6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring 1,2,3-trichloropropane 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 1,2,3-trichloropropane. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used to detect 1,2,3-trichloropropane in environmental samples are the methods approved by federal agencies 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 refine previously used methods to obtain lower detection limits, and/or to improve accuracy and precision.

6.1 BIOLOGICAL MATERIALS

No completed studies were located in the literature that reported the analysis of 1,2,3-trichloropropane in human biological matrices. Methods were located, however, for the analysis of the compound in rat biological matrices. These methods are listed in Table 6-l. With suitable modifications, the methods used to detect this chemical in animal samples may apply generally to its determination in human biological samples. Section 6.2 includes a discussion of the methods that may be most sensitive for the determination of 1,2,3-trichloropropane concentrations in environmental samples, including advantages and disadvantages of the commonly used methods. Initial testing to determine minimum detection limits, recovery, accuracy, and precision of the particular, suitably modified methods is necessary to gauge the applicability of the methods used to detect 1,2,3-trichloropropane in animal biological samples for the chemical's determination in human biological samples.

6.2 ENVIRONMENTAL SAMPLES

Methods for analyzing 1,2,3-trichloropropane in environmental samples are presented in Table 6-2. All of the methods listed use either adsorption on a sorption column (air samples) or purge-and-trap methods (solid and liquid samples), followed by thermal desorption and some form of gas chromatography (GC) with an appropriate detector as the analytical quantification technique. Purge-and-trap methods involve the purging of the vapor from the sample or its suspension in water with an inert gas and the trapping of the desorbed vapors in a sorbent trap. Particular care must be taken in sampling and storage of samples in view of the compound's high volatility. Although 1,2,3-trichloropropane was listed as a chemical that could be determined using the listed techniques, significant factors such as the detection limit and percent recovery were not reported for this chemical. Both halogen-specific detection (e.g., Hall electrolytic conductivity detectors) and mass spectrometry (MS) provide excellent detection limits (EPA 1986a; Ho 1989;

TABLE 6-1. Analytical Methods for Determining 1,2,3-Trichloropropane in Biological Materials

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Exhaled air in rats	Dry air drawn through cage and trap filled with ethyl alcohol at -15°C	GC-ECD	No data	No data	Sipes et al. 1982
Urine, feces, bile, major tissues, blood	Sample homogenized and centrifuged, extracted with n-hexane; blood added to water and bile added to ethyl alcohol prior to extraction	GC-ECD	No data	No data	Sipes et al. 1982

ECD = electron capture detection
GC = gas chromatography

TABLE 6-2. Analytical Methods for Determining 1,2,3-Trichloropropane in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Occupational air	Sample sorbed on charcoal; desorbed by CS_2	GC-FID (NIOSH method 1003)	0.3 mg/sample	95%	NIOSH 1987
Finished drinking/ raw source water	Purge and trap in Tenax/ silica/charcoal; thermally desorb	GC-HECD (EPA method 502.1)	No data	100% at 0.4 µg/L	EPA 1986a
Finished drinking/ raw source water	Purge and trap in Tenax/ silica/charcoal; thermally desorb	Subambient programmable HRGC-MS (EPA method 524.1)	No data	No data	EPA 1986a
Finished drinking/ raw source water	Purge and trap in Tenax/ silica/charcoal; thermally desorb	Cryofocusing (wide or narrow bore) HRGC-MS (EPA method 524.2)	0.03 µg/L (wide bore) 0.14 µg/L (narrow bore)	108% at 0.5-10 µg/L (wide bore) 96% at 0.5 µg/L (narrow bore)	EPA 1986a
Drinking water	Purge and trap in Tenax/ silica/charcoal; thermally desorb	GC-HECD and PID in series	0.03 µg/L	97%	Ho 1989
Liquid and solid waste, groundwater, soil, and sludge	Soil and viscous samples dispersed in water or methanol/water; purge and trap in Tenax/silica/charcoal and thermally desorb	GC-HECD (EPA method 5030 and 8010)	No data	No data	EPA 1986b
Solid and liquid waste, soil	Sample dispersed in a glycol; purged and trapped in Tenax/ silica/charcoal; thermally desorbed	GC-ECD and PID in series	No data	No data	Lopez-Avila et al. 1987
Citrus fruit (lemon, orange, grapefruit)	Sample blended with water; distilled into cyclohexane in essential oil apparatus; cleanup on Flourisil column; injected into GC	GC-ECD	No data	98%-99% at 0.01 ppm	Tonogai et al. 1986

ECD = electron capture detector
FID = flame ionization detector
GC = gas chromotagraphy
HECD = Hall electron capture detector
HRGC = high-resolution gas chromatography
MS = mass spectrometry
NIOSH = National Institute for Occupational Safety and Health
PID = photoionization detector

Lopez-Avila et al. 1987; Ramus et al. 1984). An advantage of halogenspecific detectors is that they are very sensitive and specific to halogen compounds. MS, on the other hand, provides additional confirmation of the identity of a compound through its ion fragment patterns. High-resolution gas chromatography (HRGC) with capillary columns coupled with MS provides better resolution and increased sensitivity for volatile compounds than packed columns. In this method, desorbed compounds are cryogenically trapped onto the head of the capillary column. This HRGC-MS method overcomes some common problems involved in analyses of excessively complex samples, samples with large ranges of concentrations, and samples that also contain nonvolatile compounds (Dreisch and Munson 1983; EPA 1986a).

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 1,2,3-trichloropropane 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 1,2,3-trichloropropane.

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 Data Needs

Methods for Determining Biomarkers of Exposure and Effect. No biomarker, other than possibly 1,2,3-trichloropropane itself, that can be associated quantitatively with exposure to 1,2,3-trichloropropane has been identified (see Section 2.5). Even the compound itself may not be a quantitative biomarker of exposure because the levels found have not been proven to qualitatively reflect exposure levels. Nevertheless, there are methods for analyzing 1,2,3-trichloropropane in most of the biological matrices for the rat, although important information such as detection limits and recoveries was not reported (Sipes et al. 1982). These methods may be sufficient for the analysis of human biological matrices.

No biomarkers have been identified that can be associated quantitatively with effects caused by exposure to 1,2,3-trichloropropane. Therefore, methods for biomarkers of effects are not currently available.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Analytical methods for determining 1,2,3-trichloropropane in contaminated air, water, soil, liquid and solid waste, sewage sludge, and citrus fruits are available (EPA 1986a, 1986b; Ho 1989; Lopez-Avila et al. 1987; NIOSH 1987; Tonogai et al. 1986). No methods were found for the determination of 1,2,3-trichloropropane in sediments. Most of the methods used for environmental samples, however, did not report detection limits, recovery, accuracy, and precision for 1,2,3-trichloropropane. Knowledge of these factors, as well as the development of alternative methods of analysis, would help in estimating the potential for human exposure to 1,2,3-trichloropropane. No information was found regarding degradation products of 1,2,3-trichloropropane. Consequently, no comment regarding the availability of analytical methods for determining degradation products can be made.

6.3.2 On-going Studies

The Environmental Health Laboratory Sciences Division of the Center for Environmental Health and Injury Control, Centers for Disease Control, is developing methods for analyzing 1,2,3-trichloropropane and other volatile organic compounds in blood. These methods use high resolution gas chromatography and magnetic sector mass spectrometry, which gives detection limits in the low ppt (parts per trillion) range.