6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring thallium 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 thallium. 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 thallium 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 groups 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.

Thallium is almost always determined as total metal, rather than specific thallium compounds. Among the wide range of techniques that can be used to measure thallium are spectrophotometry, mass spectrometry, voltammetry, neutron activation analysis, and x-ray fluorimetry (Sharma et al. 1986). However, direct aspiration atomic absorption analysis is the most widely used and straightforward method for determining thallium; furnace atomic absorption analysis is used for very low analyte levels and inductively coupled plasma atomic emission analysis for multianalyte analyses that include thallium.

6.1 BIOLOGICAL MATERIALS

Methods for detection of thallium in biological materials are summarized in Table 6-1. Normally, for determination in biological samples, the sample is digested in an oxidizing acid mixture, such as 3:1:1 (v/v/v) nitric:perchloric:sulfuric acid mixture (Kneip and Crable 1988), followed by atomic spectrometric determination. Alternatively, thallium can be extracted from biological samples such as blood or urine by chelating agents such as diethylthiocarbamate in methylisobutylketone and measured by atomic absorption analysis.

6.2 ENVIRONMENTAL SAMPLES

Methods for the determination of thallium in environmental samples are summarized in Table 6-2. Thallium is readily measured in multielement analyses of air, water, and solid waste samples by inductively coupled plasma atomic emission spectroscopy. For individual analyses of thallium, direct aspiration atomic absorption spectroscopy is a very convenient method of analysis; if lower detection limits are needed, furnace atomic absorption analysis can be employed. Other sensitive means of measuring thallium include anodic stripping voltammetry and laser-excited atomic fluorescence spectroscopy, which have been used for biological samples (see Table 6-2).

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Biotic materials	Combustion in oxygen stream	ASV and AAS	No data	No data	Kaiser and Tolg 1986
Blood and tissue	Acid digestion	ICP/AES	No data	131% recovery at 10 mg/sample	Kneip and Crable 1988
Blood and urine	Extraction into methyl-isobutylketone with diethyldithiocarbamate chelating agent	AAS	<3 µg/L[a]	No data	Baselt 1988
Blood and tissue	Acid digestion	ICP/AES	1 µg/100g blood, 0.2 µg/g tissue	106% 4.9% RSD	NIOSH 1984a
Bovine liver, mouse brain tissue	No data	LEAFS	No data	No data	Dougherty et al. 1988
Liver, kidney	Digestion by proteolytic enzyme	AAS	No data	No data	Carpenter 1981
Urine	Acid digestion	ASV	1 µg/L	95% recovery at 16 µg/L	Angerer and Schaller 1985
Urine	Extraction into toluene with sodium diethylthio-carbamate chelting agent	AAS	0.1 µg/L	95%-98% 3.5%-4.4% RSD	Chandler and Scott 1984
Urine	Dilution	AAS	0.5 µg/L	No data	Paschal and Bailey 1986

[a]Estimated from cited values of normal blood thallium concentration.

AAS = atomic absorption spectroscopy; ASV = anoidc stripping voltammetry (inverse voltammetry); ICP/AES = inductively coupled plasma atomic emission spectroscopy; LEAFS = laser excited atomic fluorescence spectroscopy; RSD = relative standard deviation

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Collection on filter, workup in acid	AAS	No data	No data	Sittig 1985
Air	Collection on filter; workup in acid	ICP/AES	1 µg per sample	103% recovery at 2.5 µg per sample	NIOSH 1984b
Water	Acidify with nitric acid	AAS (direct aspiration)	0.1 mg/L	98±1.7% at 3 mg/L	APHA 1985
Water	Acidify with nitric acid	AAS (direct aspiration)	0.1 mg/L	No data	EPA 1983a
Water	Acidify with nitric acid	AAS (furnace technique)	1 µg/L	No data	EPA 1983b
Water	Digestion for total thallium, filtration through 0.45 micron filter followed by digestion for dissolved thallium	AAS	No data	No data	Sittig 1985
Wastewater	Acid digestion	ICP/AES	40 µg/L	No data	EPA 1985a
Solid waste	Acid digestion	AAS (direct aspiration)	0.1 mg/L[a]	98±1.7% at 3 mg/L	EPA 1986a
Solid waste	Acid digestion	AAS (furnace technique)	1 µg/L[a]	No data	EPA 1986b
Solid waste	Acid digestion	ICP/AES	40 µg/L[a]	No data	EPA 1986c
Solid environmental samples	No data	AAS (electrothermal)	No data	No data	DeRuck et al. 1989

[a]Detection limit for thallium in liquid sample digestate.

AAS = atomic absorption spectroscopy; ICP/AES = inductively coupled plasma atomic emission spectroscopy

6.3 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 thallium 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 thallium.

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 Data Needs

Methods for Biomarkers of Exposure and Effect. The only means available to indicate exposure to thallium is detection of thallium in tissue and biological fluids. Sensitive, specific, readily used atomic spectrometric techniques are available for the detection and quantitative measurement of thallium after the sample matrix in which it is contained has been digested with oxidant acids or after thallium has been extracted with methylisobutylketone (Baselt 1988). The determination of specific compounds that contain thallium are relatively unimportant because of the uncomplicated chemistry of this element and there is no evidence in the literature for the production of metabolites. If such metabolites do in fact exist, methods for their determination would be useful in monitoring exposure to thallium. Studies are needed to determine whether solid tissues provide a "matrix effect" biasing the accuracy of determinations from tissues. Thallium exists in both stable univalent (I) and trivalent (III) states. Additional studies would be useful in clarifying if relative concentration of thallium in various tissues would be affected by the valence or if there is a biochemical conversion of Tl^{+} and $T1^{3+}$ into a single species.

Biomarkers for effects of thallium intoxication are alopecia, neurological effects, and albuminuria (Baselt 1988), which are indicative of exposure to many other toxicants as well. Therefore, methods are needed for more specific biomarkers for effects of thallium exposure.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Methods for determining the parent compound, thallium, in water, air, and waste samples with excellent selectivity and sensitivity are well developed (EPA 1983a,b, 1985a, 1986a, b,c; NIOSH 1984b), so the database in this area is good and undergoing constant improvement.

Sampling methodologies for very low-level elemental pollutants such as thallium continue to pose problems such as nonrepresentative samples, insufficient sample volumes, contamination, and labor-intensive, tedious extraction and purification procedures (Green and LePape 1987).

6.3.2 On-going Studies

Examination of the literature suggests that studies are underway to improve means for determining thallium and other heavy metals in biological samples and environmental media. Improvements continue to be made in detection limits and ease and speed of analysis.