7. ANALYTICAL METHODS

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

The analytical methods used to quantify 1,1-dichloroethane in biological and environmental samples are summarized below. Table 7-1 lists the applicable analytical methods used for determining 1,1-dichloroethane in biological fluids and tissues, and Table 7-2 lists the methods used for determining 1,1-dichloroethane in environmental samples.

7.1 BIOLOGICAL MATERIALS

The determination of trace levels of 1,1-dichloroethane in biological tissues and fluids has been restricted to gas chromatography (GC) equipped with mass spectrometry (MS) or flame ionization detection (FID).

Work conducted by Cramer and co-workers (1988) showed that 1,1-dichloroethane can be detected at nanogram per liter (ppt) levels in whole human blood using a dynamic headspace analyzer and GC/MS technique. A disadvantage of the GC/MS technique is that only limited mass scanning can be employed to obtain better sensitivity of target VOCs at ppt levels. This is because of the inherent differences in sensitivity between the full-scan MS and the limited mass scanning MS techniques (Cramer et al. 1988).

Uehori et al. (1987) developed a retention index in GC to screen and quantify VOCs in blood. A dynamic headspace analyzer and GC/FID with retention indices were employed for the detection of 1,1-dichloroethane at nanogram levels. Uehori et al. (1987) noted that this method is simple and reliable, and requires little or no sample preparation.

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Blood	Vaporize blood sample in a headspace vial and inject into GC column	GC/FID	ng range	No data	Uehori et al. 1987
Whole blood	Purge-and-trap on Tenax adsorbent	GC/MS	100 ng/L	76–110	Cramer et al. 1988
Blood and urine	Heat biological sample; purge-and-trap volatile compounds on Tenax GC adsorbent	GC/MS	No data	No data	Barkley et al. 1980
Whole blood	Collect by venipuncture, store cold; inject sample into purge-and-trap apparatus	GC/MS	0.013 ppb	102–118	Ashley et al. 1992
Breath	Collect human breath sample by means of a spirometer and analyze	GC/MS	Not detected	No data	Barkley et al. 1980
Breath	Collect human breath sample by means of a spirometer and analyze	GC/MS	Not reported	No data	Raymer et al. 1990

FID = flame ionization detector; GC = gas chromatography; MS = mass spectrometry

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Groundwater, aqueous sludges, caustic liquors, soils, sediments	Purge-and-trap (EPA method 624) or direct injection (EPA Method 5030)	GC/MS	4.7 µg/L (groundwater; 5 µg/kg (soil/sediment)	59–155%	EPA 1994a (Method 8240B), 2015a
Groundwater, surface water, waste water	Purge-and-trap (EPA method 624) or direct injection (EPA Method 5030)	GC with HECD	0.002 µg/L	47–132	EPA 1994b (Method 8010B)
Groundwater	Purge-and-trap on absorbent	GC/MS	0.0001–0.02 µg/sample	<±5 relative standard deviation	Lopez-Avila et al. 1987a
Groundwater	Purge-and-trap on absorbent	GC/FID-FID	No data	No data	Driscoll et al. 1987
Groundwater and soil	Purge-and-trap on absorbent	GC/EICD-FID	Water=0.1–0.9 µg/L; soil=1–5 µg/L	83–102	Lopez-Avila 1987b
Drinking water	Heat water sample; purge-and-trap volatile compounds on Tenax GC absorbent	GC/MS	Not detected	No data	Barkley et al. 1980
Drinking water	Pass sample through XAD-2 macroreticular resin and extract continuously with ether	GC/MS	<1 µg/L	No data	Suffet et al. 1986
Drinking water	Purge-and-trap water sample	GC/MS	0.2 µg/L	94	Otson and Chan 1987
Drinking water	Extract sample in hexane and analyze	GC-EICD	<1 µg/L	No data	Otson and Chan
Drinking water	Purge-and-trap on Tenax absorbent	GC-EICD-FID	<1 µg/L	>75	Otson and Williams 1982
Drinking water	Purge-and-trap water sample	GC/EICD	80 µg/L	84	Comba and Kaiser 1983
Drinking water	Purge-and-trap water sample	GC/EICD-FID	0.1–0.5 µg/L	No data	Kingsley et al. 1983
Water (river; sea)	Inject 1 mL into flow injection analysis system	MIMS/ITD	0.2 ppb	No data	Bauer and Solyom 1994
Waste water	Collect water sample through a permeation cell membrane and direct into GC	GC/FID	µg/L (ppb) range	<6 relative standard deviation	Blanchard and Hardy 1986

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Waste water	Collect sample through a permeation cell membrane; adsorb onto charcoal; extract with carbon disulfide	GC/FID	74–16,800 µg/L	No data	Blanchard and Hardy 1985
Waste water (municipal and industrial discharges)	Purge-and-trap (EPA method 601) with direct aqueous injection; the trap is backflushed and heated to desorb compounds onto column	GC/MS	0.07 µg/L	47–132	EPA 2001a
Waste water (municipal and industrial discharges)	Purge-and-trap (EPA method 624); the trap is backflushed and heated to desorb compounds onto column	GC/MS	4.7 µ/L	59–155	EPA 1999, 2015a
Waste water	Purge-and-trap with isotopic dilution (EPA method 1624); stable isotopes are added; the trap is backflushed and heated to desorb compounds onto column	GC/MS	10 µg/L	Labeled compound recovery: 23–191	EPA 2001b
Waste water and sludge	Purge-and-trap on adsorbent	GC/MS	No data	No data	Giabbaie et al. 1983
Drinking, ground, and surface water	Purge and trap water sample	GC/AED	0.17 µg/L	No data	Silgoner et al. 1997
Air (ambient)	Purge-and-trap on charcoal absorbent; extract with carbon disulfide	GC/ECD	0.001 ppm range	No data	Bruner et al. 1978
Air (ambient)	Collect air sample on Tenax adsorbent; vaporize thermally and analyze	GC/MS	23 µg/m^3	No data	Pellizari 1982
Air (ambient)	Collect air particulates on a glass fiber filter and Tenax GC adsorbent; extract with MeOH pentane	GC/MS	Not detected	No data	Barkley et al. 1980
Air (ambient)	Adsorb air sample onto charcoal tube; extract with carbon disulfide	GC/FID	ppm range	No data	NIOSH 2003 (method 1003)

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air (space cabin)	Dehydrohalogenate air sample with lithium hydroxide and analyze	GC/MS	0.5–4.0 ppm	No data	Spain et al. 1985
Air (high humidity atmosphere)	Collect vapor sample in a Tedlar gas bag	Portable organic vapor analyzer with PID	25 ppm	0.998 correlation coefficient	Barsky et al. 1985
Air	Air collected in cooled trap; heated upon injection	GC/IMS	No data	No data	Simpson et al. 1996
Air (ambient)	Collection on multiadsorbent traps; automated preconcentration	Capillary GC/MS	0.71 ppbv		Oliver et al. 1996
Air	Sample collected on Tenax GC/carboxene 1000 trap, separated by capillary column	GC/PID/EICD	0.1 ppb		Maeda et al. 1998
Various food (e.g., dairy products, meat, vegetables, and soda)	Food containing >70% fat: dissolve sample in isooctane and shake; cleanup on florisil column	GC/ECD-EICD	ng/g range	~70	Daft 1988
Various food (e.g., fruit juices, soda, coffees, cream, peanut butter, and butter)	Cold liquid (4 °C) and aqueous flour-based samples injected; plunge sampling tube or needle into dry/viscous foods for injection; steam distillation; purge and trap	SD/PT/GC	0.003 µg/kg	95.2	Page and Lacroix 1995
Compound formulation	Prepare dilute solution of sample in MeOH; introduce into headspace trap	GC/PID	20 pg	No data	Jerpe and Davis 1987
Fish tissue	Add water to fish sample; homogenize and extract ultrasonically; purge-and-trap on adsorbent	GC/MS	0.01 µg/g	77	Easley et al. 1981
Fish tissue	Freeze fish sample; homogenize in liquid nitrogen; distill in vacuum	GC/MS equipped with fused-silica capillary column	No data	No data	Hiatt 1983

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Fish tissue	Warm sample; purge-and-trap volatiles on activated carbon adsorbent; extract with carbon disulfide	GC/FID	No data	~32	Reinert et al. 1983
Fish tissue	Edible tissue and liver homogenized in blender; organic-free water and standard added; vial sealed and placed in ultrasonic bath; purge and trap	GC/EICD	5 pg/g	115±25	Roose and Brinkman 1998
Whole fish	Freeze fish sample and homogenize; add MeOH and extract ultrasonically; purge-and-trap on adsorbent	GC/MS equipped with fused-silica capillary column	$7.5x10^{-4}$ µg/g	6.2 relative standard deviation	Dreisch and Munson 1983
Fish and sediment	Add water containing acrolein and acrylonitrile to sample; freeze sample; extract in vacuum	GC/MS	0.025 µg/g	Sediment matrix 101; fish matrix 90	Hiatt 1981

AED = atomic emission detection; ECD = electron captive detector; EICD = electrolytic conductivity detector; FID = flame ionization detector; GC = gas chromatography; HECD = Hall electrolytic conductivity detector; IMS = ion mobility spectrometry; ITD = ion trap detector; MIMS = membrane introduction mass spectrometry; MS = mass spectrometry; PID = photoionization detector; PT = purge-and-trap; SD = steam distillation

Gas purging-and-trapping on a Tenax GC adsorbent and GC/MS technique has been employed by Barkley et al. (1980) and Ashley et al. (1992) for the determination of trace levels of volatile halogenated compounds (including 1,1-dichloroethane) in water, human blood, and urine.

7.2 ENVIRONMENTAL SAMPLES

A GC equipped with an appropriate detector is the most frequently used analytical technique for determining the concentrations of 1,1-dichloroethane in air, water, soil, fish, dairy products, and various foods. Volatile organic compounds in environmental samples may exist as complex mixtures or at very low concentrations (ppt to ppb range). Subsequently, the GC technique must be supplemented by some method of sample preconcentration. The EPA updated Method 624 with revised quality control frequencies and improved internal standards and surrogates (EPA 2015a). GC columns were changed from packed columns to open tubular capillary columns in order to increase resolution and decrease losses due to adsorption.

Gas purging-and-trapping is the generally accepted method for the isolation, concentration, and determination of VOCs in water and various environmental samples (Bellar et al. 1979; EPA 1994a, 1994b, 1996b, 1999, 2001a, 2001b; Lopez-Avila et al. 1987a, 1987b; Page and Lacroix 1995; Reding 1987; Wylie 1988). This method appears to be most adaptable for use with almost any GC detector—MS, FID, electron capture detector (ECD), and electrolytic conductivity detector (EICD). In addition, the method offers an important preliminary separation of highly volatile compounds from often highly complex samples prior to GC analysis. Detection limits at <1 µg 1,1-dichloroethane/L of sample have been achieved by this method (Dreisch and Munson 1983; Kingsley et al. 1983; Lopez-Avila et al. 1987a, 1987b; Otson and Williams 1982). Page and Lacroix (1995) successfully coupled purge-and-trap procedures with steam distillation collection methods to yield an analytical method, for various foods, with a detection limit of 0.003 µg/kg for 1,1-dichloroethane. Bruner et al. (1978) employed purge-and-trap technique on charcoal adsorbent and GC/ECD for determination at ppt levels of volatile halo organic compounds in air. A major problem is that some of the halocarbons in the atmosphere are present as ultra-trace impurities in highly pure commercial inert gases. Subsequently, these impurities may interfere with the quantitative and qualitative analysis of 1,1-dichloroethane in environmental samples.

A purge-and-trap method with cryogenic trapping (cryofocusing) for concentrating VOCs from water samples into the headspace, for analysis by capillary GC, was described by Pankow and Rosen (1988). The purge-and-trap technique offers advantages over other techniques in that it allows easy isolation and

concentration of target compounds, which reduces interference, thereby improving overall limits of detection and recovery of sample (Otson and Chan 1987). Among the other advantages of the purge-and-trap technique with cryofocusing are its simplicity and therefore its reliability; the low background contamination since no sorbent traps are needed; and the relatively short time of sample analysis (Pankow and Rosen 1988). Roose and Brinkman (1998) capitalized on these techniques to analyze fish samples in a rapid, selective, and sensitive manner. An automated GC system with dual multi-adsorbent traps was successfully operated in a mobile laboratory to collect and analyze ambient air samples. The system continuously collects air samples, uses a pre-concentration approach (cryofocusing), and recovers analytes using thermal desorption. The detection limit for 1,1-dichloroethane was reported as 0.71 ppbv (Oliver et al. 1996).

Purge-and-trap techniques have been successfully coupled with atomic emission detection (AED) for the analysis of water (Silgoner et al. 1997). Solutes eluting from the GC are atomized in a microwave-induced plasma, and individual wavelengths are measured using a photodiode array. The detection limit of this method for 1,1-dichloroethane is 0.17 µg/L. While some improvement is still needed, the purge-and-trap technique coupled with AED offers some advantages over other methods. Dynamic headspace analyzer GC has been used for the analysis and identification of 1,1-dichloroethane in water and fish tissue (Comba and Kaiser 1983; Mehran et al. 1986; Otson and Williams 1982; Reinert et al. 1983;). The analytic sample is placed in a sealed flask connected to the headspace analyzer, which is directly interfaced with the injection port of the GC system. This arrangement allows for a greater proportion of compound contained in a sample to be analyzed. Detection limits of <1 µg 1,1-dichloroethane/L water and <1 µg 1,1-dichloroethane/g fish tissue were achieved (Mehran et al. 1986; Otson and Williams 1982; Reinert et al. 1983; Trussel et al. 1983). A disadvantage of this technique is that the inherent volatility of the halo organic compounds gives rise to an excessive foaming in the headspace system, thereby forming low yields and causing interference with the GC quantification. The typical yield of 1,1-dichloroethane was approximately 32% (Reinart et al. 1983). The authors indicated that use of an antifoaming agent such as silicone surfaces greatly reduced the foam, but extraneous chromatographic components and peak masking problems were encountered.

Bauer and Solyom (1994) and Wong et al. (1995) reported that membrane introduction mass spectrometry (MIMS) offers measurements of trace-level organics in environmental media, including polluted seawater, without sample preparation, using a non-porous silicon membrane. A detection limit of 0.2 ppb was reported for 1,1-dichloroethane (Bauer and Solyom 1994).

Pellizzari (1982) initiated the development and evaluation of trace levels of VOCs in industrial and chemical waste disposal sites. Ambient air samples were collected by a sampler equipped with Tenax GC adsorbent cartridges. Compounds were thermally removed from the adsorbent and analyzed by capillary GC/MS. The detection limit was at the μg/m^3 level (Pellizzari 1982).

Simpson et al. (1996) developed a method that has potential for on-site monitoring of vapor-phase organics in air. GC is coupled with ion mobility spectrometry to offer high sensitivity and the ability to operate at ambient pressure. While a detection limit for 1,1-dichloroethane was not reported, detection limits for several other EPA priority pollutants ranged from 0.05 to 140 pg/second. Maeda et al. (1998) also investigated analytical methods that may be applied to on-site monitoring techniques of HAPs. The analytical methods that they employed included a Tenax GC and Carboxene 1000 trap, followed by capillary separation and either photo ionization detector (PID) or EICD detection methods. The detection limit of the system was reported as 0.1 ppb. Another method for sampling and analyzing VOCs in air is proposed to have some advantages for use in field situations and may provide satisfactory results. The method uses teraglyme as a sample enrichment tool and employs purge-and-trap methods along with GC/MS (Huybrechts et al. 2001).

Blanchard and Hardy (1985, 1986) developed a method that allows for continuous monitoring or intermittent analysis of volatile organic priority pollutants in environmental media. The method is based on permeation of VOCs through a silicone polycarbonate membrane from wastewater sample matrix, into an inert gas stream and directed into a capillary GC/FID via a sampling loop (Blanchard and Hardy 1986). Advantages of this procedure are that it is simple, it does not require time-consuming preconcentration steps, and it can be used either in the field or in the laboratory.

The liquid-liquid extraction procedure provides a simple, rapid, screening method for semiquantitative determination of 1,1-dichloroethane in aqueous samples containing limited number of VOCs. It is less effective for aqueous samples containing large numbers of VOCs. Furthermore, interference from the organic (hexane) extraction solvent makes it more difficult to identify completely all compounds (Otson and Williams 1981). GC/EICD was employed by Otson and Williams (1981) for the detection of trace amounts (<1 μg/L of sample) of 1,1-dichloroethane in drinking water.

Daft (1988) employed a photoionization detector and an electrolytic conductivity detector connected in series to a capillary GC to detect 1,1-dichloroethane at ng/g levels in fumigants and industrial chemical residues of various foods (e.g., dairy products, meat, vegetables, and soda). Typically, foods were

extracted with isooctane and injected in GC column for analysis. However, foods containing lipid and fat were subjected to further clean-up on micro-florisil column prior to GC analysis.

A procedure was developed by Hiatt (1983) and Dreisch and Munson (1983) to identify and quantify 1,1-dichloroethane in fish tissue samples by GC/MS, employing a fused-silica capillary column (FSCC) and vacuum distillation (extraction). An advantage of the vacuum extraction is that the system does not require elevated temperatures or the addition of reagents, which could produce unwanted degradation products (Hiatt 1981). The FSCC provides a more attractive approach than packed column for chromatographic analysis of VOCs, because FSCC can be heated to a higher-temperature (350 °C) than that recommended for packed column thereby improving the resolution (at the ng/g level) of compounds at a lesser retention time. A physical limitation for compounds that can be detected, however, is that the vapor pressure of the compounds must be >0.78 torr (approximately 50 °C) in the sample chamber (Hiatt 1983).

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 1,1-dichloroethane 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 1,1-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. Reliable methods are available for detecting and quantifying 1,1-dichloroethane in the tissues and body fluids of humans. GC/MS or GC/FID has been employed to detect 1,1-dichloroethane at nanogram to picogram levels in blood and tissue samples of humans. No additional analytical methods for determining trace levels of 1,1-dichloro-

ethane in the blood of humans are needed. Also, no detection limits for detecting 1,1-dichloroethane in urine samples by GC/MS were indicated by Barkley et al. (1980). Therefore, additional research and development of sensitive and selective methods for detecting and quantifying the levels of 1,1-dichloroethane and its metabolites in the tissues and urine of humans would be useful. If methods were available, it would assist investigators in determining whether specific levels of 1,1-dichloroethane found in the tissues/fluids of exposed persons correlate with any adverse health effects.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Analytical methods are available to detect 1,1-dichloroethane in environmental samples. Purge-and-trap or direct injection followed by analysis with GC/ECD and GC/MS have been used to detect and quantify 1,1-dichloroethane in water samples at ppt and ppb levels (methods 5030, 8240, 8010B [EPA 1994a, 1994b, 1996b]; method 601, 624, 1624 [EPA 1999, 2001a, 2001b]). GC equipped with FID, PID, or EICD has also been used to detect and quantify 1,1-dichloroethane in air, water, milk, vegetables, and fish at ppb levels NIOSH (method 1003 [NIOSH 2003]). No additional analytical methods for determining trace levels of 1,1-dichloroethane in environmental media are needed.

7.3.2 Ongoing Studies

No ongoing studies regarding sponsored by NIH or EPA were identified for 1,1-dichloroethane.