6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring vinyl acetate 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 vinyl acetate. 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 vinyl acetate 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

The only method of analysis described in the literature for detecting vinyl acetate and metabolites in biological media is by administration of radioactive vinyl acetate (Hazleton 1979a, 1980a). Vinyl acetate is a volatile organic compound that is very rapidly hydrolyzed to acetaldehyde (via the unstable intermediate, vinyl alcohol) and acetate in the bodies of humans and animals (Simon et al. 1985a; Vinegar 1983). The acetaldehyde is converted to acetate and incorporated into the normal biochemical pathways and primarily excreted as carbon dioxide in expired air (Vinegar 1983). Section 2.3 contains more detailed information on the toxicokinetics of vinyl acetate.

6.2 ENVIRONMENTAL SAMPLES

Most analysis of vinyl acetate has been done on workplace air, especially in factories that make or use vinyl acetate. The primary method of analysis for vinyl acetate in air is gas chromatography with flame ionization detection (GC/FID). Infrared spectroscopy and gas chromatography/mass spectrometry (GC/MS) are also frequently used. Problems encountered when analyzing for vinyl acetate include volatility of the sample, interference from other organic chemicals, degradation of vinyl acetate by hydrolysis and polymerization, and desorption (extraction) of the sample. Most of the variation in methodology occurs with sample collection and desorption. Samples have been collected by grab-sampling, by midget impingers, and on solid sorbent tubes.

Grab-sampling of air in Houston followed by analysis by GC/FID or Fourier transform infrared spectroscopy (FTIR), showed that vinyl acetate could be detected in the samples in the presence of a large number of other organic compounds when analyzed by FTIR (Gordon and Meeks 1977). Disadvantages of this method are possible loss of sample through leakage from or decomposition in the collection bags and contamination of the sample by bag

components. Problems encountered with the FTIR hardware under field conditions led the authors to conclude the technique was better suited for laboratory use.

Midget impingers, as well as large-scale impingers, containing toluene have been used to sample the air in a vinyl acetate production plant (Deese and Joyner 1969). Analysis of samples was conducted by GC/FID. Several evaluations indicated that the method was accurate (mean recovery of 99.2%) and reliable for concentrations in the low ppm range. The main problems with this method are that the liquid used in the impingers is subject to spillage (however, unspillable impingers are now available) and it is difficult to scale the impingers down to a suitable size for personal use.

Solid sorbents are the usual collection media for personal sampling tubes used in occupational exposure situations because they are efficient, simple to use, and can be easily be scaled down to a convenient size. Solid sorbents are also the most frequently used for concentrations of organics from air. One of the most commonly used solid sorbents is activated carbon (Foerst and Teass 1980; Kollar et al. 1988; Krajewski et al. 1980; Sidhu 1981). Recoveries on this sorbent can be low due to hydrolysis or polymerization, depending on humidity conditions. Recoveries have ranged from 40% to 101% depending on desorption technique, humidity level, sample storage time, and how the sample was introduced to the sampler (Foerst and Teass 1980; Kollar et al. 1988; Krajewski et al. 1980; Sidhu 1981). Modifications to the activated carbon sampler were made to alleviate some of the problems associated with them (Kimble et.al. 1982). Recoveries approaching 100% were reported with activated charcoal sorbent treated with a polymerization inhibitor (hydroquinone) and preceded by a drying agent (calcium sulfate). When desorbed with carbon disulfide-acetone and analyzed by GC/FID, good sensitivity and precision were obtained (see Table 6-l). Advantages of this technique are apparent sample stability, high breakthrough volume, and readily available desorption and detection techniques. When this approach was repeated by others (Andersson and Andersson 1988), however, both recovery and precision were poor at humidities below 50%. A more recent GC/FID method using collection on the solid sorbent, Ambersorb® XE-347, followed by desorption with dichloromethane containing 5% methanol, yielded excellent recovery and precision over humidities ranging from 20 to 85% (Andersson and Andersson 1990).

The NIOSH-recommended procedure for determining vinyl acetate in air calls for collection on Chromosorb® 107, followed by thermal desorption and analysis by GC/FID (NIOSH 1990a). The lowest quantifiable level with this method is in the low ppb range with an average precision of 8.1% relative standard deviation (RSD) at humidity levels greater than 80%. The NIOSH method was developed and compared to activated charcoal by Foerst and Teass (1979). Although activated charcoal had a higher affinity for vinyl acetate, as demonstrated by its higher breakthrough volume (about 167 L compared to 4L for Chromosorb® 107), vinyl acetate was considerably less stable on the

TABLE 6-1. Analytical Methods for Determining Vinyl Acetate in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Collect in midget impingers; inject toluene collection medium	GC/FID	Low mg/m^3 (ppm)	99.2	Deese and Joyner 1969
	Collect on Chromosorb® 107; desorb thermally directly to GC	GC/FID	7 mg/m^3 (2 ppm)	106-110	NIOSH 1990a (NIOSH Method P&CAM 278)
Air	Collect sample on activated charcoal; desorb with carbon disulfide or acetonitrile; inject desorption solvent into GC	GC/FID	NR	40-100	Foerst and Teass 1979
	Collect on activated charcoal; desorb with carbon disulfide	GC/FID	0.35 mg/m^3 (0.1 ppm)	83.2	Sidhu 1981
	Collect on calcium sulfate-hydroquinone inhibited charcoal; desorb with carbon disulfide-acetone	GC/FID	1.33 mg/m^3 (0.38 ppm)	98.6-99.7	Kimble et al. 1982
Air	Collect sample on Ambersorb® XE-347; desorb with methanol/dichloro-methane	HRGC/FID	No data	82-100	Andersson and Andersson 1990
	Collect on Tenax®-GC; desorb thermally directly to GC	GC/MS	No data	>75	Pellizzari 1982
	Collect on calcium sulfate-hydroquinone inhibited carbon; desorb with carbon disulfide-acetone	GC/FID GC/MS	No data	16-96	Andersson and Andersson 1988

Table 6-1 (Continued)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
	Collect on trans-platinum chloride (ethylene); (pyridine) coated SAW	SAW sensor	No data	No data	Zellars 1989
Waste water effluent	Purge sample and trap volatiles on Tenax®-GC/ silica gel; thermally desorb to GC	GC/MS	No data	No data	EPA 1979 (EPA Method 624)
Waste water effluent	Purge and trap sample on total organics concentrator (Tenax® GC-silica gel-glass wool); desorb thermally to GC	GC/MS	1 µg/L (1 ppb)	96-110	Spingarn 1982 (EPA Method 624)
Coal combustion leachate	Purge sample and trap volatiles on Tenax®-GC/ silica gel; thermally desorb to GC	GC/MS	10 µg/L (10 ppb)	No data	Sorini and Jackson 1988 (EPA Method 624)

EPA = Environmental Protection Agency; FID = flame ionization detector; GC = gas chromatography; HRGC = high-resolution gas chromatography; MS = mass spectrometry; SAW = surface acoustic wave

activated charcoal. Advantages of the Chromosorb® 107 collection technique are improved sample stability, better recovery, and improved precision through a wider humidity range. Disadvantages are a lower breakthrough volume and limited access of most field sites to the thermal desorption technique.

Vinyl acetate has also been determined in air at industrialized areas and near waste disposal sites using Tenax® GC sorbent with thermal desorption. Separation and detection was on a high resolution GC/MS coupled to a computer containing a mass spectra database. Recoveries for this method were greater than 75%. Advantages of this method are its specificity in the presence of large numbers of potentially interfering chemicals and ability to quantify results (Pellizzari 1982). A disadvantage is the requirement for sophisticated and expensive equipment and the expertise to use the method. In addition, the effect of humidity is not known.

A more recently developed technique for use in industrial hygiene situations depends on detection of vinyl acetate by coated surface acoustic wave sensor. The special trans-$PtCL_2$(ethylene)(pyridine) coating makes the technique selective for vinyl acetate, and the apparatus can easily be scaled down for personal use. In addition, the coating is regenerative, increasing the cost/benefit ratio (Zellers 1989). More information is needed to compare this method to those currently in use.

Very little information was found concerning analysis of vinyl acetate in water and soil and no information was found for other media. The EPA recommended method for water (Method 624) specifies sampling on a total organics concentrator (Tenax® -silica gel) used as a purge-trap device (EPA 1979). The sample is thermally desorbed and analyzed by GC/MS. This method was used to detect vinyl acetate in secondary effluent from a publicly owned treatment works (Spingarn et al. 1982). It proved to be sensitive, accurate, and fairly precise. This method was also used to measure vinyl acetate in coal combustion leachate with a detection limit of 10 μg/L (Sorini and Jackson 1988).

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 vinyl acetate 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 vinyl acetate.

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. There are no reliable biomarkers of exposure for vinyl acetate (see Sections 2.5.1 and 2.9.2). Vinyl acetate is rapidly absorbed and metabolized in the body (Hazleton 1979a, 1980a; Simon et al. 1985a). The metabolites formed, acetaldehyde and acetate, are commonly found in humans and animals, and thus are not specific for exposure to vinyl acetate. Acetaldehyde and acetate are incorporated into the biochemical cycles and converted primarily to carbon dioxide and water. There are no tests currently available for measuring vinyl acetate or its metabolites in biological tissues.

There are no established biomarkers of effect for vinyl acetate; thus, there are no methods for determining biomarkers of effect for this compound. No changes in enzyme levels or body fluids have been documented following exposure to this compound. Genotoxic effects have been found in in vitro tests, but these are not specific for vinyl acetate and there is no established method for monitoring such effects in vivo.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Given vinyl acetate's high volatility, the media of most concern for human exposure is most likely air, with exposure also occurring by both oral and dermal routes (Deese and Joyner 1969; NIOSH 1978; Smyth and Carpenter 1973). Sensitive, reliable, and accurate methods exist for determining vinyl acetate in air (Deese and Joyner 1969; Foerst and Teass 1979; Gordon and Meeks 1977; Kimble et al. 1982; Kollar et al. 1988; NIOSH 1990a). The detection limits of these methods are probably too high for monitoring ambient air, but are sufficient for measuring levels present in occupational settings. At least one sensitive and accurate method exists for detecting vinyl acetate in water (Springarn et al. 1982). Routine methods of analysis for other environmental media were not located. Further studies on measurement of vinyl acetate in air, water and soil would be useful in determining the potential for exposure to this chemical at hazardous waste sites.

6.3.2 On-going Studies

No on-going studies concerning methods for measuring and determining vinyl acetate in biological and environmental samples were located.