

6. ANALYTICAL METHODS

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

6.1 BIOLOGICAL MATERIALS

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) has been used for measuring low levels of barium in the blood, urine, and bones of humans and animals (Mauras and Allain 1979; Schramel 1988; Shiraishi et al. 1987) (see Table 6-1). In general, biological samples are nebulized and the resulting aerosol is transported to the plasma torch. Atomic-line emission spectra are produced by the inductively coupled plasma for specific element and the intensities of the lines (bands) are monitored by a photomultiplier tube. A line emission at 455.50 nm was observed for barium (Mauras and Allain 1979; Oppenheimer et al. 1984). Detection limits of 0.25 µg barium/L of urine, 0.6 µg barium/L of blood, and 0.0005 µg of barium per gram of bone were achieved (Mauras and Allain 1979; Shiraishi et al. 1987). Advantages of ICP-AES technique include moderate costs, fairly rapid analysis time, and high sensitivity (Mauras and Allain 1979; Oppenheimer et al. 1984). The presence of spectral interferences is a disadvantage of ICP-AES technique. These interferences are caused when a sample contains elements or compounds that have analytical emission lines (bands) that overlap the line chosen for the analyte. Boric acid or sodium borate (at a concentration of greater than 100 mg boron/L of sample) was reported to interfere with the line emission spectra of barium at 455.50 nm (Mauras and Allain 1979).

Neutron activation analysis (NAA) technique has also been used for determining low levels of barium in human blood (Olehy et al. 1966). This technique is based on the interaction of the nuclei of individual barium atoms with neutron irradiation, resulting in the emission of x-rays (photons). Detection limits of 7 µg barium/L of erythrocyte and 66 µg barium/L of plasma were obtained (Olehy et al. 1966). The advantages of the NAA technique are its nondestructive nature of sample and minimum sample manipulation. Disadvantages of this technique include its high costs and a nuclear reactor may not be readily available to many laboratories.

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Urine and blood	Dilute sample with demineralized water, introduce into the plasma and analyze	ICP-AES	0.25 µg/L (urine) 0.6 µg/L (blood)	3%-7% coefficient of variation	Mauras and Allain 1979
Plasma and erythrocyte	Ash sample, digest with acid and irradiate	NAA	7 µg/L (erythrocyte) 66 µg/L (plasma)	28.5% RSD (erythrocyte) 7.6% RSD (plasma)	Olehy et al. 1960
Biological tissues	Digest sample in acid; precipitate as the sulfate and analyze	Gravimetry	No data	No data	Borchardt et al. 1961
Visceral materials (intestine, stomach, liver, spleen, and kidney)	Ash sample and analyze	Spectrography	No data	No data	Baisane et al. 1978
Fetus bones	Ash sample and digest with acid	ICP-AES	0.0005 µg/g	0.5% RSD	Shiraishi et al. 1987

ICP-AES = inductively coupled plasma-atomic emission spectrometry; NAA = neutron activation analysis; RSD = relative standard deviation.

6. ANALYTICAL METHODS

6.2 ENVIRONMENTAL SAMPLES

Atomic absorption spectroscopy (AAS) is the most prevalent analytical technique for measuring low levels of barium and its compounds (i.e., barium carbonate, barium sulfate, and barium chloride) in air, water, waste water, geological materials (calcium carbonate), unused lubricating oil, and diagnostic meals containing barium sulfate (see Table 6-2).

Samples may be prepared for AAS in a variety of ways (Hui-Ming and Yao-Han 1984; Johnson et al. 1983; Murata and Noguchi 1974; Pierce and Brown 1977; Renshaw 1973; Sharp and Knevel 1971; Sugiyama et al. 1984). Acid digestion with nitric acid is the most common method of preparation. Sample dilution with nitric acid or other agents to solubilize barium from the matrix can also be employed. If the concentration of barium in the dissolved sample is very low, preconcentration techniques such as chelation or extraction may be employed.

Flame atomic absorption spectroscopy (FAAS) (Methods 208.1 and 7080) and graphite furnace atomic absorption spectroscopy (GFAAS) (Methods 208.2 and 7081) are the techniques recommended by the Office of Solid Waste and Emergency Response of EPA for determining ppb ($\mu\text{g/L}$) levels of barium in water and waste water (EPA 1979a, 1979b, 1986c). Parts-per-trillion (sub $\mu\text{g/L}$) levels of barium in sea and freshwater have been detected by GFAAS (Epstein and Zander 1979; Roe and Froelich 1984). The advantages that GFAAS and FAAS techniques offer are that they are sensitive techniques, use relatively simple and inexpensive instrumentation, and have high accuracy and precision. In addition, GFAAS technique requires a small amount of sample and is more sensitive than FAAS methodology for determining barium in aqueous media (Edelbeck and West 1970; Oppenheimer et al. 1984).

FAAS (Method 7056) is the technique recommended by NIOSH for detecting soluble barium compounds in air (NIOSH 1987b). Atomic absorption spectroscopy has also been employed for detecting barium in air at 20 ppb (Miner 1969a).

Other analytical techniques that have been employed for measuring barium and its compounds in environmental media include x-ray fluorescence spectroscopy (XFS), neutron activation analysis (NAA), scintillation spectroscopy, and spectrography (Boothe and James 1985; Landis and Coons 1954; Larsen 1973; Murata and Noguchi 1974; Oppenheimer et al. 1984). XFS and NAA methods are less sensitive than other available analytical methods for measuring barium or its compounds in environmental media. Scintillation spectroscopy and spectrography are less commonly used to measure barium in the environment relative to other analytical methods.

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Collect sample on cellulose and extract with hot acid; evaporate extract to dryness and dissolve residue in acid	FAAS	No data	No data	NIOSH 1987b (Method 7056)
Water	Acidify sample and pass through ion-exchange resin	FAAS	3 µg/L	11.6% RSD	Pierce and Brown 1977
	Pass sample through ion-exchange resin	FAES	µg/L levels	No data	Johnson et al. 1983
	Extract sample with buffered HFA solution	FAAS	5 µg/L	No data	Edelbeck and West 1970
	No data	GFAAS	7 µg/L	No data	Fagioli et al. 1984
	Inject sample directly into graphite furnace	GFAAS	0.6 µg/L (seawater) 0.2 µg/L (freshwater)	13% RSD	Roe and Froelich 1984
Water and wastewater	Digest sample and evaporate to dryness; dissolve residue in acid	FAAS, GFAAS	100 µg/L (FAAS) 2 µg/L (GFAAS)	94%-113% (FAAS) 96%-102% (GFAAS)	EPA 1979a, 1979b, and 1986c (Methods 208.1, 208.2, 7080 and 7081)
Industrial wastewater	Digest sample; mix with cation-exchange resin, dry, and analyze	XFS	290 µg/L (on a 500 ml samples)	5.1% RSD	Murata and Noguchi 1974
Unused lubricating oil	Dissolve sample in 2-methylpropan-2-ol: toluene (3:2); add potassium naphthenate solution	FAAS	No data	No data	Holding and Rowson 1975
Rocks and minerals (calcium carbonate)	Precipitate barium from sample; dissolve in ammoniacal solution of EDTA	FAAS	Low µg/g levels	118%	Bano 1973

TABLE 6-2 (Continued)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Diagnostic meals containing barium sulfate	Add sample to EDTA solution and warm	FAAS	No data	98.6%-102.5%	Sharp and Knevel 1971
Compound formulation (Ba ¹⁴ CO ₃)	Prepare solution of sample in EDTA and count	Scintillation spectrometry	No data	No data	Larsen 1973

Ba¹⁴CO₃ = radiolabeled barium carbonate; EDTA = ethylenediamine tetraacetic acid; FAAS = flame atomic absorption spectroscopy; FAES = flame atomic emission spectroscopy; GFAAS = graphite furnace atomic absorption spectroscopy; HFA = hexafluoroacetylacetone; RSD = relative standard deviation; XFS = x-ray fluorescence spectroscopy

6. ANALYTICAL METHODS

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 barium 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 barium.

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 Determining Biomarkers of Exposure and Effect. Several methods are available for measuring biomarkers of exposure. ICP-AES is the analytical method used for measuring barium in blood, urine and bone of humans and animals at ppt (sub $\mu\text{g/L}$) levels (Mauras and Allain 1979; Schramel 1988; Shiraishi et al. 1987). NAA technique has also been employed for measuring barium in blood of humans and animals at ppb ($\mu\text{g/L}$) levels (Olehy et al. 1966). These techniques are sensitive for measuring background levels of barium in the population. However, it is not known whether data collected using these techniques have been used to correlate the levels of barium in biological tissues and fluids to exposure levels.

At present, no biomarkers of effect are available for barium. There are no data to indicate whether a biomarker, if available, would be preferred over chemical analysis for monitoring effects from long-term and short-term exposure to barium.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. GFAAS and FAAS are the most widely used analytical techniques for measuring barium and its compounds in air (NIOSH 1987b), water (Edelbeck and West 1970; Fagioli et al. 1988; Johnson et al. 1983; Pierce and Brown 1977; Roe and Froelich 1984), waste water (EPA 1979a, 1979b, 1986c; Murata and Noguchi 1974), rocks and minerals (Bano 1973), unused lubricating oil (Holding and Rowson 1975), and diagnostic meals (Sharp and Knevel 1971). The media of most concern for potential human exposure to barium is water. GFAAS and FAAS techniques are sensitive for measuring background levels of barium in aqueous media (Epstein and Zander 1979; Roe and Froelich 1984).

6. ANALYTICAL METHODS

However, it is not known whether these techniques are sensitive for measuring levels of barium at which health effects might begin to occur. FAAS and GFAAS are the methods (Methods 208.1, 208.2, 7080, and 7081) recommended by EPA for detecting ppb levels of barium in water and waste water (EPA 1979a, 1979b, 1986c). GFAAS has also been employed to detect ppt levels of barium in aqueous media (Epstein and Zander 1979; Roe and Froelich 1984). No additional methods for detecting barium and its compounds in environmental media appear to be useful at this time.

6.3.2 On-going Studies

No on-going studies regarding techniques for measuring and determining barium in biological and environmental samples were located.

