6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring 1,2-dibromoethane 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 1,2-dibromoethane. 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 1,2-dibromoethane 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

Gas chromatography (GC) equipped with a flame ionization detector has been employed for measuring the concentration of 1,2-dibromoethane in the tissues of two workers following exposure (Letz et al. 1984). A detection limit of 0.5 μg of 1,2-dibromoethane per gram of tissue was achieved. In the same report, Letz et al. (1984) detected ppm (mg/L) levels of bromide ion (a metabolite of 1,2-dibromoethane) in the serum and whole blood before and after the death of two individuals, respectively. Detection limits of 50 mg of bromide ion per liter of serum and 8 mg of bromide ion per liter of whole blood were obtained using gold chloride calorimetry and high-performance liquid chromatography, respectively. GC has also been used for quantifying ppm levels of 1,2-dibromoethane in blood and liver of rats and chicks (Nachtomi and Alumot 1972). See Table 6-l for details.

6.2 ENVIRONMENTAL SAMPLES

High-resolution GC equipped with an appropriate detector is the most common analytical technique for determining the concentrations of 1,2-dibromoethane in air, water, wastewater, soil, leaded gasoline, and various foods (e.g., grains, grain-based foods, beverages, and fruits). The choice of a particular detector will depend on the nature of the sample matrix, the detection limit, and the cost of the analysis. Because volatile organic compounds in environmental samples may exist as complex mixtures or at very low concentrations, concentrations of these samples prior to quantification are usually necessary.

Gas purging and trapping is the most commonly used method for the preconcentration of 1,2-dibromoethane from water, waste water, soil, and various foods. This method also provides a preliminary separation of 1,2-dibromoethane from other less volatile and nonvolatile components in the

TABLE 6-1. Analytical Methods for Determining 1,2-Dibromoethane in Biological Materials

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Biological tissues	Add water to tissue sample (at 50°C) and homogenise; extract with carbon disulfide and analyze	Gas chromatography flame ionization detector	0.5 µg/g	No data	Letz et al. 1984
Bromide ion in serum (before death of workers)	No data	Gold chloride colorimetry	50 mg/L	No data	Letz et al. 1984
Bromide ion in whole-blood (after death of workers)	No data	High-performance liquid chromatography	8 mg/L	3.6% coefficient of variation	Letz et al. 1984
Blood and liver (rats and chicks)	No data	Gas chromatography	ppm levels	No data	Nachtomi and Alumot 1972

samples, thereby alleviating the need for extensive separation of the components by a chromatographic column prior to quantification.

The best sensitivity for 1,2-dibromoethane quantification is obtained by either electron capture detector (ECD) or Hall electrolytic conductivity detector (HECD) in the halide detection mode, since these detectors are relatively insensitive to nonhalogenated species and very sensitive to halogenated species. Another common detection device is a mass spectrometer (MS) connected to a GC. The GC/MS combination provides unequivocal identification of 1,2-dibromoethane in samples containing multiple components having similar GC elution characteristics (see Table 6-2). To date, GC equipped with either ECD or HECD has provided the greatest sensitivity for detecting 1,2-dibromoethane. However, GC/MS employing the techniques of selective ion monitoring and isotope dilution have produced sensitivities in the parts-per-quadrillion range for some organic pollutants (Patterson et al. 1987), and could be used for 1,2-dibromoethane analysis.

The primary method of analyzing 1,2-dibromoethane in air is by adsorption on a solid phase (i.e., activated charcoal tube or Tenax adsorbent followed by thermal or solvent elution for subsequent quantification. GC/ECD and GC/MS are the most commonly used analytical techniques for 1,2-dibromoethane after elution from the solid phase (Clark et al. 1982; Collins and Barker 1983; Erikson and Pellizzari 1978; Girish and Kumar 1975; NIOSH 1987; Scott et al. 1987). NIOSH has recommended GC/ECD (method 1008) for determining 1,2-dibromoethane in air (NIOSH 1987). The range of quantification is 0.3-1,000 ppb for a 25-L air sample.

1,2-Dibromoethane is usually isolated from aqueous media by the purgeand-trap method or liquid-liquid extraction. GC/ECD or GC/MS is the technique employed for measuring 1,2-dibromoethane in water and waste water at ppt levels (Kroneld 1985; Marti et al. 1984; Simmonds 1984). GC/ECD is also the technique (method 8011) recommended by the EPA Office of Solid Waste and Emergency Response for determining 1,2-dibromoethane in drinking water and groundwater at ppt levels (EPA 1987b).

1,2-Dibromoethane can be isolated from soil samples by liquid-liquid extraction and subsequent quantification by GC/MS (Sawhney et al. 1988). Low ppb levels of 1,2-dibromoethane in soil were reported using this technique. Sample collection and preparation for the analysis of 1,2-dibromoethane in foods includes the purge-and-trap method, headspace gas analysis, liquid-liquid extraction, and steam distillation (Alleman et al. 1986; Anderson et al. 1985; Bielorai and Alumot 1965, 1966; Cairns et al. 1984; Clower et al. 1985; Pranoto-Soetardhi et al. 1986; Scudamore 1985). GC equipped with either ECD or HECD is the technique used for measuring 1,2-dibromoethane in foodstuffs at ppt levels (Clower et al. 1985; Entz and Hollifield 1982; Heikes and Hopper 1986; Page et al. 1987; Van Rillaer and Beernaert 1985).

TABLE 6-2. Analytical Methods for Determining 1,2-Dibromoethane in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Adsorb air sample onto charcoal tube; extract sample and analyze	GC/ECD	0.0003-1 ppm (for a 25-L air sample)	No data	NIOSH 1987 (Method 1008)
	Collect air sample on Tenax adsorbent; desorb thermally and analyze	GC/ECD or GC/FID	No data	1.4% RSD	Clark et al. 1982
	No data	GC/PID	0.019 ppm	No data	Dumas and Bond 1982
Water	Purge and cryotrap on adsorbent	GC/ECD	0.01-0.004 µg/L	12.1% RSD	Simmonds 1984
	Purge and trap on adsorbent	GC/MS	0.05 µg/L	95%	Marti et al. 1984
	Add sodium chloride to sample and extract with hexane	GC/ECD	0.01 µg/L	95%-114%	EPA 1987b (Method 8011)
Water and waste water	Purge and trap on adsorbent	GC/MS	1 µg/L (drinking water)	68% (drinking water)	Michael et al. 1988
Soil	Extract sample with methanol	GC/MS	≤0.0018 µg/g	No data	Sawhney et al. 1988
	Decompose 1,2-dibromoethane in sample by distillation and cooling in acetone:isooctane (1:1); analyze resulting hydrogen bromide at 376 nm	MEC	<0.5 µg/g	>96%	Abdel-Kader et al. 1979
Leaded gasoline	Derivatize 1,2-dibromoethane in sample with silica-supported silver picrate column; analyze derivative	HPLC/ED	0.28 µg/L	No data	Colgan et al. 1986

TABLE 6-2 (Continued)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Various foods (e.g., grains, grain-based foods, fruits, and beverages)	Ground sample in water (water-soluble foods or sulfuric acid (water-immiscible foods) and introduce in headspace analyzer	GC/MS	<0.001 µg/g (water-soluble foods) 0.01-0.05 µg/g (lipid-containing foods)	90%-100%	Entz and Hollifield 1982
	Ground sample in water or sulfuric acid and introduce in headspace analyzer	GC/ECD	0.001 µg/g	70%-82%	Pranoto-Soetardhi et al. 1986
	Extract 1,2-dibromoethane from sample by steam distillation	GC/ECD	0.0005-0.1 µg/g	95.1%-117%	Page et al. 1987; Van Rillaer and Beernaert 1985
	Add isooctane and sodium chloride solution to sample and shake; extract with methanol and analyze	GC/ECD or HECD	0.002 µg/g	62%	Daft 1988
	Extract sample by soaking in acetone: water (5:1) and dry (calcium chloride)	GC/ECD	low ng/g levels	90%-100%	Daft 1988
	Purge-and-trap on adsorbent	GC/ECD or HECD	0.0009 µg/g	82%-99%	Heikes and Hopper 1986
	Extract with acetone-water, or by triple hexane codistillation	GC/ECD	0.0004-0.005 µg/g	94%-106%	Clower et al. 1985

ECD = electron capture detector; ED = electrochemical detector; FID = flame ionization detector; GC = gas chromatography; HECD = Hall's electrolytic conductivity detector; HPLC = high performance liquid chromatography; MEC = molecular emission cavity analysis; MS = mass spectrometry; PID = photo-ionization detector

A highly sensitive and specific liquid chromatographic method for determining 1,2-dibromoethane in leaded gasoline has been developed by Colgan et al. (1986). The method involves the reaction between silver picrate adsorbed on silica gel and 1,2-dibromoethane to form 1-bromo-2-(picryloxy)-ethane and/or 1,2-bis(picryloxy)ethane. The derivatives formed were analyzed by high-performance liquid chromatography (HPLC) equipped with an oxidative electrochemical detector (ED). A detection limit of 280 ppt of 1,2-dibromoethane was reported (Colgan et al. 1986).

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 1,2-dibromoethane 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 1,2-dibromoethane,

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. GC, HPLC, and gold chloride calorimetry have been used for measuring low ppt levels of 1,2-dibromoethane and bromide ion. These techniques are sensitive for measuring background levels of 1,2-dibromoethane in the population (Letz et al. 1984). However, it is not known whether these techniques are sensitive for measuring levels of 1,2-dibromoethane at which health effects may begin to occur. Although analytical methods are available to detect exposures to 1,2-dibromoethane, it is difficult to monitor for exposure to 1,2-dibromoethane in humans. This is because 1,2-dibromoethane is volatile and has a short half-life in biological materials (Plotnick et al. 1979; Windholz 1983). Monitoring for bromide ion in biological media is also problematic in that the presence of this metabolite may result from the metabolism of other brominated hydrocarbons (see Chapter 2). Furthermore, information on the precision and accuracy of the gas chromatographic technique would be useful for interpreting monitoring data in biological tissues and fluids.

Biochemical assays have been employed to measure changes in enzyme levels (e.g., aspartate aminotransferase, lactic dehydrogenase) as an indication of exposure to 1,2-dibromoethane in humans and animals (Albano et al. 1984; Botti et al. 1989; Letz et al. 1984; Van Iersel et al. 1988). Decreased sperm counts per ejaculate and increased numbers of sperm with abnormal morphology have also been identified in workers following exposure to 1,2-dibromoethane (Ratcliffe et al. 1987; Wyrobek 1984). In general, these techniques are nonspecific for 1,2-dibromoethane exposure (see Chapter 2). There are no data to indicate whether a biomarker, if available, would be preferred over chemical analysis for monitoring exposure to 1,2-dibromoethane.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. GC equipped with either ECD, HECD, or MS and HPLC/ED are the analytical techniques used for measuring low levels of 1,2-dibromoethane in air, water, waste water, soil, leaded gasoline, and foodstuffs (Colgan et al. 1986; Daft 1988; EPA 1987b; Marti et al. 1984; Michael et al. 1988; NIOSH 1987; Sawhney et al. 1988; Simmonds 1984). The media of most concern for potential human exposure to 1,2-dibromoethane are drinking water, air, and foodstuffs. Gas chromatographic techniques are sensitive for measuring background levels of 1,2-dibromoethane in these media and levels of 1,2-dibromoethane at which health effects might begin to occur. GC/ECD is the technique (method 8011) recommended by EPA for measuring ppt levels of 1,2-dibromoethane in water (EPA 1987b). NIOSH has also recommended GC/ECD as the method (method 1008) for measuring low-ppm to sub-ppb levels of 1,2-dibromoethane in air (NIOSH 1987). GC/HECD or ECD has been employed for detecting 1,2-dibromoethane in various foodstuffs at low- to sub-ppb levels. No additional analytical methods for measuring 1,2-dibromoethane in environmental media appear to be necessary at this time.

6.3.2 On-going Studies

The Environmental Health Laboratory Sciences Division of the National Center for Environmental Health and Injury Control, Centers for Disease Control, is developing methods for the analysis of 1,2-dibromoethane and other volatile organic compounds in blood. These methods use high resolution gas chromatography and magnetic sector mass spectrometry which gives detection limits in the low parts-per- trillion range.