7. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting, measuring, and/or monitoring boron, its metabolites, and other biomarkers of exposure and effect to boron. 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

Methods for the determination of boron in biological materials are summarized in Table 7-1. Methods for the determination of boron in samples of toxicological interest have been summarized (Stokinger 1981; Van Ormer 1975). Total boron is usually determined after the material is digested or ashed. No techniques are available to quantitatively analyze for specific boron compounds in biological matrices (Culver et al. 1994a). The most common analytical procedure to analyze boron in biological materials involves digestion of the sample in hot acid or base, followed by analysis of the resulting solution by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Culver et al. 2001).

Goullé et al. (2005) assessed inductively coupled plasma–mass spectrometry (ICP-MS) for detecting metals and metalloids in whole blood, plasma, urine, and hair. ICP-MS is a fast, sensitive method that requires a small sample size. Analysis required 0.4 mL of blood, plasma, or urine and 25 mg of hair. Usuda et al. (1998) noted that boron levels in urine can be influenced by dietary intake of boron and recommended that the intake of large amounts of boron-rich foods or drinks should be avoided if the boron status is being evaluated for possible environmental- or labor-related exposure. Xing et al (2008) suggested that creatinine-corrected, post-shift urine boron concentration can be used as a biomarker of human boron exposure in worker populations when monitored by ICP-MS.

Colorimetric analysis can also be used to determine boron concentrations in biological samples; however, colorimetric procedures are more time-consuming and require more laboratory care and technical skill

Table 7-1. Analytical Methods for Determining Boron in Biological Materials

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Urine	Dilution; direct analysis	ICP-AES	6.24 µg/L	100.8–104.2%	Usuda et al. 1998
Whole blood, plasma, urine	Dilution with purified water, acid, buffer, and butanol	ICP-MS	1.33 µg/L (blood) 1.26 µg/L (plasma) 0.25 µg/L (urine)	No data	Goullé et al. 2005
Hair	Mineralization after decontamination with water/acetone	ICP-MS	0.14 ng/mg	No data	Goullé et al. 2005
Blood	Ashed by oxygen in a Parr bomb, dissolved	Colorimetric carmine method	<100 µg/L	84% at 5 µg/mL	Hill and Smith 1959
Serum (borate)	Deproteinized, allowed to react with reagent	Colorimetric carmine method	Greater than endogenous levels, which are <20 mg/L	92–104%	Baselt 1988

ICP-AES = inductively coupled plasma-atomic emission spectroscopy; ICP-MS = inductively coupled plasma-mass spectrometry

(Culver et al. 2001). Spectrophotometric methods suffer from interferences from other elements (e.g., Al, Cu, Fe, Zn, and Mo), as well as pH (Sah and Brown 1997).

Neutron activation analysis (NAA) is another analytical technique used to determine boron in biological samples. In NAA, the sample is bombarded with neutrons, and the element of interest is made radioactive. The amount of the element present in the sample is then determined by measurement of the radioactivity or radioactive decay products. This process involves ^{10}B, which is a naturally occurring, stable isotope of boron that occurs with about 20% abundance. When ^{10}B is bombarded with neutrons, it does not become radioactive, but results in a neutron-capture reaction, resulting in the emission of a α-particle and γ-photon. NAA methods for boron determination are based on the measurement of one of more of the products (α-particle and γ-photon), using techniques such as neutron activation mass spectrometry (NA-MS) or prompt γ-ray spectroscopy. An advantage of NAA is that it is a nondestructive method. However, the requirements of a neutron source and the abundance of ^{10}B restrict its use (Culver et al. 2001; Sah and Brown 1997).

7.2 ENVIRONMENTAL SAMPLES

Methods for the determination of boron in environmental samples are summarized in Table 7-2.

Boron is readily measured in multielement analyses of air, water, and solid waste samples by ICP-AES atomic emission spectroscopy, the method of choice for the determination of boron in modern practice. Although not multielement procedures, colorimetric cucumin and colorimetric carmine methods are still reliable methods for the determination of boron in water, air, and solid waste samples (APHA 1998b; 1998c; EPA 1983). These colorimetric procedures provide adequate methods when ICP instrumentation is not available. Alkali fusion or wet digestion with hydrofluoric acid or a mixture of hydrofluoric acid and other acids are used to digest soils and other geological and silica-rich materials (Sah and Brown 1997). A highly sensitive and selective method for determining boron at ng/dm^3 levels was developed by Takahashi et al. (2008) by derivatization reaction of boron with reversed-phase partition high-performance liquid chromatography (HPLC) separation and ultraviolet spectrophotometric detection. A detection limit as low as 22 ng/dm^3 was achieved without any preconcentration. No significant interference was observed in the determination of 16 μmol/dm^3 of boron with the addition of nine metal ions (Al^{3+}, CuI^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, V^{5+}, and Zn^{2+}) at concentrations 100 times greater than that of boron (Takahashi et al. 2008).

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Collection on filter, hot block/HCl/HNO_3 digestion followed by dilution with water	NIOSH Method 7303 ICP-AES	0.0094 µg/L 0.71 µg/sample	No data	NIOSH 2003
Air (boron carbide)	Collection on filter, ashed, suspended in 2-propanol, redeposited on silver membrane filter	NIOSH Method 7506 X-ray powder diffraction	0.05 mg/ sample	No data	NIOSH 1994
Air (boron trifluoride)	A known volume of air is drawn through a solution of ammonium fluoride; fluoroborate ion is measured using an ion specific electrode	OSHA Method ID216SG Fluoroborate ion specific electrode	10 µg or 0.4 µg/mL of solution	No data	OSHA 1989b
Water	Acidify, inject	APHA Method 3120 ICP-AES	5 µg/L	115.46%[a] 27% RDS[a]	APHA 1998a
Water	Direct analysis	APHA Method 4500-B Colorimetric curcumin	0.2 µg	22.8% RSD	APHA 1998b
Water	Ash, dissolve in acid	APHA Method 4500-B Colorimetric carmine	2 µg	35.5% RSD	APHA 1998c
Water	Direct analysis	EPA Method 212.3 Colori-metric curcumin[b]	0.1–1.0 mg/L (optimal range)	22.8% RSD	EPA 1983
Water	Filter, acidify	EPA Method 200.7 ICP-AES	3 µg/L	115%[a] 27% RSD[a]	EPA 1994
Water, sediments, solid wastes, sludges	Aqueous and solid matrices require acid digestion prior to analysis; pre-filtered, acidified groundwater samples do not need acid digestion	EPA Method 6010C ICP-AES	3.8 µg/L	No data	EPA 2000
Water	Direct analysis	USGS-NWQL Method I-1114 DCP-AES	Applicable range: 10–1,000 µg/L	5.8% RSD	USGS 1989
Aquatic biological material	Nitric acid digestion followed by treatment with 30% hydrogen peroxide	USGS-NWQL Method B-9001-95 ICP-AES	Not calculable	95–96%	USGS 1996a

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Water	Acidify to a pH <2.0 with nitric acid	USGS-NWQL Method I-1472-95 ICP-AES	Method reporting limit: 4 µg/L	91.6–109%	USGS 1996b
Water	Filter, acidify	USGS-NWQL Method I-2477-92 ICP-AES	0.5 µg/L	70–103%	USGS 1999
Water	Acidify, filter	USGS-NWQL Method I-4471-97 ICP-OES	13 µg/L	98% (average)	USGS 1998

[a]Percent recovery and relative standard deviation were reported by NEMI (2007).
[b]Same method as APHA (1998b).

APHA = American Public Health Association; DCP = direct current plasma; EPA = U.S. Environmental Protection Agency; ICP-AES = inductively coupled plasma-atomic emission spectroscopy; ICP-OES = inductively coupled plasma-optical emission spectroscopy; NIOSH = National Institute for Occupational Safety and Health; NWQL = National Water Quality Laboratory; OSHA = Occupational Safety and Health Administration; RSD = relative standard deviation; USGS = U.S. Geological Survey

Anthropogenic-derived boron concentrations can be effectively distinguished by the the measurement of the ^{10}B to ^{11}B isotopic ratio (Chetelat and Gaillardet 2005; Moore et al. 2008). The natural abundance of ^{10}B and ^{11}B is specific to location, making anthropogenic boron isotopic ratios distinctly different than groundwater (Davidson and Bassett 1993). This allows utilization of the boron isotopic ratio to determine potential contamination in groundwater (Vengosh et al. 1994), river water (Chetelat and Gaillardet 2005), marine water (Xiao et al. 2007), and effluent (Kloppmann et al. 2008).

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 boron is available. Where adequate information is not available, ATSDR, in conjunction with 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 boron.

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

Analytical methods are available and are adequately sensitive to detect boron in biological materials (e.g., blood and urine) and in environmental samples (e.g., water, sediments, and air). No data needs are identified at this time.

Methods for Determining Biomarkers of Exposure and Effect.

Exposure. Boron can be determined sensitively and selectively by ICP-AES and ICP-MS in urine and blood (Goullé et al. 2005; Sah and Brown 1997; Usuda et al. 1998). Analytical methods with satisfactory sensitivity and precision are available to determine levels of boron in human tissues and body fluids.

Effect. Existing methods are sensitive enough to measure background levels for boron in the population and levels at which biological effects occur.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. ICP-AES is a satisfactory multielement method available for the determination of boron in water, air, and solid waste samples (APHA 1998a; EPA 1994; 2000; NIOSH 2003; USGS 1989, 1996a, 1996b, 1999). Colorimetric procedures are as sensitive and precise, but are more labor intensive. Colorimetric procedures do provide adequate methods for those laboratories that do not have ICP instrumentation. An alternative method to the expensive and highly skill-dependent ICP-MS has been developed by boron derivatization and analysis by standard reverse-phase HPLC without sacrificing sensitivity (Takahashi et al. 2008).

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

7.3.2 Ongoing Studies

No ongoing studies pertaining to analytical methods for boron were identified in a search of the Federal Research in Progress database (FEDRIP 2009).