6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring l,l-dichloroethane 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 l,l-dichloroethane. Rather, the intention is to identify wellestablished methods that are used as the standard methods of analysis by various Federal agencies. Many of the analytical methods used to detect l,l-dichloroethane in environmental samples are methods approved by federal agencies such as EPA and NIOSH. Other methods presented in this chapter are those that are approved by trade associations such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). A third category of analytical methods emphasizes research and development activities, where efforts are underway to refine previously used methods, to obtain lower detection limits, and to increase accuracy and precision.

The analytical methods used to quantify l,l-dichloroethane in biological and environmental samples are summarized below. Table 6-l lists the applicable analytical methods used for determining l,l-dichloroethane in biological fluids and tissues, and Table 6-2 lists the methods used for determining l,l-dichloroethane in environmental samples.

6.1 BIOLOGICAL MATERIALS

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

Recent work conducted by Cramer and co-workers (1988) showed that l,l-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 volatile organic compounds 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).

Hara et al. (1980) employed GC/MS for the analysis of trace amounts of mixed halogenated compounds in the blood and tissue of humans. Identification and quantitative analysis of various compounds was achieved by monitoring the mass fragments for selectively molecular, abundant or characteristic ions for each compound. Thus, the monitoring ion (m/z) for quantification of l,l-dichloroethane was set at 83 [$(M)^{+}$-CH_3]. A lower detection limit of 20 to 20 pg per sample was achieved.

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

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
Blood and tissue specimen	Warm sample and inject vapor phase into GC column	GC/MS	0.01-0.02 ng/sample	<6% relative standard deviation	Hara et al. 1980
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% recovery	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
Breath	Collect human breath sample by means of a spirometer and analyze	GC/MS	Not detected	No data	Barkley et al. 1980

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

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

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
Groundwater	Purge-and-trap on absorbent	GC/MS	<1 μg/L	~ 90% recovery	Krasner et al. 1981
	Purge-and-trap on absorbent	GC/MS	0.0001-0.02 μg/sample	<±5% RSD	Lopez-Avila et al. 1987a
	Purge-and-trap on absorbent	GC/PID-FID	No data	No data	Driscoll et al. 1987
Groundwater and soil	Purge-and-trap on adsorbent	GC/EICD-PID	water = 0.1 to 0.9 μg/L; soil = 1 to 5 μg/L	83 to 102% recovery	Lopez-avila et al. 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
	Pass sample through XAD-2 macroreticular resin and extract continuously with ether	GC/MS	<1 μg/L	No data	Suffet et al. 1986
	Purge-and-trap water sample	GC/MS	0.2 μg/L	94% recovery	Otson and Chan 1987
	Extract sample in hexane and analyze	GC/EICD	<1 μg/L	No data	Otson and Chan 1987
	Purge-and-trap on Tenax absorbent	GC/EICD-FID	<1 μg/L	>75% recovery	Otson and Williams 1982
	Purge-and-trap water sample	GC/EICD	80 μg/L	84% recovery	Comba and Kaiser 1983
	Purge-and-trap water sample	GC/EICD-PID	0.1 to 0.5 μg/L	No data	Kingsley et al. 1983
Wastewater	Collect water sample through a permeation cell membrane and direct into G.C.	GC/FID	μg/L (ppb) range	<6% RSD	Blanchard and Hardy 1986
	Collect sample through a permeation cell membrane; adsorb onto charcoal; extract with carbon disulfide	GC/FID	74 to 16800 μg/L	No data	Blanchard and Hardy 1985
Wastewater and sludge	Purge-and-trap on adsorbent	GC/MS	No data	No data	Giabbaie et al. 1983

TABLE 6-2 (Continued)

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
Air (ambient)	Purge-and-trap on charcoal absorbent; extract with carbon disulfide	GC/ECD	0.001 ppm range	No data	Bruner et al. 1978
	Collect air sample on Tenax adsorbent; vaporize thermally and analyze	GC/MS	23 $\mu g/m^3$	No data	Pellizari 1982
	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
	Adsorb air sample onto charcoal tube; extract with carbon disulfide	GC/FID	ppm range	No data	NIOSH 1987 (method 1003)
Air (Space cabin)	Dehydrohalogenate air sample with lithium hydroxide and analyze by GC/MS	GC/MS	0.5 to 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
Garbage dump	Collect sample on headspace cold trap system	GC/MS and GC/ECD	0.12 μg/ sample	No data	Hoefler et al. 1986
Various food (e.g., diary products, meat, vegetables and soda)	Food containing <70% fat: add sample to acetone: isooctane (10:1) and 1% phosphoric acid, shake and add MeOH; clean-up on florisil column Food containing >70% fat: dissolve sample in isooctane and shake; clean-up on florisil column	GC/ECD-EICD	ng/g range	~70% recovery	Daft 1988
Compound formulation	Prepare dilute solution of sample in MeoH; introduce into headspace trap	GC/PID	20 pg	No data	Jerpe and Davis 1987

TABLE 6-2 (Continued)

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
Fish tissue	Add water to fish sample; homogenize and extract ultrasonically; purge-and-trap on adsorbent	GC/MS	0.01 μg/g	77% recovery	Easley et al. 1981
	Freeze fish sample; homogenize in liquid nitrogen; distil in vacuum	GC/MS equipped with fused-silica capillary column	No data	No data	Hiatt 1983
	Warm sample,purge-and-trap volatiles on activated carbon adsorbent; extract with carbon disulfide	GC/FID	No data	~32% recovery	Reinert et al. 1983
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% RSD	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% recovery. Fish matrix 90% recovery	Hiatt 1981

GC = gas chromatography; GC/MS = gas chromatography/mass spectrometry; GC/EICD = gas chromatography/electrolytic conductivity detector; GC/PID = gas chromatography/photoionization detector; GC/ECD = gas chromatography/electron captive detector; GC/FID = gas chromatography/flame ionization detector; RSD = relative standard deviation; ppb = part per billion; ppt = parts per trillion.

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

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

6.2 ENVIRONMENTAL SAMPLES

A GC equipped with an appropriate detector is the most frequently used analytical technique for determining the concentrations of l,l-dichloroethane in air, water, soil, fish, diary 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.

Gas purging-and-trapping is the generally accepted method for the isolation, concentration, and determination of volatile organic compounds in water and various environmental samples (Bellar et al. 1977; EPA 198613, 1987; Krasner et al. 1981; Lopez-Avila et al. 1987a, 1987b; Reding 1987; Wylie 1987, 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 less than 1 μg of l,l-dichloroethane per liter of sample have been achieved by this method (Dreisch and Munson 1983; Kingsley et al. 1983; Krasner et al. 1981; Lopez- Avila et al. 1987a, 1987b; Otson and Williams 1982). 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 l,l-dichloroethane in environmental samples.

Recently, Badings et al. (1985) and Pankow and Rosen (1988) employed the purge-and-trap technique with cryogenic trapping (cryofocusing) of volatile organic compounds in water samples as an effective concentration method prior to capillary GC analysis. 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).

Dynamic headspace analyzer GC has been used for the analysis and identification of l,l-dichloroethane in water and fish tissue (Comba and Kaiser 1983; Mehran et al. 1985, 1986; Otson and Williams 1982; Reinert et al. 1983; Trussell 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. This method is simple and does not require any sample preparation (Mehran et al. 1985). Detection limits of less than 1 μg l,l-dichloroethane/L water and less than 1 μg l,l-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 l,l-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 comp.Fnents and peak masking problems were encountered.

Pellizzari (1982) initiated the development and evaluation of trace levels of volatile organic compounds 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 $\mu g/m^3$ level (Pellizzari 1982).

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 volatile organic compounds 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 l,l-dichloroethane in aqueous samples containing limited number of volatile organic compounds. It is less effective for aqueous samples containing large numbers of volatile organic compounds, 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 (less than 1 μg/L of sample) of l,l-dichloroethane in drinking water.

Daft (1988) employed a photoionization detector and an electrolytic conductivity detector connected in series to a capillary GC to detect l,l-dichloroethane at rig/g levels in fumigants and industrial chemical residues of various foods (e.g., diary 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 volatile organic compounds, because FSCC can be heated to a higher-temperature (350°C) than that recommended for packed column thereby improving the resolution (at the g/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 greater than 0.78 torr (approximately 50°C) in the sample chamber (Hiatt 1983).

6.3 ADEQUACY OF THE DATABASE

Section 104(i) of CERCLA 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 l,l-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 l,l-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 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 Identification of Data Needs

Methods for Determining Biomarkers of Exposure and Effect. Reliable methods are available for detecting and quantifying l,l-dichloroethane in the

tissues and body fluids of humans. GC/MS or GC/FID has been employed to detect l,l-dichloroethane at nanogram to picogram levels in blood and tissue samples of humans. No additional analytical methods for determining trace levels of l,l-dichloroethane in the blood of humans are needed. However, the report by Hara et al. (1980) did not identify what tissues were analyzed to detect l,l-dichloroethane by GC/MS. Also, no detection limits for detecting l,l-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 l,l-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 l,l-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 l,l-dichloroethane in environmental samples. GC/ECD and GC/MS have been used to detect and quantify l,l-dichloroethane in air and water samples at ppt and ppb levels [EPA methods 5030, 8240 (1986); method 601, 624, 1624 (1987)]. GC equipped with FID, PID, or EICD has also been used to detect and quantify l,l-dichloroethane in air, water, milk, vegetables, and fish at parts-per-billion levels NIOSH [method 1003 (1987)]. No additional analytical methods for determining track levels of l,l-dichloroethane in environmental media are needed.

6.3.2 On-going Studies

No on-going studies concerning methods for measuring and determining l,l-dichloroethane in biological and environmental samples were reported.

The Environmental Health Laboratory Sciences Division of the Center for Environmental Health and Injury Control, Centers for Disease Control, is developing methods for the analysis of l,l-dichloroethane and other volatile organic compounds in blood. These methods use purge and trap methodology and magnetic mass spectrometry which gives detection limits in the low parts per trillion range.