

7. ANALYTICAL METHODS

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

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 7-1). 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 >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 include minimal sample preparation and the fact that destruction of the

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Table 7-1. 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
Urine	Dilute sample with demineralized water, introduce into the plasma and analyze	ICP-AES	0.2 µg/L	No data	Schramel 1988
Erythrocyte and plasma	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. 1966
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	AES	No data	86.8–130.5%	Baisane et al. 1979
Fetus bones	Ash sample and digest with acid	ICP-AES	0.0005 µg/g	0.5% RSD	Shiraishi et al. 1987

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

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sample is not needed to conduct the analysis. Disadvantages of this technique include its high costs and a nuclear reactor may not be readily available to many laboratories.

Gravimetric and spectrometric techniques have also been described for quantifying barium in tissues. Borchardt et al. (1961) measured barium in tissues gravimetrically following digestion of 15–20 grams of sample in a 2:1 (by volume) mixture of sulfuric and nitric acids. The barium in the samples was precipitated out as the sulfate, dried, and weighed. No limits of detection were given. Recovery of barium from acid-digested tissues can be impaired when organic ions react with barium and interfere with the formation of the barium sulfate precipitate. However, Borchardt et al. (1961) reported that no such interferences were observed in their assay and that complete recovery of barium from the sample was obtained. In another method, Baisane et al. (1979) used atomic emission spectroscopy to measure barium in visceral material. The method required ashing of tissue samples by heating with a burner or a muffle furnace and then fusing the ash with graphite and lithium carbonate. The barium in the fused ash was quantified by using an electric arc as an excitation source and monitoring the barium emission at 2,335 Å. Limits of detection were not given, but recoveries ranged from 86.8 to 130.5%.

7.2 ENVIRONMENTAL SAMPLES

Atomic absorption spectroscopy (AAS) is the most prevalent analytical technique for measuring low levels of barium in air, water, waste water, geological materials (calcium carbonate), unused lubricating oil, and diagnostic meals containing barium sulfate (see Table 7-2).

Samples may be prepared for AAS in a variety of ways (EPA 1974, 1994a, 1994b, 1996; 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 1974, 1979, 1992, 1994a, 1994b). Parts-per-trillion (sub $\mu\text{g/L}$) levels of barium in seawater and freshwater have been detected by GFAAS (Epstein and Zander 1979; Roe and Froelich

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Table 7-2. 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 membrane and extract with hot acid; evaporate extract to dryness and dissolve residue in acid	FAAS	2 µg per sample	102%	NIOSH 1994 (Method 7056)
Air	Collect sample on cellulose or PVC membrane; extract with hot acid and evaporate at 150 °C to near dryness; dissolve residue in acid	ICP-AES	0.005 µg per sample	97.7–102.4%	NIOSH 2003 (Method 7300)
Water	Reflux with addition of HNO ₃ and HCl; filter	ICP-MS	0.8 µg/L	95%	EPA 1994a (Method 200.8)
	Reflux with addition of HNO ₃ and HCl; filter	ICP-AES	1 µg/L	92%	EPA 1994b (Method 200.7)
	Acidify with HNO ₃ ; filter	FAAS	100 µg/L	94%	EPA 1974 (Method 208.1)
	Reflux with addition of HNO ₃ and HCl	FAAS	33.5–132 µg/L (working range)	104.5–106.9% (33.5 µg/L)	ASTM 2000 (Method D4382)
	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	90–110%	Fagioli et al. 1988
Inject sample directly into graphite furnace	GFAAS	0.6 µg/L (seawater); 0.2 µg/L (freshwater)	13% RSD	Roe and Froelich 1984	
Seawater and brackish water	Acidify and inject	DCAP-AES	10–20 mg/L (working range)	108.8% (10 mg/L)	ASTM 1999 (Method D3986)
Water and waste water	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 1974, 1979, 1992, 1994 (Methods 208.1, 208.2, 7080, and 7081)
Industrial waste water	Digest sample; mix with cation-exchange resin; dry and analyze	XFS	290 µg/L (in 500 mL samples)	5.1% RSD	Murata and Noguchi 1974

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Unused lubricating oil	Dissolve sample in 2-methyl-propan-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
Soil	Digest sample in HNO ₃ and H ₂ O ₂ , filter, dilute with acid	GFAAS	0.2 µg/g dry weight	96%	EPA 1978, 1996 (Methods 3050B and 208.2)
Sediment, soil, rocks	Digest sample in a mixture of HCl, HNO ₃ , and HClO ₄ by heating to dryness; resuspend residue in HNO ₃ and H ₂ O ₂ and heat; cool and dilute in 1% HNO ₃	ICP-MS	0.15 ppm	96–102%	USGS 2002a (Method T20)
Sediment, rocks, plants	Digest sample in a mixture of HF, HNO ₃ , and HClO ₄ by heating to dryness; resuspend residue in HClO ₄ and heat to dryness; resuspend in aqua regia, dilute with 1% HNO ₃ , and reheat	ICP-AES	0.3 ppm	95–106%	USGS 2002b (Methods E011 and T01)
Food, beverage	Homogenize sample; microwave digestion of sample in HNO ₃ ; centrifuge	ICP-AES	0.03 mg/kg (food) 0.004 mg/kg (beverage)	86–94% (food) 86–92% (beverage)	EPA 1995b
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; DCAP-AES = direct-current argon plasma-atomic emission spectroscopy; EDTA = ethylenediamine tetraacetic acid; FAAS = flame atomic absorption spectroscopy; FAES = flame atomic emission spectroscopy; GFAAS = graphite furnace atomic absorption spectroscopy; HCl = hydrochloric acid; HClO₄ = perchloric acid; HF = hydrofluoric acid; HFA = hexafluoroacetylacetone; HNO₃ = nitric acid; H₂O₂ = hydrogen peroxide; ICP-AES = inductively coupled plasma-atomic emission spectroscopy; ICP-MS = inductively coupled plasma-mass spectrometry; PVC = polyvinyl chloride; RSD = relative standard deviation; XFS = x-ray fluorescence spectroscopy

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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 1994). AAS 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), direct current argon plasma-atomic emission spectroscopy (DCAP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), 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 in environmental media. Scintillation spectroscopy and spectrography are less commonly used to measure barium in the environment relative to other analytical methods. ICP-MS and ICP-AES offer low detection sensitivities that are typically at the ppb level and are becoming more routinely used for analysis of samples with complex mixtures of metals and metal complexes. For example, ICP-AES (Method 7300) is a technique recommended by NIOSH for analyzing soluble barium compounds in air with a limit of detection of 0.005 μg per sample (approximately 0.005 $\mu\text{g}/\text{m}^3$), which is 400 times less than the detection limit for another NIOSH method (7056) that uses FAAS as the technique to quantify barium in air (NIOSH 1994, 2003). ICP-AES (Methods E011 and T01) and ICP-MS (Method T20) are recommended by the U.S. Geological Survey (USGS) for measuring the barium content in sediments and rocks (USGS 2002a, 2002b). ICP-AES is also used to quantify barium and other trace metals in food and beverages with minimum detection limits of 0.004–0.3 mg/kg (ppm) and recoveries of 86–94% (EPA 1995b). ICP-MS is a useful technique for isotopic analysis of barium to determine sources of environmental emissions of barium compounds.

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 barium is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research

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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 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

Methods for Determining Biomarkers of Exposure and Effect.

Exposure. 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, information is needed on whether data collected using these techniques can be used to correlate the levels of barium in biological tissues and fluids with exposure levels.

Effect. 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- 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 1987), water (ASTM 2000; Edelbeck and West 1970; EPA 1974, 1994a, 1994b; Fagioli et al. 1988; Johnson et al. 1983; Pierce and Brown 1977; Roe and Froelich 1984), seawater and brackish water (ASTM 1999), waste water (EPA 1974, 1979, 1992, 1994b), rocks and minerals (Bano 1973), unused lubricating oil (Holding and Rowson 1975), soil (EPA 1978, 1996), 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). However, it is not known whether

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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 1974, 1979, 1992, 1994c). GFAAS has also been employed to detect ppt levels of barium in aqueous media (Epstein and Zander 1979; Roe and Froelich 1984). ICP-MS and ICP-AES quantitative methods are increasing in use for routine analysis of barium at ppb levels and are capable of ppt levels of detection when ion chromatographic and other prepurification methods are used in sample preparation and analysis. Therefore, analytical methods are available that are sufficiently specific and sensitive to measure barium in the environment, and no data needs have been identified at this time.

7.3.2 Ongoing Studies

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