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 1,1-dichloroethene, its metabolites, and other biomarkers of exposure and effect to 1,1-dichloroethene. 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.

6.1 BIOLOGICAL MATERIALS

The analytical methods used to quantify 1,1-dichloroethene in biological samples are summarized below. Table 61 lists the applicable analytical methods for determining 1,1-dichloroethene in biological specimens.

1,1-Dichloroethene exposure can be monitored by measuring the levels in blood, expired air and urine (Ashley et al. 1992; McKenna et al. 1978a; Pellizari et al. 1985; Raymer et al. 1990, 1991; Wallace et al. 1984). 1,1-dichloroethene also distributes preferentially to liver, kidney, and to a lesser extent, adipose tissue. Methods are available to measure 1,1-dichloroethene and/or its metabolites in these tissues as well (Lin et al. 1982). Purge-and-trap gas chromatography/mass spectrometry (GC/MS) is the most commonly used method to detect 1,1-dichloroethene in biological samples. The purge-and-trap technique involves bubbling an inert gas through the sample to purge the volatile compounds out of solution. The compounds are then trapped in a cold trap (cry&rapping) or adsorbed on a suitable adsorbent such as Tenax. The next step is thermal desorption of the trapped solutes and their subsequent transfer to an analytical column. GC/MS allows the detection of compound at the ppb level. Capillary GC affords the highest resolution of complex mixtures, even when other volatile organic compounds are present that

could conceivably mask or interfere with the detection of 1,1-dichloroethene. Furthermore, specific GC-detectors, as well as mass selective detectors, enable the quantitation of 1,1-dichloroethene even when it is not fully separated from other compounds. It is difficult to accurately measure biological concentrations of 1,1-dichloroethene and correlate these measurements to actual exposure concentrations because of the chemical's short half-life and conversion into metabolites. The concentration of 1,1-dichloroethene in biological media is continually changing by virtue of its rapid release into the air or biotransformation into other compounds. More information on methods for the analysis of 1,1-dichloroethene in biological materials, including sample preparation techniques, can be found in the references cited in Table 6-1.

Environmental exposure to 1,1-dichloroethene at hazardous waste sites may often include exposure to other chlorinated hydrocarbons. 1,1-dichloroethene exposure can be monitored by direct measurement of the parent compound or its metabolites. It is difficult to distinguish metabolites of 1,1-dichloroethene in the body because some of the same metabolites may be formed as a result of exposure to other chlorinated hydrocarbons.

Determination of 1,1-dichloroethene in breath samples by GC/MS is the most commonly used method of monitoring exposure to 1,1-dichloroethene (Pellizzari et al. 1985; Raymer et al. 1990, 1991). Sensitivity is in the low ppb range. Recovery is adequate. Various other techniques are being studied and developed to monitor 1,1-dichloroethene in expired air using reversible adsorption (Contant et al. 1984) and impregnated tape methods for continuous monitoring (Denenberg and Miller 1974). Recently, a portable device for measuring 1,1-dichloroethene in alveolar breath was described (Raymer et al. 1990).

1,1-dichloroethene has been measured in whole blood samples using purge-and-trap GC/MS (Ashley et al. 1992). This method shows excellent sensitivity (low ppt levels) and good precision (<20% coefficient of variation). Recoveries were high (> 100%). The reason for the high recoveries was not clear but was suggested to be due to the inability to accurately assess the levels of the volatile compounds in the unspiked blood which served as a baseline for recovery calculation. The measurement of 1,1-dichloroethene adducts with DNA in lymphocytes or hemoglobin may also be useful in monitoring exposure to 1,1-dichloroethene. Such a method has been established in hemoglobin for another volatile organic compound, ethylene oxide (Tornqvist et al. 1986). Because human hemoglobin has a half-life of ≈60 days (although half-lives of

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Human tissue (adipose, kidney, liver, and brain)	Mince tissue, add isooctane/water; extract, purge-and-trap	GC/ECD	≈50 pg	>50	Lin et al. 1982
Human Breath	Thermal desorption	GC/MS	1 $\mu g/m^3$	40–60	Pellizari et al. 1985; Wallace et al. 1984
Human Breath	Collect alveolar breath samples in 6-L cannister using a spirometer followed by cryogenic trapping; collect whole breath samples in Tedlar bags; preconcentrate onto Tenax; thermally desorb	GC/MS	NR	NR	Raymer et al. 1991
Human alveolar breath	Breath collection in evacuated 1.8-L canister using a spirometer, cryogenic concentration	GC/MS	<5 $\mu g/m^3$	95	Raymer et al. 1990
Human blood	Purge-and-trap volatile compounds from blood	GC/MS	3.1 ppt	>100	Ashley et al. 1992
Rat urine	None	GC/MS	No data	≥35	McKenna et al. 1978b

ECD = electron capture detector; GC = gas chromatography; MS = mass spectrometry; NR = not reported

hemoglobin adducts are somewhat reduced), monitoring of 1,1-dichloroethene adducts with hemoglobin can be a valuable tool for estimating exposure over longer periods.

1,1-dichloroethene has been detected in urine using GC/MS; however, low recoveries were obtained (McKenna et al. 1978a). Sensitivity and precision data were not reported.

6.2 ENVIRONMENTAL SAMPLES

The analytical methods used to quantify 1,1-dichloroethene in environmental samples are listed in Table 6-2. The analytical methods required by EPA (1984a, 1984b, 1984c) for the analysis of 1,1-dichloroethene in water and waste water are described in procedures 601 (GC/ECD), 624 (GC/MS), and 1624 (GC/MS). The sensitivity for these methods is in the ppb range. These are testing procedures required under the Clean Water Act for sites discharging municipal and industrial waste water. The method required by the EPA Contract Laboratory Program (CLP) for analysis of 1,1-dichloroethene and other volatile organic compounds is hexadecane extraction, fc>llowed by determination of approximate concentration using GC and flame ionization detection (FID), and final quantitative analysis using GC/MS (EPA 1986a, 1986b).

GC/FID is used to detect 1,1-dichloroethene in air samples (Foerst 1979; NIOSH 1984; Taylor 1978). The sensitivity of this procedure is in the low ppm range. Recovery is good. GC/MS is used to determine 1,1-dichloroethene in water, waste water discharges, and soil samples with sensitivities in the ppb-range. DeLeon et al. (1980) measured levels of 1, 1-dichloroethene in soil and chemical waste; this method had a limit of detection of 10 ppm. In addition, GC/MS is used to determine levels of 1,1-dichloroethene in fish tissue (Easley et al. 1981 and Hiatt 1983). GC/ion trap detection (ITD) is used for drinking water. Sensitivity is in the ppb range and recovery is good. Purge-and-trap GC/MS is used for measuring volatile chlorinated hydrocarbons in ground water (Barber et al. 1992). The detection limit for this method is 0.2 μg /L. At concentrations 1, 1-dichloroethene ranging from 0.2 to 100 μg /L, recoveries were good, ranging from 85% to 142%. The high recoveries (>100%) o were the result of using a calibration curve that spanned more than three orders of magnitude. Precision was excellent (33% RSD). Purgeable organic chloride (POCl) analysis can be used as a complimentary method for use with GC/MS. Purge-and-trap CC/MS and POCl analysis gave data of similar accuracy and precision at spiked concentrations of >l μg /L. Lower recoveries and poor precision were obtained at a

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery[a]	Reference
Air	Adsorb (charcoal); desorb carbon disulfide	GC/FID	1 mg/m^3	85	Foerst 1979; NIOSH 1984 (method 1015); Taylor 1978
Air	Solid sorbent collection	GC/FID	7 μg/sample	>80	Foerst 1979
Air	Reversible adsorption	GC/MS	No data	No data	Coutant 1984
Water	Purge-and-trap method	GC/HECD	0.13 μg/L	0.98C–0.87	EPA 1984a (method 601)
Water	Purge-and-trap method	GC/MS	2.8 μg/L	1.12C+0.61	EPA 1984c (method 624)
Water	Isotope dilution	GC/MS	10 μg/L	No data	EPA 1984c (method 624)
Tap water	Purge-and-trap method	GC/FID	NR	76.6	Driss and Bouguerra 1991
Drinking water	Purge-and-trap on solid absorbent, thermal desorption, capillary column GC separation	GC/ITD	<0.2 μg/L	87	Eichelberger et al. 1990 (EPA method 524.2)
Groundwater	Purge-and-trap method	GC/HECD	0.13 μg/L	0.98C–0.87	EPA 1986a (method 8010)
Ground water	Purge-and-trap method	GC/MS	0.2 μg/L	85–142	Barber et al. 1992
Groundwater	Purge-and-trap method	GC/MS	5 μg/L	1.12C+0.61	EPA 1986b (method 8240)

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

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery[a]	Reference
Solids/sludges/ soils/sediments/ wastes	Purge-and-trap method	GC/MS	Soil, sediment, 5 μg/L (ww); wastes, 0.5 mg/kg	1.12C+ 0.61	EPA 1986b (method 8240)
Soil/chemical waste	Hexane extraction; temperature programmed GC determination	GC/MS	10 ppm	80–90	DeLeon et al. 1980
Fish tissue	Homogenize, add liquid N_2 to prevent evaporation of volatiles, vacuum distillation	GC/MS using a fused-silica capillary column	No data	No data	Hiatt 1983
Fish tissue	Purge-and-trap method to release volatile compounds trapped in the fish tissue	GC/MS	10 μg/kg	70	Easley et al. 1981
Packaging films	Heat hypovials containing film at 120°C; collect headspace vapor	GC/ECD	0.04 ppm	No data	Crosby 1982; Gilbert et al. 1980
Food (potato crisps, cakes, snack products, cheeses, biscuits)	Crush or grind and heat food samples	GC/ECD	<0.005 ppm	No data	Gilbert et al. 1980

[a]Recovery is sometimes expressed as a function of C which denotes the true value for the concentration

ECD = electron capture detection; FID = flame ionization detection; GC = gas chromatography; HECD = Hall electrolytic conductivity detector; ITD = ion trap detection; MS = mass spectrometry; N_2 = nitrogen; ww = wet weight

spiked concentration <1 μg /L. Detection limits using POCL analysis were 0.2 μg /L as well. POCI analysis is useful for screening samples for volatile chlorinated hydrocarbons; however, it is not suitable as an independent method of analysis. Purge-and-trap GC/flame ionization detector (ECD) has also been used to measure 1,1-dichloroethene in tap water (Driss and Bouguerra 1991). Recovery (76.6%) and precision (1.6% RSD) for this method were good. The detection limit was not reported. Gilbert et al. (1980) detected 1,1-dichloroethene in food at levels <5 ppm using headspace GC/ECD. These food products were packaged in polyvinylchloride films. Birkel et al. (1977), using GSC/MS, detected levels of between 6.5 and 10.4 ppm of 1,1-dichloroethene in Saran® food packaging films. Complete descriptions of these techniques can be found in the references cited in Table 6-2.

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 1,1-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 1,1-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. Except for the measurement of 1,l-dichloroethene in breath within a short period after exposure, there are no other biomarkers of exposure or effect unique to 1,1-dichloroethene. Analytical methods exist for determining 1,1-dichloroethene in breath (Contant et al. 1984; Denenberg and Miller 1974;

Pellizzari et al. 1985; Raymer et al. 1990; Wallace et al. 1984), blood (Ashley et al. 1992), and urine (McKenna et al. 1978a). These methods have acceptable quantification limits and are capable of determining exposure.

There are few analytical methods used to determine 1,1-dichloroethene in biological samples. The current emphasis is on (a) measuring the compound of interest at the ppb level accurately and consistently, (b) refining sample preparation techniques, and (c) modifying the analytical procedure to obtain better resolution with higher sensitivity. Analytical methodology to distinguish exposure to 1,1-dichloroethene from compounds with similar metabolic profiles is not available. Accuracy, precision, and recovery data are also lacking since the available information concentrates on the extension of detection limits of 1,1-dichloroethene rather than meeting quality control objectives necessary for analytical method standardization.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. There are media-specific standardized methods available for detecting 1,1-dichloroethene in environmental samples. Accuracy data and sample detection limit data are available for the EPA-approved methods; however, this information is incomplete for other analytical methods. This may be because of the lack of adequate data to determine method accuracy, precision, or recovery values. A better resolution and sensitivity are achievable with the application of the proper GC capillary column and selection of the correct detector or detector combination (Kirshen 1984).

Methods are available to detect 1,1-dichloroethene in air, water, sediment, soil, sludge, liquid waste, food, and fish (Barber et al. 1992; Coutant 1984; DeLeon et al. 1980; Driss and Bouguerra 1991; Easley et al. 1981; Eichelberger et al. 1990; EPA 1984a, 1984c, 1986a, 1986b; Foerst 1979; Gilbert et al. 1980; Hiatt 1983; NIOSH 1984; Taylor 1978). The standardized methods can detect 1,l-dichloroethene at ppt levels in air and mg/L levels in water. In addition, numerous techniques for the analysis of 1,1-dichloroethene are reported in the open literature (Constant et al. 1984; EPA 1986a, 1986b; Gilbert et al. 1980; Pellizzari et al. 1985; Tornqvist et al. 1986).

The known degradation products of 1,1-dichloroethene containing chlorine are volatile organic compounds and are often detected and quantified along with 1,1-dichloroethene in monitoring experiments (although they likely arose from anthropogenic sources). Thus, experimental

methods used to detect 1,1-dichloroethene are sufficient to quantify its chlorinated degradation products.

6.3.2 On-going Studies

No on-going studies concerning techniques for measuring and determining 1,1-dichloroethene in environmental samples were identified.

One on-going study on the development of analytical methods for human monitoring exposure to 1,1-dichloroethene was located (EXICHEM 1993). The study is being conducted by the EPA. Further details are not available .

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 1,1-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.