydroxide, cleaned up by complexation and solvent extracted and electro-deposited.	α-Spectrometry	0.01 pCi	18%	Singh and Wrenn 1988
Microelectronic constituent	Sample dissolved in HNO_3, cleaned by solvent extraction.	Colorimetric with Arsenazo III or ICP/MS	Not reported	98.9-100.3%	Saisho et al. 1988
Whole rock	Sample dissolved by alkali and acid digestion, cleaned up by solvent extraction.	ICP/ES	Not reported	97-103%	Korte et al. 1983
Sediment	Sample dissolved in a mixture of acids, cleaned up by anion-exchange resin.	α-Spectrometry	Not reported	20%	Inn 1987
Groundwater	Concentrated Th in sample by column chromatography and coprecipitated with LaF_3.	α-Spectrometry	0.03 pCi/L	102%	Lauria and Godoy 1988

[a]Where accuracy is not available, the recovery data are given.

AAS = atomic absorption spectrometry; DTPA = diethylenetriaminepentaacetic acid; ES = emission spectrometry; fCi = 10^{-15} Ci; ICP = inductively coupled plasma; MS = mass spectrometry.

6.3.1 Identification of Data Needs

Methods for Determining Biomarkers of Exposure and Effect. A few authors have found elevated levels of thorium in tissues of thorium workers and these studies have been discussed in Sections 2.6 and 5.4.4. However, there are no data in the literature that correlate the concentrations of thorium in any human tissue or body fluid with its level of exposure. If a biomarker for thorium in human tissue or fluid were available, the level of the biomarker in a tissue could be used as an indicator of exposure to thorium. Analytical methods with satisfactory sensitivity are available to determine the levels of thorium in most human tissues and body fluids of exposed and background population, but the recovery of thorium by these methods needs further refinement.

No studies were located that identified biomarkers specific to thorium-induced disease states. If a biomarker for thorium-induced effect in humans were found, this effect could also be used as an indicator of exposure to thorium. Therefore, there is a need to develop biomarkers that will serve as indicators of exposure and effect from exposure to uranium. It may be necessary to develop analytical methods of satisfactory sensitivity and precision for the quantification of thorium-induced effects in humans.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Analytical methods with required sensitivity and precision are available for the quantification of thorium in most environmental samples. However, some of the more sensitive analytical methods have not always been used for the determination of thorium concentrations in drinking water and food. Knowledge of the levels of thorium compounds in environmental media can be used to indicate human exposure to thorium through inhalation of air and ingestion of drinking water and foods containing these compounds. The concentration of thorium is usually very low in drinking water and food and the more sensitive methods may not always have been used for quantification. Because of this, there is controversy in the literature about the relative importance of drinking water and food in contributing to the total dietary daily intake of thorium. It will be helpful to reevaluate the concentrations of thorium in drinking water and food by using the more sensitive analytical methods.

In the environment, thorium and its compounds do not degrade or mineralize like many organic compounds, but instead speciate into different chemical compounds and form radioactive decay products. Analytical methods for the quantification of radioactive decay products, such as radium, radon, polonium and lead are available. However, the decay products of thorium are rarely analyzed in environmental samples. Since radon-220 (thoron, a decay product of thorium-232) is a gas, determination of thoron decay products in some environmental samples may be simpler, and their concentrations may be used as an indirect measure of the parent compound in the environment if a secular equilibrium is reached between thorium-232 and all its decay

products. There are few analytical methods that will allow quantification of the speciation products formed as a result of environmental interactions of thorium (e.g., formation of complex). A knowledge of the environmental transformation processes of thorium and the compounds formed as a result is important in the understanding of their transport in environmental media. For example, in aquatic media, formation of soluble complexes will increase thorium mobility, whereas formation of insoluble species will enhance its incorporation into the sediment and limit its mobility.

6.3.2 On-going Studies

Under the sponsorship of the National Science Foundation and in collaboration with scientists in New Zealand, Burnett of Florida State University is attempting to develop a chemical separation technique for uranium, thorium, and their daughter products (Federal Research in Progress 1990). Other than this research, no studies are in progress for improving the method for the quantification of thorium and daughter products in biological and environmental samples.