6. ANALYTICAL METHODS

6.1 BIOLOGICAL MATERIALS

The analytical methods for the determination of 1,1,2-trichloroethane in biological matrices are given in Table 6-1. Very few studies exist in the literature that report the analyses of this compound in biological matrices. The discussion about the methods that may be most sensitive for the determination of 1,1,2-trichloroethane levels in environmental samples and the advantages and disadvantages of the commonly used methods as given for environmental samples are thought to be applicable for biological samples because identical quantification methods are used for both kinds of samples. Most biological samples, however, pose unique problems during quantification. For example, the binding of the analytes to protein in samples containing high protein (e.g., whole blood) may result in reduced recovery (Cramer et al. 1988). Both blood and urine are very susceptible to foaming, especially at-high temperatures used during purging (Cramer et al. 1988; Michael et al. 1980). Poor and variable recovery has also been observed for tissue samples with high lipid content (Michael et al. 1980).

6.2 ENVIRONMENTAL SAMPLES

The common methods used for the determination of 1,1,2-trichloroethane in environmental samples are given in Table 6-2. The two common methods that are used for the preconcentration of 1,1,2-trichloroethane for the determination of its levels in air are adsorption on a sorbent column or collection in a cryogenically-cooled trap. The disadvantage with the cryogenic cooling is that the method is cumbersome and condensation of moisture in the air may block the passage of further air flow through the trap. The disadvantages with the sorption tubes are that the sorption and desorption efficiencies may not be 100% and that the background impurities in the sorbent tubes may limit detection in samples containing low concentrations (Cox 1983).

The most common method for the determination of 1,1,2-trichloroethane levels in water, sediment, soil, and aquatic species is the purging of the vapor from the sample or its suspension in water with an inert gas and trapping the desorbed vapors in a sorbent trap. Subsequent thermal desorption is used for the quantification of its concentration.

The two quantification methods that provide the lowest detection limits are halide-specific detection (e.g., Hall electrolytic conductivity detector) and mass spectrometry. Since the compound has three chlorine atoms, electron capture detection is also very sensitive for this compound. The advantages of halide-specific detectors are that they are not only very sensitive but are also specific for halide compounds. The mass spectrometer, on the other hand, provides an additional confirmation of the presence of a compound through the ionization patterns, and is desirable

TABLE 6-1. Analytical Methods for 1,1,2-Trichloroethane in Biological Samples[a]

Sample Matrix	Sample Preparation	Analytical Method	Detection Limit	Accuracy	Reference
Exhaled air	Collected in Tedlar bag, adsorbed on Tenax and thermally desorbed	Cryofocussing HRGC-MS	NG	NG	Barkley et al. 1980
Blood and urine	Purge at 50°C, trap in Tenax, thermal desorption	Cryofocussing HRGC-MS	NG	NG	Barkley et al. 1980
Blood	Purge and trap in Tenax, thermally desorb	GC-MS	NG	NG	Cramer et al. 1988
Urine	Equilibriate in sealed vial at 37°C and headspace gas analyzed	HRGC-MS	NG	NG	Ghittori et al. 1987
Human milk	Purge at 70°C, trap in Tenax, desorb thermally	Cryofocussing HRGC-MS	NG	NG	Pellizzari et al. 1982 Michael et al. 1980

[a]Although the analytical methods given were used for 1,1,1-trichloroethane, these methods should be applicable to 1,1,2-trichloroethane.

NG = Not given; GC = gas chromatography; HRGC = high resolution gas chromatography; MS = mass spectrometry

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

Sample Matrix	Sample Preparation	Analytical Method	Detection Limit	Accuracy	Reference
Ambient air	Direct injection.	Subambient air MG-MS	<5 ppt	NG	Grimsrud and Rasmussen 1975
	Adsorption on Tenax, thermal desorption into a stainless steel cylinder.	Subambient HRGC-MS	0.01-0.1 ppb	NG	Harkov et al. 1985, Kebbekus and Bozzelli 1982
	Sample collected in a cryogenically cooled trap.	GC-ECD	<0.01 ppb	85-115%	Singh et al. 1982
Occupational air	Adsorption on charcoal, desorption by CS_2.	GC-FID (NIOSH Methods P & CAM 127 and 5134)	0.05 mg/sample	92.3%	NIOSH 1977a,b
Landfill air	Adsorption on Tenax, thermal desorption into a stainless steel cylinder.	Cryofocussing GC-MC	0.1 ppb[a]	NG	LaRegina et al. 1986
Drinking, ground and surface water	Vacuum distillation with cryogenic trapping.	HRGC-ECD	0.2 µg/L	54%	Comba and Kaiser 1983
Finished water and raw source water	Purge at ambient temperature, trap in Tenax/silica/charcoal and desorb thermally.	GC-HECD (EPA Method 502.1)	0.007 µg/L	95% at 0.4 µg/L	EPA 1986a
	Purge at ambient temperature, trap in Tenax/silica charcoal,	subambient programmable GC-MS (EPA Method 524.1)	NG desorb thermally.	NG	EPA 1986a
	Purge at ambient temperature, trap in Tenax/silica charcoal, thermally desorb.	Cryofocussing HRGC-MS (wide or narrow bore) (EPA Method 524.2)	0.1 µg/L (wide bore) 0.08 µg/L (narrow bore)	104% (wide bore) at 0.5-10.0 µg/L 102% (narrow bore) at 0.5 µg/L	EPA 1986a
Water/wastewater	Purge at ambient temperature, trap in Tenax/silica charcoal, thermally desorb.	GC-HECD (EPA Method 601)	0.02 µg/L	91% at 0.45-50.0	EPA 1982a

TABLE 6-2 (continued)

Sample Matrix	Sample Preparation	Analytical Method	Detection Limit	Accuracy	Reference
Water/wastewater	Purge at ambient temperature, trap in Tenax/silica, thermally desorb.	GC-MS (EPA Method 624)	5.0 µg/L	101-104%	EPA 1982a
Groundwater/ leachate	Purge at ambient temperature, trap in Tenax/silica, desorb thermally.	GC-MS (EPA-CLP Method)	5 µg/L	NG	EPA 1987a
	Purge at ambient temperature, trap in Tenax/silica/charcoal, desorb thermally.	GC-HECD (EPA Methods 5030 and 8010)	0.2 µg/L	0.86c + 0.30 (where c is the concentration	EPA 1982b, 1986b
Sediment	Closed-loop purging and steam distillation, trap in Porapak N, solvent desorption.	GC-MS	1 µg/L	77-91%	Amin and Narang 1985
Sediment/fish	Vacuum distillation and cryogenic condensation.	HRGC-MS	NG	98% (sediment) 66% (fish)	Hiatt 1981, 1983
Soil/sediment	Purge suspension in water at 50°C, trap in Tenax/silica, desorb thermally.	GC-MS (EPA-CLP Method)	5 µg/L	NG	EPA 1987a
Soil, sludge, liquid and solid	Sample dispersed in a glycol, purge at ambient temperature, trap in Tenax/silica, desorb thermally.	GC-HECD (EPA Method 5030 and 8010)	0.2 µg/kg (soil) 10 µg/kg (liquid waste) 25 µg/kg (sludge and solid waste)	0.86c + 0.30	EPA 1982b, 1986b

[a]Based on a detection limit equivalent to twice the laboratory and field blank samples.

GC = Gas chromatography; MS = mass spectrometry; NG = not given; HRGC = high resolution gas chromatography; FID = flame ionization detector; ECD = electron capture detector; HECD = Hall electrolytic conductivity detector

when a variety of compounds must be quantified. The inability of halide-specific detectors to detect and quantify non-halogen compounds can be greatly overcome by using other detectors (e.g., photoionization detector) in series (Lopez-Avila et al, 1987; Driscoll et al. 1987). High-resolution gas chromatography with capillary columns is a better method for volatile compounds than are packed columns because they provide better resolution of closely eluting compounds and increase the sensitivity of detection. In addition, purge and whole-column cryotrapping eliminates the need for the conventional purge-and-trap unit and reduces the time of analysis (Pankow and Rosen 1988). The plugging of the trap by the condensation of moisture during cryotrapping may be avoided by the use of a very wide-bore capillary column, although the chromatographic resolution of such a column is inferior to narrow-bore capillary columns (Pankow and Rosen 1988; Mosesman et al. 1987). Regardless of the analytical method used for biological and environmental samples, precautions should be taken during sampling, preservation, and storage of samples to prevent loss from volatilization.

6.3 Adequacy of the Database

6.3.1 Data Needs

Methods for Determining Parent Compounds and Metabolites in Biological Materials. The analytical methods for determining levels of volatile chlorinated compounds in biological media are general ones, applicable to the entire class of chemicals. The publications that describe these methods do not report either the recovery or the detection limit of 1,1,2-trichloroethane in different biological matrices. The study of the levels of the parent compound in human blood, urine or other biological matrices can be useful in deriving a correlation between the level of this compound found in the environment and those found in human tissue or body fluid. Such correlation studies are unavailable for this compound, although the parent compound has been detected in human breath and urine (see Subsection 2.4).

No metabolite of 1,1,2-trichloroethane from human exposure to this compound has yet been identified (see Subsection 2.6.3). The changes in metabolite concentrations with time in human blood, urine, or other appropriate biological medium may be useful in estimating its rate of metabolism in humans. In some instances, a metabolite may be useful in correlating the exposed doses to the human body burden. Such studies on the levels of metabolites in human biological matrices are not available for this compound, although metabolic products of this compound from animal and in vitro studies have been identified (see Subsection 2.6.3) and analytical methods for their quantification are available.

Methods for Biomarkers of Exposure. No studies were located that identified biomarkers specific for 1,1,2-trichloroethane-induced disease states (see Subsection 2.9.2). If a biomarker for this compound in a human biological tissue or fluid were available and a correlation were found to

exist between the level of biomarker and a certain health effect, it could be used as an indication of a health effect caused by the exposure to this chemical.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. As shown in Table 6-2, methods are available for the analysis of 1,1,2-trichloroethane in environmental samples. The levels of this compound in different environmental media can be used to indicate whether there could be human exposure to this compound through the inhalation of air and ingestion of drinking water and foods containing 1,1,2-trichloroethane. If a correlation with human tissue or body fluid levels were available, the intake levels from different environmental sources can be used to estimate the body burden of the chemical in humans.

Although the products of biotic and abiotic processes of this compound in the environment are adequately known, no systematic study is available that measured the concentrations of its reaction products in the environment. In instances where the product(s) of an environmental reaction is more toxic than the parent compound, it is important that the level of the reaction products in the environment be known. It is known that 1,1,2- trichloroethane under anaerobic conditions (e.g. in anaerobic soils leading to contamination to groundwater) may dehydrochlorinate to vinyl chloride (see Section 5.3), a compound more toxic than the parent compound. The analytical methods for the determination of the levels of these and other environmental degradation products of 1,1,2-trichloroethane are available.

6.3.2 Ongoing Studies

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 1,1,2-trichloroethane 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.