6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring acrylonitrile 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 acrylonitrile. 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 acrylonitrile 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 a trade association 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

Acrylonitrile in both biological and environmental samples is most commonly determined by gas chromatography with a nitrogen-phosphorus detector (GC/NPD) (Page 1985), gas chromatography/flame ionization detection (GC/FID) (EPA 1982a), or gas chromatography/mass spectroscopy (GC/MS) (Anderson and Harland 1980). Infrared spectroscopy (Jacobs and Syrjala 1978) may also be used. In the handling of samples and standards, acrylonitrile should be treated with precautions appropriate for a probable human carcinogen.

Comparatively little information is available in the literature on the determination of acrylonitrile in biological materials. Methods have been published for the determination of acrylonitrile in blood (Anderson and Harland 1980; Freshour and Melcher 1983) and urine (Houthuijs et al. 1982; Sakurai et al. 1978). Acrylonitrile was widely used in the past as a fumigant, and it is possible that methods used for the determination of other fumigants in biological materials (Walters 1986) could be adapted to the determination of acrylonitrile in such samples.

Methods for detection of acrylonitrile in biological materials are summarized in Table 6-1.

6.2 ENVIRONMENTAL SAMPLES

The methods of choice for the determination of acrylonitrile in environmental samples are GC/NPD (Page 1985), GC/FID (EPA 1982a), and GC/MS (EPA 1982b). Multiple internal reflectance infrared spectrometry (Jacobs and Syrjala 1978) is useful for monitoring low levels of acrylonitrile in air.

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

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy (% Recovery)	Reference
Blood	Perfusion of whole blood with nitrogen at 95°C in a perfusion flask, collection on Tenax	GC/MS	1 ng/mL	50-80	Anderson and Harland 1980
Plasma	Sample injected onto precolumn, water evaporated, analyte flushed from precolumn by heating	GC/NPD	2 ng/mL	No data	Freshour and Melcher 1983
Urine	Headspace gas	GC/NPD	2 ng/mL	3.3%[a]	Houthuijs et al. 1982
Urine	Azeotropic distillation	GC	5 ng/mL	No data	Sakurai et al. 1982

[a]Coefficient of variation

GC = gas chromatography; MS = mass spectrometry; NPD = nitrogen-phosphorus detector.

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The determination of acrylonitrile in air may be accomplished by collection on a solid sorbet, such as activated charcoal, followed by elution and gas chromatographic measurement (NIOSH 1984).

EPA has published a method of analysis specific for acrylonitrile in water (EPA 1982a) and a method applicable to its determination in water along with other purgeable organics (EPA 1982b). Other standard EPA methods are adaptable for the determination of acrylonitrile in wastes (EPA 1986b).

Methods for the determination of acrylonitrile in environmental samples are summarized in Table 6-2.

6.3 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, 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 acrylonitrile 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 acrylonitrile.

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 Identification of Data Needs

Method for Determining Biomarkers of Exposure and Effect. Exposure to acrylonitrile can be determined by measuring parent acrylonitrile, acrylonitrile metabolites and adducts. Good methods exist for detecting and quantifying acrylonitrile in biological materials. These methods are based on capillary gas chromatography, where a special problem is introduction of analytes quantitatively and in a narrow band onto the capillary GC. One of the most promising approaches to analyte transfer is the use of cyrofocusing, in which analytes are condensed in a narrow band on a trap or on the GC column itself. Improvements in cryofocusing of volatile organic analytes for capillary GC determination (Washall and Wampler 1988) should improve sensitivity for the determination of acrylonitrile.

TABLE 6-2. Analytical Methods for Determining Acrylonitrile in Environmental Samples

Sample Matrix	Sample Preparation	Analytical Method	Sample Detection Limit	Accuracy	Reference
Air	Direct monitoring in ambient air	IR	0.2 ppm (volume)	±5% at 20 ppm	Jacobs and Syrjala 1978
Air	Collect on charcoal, elute to GC	GC/FID	0.015 mg/ sample	Not evaluated	NIOSH 1984
Air	Charcoal adsorption, elute with acetone, inject acetone solution	GC/NPD	10 ppb (volume, estimated)	70-82% recovery	Marano et al. 1978
Water	Purge, trap on soil sorbent trap, heat and desorb, backflush to GC	GC/IDMS	50 µg/L	Not evaluated	EPA 1980b
Water	Purge at 85°C, trap on Tenax sorbent trap, heat and desorb, backflush to GC	GC/FID	0.5 µg/L	107 ± 5.6% recovery	EPA 1982a
Water	Purge, trap on Tenax and silica gel, heat and desorb, backflush to GC	GC/MS	No data	Not evaluated	EPA 1982b
Soil, sediment, solid waste	Isolation of volatile acrylonitrile from sample followed by GC separation	GC/FID	0.5 µg/L	84 - 104% recovery	EPA 1986b

IR = infrared spectrometry; GC = gas chromatography; FID = flame ionization detector; NPD = nitrogen-phosphorous detector; IDMS = isotope dilution mass spectrometry; MS = mass spectrometry.

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Acrylonitrile metabolites have been measured in blood and urine, but, except for measurement of thiocyanate, these methods have not been developed for routine monitoring of exposed humans. Supercritical fluid extraction/chromatography and immunoassay analysis are two areas of intense current activity from which substantial advances in the determination of acrylonitrile and its metabolites in biological samples can be anticipated. The two techniques are complementary because supercritical fluid extraction is especially promising for the removal of analytes from sample material and immunoassay is very analyte- selective and sensitive (Vanderlaan et al. 1988).

Studies using radioactivity-labeled acrylonitrile indicate that acrylonitrile or its metabolites form covalent adducts with cellular macromolecules in most tissues. Studies to develop chemical or immunological methods for measuring these adducts would be especially valuable in detecting and perhaps even quantifying human exposure to acrylonitrile. Adverse health effects demonstrated following exposure to acrylonitrile, particularly acute exposures, were characteristic of cyanide toxicity. Because these effects are also indicative of exposure to many other toxicants, additional methods are needed for more specific biomarkers of effects of acrylonitrile exposure.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Methods for determining acrylonitrile in environmental samples are quite good. It may be assumed that the normal incentives for both research and the development of commercial methods of analysis will result in new analytical methods for acrylonitrile that have improved sensitivity and selectivity. Degradation products of acrylonitrile in environmental media are difficult to determine. This difficulty is not as much an analytical problem as it is a problem of knowing the fundamental environmental chemistry of these compounds in water, soil, air and biological systems.

6.3.2 On-going Studies

There exists an ongoing effort to develop a "Master Analytical Scheme" for organic compounds in water (Michael et al. 1988). The overall goal is the development of technology capable of detecting and quantitatively measuring organic compounds at 0.1 μg/L in effluent waters. Analytes are to include numerous semivolatile compounds and some compounds that are only "semisoluble" in water, as well as volatile compounds (boiling point, less than 150°C).

Studies designed to improve the determination of environmental contaminants will continue to provide refinements and improvements in the determination of acrylonitrile. The current high level of activity in supercritical fluid extraction of solid and semisolid samples should

yield improved recoveries and sensitivities for the determination of acrylonitrile in solid wastes, and the compound should be amenable to supercritical fluid chromatographic analysis. Immunoassay analysis is another area of intense current activity from which substantial advances in the determination of acrylonitrile in environmental samples can be anticipated (Vanderlaan et al. 1988).