7. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting, measuring, and/or monitoring 1,2-dichloroethane, its metabolites, and other biomarkers of exposure and effect to 1,2-dichloroethane. 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

Table 7-1 lists the analytical methods used for determining 1,2-dichloroethane in biological fluids and tissues. Gas chromatography/mass spectrophotometry (GC/MS) is the most commonly used analytical method for measuring 1,2-dichloroethane in breath, blood, and urine samples (Ashley et al. 1992; Barkley et al. 1980; Wallace et al. 1984, 1986). Sensitivity is in the low- to sub-ppb range. For blood samples, recovery is >74% (Ashley et al. 1992). Precision is adequate (<30% relative standard deviation [RSD]) (Ashley et al 1992). Recovery data were not reported for breath or urine samples.

Glutathione-*S*-transferase (GST) was suggested as a biological marker to detect 1,2-dichloroethane in human erythrocytes (Ansari et al. 1987). 1,2-Dichloroethane inactivates GST in human erythrocytes. A dose-dependent reduction in GST with levels of 1,2-dichloroethane in human erythrocytes *in situ* was reported. However, because a similar response is also reported for acrolein, propylene oxide, styrene oxide, and ethylene dibromide, it is not possible to use measurement of GST activity in human erythrocytes to monitor exposure to 1,2-dichloroethane alone (Ansari et al. 1987).

The presence of metabolites of 1,2-dichloroethane, such as 2-chloroethanol and monochloroacetic acid, in blood and urine could be used as an indicator of exposure to 1,2-dichloroethane (Monster 1986). However, similar metabolites may be found following exposure to other volatile organic compounds. This method is not presently used to determine exposure to 1,2-dichloroethane. Levels of thioethers could be determined analytically in the urine. No analytical measurement for these metabolites are given.

Table 7-1. Analytical Methods for Determining 1,2-Dichloroethane in Biological Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Breath	Collect exhaled air in Tenax cartridge	GC/MS-thermal desorption in a fused silica capillary column	1 µg/m^3	No data	Wallace et al. 1984, 1986
Breath	Collect exhaled air in Tenax cartridge	GC/MS-thermal desorption	0.12 µg/m^3	No data	Wallace et al. 1984
Human erythrocytes	Separate erythrocytes from blood; wash and hemolyze; collect GST enzyme	GST activity; not specified	No data	No data	Ansari et al. 1987
Blood/urine	Heat at 50 EC; purge with helium; trap on Tenax GC sorbent	GC/MS	No data	No data	Barkley et al. 1980
Blood	Purge-and-trap blood sample	GC/MS	0.012 ppb	74–116	Ashley et al. 1992

GC = gas chromatography; GST = glutathione-S-transferase; MS = mass spectrophotometry

A pilot study attempted to show a correlation between the levels of halogenated compounds found in the environment and levels measured in blood and urine. The results, however, were not statistically significant (Barkley et al. 1980). The lack of correlation was attributed to differences in body metabolism between the individuals and small sample size. However, the applicability of GC/MS towards correlating environmental levels with body burden levels, given a large enough sample size, was demonstrated.

More information on methods for the analysis of 1,2-dichloroethane in biological materials, including sample preparation techniques can be found in the references cited in Table 7-1.

7.2 ENVIRONMENTAL SAMPLES

Table 7-2 lists the methods used for analyzing 1,2-dichloroethane in environmental samples. GC/MS and GC combined with electron capture detection (ECD) are the most commonly used analytical methods for detecting 1,2-dichloroethane in air (Class and Ballschmiter 1986; Driss and Bouguerra 1991; EPA 1999d; Grimsrud and Rasmussen 1975; Hoyt and Smith 1991; Hsu et al. 1991; Jonsson and Berg 1980; Kessels et al. 1992; Kirshen and Almasi 1992; McClenny et al. 1991; NIOSH 1994; Pleil et al. 1988; Wallace et al. 1984), water, including drinking water, waste water, and tap water (EPA 1982b, 1984c, 1997; Garcia et al. 1992; Otson and Williams 1982; Wallace et al. 1984), sediment (Hiatt 1981), fish (Easley et al. 1981; Hiatt 1981), and food (Daft 1987, 1988, 1989, 1991; Heikes 1987; Heikes and Hopper 1986). Air samples are generally collected on filters and desorbed or collected in canisters. For measuring 1,2-dichloroethane in air samples, sensitivity is in the sub-ppb to low-ppt range for both GC/MS and GC/ECD. Recovery (>90%) and precision (3% RSD) are good (Hsu et al. 1991; Jonsson and Berg 1980).

Purge-and-trap extraction methods are generally used when measuring volatile compounds such as 1,2-dichloroethane in water samples. Sensitivity is in the low-to-sub-ppb and low-ppt range for GC/MS and GC/ECD. High performance gas chromatography (HRGC)/MS has also been used to measure the compound in water with similar sensitivity. Recovery and precision data were not reported. HRGC, with dual detection by ECD and flame ionization detectors (FID) or GC/FID can also be used to measure 1,2-dichloroethane in drinking water and tap water (Driss and Bouguerra 1991; Kessels et al. 1992). Sensitivity for HRGC/ECD-FID is in the sub-ppb range with excellent recovery (100%) (Kessels et al. 1992). Sensitivity data were not reported for GC/FID; however, recoveries were adequate (77.5%) (Driss and Bouguerra 1991). For both methods, precision was good (3.1-21% RSD) (Driss and Bouguerra 1991; Kessels et al. 1992).

Table 7-2. Analytical Methods for Determining 1,2-Dichloroethane in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Collect whole air sample in canister; preconcentrate volatile organics from air; treatment of water vapor	GC/MS	0.3 ppb	No data	McClenny et al. 1991
Air	Draw ambient air through a cartridge containing approximately 1–2 g of Tenax. Certain volatile organic compounds are trapped on the Tenax while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge	GC/MS	In general the detection limit should be 20 ng or less	No data	EPA 1999d (Method TO-1)
Air	Draw ambient air through a cartridge containing approximately 0.4 g of a carbon molecular sieve (CMS) adsorbant. Volatile organic compounds are captured on the adsorbant while major inorganic atmospheric constituents pass through (or are only partially retained)	GC/MS	No data	85	EPA 1999d (Method TO-2)
Air	Purge-and-trap	GC/ECD/FID	For many compounds detection limits of 1–5 ng are found using FID	100	EPA 1999d (Method TO-3)

Table 7-2. Analytical Methods for Determining 1,2-Dichloroethane in Environmental Samples *(continued)*

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Draw a sample of ambient air through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated SUMMA passivated canister	GC/MS	>1 ppb	90–110	EPA 1999d (Method TO-14A)
Workplace air	Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs. Add 1 mL carbon disulfide to each vial	GC/FID	0.2 mg/m^3	No data	NIOSH 1994 (Method 1003)
Air and soil gas	Collect air or soil gas sample in evacuated canister or Tedlar bag through a cryogenically cooled trap to freeze out and preconcentrate volatile compounds; heat trap and transfer volatile analyte to cryogenically cooled column	HRGC/PID-ECD or ELCD	0.05 ppb (ELCD); 0.19 ppb (ECD)	No data	Kirshen and Almasi 1992
Drinking water	Purge-and-trap	GC/MS	5 ng/L	No data	Wallace et al. 1984
Drinking water	Liquid-liquid extraction using *n*-pentane	HRGC/ECD	2.6 µg/L	No data	Garcia et al. 1992
Water and waste water	Purge-and-trap	GC	0.03 µg/L	1.04–1.06C 97.8	EPA 1982b, 1984c (Method 601)
Water and waste water	Purge-and-trap	GC/PID	0.03 µg/L	No data	EPA 1997 (Method 8021B)

Table 7-2. Analytical Methods for Determining 1,2-Dichloroethane in Environmental Samples *(continued)*

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Water and waste water	Purge-and-trap	GC/MS	0.06 µg/L	No data	EPA 1997 (Method 8260B)
Water and waste water	Grab sample	GC/MS	4.7 µg/L	1.02+0.45C 99	EPA 1982b, 1984c (Method 624)
Water and waste water	Purge-and-trap	GC/MS	10 µg/L	7.7 µg/L	EPA 1984c (Method 1624B)
Water and waste water	Modified purge-and-trap	GC/HECD and FID simultaneous	0.1 µg/L (FID); <0.1 µg/L (HECD)	78 (FID); 79 (HECD)	Otson and Williams 1982
Water, waste water, and solid waste	Purge-and-trap	GC/MS	5 µg/kg (soil/sediment); 0.5 µg/kg (wastes); 5 µg/L (water)	No data	EPA 1997 (Method 8240B)
Water and waste water	Purge-and-trap	GC	0.002µg/L	No data	EPA 1997 (Method 8010B)
Drinking water	Purge-and-trap extraction technique	HRGC/ECD-FID	0.03 µg/L (ECD); 0.07 µg/L (FID)	100 (ECD); 104–116 (FID)	Kessels et al. 1992
Tap Water	Purge-and-trap extraction technique	GC/FID	No data	77.5	Driss and Bouguerra 1991
Water, solid waste, and tissue	Vacuum distillation extraction technique	GC/MS	No data	No data	EPA 1997 (Method 5032)

Table 7-2. Analytical Methods for Determining 1,2-Dichloroethane in Environmental Samples *(continued)*

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Fish	Add fish tissue to reagent grade water; disrupt cells ultrasonically; analyze sample by a purge-and -trap method	GC/MS	10 µg/kg	85±11	Easley et al. 1981
Fish	Spiked samples of ground fish tissue; vaporize VOCs from fish under vacuum and condense in purge-and-trap	GC/MS	No data	85±11[a]	Hiatt 1981
Fish	Homogenize fish sample; remove residual moisture by vacuum distillation	GC/MS-fused silica capillary column	No data	No data	Hiatt 1983
Sediment	Spiked samples; vaporize VOCs under vacuum and condense in purge-and-trap	GC/MS	No data	96±17[a]	Hiatt 1981
Grains, legumes, spices, citrus fruits, beverages, dairy products, meat	Acidified acetone-water extraction; isooctane back extraction	GC/ECD	No data	14–75	Daft 1987, 1988, 1989, 1991
Table ready foods	Stirred with water; purge-and-trap on Tenax GC; hexane desorption	GC/ECD	6 ppb	85–104	Heikes 1987; Heikes and Hopper 1986

[a]Reported as percent spike recoveries for 25 ppb spikes

ECD = electron capture detector; ELCD = electrolytic conductivity detector; FID = flame ionization detector; GC = gas chromatography; HECD = Hall electron capture detector; HRGC = high resolution gas chromatography; MS = mass spectrometry; PID = photoionization detector; VOCs = volatile organic carbon compounds

The EPA recommends GC/MS for the determination of 1,2-dichloroethane in water and waste water; this method can detect 1,2-dichloroethane levels of $0.03 µg/L (EPA 1997). Under EPA's Contract Laboratory Program, all contract laboratories are required to maintain certain levels of performance to meet specific quantitation levels (EPA 1988c). For volatiles such as 1,2-dichloroethane, the Contract Required Quantitation Level (CRQL) for water and low soil/sediment is 5 µg/L (EPA 1986a). Complete descriptions of these techniques can be found in the references cited in Table 7-2.

GC/MS is adequate for measuring 1,2-dichloroethane in fish samples with sensitivities in the low-ppb range. Good recoveries (>85%) were achieved (Easley et al. 1981; Hiatt 1981). Sensitivity data were not reported for measuring 1,2-dichloroethane in sediment; however, good recovery (96%) was obtained (Hiatt 1981).

GC/ECD is generally used to measure 1,2-dichloroethane in foodstuffs (Daft 1987, 1988, 1989, 1991; Heikes 1987; Heikes and Hopper 1986). For table-ready foods, sensitivity is in the low-ppb range with good recoveries achieved (>85%) (Heikes 1987; Heikes and Hopper 1986). Precision data were not reported.

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 1,2-dichloroethane is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (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-dichloroethane.

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. The activity of the biomarker GST in blood (Ansari et al. 1987) cannot be used reliably as an indication of exposure to 1,2-dichloroethane because similar effects have been noted following exposure to other organic compounds. No method is routinely used to monitor 1,2-dichloroethane metabolites in human urine. Although it has been suggested that measurement of 2-chloroethanol and monochloroacetic acid in urine may provide evidence of exposure to chlorinated hydrocarbons (Monster 1986), these metabolites are not specific to 1,2-dichloroethane. Methods are available to detect and quantify 1,2-dichloroethane in human breath, blood, and urine (Ashley et al. 1992; Barkley et al. 1980; Wallace et al. 1984). There are no quantitative techniques available to correlate the concentration of 1,2-dichloroethane measured in expired air, blood, or urine to levels of environmental exposure or health effects.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Methods are available to detect 1,2-dichloroethane in air (Class and Ballschmiter 1986; Driss and Bouguerra 1991; EPA 1999d; Grimsrud and Rasmussen 1975; Hoyt and Smith 1991; Hsu et al. 1991; Jonsson and Berg 1980; Kessels et al. 1992; Kirshen and Almasi 1992; McClenny et al. 1991; NIOSH 1994; Pleil et al. 1988; Wallace et al. 1984), water, including drinking water, waste water, and tap water (EPA 1997; Garcia et al. 1992; Otson and Williams 1982; Wallace et al. 1984), sediment (Hiatt 1981), fish (Easley et al. 1984; Hiatt 1981), and food (Daft 1987, 1988, 1989, 1991; Heikes 1987; Heikes and Hopper 1986). The standardized methods can detect 1,2-dichloroethane levels of $5 ppt in air and of $2 ng/L in water. In addition, numerous techniques for the analysis of 1,2-dichloroethane are reported in the open literature.

The known degradation products of 1,2-dichloroethane that contain chlorine are volatile organic compounds and are often detected and quantified along with 1,2-dichloroethane in monitoring experiments (although they probably arose from anthropogenic sources). Thus, experimental methods used to detect 1,2-dichloroethane are sufficient to quantify its chlorinated degradation products.

7.3.2 Ongoing Studies

No ongoing studies were located regarding techniques for measuring or detecting 1,2-dichloroethane in biological materials or environmental samples.

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-dichloroethane and other volatile organic compounds in blood. These methods use purge and trap methodology, high resolution gas chromatography, and magnetic sector mass spectrometry that permit detection limits in the low parts per trillion (ppt) range.