# 6. ANALYTICAL METHODS

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

To determine dichloroethenes in various matrixes, most approaches involve purge procedures. Since these analytes are volatile (bp: 60.3 °C cis; 48.0-48.5 °C trans), removing them from an often complex matrix has very distinct advantages, particularly for biological and environmental samples. Virtually all standard methods use purge and trap procedures, in which the compounds are volatilized by passing an inert gas through a sample solution or suspension and the purged components are trapped on a solid sorbent for subsequent removal and analysis by gas chromatography (GC). Because of the presence of halogens, dichloroethenes can be selectively detected using devices such as electron capture, Hall electrolytic conductivity, or photoionization detectors. The most common detection technique specified by the standard methods is mass spectrometry (MS), which can readily achieve a high degree of selectivity and sensitivity.

## 6.1 BIOLOGICAL SAMPLES

Methods of analysis for 1 ,2dichloroethene in biological materials are presented in Table 6- 1. The purge and trap method of Lin et al. (1982) is a suitable method for extraction and measurement of cisand trans- 1,2-dichloroethene in body tissues. However, recovery of trans- 1,2-dichloroethene varies with the type of body tissue. This finding generally agrees with those of the investigators who have attempted to measure levels of volatile halocarbons in body tissues. In addition to purge and trap, the headspace analysis methods of Hara et al. (1980) and Uehori et al. (1987) allow qualitative

## Table 6-1. Analytical Methods for Determining 1,2-Dichloroethene in Biological Samples

| Sample matrix | Preparation method | Analytical method | Sample detection limit | Percent recovery | Reference |
|---|---|---|---|---|---|
| Adipose, kidney, and brain tissue | Mince and purge tissue at 60 °C; trap on Tenax®; thermal desorption | GC/HECD | 50 pg | 93.3±12.4[a](adipose)<br>53.4±2.4[a](kidney)<br>62.6±2.6[a] (brain) | Lin et al. 1982 |
| Blood | Heat in a closed vial | GC/FID | No data | No data | Uehori et al. 1987 |
| Blood | Mix with water; heat in a closed vial at 40 °C; headspace analysis | GC/MS | 10–20 pg | No data | Hara et al. 1980 |
| Blood | Purge and trap with antifoaming agent; thermal desorption | GC/MS | 20 ppt | ~ 125 | Ashley et al. 1992 |
| Blood, urine, solid tissue | Sample in sealed vial heated to 65 °C; headspace analysis | GC/FID<br>GC/ECD | No data | No data | Streete et al. 1992 |
| Body tissue | Homogenize and mix tissue with water; heat in a closed vial at 40 °C; headspace analysis | GC/MS | 10–20 pg | No data | Hara et al. 1980 |
| Breath | Portable spirometer into canisters | GC/MS | No data | 99 (trans)<br>90 (cis) | Raymer et al. 1990 |

[a]For trans-1,2-dichloroethene

ECD = electron capture detector; FID = flame ionization detector; GC = gas chromatography; HECD = Hall electroconductivity detection; MS = mass spectrometry

identification of 1,2-dichloroethene in biological materials. A combination of detectors enabled Streete et al. (1992) to determine dichloroethenes in the headspace of blood, urine, and solid tissues. Dichloroethenes in breath can be determined by GUMS after collection with a portable spirometer (Raymer et al. 1990). In this approach, recoveries exceeded 90% for the dichloroethene isomers. The detection limit for dichloroethenes in human blood has been extended to part-per-trillion levels by Ashley et al. (1992), using an automated purge and trap technique that suppresses sample foaming with an antifoaming agent. High resolution GUMS can be used to enhance the contaminant separation abilities of gas chromatography on blood samples (Ashley et al. 1992; Bonin et al. 1992).

## 6.2 ENVIRONMENTAL SAMPLES

Analytical methods for determining cis- and trans- 1,2 dichloroethene in environmental samples are presented in Table 6-2. Analysis of 1,2 dichloroethene in workplace air samples can be determined by NIOSH method 1003 (NIOSH 1987).

Methodologies appearing in the literature for sampling 1,2-dichloroethene in air are essentially the same with minor variations. Capillary columns are versatile in separating contaminants of interest, and usually offer superior resolution and limits of detection (Oxenford et al. 1989). Various detectors are used, such as flame ionization detectors (FID), electron capture detectors (ECD), Hall electroconductivity detectors (HECD), and mass spectrometers. Multiple detectors are often employed in series or in parallel to increase the number and types of compounds detectable by purge and trap methods (Ho 1989; Kessels et al. 1992). Of the four listed, the FID is the least sensitive to halogenated hydrocarbons, yet it is sensitive enough for environmental samples.

For 1,2-dichloroethene, adsorption to the solid sorbent is a significant analytical concern because of its volatility. It may be difficult to completely remove highly volatile compounds such as 1,2-dichloroethene from the air stream. Solid sorbents other than charcoal appear in some analytical methods; the most popular is the resin, Tenax® GC. In addition to Tenax, Mehran et al. (1990) usedCarbosieve® with capillary chromatography to decrease the analysis time for EPA method 502.2. Pollack and coworkers (1991) provide for automating the collection and analysis of cis-1,2-dichloroethene by focusing the sample on a trap consisting of Carbopack-B and Carbosieve S-III instead of on glass beads. Substituting spray and trap for purge and trap enhances extraction efficiencies by a factor of 2-5 and eliminates difficulties associated with sample foaming (Matz and Kesners 1993).

## Table 6-2. Analytical Methods for Determining 1,2-Dichloroethene in Environmental Samples

| Sample matrix | Preparation method | Analytical method | Sample detection limit | Percent recovery | Reference |
|---|---|---|---|---|---|
| Air | Charcoal tube collection and $CS_2$ desorption | GC/FID | 16 ppm | No data | NIOSH 1987 |
| Air | Stainless steel canister (modified EPA method TO-14) | GC/MS | 0.3 ppb (cis) | No data | McClenny et al. 1991 |
| Air | Gas sampling loop | Fast GC/FID | 4.3 ppb (cis) | No data | Ke et al. 1992b |
| Drinking water | Purge and trap onto adsorbent; backflush to cryogenically-cooled trap | GC/HECD | 0.002 µg/L | 80±7 | EPA 1986e |
| Drinking water | Automated purge and trap; thermal desorption | GC/PID; GC/HECD (capillary) | No data | No data | Ho et al. 1989 |
| Drinking water | Purge and trap (modified EPA method 524.2) | GC/ITD (capillary) | <0.2 µg/L | 100 (cis)<br>92 (trans) | Eichelberger et al. 1990 |
| Drinking water | Purge and trap (modified EPA method 524.2) | GC/FID; GC/ECD (capillary) | 0.01 µg/L (trans)[a]<br>0.03 µg/L (cis)[a] | 100 (trans)<br>99 (cis) | Kessels et al. 1992 |
| Water | Purge and trap; thermal desorption | GC/MS (method 6210) | 1.6 µg/L (trans) | 1.05*C*+0.03[b] (trans) | APHA/AWWA/WEF 1992 (Standard Methods) |
| Water | Purge and trap onto adsorbent; thermal desorption | GC/HECD (method 6230) | 0.10 µg/L (trans) | 0.97*C*-0.16 (trans) | APHA/AWWA/WEF 1992 (Standard Methods) |
| Water | Flow injection | MIMS (uses ion trap MS) | 0.5 ppt (trans) | No data | Bauer and Solyom 1994; Soni et al. 1995 |
| Groundwater, soil, sediment, solid waste | Purge and trap onto adsorbent; thermal desorption | GC/MS (SW846 method 8240B) | 5 µg/L (trans) | 1.05*C*+0.03 | EPA 1986 |
| Groundwater, soil, sediment, solid waste | Purge and trap onto adsorbent; thermal desorption | GC/MS (SW846 method 8260A) | 60 ng/L (trans), 120 ng/L (cis) | 93±5.2 (trans), 101±6.7 (cis) | EPA 1986 |

## Table 6-2. Analytical Methods for Determining 1,2-Dichloroethene in Environmental Samples (continued)

| Sample matrix | Preparation method | Analytical method | Sample detection limit | Percent recovery | Reference |
|---|---|---|---|---|---|
| Groundwater, soil, sediment, solid waste | Purge and trap onto adsorbent; thermal desorption | GC/HECD (SW846 method 8010B) | 2 ng/L (optimum conditions for trans) | 0.97*C*-0.16 (trans) | EPA 1986 |
| Groundwater, soil, sediment, solid waste | Purge and trap onto adsorbent; thermal desorption | GC/PID<br>GC/HECD (SW846 method 8021A) | 50 ng/L (trans)<br>60 ng/L (trans) | 93±3.7 (trans)<br>99±3.7 (trans) | EPA 1986 |
| Wastewater | Purge and trap onto adsorbent; backflush to cryogenically-cooled trap | GC/HECD (EPA 601) | 0.1 µg/L | 91±19 | EPA 1982 |
| Wastewater | Purge and trap onto adsorbent; backflush to cryogenically-cooled trap | GC/MS (EPA 624) | 1.6 µg/L | 99±12 | EPA 1982 |
| Wastewater | Purge and trap (EPA Master Analytical Scheme) | GC/MS (capillary) | ~1 ppb | No data | Michael et al. 1991 |
| Landfill leachate | Homogenized sample; heated at 40 °C; headspace sampled | GC/MS (qual.)<br>GC/FID (quant.) | ~1 ppb | No data | Först et al. 1989 |
| Soil | Purge and trap onto adsorbent; rapid heating desorption | GC/MS | 5 µg/kg | No data | EPA 1987b |
| Food | Headspace with solid-phase microextraction | GC/HECD | ~100 µg/kg | No data | Page and Lacroix 1993 |
| Food | Homogenize sample in alcohol | GC/MCD | No data | No data | AOAC 1990a |

[a]ECD
[b]This formula has concentration entered as µg/L in place of *C* (true concentration) then calculated as a percentage.
Example: For 0.97*C*-0.16 at a concentration of 10 µg/L: (0.97×10) - 0.16 = 9.54. 9.54 of 10 is equivalent to 95.4% recovery.

AOAC = Association of Official Analytical Chemists; APHA = American Public Health Association; AWWA = American Water Works Association; ECD = electron capture detection; EPA = Environmental Protection Agency; FID = flame ionization detection; GC = gas chromatography; HECD = Hall electrolytic conductivity detection; ITD = ion trap detection; MCD = microcoulometric detection; MIMS = membrane introduction mass spectrometry; MS = mass spectrometry; NIOSH = National Institute of Occupational Safety and Health; PID = photoionization detection; WEF = Water Environment Federation

## 6. ANALYTICAL METHODS

EPA method 601 (purgeable halocarbons) and EPA method 524 (purgeables) describe analysis of 1,2-dichloroethene in municipal and industrial waste water (EPA 1982). In both methods, a 5 mL grab sample of water is connected to a purging chamber. This chamber allows an inert gas to bubble through the water sample; the gas flow is directed through an adsorbent tube. In EPA method 601, nitrogen or helium.is the purging gas, and the adsorbent column consists of two different adsorbents and a drying agent. In EPA method 624, helium is the purging gas, and the adsorbent column is made up of one adsorbent and a drying agent. The collected organics are liberated from the sorbent by heating the sorbent column while backflushing with an inert gas; these organics are then introduced into the gas chromatograph. EPA methods 601 and 624 were developed to analyze volatile priority pollutants. In EPA method 601, analysis by GC uses a Carbopack B column, a Poracil C column, and a HECD detector. In EPA method 624, analysis by GC uses a Carbopack B column and a mass spectrometer. Since trans-1,2-dichloroethene is a priority pollutant and cis- 1,2-dichloroethene is not, only the trans isomer is mentioned in this method.

EPA method 502.1 is used to analyze 1,2-dichloroethene in finished or raw source water (EPA 1986e). This method is similar to EPA method 601. However, once the compound has been purged from the water sample to the adsorbent tube, the compound is introduced to the gas chromatograph by rapidly heating the adsorbent tube, with no intermediate cryogenic trapping.

Numerous researchers have applied modifications of the EPA methods to environmental samples. EPA's Master Analytical Scheme (Michael et al. 1991) incorporates automated purge and trap and capillary chromatography into method 624 to achieve sensitivity of 1 ppb. Method 624 was compared to purgeable organic chloride analysis by Barber et al. (1992) and found to be superior by virtue of its contaminant identification capabilities. Eichelberger et al. (1990) modified method 524 by using a capillary column and an ion trap detector (ITD) to achieve detection levels below 200 ppt. Headspace sampling coupled with capillary GUMS offers a promising screening tool since it requires minimal sample preparation (Gryder-Boutet and Kennish 1988). Headspace GUMS can also been used for determining dichloroethenes in landfill leachate (Forst et al. 1989).

Purge and trap methodology sometimes involves direct trapping of the bubbled compound cryogenically. Water contamination can become a problem in this method. The cryogenic trap described in EPA methods 601 and 624 is a specialized item and may not be adaptable to all gas

chromatographs. The considerations discussed above regarding use of different columns and detectors also apply here.

The EPA guidelines for contract laboratories include methodology for water and soil sample analysis (EPA 1987c). The method listed in Table 6-2 is identical to EPA method 502.1 for the purpose of this discussion (except for the use of a mass spectrometer as the detector). The procedure for analyzing low-level contamination in soil is also similar to EPA method 502.1, except that the purging gas passes through a soil sample rather than a water sample. For higher-level soil contamination, the soil sample is first extracted with methanol. An aliquot of the extract is diluted with water; then the purge and trap methodology is followed. With respect to dichloroethene recoveries, Hewitt et al. (1991) found a headspace technique that is comparable to EPA SW-846 method 8240 for soil. It is practical for sample screening where contaminant identities were not required. The various SW-846 methods for 1,2-dichloroethene presented in Table 6-2 are similar except for detection method.

EPA method TO-14 uses an evacuated stainless steel canister to collect ambient air samples. Sample aliquots are analyzed by GUMS. McClenny et al. (1991) report a method detection limit of 0.3 ppb for this method. A method which represents a significant departure from more traditional methods for environmental samples is solid-phase microextraction (SPME). Solid phase microextraction uses a coated fused-silica fiber to collect contaminants from air and water samples. Chai et al. (1993) describe a simple non-purge and trap technique for determining dichloroethenes in air and water using this approach. The contaminants on the coated fused-silica fiber can then be thermally desorbed directly into the gas chromatograph for analysis. Page and Lacroix (1993) show the utility of headspace sampling coupled with fused-silica fiber adsorption in determining dichloroethenes at the 100 ppt level in foods. Their method satisfies the detection limit requirements of EPA method 524.2 for chloroethenes. Bauer and Solyom (1994) have developed a method to directly analyze waters in an ion trap mass spectrometer and have achieved a limit of detection for trans-1,2-dichloroethene of 0.5 ppt using single ion monitoring of *m/z* 96 (Soni et al. 1995).

## 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-dichloroethene 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-dichloroethene.

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.

### 6.3.1 Identification of Data Needs

**Methods for Determining Biomarkers of Exposure and Effect.** The available database provides several analytical methods adequate for the measurement of cis- and trans- 1,2dichloroethene in body tissue (see Section 6.1). Accuracy measurements for 1,2dichloroethene by Lin et al. (1982) show excellent recovery from adipose tissue but marginal recoveries from kidney and brain tissues. 1,2Dichloroethene was recovered at 88-150% from blood (Ashley et al. 1992). Limits of detection for all biological matrices ranged from 10 to 50 pg. Additional recovery data in all condensed biological media are needed. Other than the parent compounds, there are no known biomarkers of exposure or the effects of exposure that are unique to 1,2-dichloroethene. Consequently, biomarkers of exposure or the effect of exposure should be identified; standardized analytical methods for their determination should be identified or developed in response. These biomarkers could allow an easier route for identification of exposure, especially for some tissues where bioconcentration of 1,2-dichloroethene does not occur.

**Methods for Determining Parent Compounds and Degradation Products in Environmental Media.** Numerous analytical methods exist for analysis of cis- and trans-1,2-dichloroethene in environmental matrices (see Section 6.2). These analytical methods may be used to identify areas of 1,2-dichloroethene contamination, and to determine the potential threat to human health of 1,2-dichloroethene in the environment. Standardized methods exist for the analysis of drinking water, waste water, soil and air (APHA 1992; EPA 1986, 1987b; NIOSH 1987). Standardized methods for analyzing other media such as sediments and surface water will aid in establishing levels of human exposure to 1,2-dichloroethene. Inhalation is the most probable route of

exposure, and atmospheric exposure is likely to be of greatest concern to humans. However, the standardized methods for detecting 1,2-dichloroethene in air appear to be weak. For example, its detection limit of 16 ppm, outlined by the NIOSH technique (NIOSH 1987), is relatively high. Conversely, the stainless steel canister method of McClenny et al. (1991) purports to have a detection limit of 0.3 ppb and although not rigorously standardized, shows promise in detecting ambient background levels of 1,2-dichloroethene. Information regarding the recovery efficiencies of the NIOSH (1987), McClenny (1991), and Ke et al. (1992b) procedures for detecting 1,2-dichloroethene in air were lacking. Additional data is needed to assess both accuracy and precision in the analysis of 1,2-dichloroethene in air.

Contamination of surface water, groundwater, and foods in the vicinity of waste sites poses a threat to humans through oral exposure to 1,2-dichloroethene. Near quantitative recoveries and <.02 ppb detection limits were reported by Eichelberger et al. (1990). Low part-per-trillion detection limits were reported by Kessels et al. (1992) and an 0.5 ppt detection limit was reported by Soni et al. (1995). These recoveries and detection limits for 1,2-dichloroethene in water, coupled with the specificity offered by capillary gas chromatography and selective detection used by these researchers provide a means for determining 1,2-dichloroethene at very low levels in water.

Currently, no viable method exists for determining 1,2-dichloroethene in food. The detection limit of 100 μg/kg reported by Page and Lacroix (1993) is at least two orders of magnitude higher than what is required to be comparable to existing air and water methods for 1,2-dichloroethene. Appreciable additional work is needed in this area.

### 6.3.2 Ongoing Studies

The Environmental Health Laboratory Sciences Division of the National Center for Environmental Health, Centers for Disease Control and Prevention, is developing methods for the analysis of both cisand trans-1,2-dichloroethene and other volatile organic compounds in blood. These methods use purge and trap methodology, high resolution gas chromatography, and magnetic sector mass spectrometry which gives detection limits in the low parts per trillion (ppt) range.

Ongoing studies for developing new analytical methods for 1,2-dichloroethene in environmental matrices could not be located.