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Health Assessment Document for Acrylonitrile

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HEALTH ASSESSMENT DOCUMENT FOR ACRYLONITRILE

NOTICE

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.

U.S. ENVIRONMENTAL PROTECTION AGENCY
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The report is an internal draft for review purposes only and does not constitute Agency Policy. Mention of trade names or commerical products does not constitute endorsement or recommendation for use.

PREFACE

The Office of Health and Environmental Assessment has prepared this health assessment to serve as a "source document" for Agency-wide use. The health assessment document was originally developed at the request of the Office of Air Quality Planning and Standards; however, the scope of the assessment has since been expanded to address multimedia aspects. This assessment will help ensure consistency in the Agency's consideration of the relevant scientific health data associated with acrylonitrile.

In the development of the assessment document, the scientific literature has been inventoried, key studies have been evaluated and summary/conclusions have been prepared so that the chemical's toxicity and related characteristics are qualitatively identified. Observed effect levels and other measures of dose-response relationships are discussed, where appropriate, so that the nature of the adverse health responses are placed in perspective with observed environmental levels.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (Cont.)

LIST OF TABLES (Cont.)

LIST OF FIGURES

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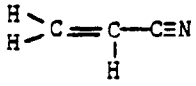
1. SUMMARY AND CONCLUSIONS

Acrylonitrile is a clear, colorless, and highly flammable liquid that has an unpleasant and irritating odor (Fassett, 1963). The boiling point of acrylonitrile is between 77.5 and 79°C; the melting point is -83.5°C (Weast, 1976), and the density of the vapor at 20°C is 0.8060 (Groet, 1976). Acrylonitrile is soluble in water between 7.2 and 9.1% at temperatures of 0°C and 60°C, respectively. The open cup flash point of acrylonitrile is 0°C, and the explosive limits are between 3.0 and 17% by volume in air at 25°C (Steere, 1968). Synonyms for acrylonitrile include 2-propenenitrile, cyanoethylene, and vinyl cyanide. Acrylonitrile has a molecular weight of 53.06 and a molecular formula of C_3H_3N. The structural formula is given below.



Acrylonitrile monomer production capacity in the United States is approximately 1,000,000 metric tons, and the estimated 1980 demand would utilize 86.2% of the total capacity (Anonymous, 1980). Of the anticipated 862,000 metric tons of acrylonitrile produced, approximately 77% (664,000 metric tons) will be used domestically; the remainder is exported. Acrylonitrile is used primarily as a raw material in the synthesis of acrylic and modacrylic fibers, ABS and SAN resins, nitrile rubbers, adiponitrile, acrylamide, and barrier resins (Suta, 1979). A small percentage of the acrylonitrile produced is used as a chemical intermediate.

Acrylonitrile is emitted to the atmosphere during monomer production, polymer production, transport, and end-product usage; however, the major sources of acrylonitrile emissions are monomer and polymer production facilities. These facilities are estimated to emit 10,872 metric tons of acrylonitrile per year.

The atmospheric half-life of acrylonitrile has been estimated to be between 9 and 10 hours (Suta, 1979), which is long enough to allow transport of acrylonitrile from emission sources to nearby populations. In natural water, acrylonitrile was decomposed. This may occur by either chemical decomposition or microbial degradation (Going et al., 1979; Mills and Stack, 1955). Evaporation may also lower the concentration of acrylonitrile in water; the calculated half-life for acrylonitrile by evaporation alone from water 1 m deep is 795 minutes (Dilling, 1977). If evaporation from water occurs at this rate in the environment, at least some of the acrylonitrile released in water will be emitted into the atmosphere.

The acrylonitrile levels in the vicinity of acrylonitrile production and polymer manufacturing plants were investigated by Hughes and Horn (1977) and Going et al. (1979). Acrylonitrile was detected in the air at distances up to 5 km; however, the concentrations of acrylonitrile were dependent on meteorological conditions and the production stage within the plant at the time of sampling. No acrylonitrile was detected in the soil near these plants. Variable low levels of acrylonitrile were generally detected in the water downstream from the plants, except for high levels of 35 to 4300 µg/l detected in some samples near wastewater discharge points. Acrylonitrile has also been detected in drinking water, although the levels were not quantified (Kopfler et al., 1976). The inhalation exposure of acrylonitrile in the vicinity of a plant site estimated by dispersion modelling does not agree well with the experimental monitoring data obtained from the same site (Going et al., 1979; Suta, 1979). There are insufficient data with which to determine the human intake of acrylonitrile through food and drinking water.

Limited data suggest that both aerobic and anaerobic microorganisms are capable of degrading acrylonitrile, especially acclimated microorganisms. Certain isolated bacteria can tolerate 10,000 ppm acrylonitrile and use it as a

sole source of nitrogen. In natural water, a concentration of 50 ppm may inhibit aerobic microbial degradation of acrylonitrile. The breakdown products of aerobic microorganisms may include ammonia and organics, followed by nitrification of ammonia.

Acrylonitrile has been shown to affect some terrestrial and aquatic plants at exposure concentrations of 9 to 100 mg/l. Acrylonitrile is toxic to aquatic animals at exposure concentrations in the low milligrams per liter range. The reported acute LC50 values for fish ranged between 10.1 and 70 mg/l. Subchronic exposure of fish for 30 to 100 days resulted in LC50 values of about 2 mg/l, with no evidence that a threshold concentration had been reached. Although the only tested invertebrate, Daphnia magna, had the lowest acute LC50 value (7.6 mg/l), this species was not adversely affected by chronic exposure to 3.6 mg/l throughout its whole life cycle.

Use of acrylonitrile as a fumigant has shown that the vapor concentrations required to kill 95% or more of many species of pest insects is between about 1 and 10 mg/l. No other information was found concerning the effects of acrylonitrile on wildlife.

Acrylonitrile is readily absorbed in animals following ingestion or inhalation, while dermal absorption is poor and occurs at about 1% of that of the lungs. Following absorption of radiolabeled acrylonitrile, the radioactivity disappears in a biphasic manner, with a half-life for the first phase of 3.5 to 3.8 hours and the second phase of 50 to 77 hours (Young et al., 1977). The predominant route of elimination is through the urine. The routes of elimination are dose-related with the percent eliminated through the urine less for small doses as compared to larger doses, while the relative amount retained by the carcass is greater for the small dose as compared to a larger dose. Acrylonitrile is metabolized to cyanide, which is transformed to thiocyanic and by

cyanoethylation of sulfhydryl groups to S-(2-cyanoethyl)cysteine, followed by elimination of these metabolites in the urine. Other minor metabolites are formed from acrylonitrile. The toxicity of acrylonitrile is caused by both the acrylonitrile molecule itself and its metabolites.

Acrylonitrile intoxication in humans results in irritation of the eyes and nose, weakness, labored breathing, dizziness, impaired judgement, cyanosis, nausea, and convulsions. The TLV of acrylonitrile is 45 mg/m^3 for humans. Acrylonitrile also causes severe burns to the skin. In experimental animals, there is considerable species variation in susceptibility to acrylonitrile intoxication; the guinea pig is the most resistant and the dog is the most sensitive. In animals, effects of intoxication include respiratory changes, cyanosis, convulsions, and death. In rats, the LD50 for acrylonitrile is between 80 and 113 mg/kg (Knoblock et al., 1971; Smyth et al., 1969). There is some evidence that acrylonitrile produces abnormal function of both the peripheral and central nervous systems and that acrylonitrile causes damage to the adrenals. With subchronic exposure of animals to acrylonitrile, some signs of functional disorders of the liver and kidney are observed. Chronic exposure of dogs and rats results in unthrifty appearance, weight loss, and early death. Some of these signs may be related to low food and water consumption resulting from the unpleasant taste of acrylonitrile in the water. Pathological changes in the rats believed to be treatment related included hyperplasia and hyperkeratosis of the squamous epithelium of the nonglandular portion of the stomach, proliferation of glial cells in the brain, and mammary gland hyperplasia in females.

Acrylonitrile adversely affected pup survival following exposure of pregnant rats and, in one study, produced teratogenic events. In a three-generation study in which rats were exposed to 500 ppm acrylonitrile in the drinking water, there was reduced pup survival in the first generation (Beliles

et al., 1980). This was a maternal effect inasmuch as fostering the pups on untreated dams eliminated the poor survival. Reproductive capacity was unchanged in the other generations, and the offspring showed no adverse effects on development. Similarly, rats exposed by inhalation to 40 or 80 ppm of acrylonitrile for 6 hours a day on days 6 to 15 of gestation had no statistically significant changes in reproductive success or fetal development (Murray et al., 1978). Only the pups of rats administered acrylonitrile per os (65 mg/kg) for days 6 to 15 of gestation had an increase in malformations (Murray et al., 1976). This increase was in total malformations, with no statistically significant increase occurring in any single malformation. It was concluded that these fetal abnormalities were the result of acrylonitrile and not the result of toxicity in the dams.

Acrylonitrile is difficult to assay for mutagneicity with in vitro assays because of its high vapor pressure. Acrylonitrile is positive in the Ames mutagenicity assay using S. typhimurium when the bacteria are exposed to the vapors of the compound and a mammalian metabolic activating system is present. Using E. coli and the fluctuation assay, there was no requirement for a metabolic activation system. Although it is not clear whether metabolic activation is required, it is clear that acrylonitrile is a mutagen in these bacterial assays. Acrylonitrile did not cause recessive lethal mutation in Drosophila melanogaster nor did it cause chromosomal aberrations in root tip meristerm. The lymphocytes of workers exposed to 5 ppm of acrylonitrile for an average of 15.3 years also showed no increase in chromosomal aberration (Thiess and Fleig, 1978). Although mutations and chromosomal aberrations have not been demonstrated in higher organisms after exposure to acrylonitrile, these systems have not been investigated as extensively as the bacterial assays.

Acrylonitrile has been shown to cause excessive numbers of tumors in rats in several assays as indicated in Table 1-1 (Quast et al., 1980a; Beliles, 1980; Bio/Dynamics Inc., 1980a, 1980b, 1980c; Maltoni, 1977; Quast et al., 1980b). Tumors occurred when the animals were exposed to acrylonitrile by inhalation, gavage, or ingestion of the compound in the drinking water. Common tumors, most notably mammary gland tumors in females, that occur with appreciable spontaneous rates in rats were observed at higher incidence and with shorter latency periods in treated animals as compared with control groups. In addition, treated animals developed brain astrocytomas, stomach (nonglandular portion) papillomas, and Zymbal gland (ear canal) tumors that are not commonly observed in control animals. Increased incidences of tumors at these sites occurred in nearly all the bioassays; however, increased incidences of tumors at additional sites were reported in some of the studies. It is clear that acrylonitrile is a carcinogen in rats, by several routes of exposure.

An occupational epidemiology study has been performed by O'Berg (1980). This study included 1345 male workers exposed to acrylonitrile in a textile fiber plant. An observed increased cancer rate in exposed workers as compared with the expected number was reported for both cancer at all sites and respiratory cancer. This increased cancer rate was crudely related to both the estimated extent of exposure and the length of exposure. Monitoring data, however, was unavailable with extent of exposure indicated only as high, medium, or low and without more precise data a dose-response relationship for exposure to acrylonitrile and human risk of cancer cannot readily be derived from this study. The Cancer Assessment Group (CAG) in an appendix to this report has estimated, after consultation with DuPont representatives, that high, medium, and low correspond to exposures of 20, 10, and 5 ppm, respectively. These values were supported by a recent NIOSH industrial hygiene survey. Although monitoring data is preferred

Table 1-1. Carcinogenicity Bioassays of Acrylonitrile

Reference	Strain of Rat	Route of Administration	Effect Level[a]	Treatment Schedule	Site of Tumors	No-Effect Levels
Quast et al. (1980a)	Sprague-Dawley	ingestion in drinking water	35-300 ppm	24 months	Brain (astrocytomas) Ear canal (Zymbal gland) Stomach (nonglandular portion) Mammary gland (females only) Tongue Pituitary gland Pancreas (males only) Uterus (females only)	not determined
Nelliles et al. (1980)	Charles River	ingestion in drinking water	500 ppm	45 weeks[b]	Brain (astrocytomas) Ear canal (Zymbal gland)	100 ppm
Bio/dynamics Inc. (1980a)	Spartan	ingestion in drinking water	100 ppm	19-20 months	Brain (astrocytomas) Ear canal (Zymbal gland) Stomach	1 ppm
Bio/dynamics Inc. (1980c)	Fischer 344	ingestion in drinking water	10-100 ppm	23-26 months	Brain (astrocytomas) Ear canal (Zymbal gland) Stomach Mammary gland (females only)	1 and 3 ppm
Bio/dyamics Inc. (1980b)	Spartan	gavage	10 mg/kg/day	19-20 months	Brain (astrocytomas) Ear canal (Zymbal gland) Stomach Mammary gland (females only)	0.1 mg/kg/day
Maltoni et al. (1977)	Sprague-Dawley	inhalation	5-40 ppm	4 hours/day, 5 days/week, for 12 months	Stomach (males only) Mammary gland (females only) Skin (females only)	not determined
Quast et al. (1980b)	Sprague-Dawley	inhalation	20-80 ppm	6 hours/day, 5 days/week, for 24 months	Central nervous system Ear canal (Zymbal gland) Gastrointestinal tract (male only; mammary gland (female only; tongue (male only)	not determined

[a]Not all the tumors indicated for each study were observed at the lower dose.

[b]This was a three-generation reproductive study; the tumors were observed in the second generation.

for human risk assessment, the CAG used these estimates of exposure in lieu of any other available data to determine human cancer risk.

In a second epidemiology study conducted for B.F. Goodrich, an association between acrylonitrile exposure and cancer are inconclusive because the workers were exposed to other carcinogens in the workplace (Federal Register, 1978b). Although the epidemiology studies cannot by themselves support the association between acrylonitrile and human cancer, they are suggestive that acrylonitrile is a human carcinogen and are consistent with the carcinogenic response that acrylonitrile has demonstrated in animal studies. A human carcinogenic risk assessment for acrylonitrile has been derived by the U.S. EPA Carcinogen Assessment Group (CAG) and is presented in an appendix to this document.

2. INTRODUCTION

Human exposure to acrylonitrile has for some time been a matter of public health concern. Until recently, approaches to the evaluation of this potential problem have generally taken a rather narrowly focused view, considering only one mode of exposure or a limited range of biologic effects. The U.S. Environmental Protection Agency, through its Environmental Criteria and Assessment Office in Research Triangle Park, NC, realized the need for a comprehensive assessment of all environmental and public health aspects associated with acrylonitrile.

The present document represents a comprehensive data base that considers all sources of acrylonitrile in the environment, the likelihood for its exposure to humans, and the possible consequences to man and lower organisms from its absorption. This information is integrated into a format that can serve as the basis for qualitative and quantitative risk assessments, while at the same time identifying gaps in our knowledge that limit present evaluative capabilities. Thus, it is expected that this document may serve the information needs of many government agencies and private groups that may be involved in decision making and regulatory activities.

3. PHYSICAL AND CHEMICAL PROPERTIES

3.1 SYNONYMS AND TRADE NAMES

Chemical Abstracts Name: 2-propenenitrile

CAS No.: 107-13-1

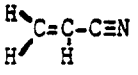
EPA Toxic Substances List No.: RO37-2101

RTECS No.: AT52500

Standard Industrial Code: 2822; 2824

The compound is also known as acrylonitrile (AN), cyanoethylene, propenenitrile, and vinyl cyanide (VCN). Fumigant formulations containing acrylonitrile with names Acrylon, Carbacryl, Fumigrain, Ventox, and ENT-54 are no longer manufactured in the United States.

3.2 STRUCTURAL AND MOLECULAR FORMULAS AND MOLECULAR WEIGHT



C_3H_3N Molecular Weight: 53.06

3.3 BOND ANGLES AND BOND DISTANCES

A molecule of acrylonitrile is planar; all the bond angles are close to 120°. Estimated bond distances are as follows (Wilcox and Goldstein, 1954): C-H: 1.09 Å; C-C: 1.46 Å; C=C: 1.38 Å; and C≡N: 1.16 Å.

3.4 PHYSICAL PROPERTIES

3.4.1 Description

Acrylonitrile is a clear, colorless, and highly flammable liquid that has an unpleasant and irritating characteristic odor (Fassett, 1963).

3.4.2 Boiling Point

77.5 - 79°C (Weast, 1976).

3.4.3 Melting Point

-83.5°C (Weast, 1976).

3.4.4 Density

d_4^{20} : 0.8060; vapor density: 1.83 (air=1) (Groet, 1978).

3.4.5 Refractive Index

n_D^{20} : 1.3911 (Weast, 1976).

3.4.6 Spectroscopic Data

The λ_{max} is at 203 nm with a molar extinction coefficient of 6100; a compilation of infrared, Raman, NMR, and mass spectral data is available in Grasselli and Ritchey (1975).

3.4.7 Solubility

Acrylonitrile is soluble in water, acetone, and benzene (Weast, 1976); miscible with ethanol, carbon tetrachloride, ethyl acetate, ethylene cyanohydrin, liquid carbon dioxide, ether, toluene, petroleum ether, and xylene (Miller and Villaume, 1978).

The solubility in water is given below (Groet, 1978):

0°C:	7.2%
20°C:	7.35%
40°C:	7.9%
60°C:	9.1%

3.4.8 Volatility in Water

Henry's law constant: 0.063 at 25°C (Bocek, 1976). Partial vapor pressure (water azeotrope): $\log P = 7.518 - \frac{1644.7}{T(\text{in K})}$ i.e., 80 mm at 20°C (Miller and Villaume, 1978). The half-life of evaporation of acrylonitrile from water with an assumed 1 meter depth can be calculated, using the method of Dilling (1977), to be 795 minutes.

3.4.9 Volatility

Values for the vapor pressure of acrylonitrile (mm of mercury) at different temperatures are given below (Patterson et al., 1976; Norris, 1967; Perry and Chilton, 1973; Miller and Villaume, 1978):

8.7°C:	50
20°C:	83
23.6°C:	100
25°C:	110-115
45.5°C:	250
64.7°C:	500

3.4.10 Stability

Flash-point (open cup): 0°C (Steere, 1968); Flash-point (closed cup): -1°C (Patterson et al., 1976), -4.4°C (Miller and Villaume, 1978).

Explosive limits: 3.0 to 17% by volume in air at 25°C (Steere, 1968).

Ignition temperature: 481°C (Steere, 1968).

3.4.11 Octanol-water Partition Coefficient

k = 0.12 (Leo et al., 1971).

3.4.12 Conversion Factor

1 ppm in air = 2.17 mg/m^3 at 25°C.

3.5 CHEMICAL PROPERTIES

3.5.1 Reactivity

Undergoes reactions at both the nitrile group and the double bond (Maltoni et al., 1977). Some of these reactions are used for the quantification of acrylonitrile and have been discussed in Section 4. Acrylonitrile also undergoes the following reactions (Miller and Villaume, 1978), many of which are important commercially.

3.5.2 Polymerization

Polymerization, forming high molecular weight products, is the most important commercial reaction of acrylonitrile. The polymerization usually requires the presence of free radical initiators, such as peroxydisulfate. Heat or light ($\lambda < 2900$ Å) can also initiate polymerization reactions. Oxygen and methylhydroquinone are powerful inhibitors of the polymerization reaction.

Pure polyacrylonitrile cannot be dyed using conventional techniques. Copolymerization of acrylonitrile with small amounts of methyl methacrylate or vinyl pyridine introduces reactive dyeing sites. Acrylonitrile can be copolymerized with other monomers as well; examples of other acrylonitrile copolymers include nitrile rubber, acrylonitrile-butadiene-styrene (ABS), and styrene-acrylonitrile (SAN) resins. Terpolymers of acrylonitrile or methacrylontrile are the so-called barrier resins.

3.5.3 Reaction at the Nitrile Groups

Acrylonitrile reacted with 84.5% H_2SO_4 at 100°C produces acrylamide sulfate, which yields acrylamide upon neutralization:

$$CH_2{=}CHCN + H_2O + H_2SO_4 \longrightarrow CH_2{=}CHCONH_2 \cdot H_2SO_4$$

$$CH_2{=}CHCONH_2 \cdot H_2SO_4 + 2NaOH \longrightarrow CH_2{=}CHCONH_2 + Na_2SO_4 + 2H_2O$$

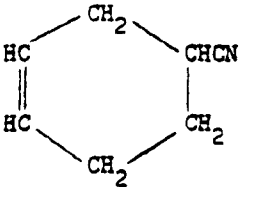
Until recently, the above process was used exclusively for the commercial production of acrylamide. The catalytic hydration of acrylonitrile is the currently used method for the production of acrylamide. When acrylontrile is heated with less concentrated H_2SO_4 or with water, acrylic acid ($CH_2{=}CHCOOH$) is formed. In aqueous NaOH, NH_3 is the reaction product. The hydrolysis constant for this reaction was measured as 3.8×10^{-3} min^{-1} at 60°C and 1.39 min^{-1} at 100°C (Linetskii and Serebryakov, 1965). Violent polymerization, however, has been reported to occur with concentrated alkali (Steere, 1968). Acrylonitrile allowed to react with alcohols in the presence of concentrated H_2SO_4

produces esters of acrylic acid. With olefins, it forms N-substituted acrylamides in the presence of concentrated H_2SO_4.

3.5.4 Reactions at the Double Bond

The double bond in acrylonitrile acts as a dienophile in the Diels-Alder reaction. Cyclic products are produced when acrylonitrile is treated with aliphatic or alicyclic compounds containing conjugated carbon-to-carbon double bonds. An example is the reaction with butadiene:

$$CH_2{=}CHCN + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow$$



Δ-3-tetrahydrobenzonitrile

In the presence of catalyst, acrylonitrile can be hydrogenated to propionitrile, which can be further hydrogenated to n-propylamine:

$$CH_2{=}CHCN \xrightarrow{H_2} CH_3CH_2CN \xrightarrow{H_2} CH_3CH_2CH_2NH_2$$

It can also be reduced, in the presence of magnesium and methanol, in the following manner to produce adiponitrile:

$$2CH_2{=}CHCN + 2CH_3OH + Mg \longrightarrow \begin{matrix} CH_2CH_2CN \\ | \\ CH_2CH_2CN \end{matrix} + (CH_3O)_2Mg$$

This is then further reduced to hexamethylenediamine, which is used in the production of nylon.

3.5.5 Cyanoethylation Reactions

These reactions involve the interaction of acrylonitrile with compounds containing active hydrogen. Examples of compounds containing active hydrogen are water, alcohols, ammonia, amines, mercaptans, aldehydes, and inorganic acids

and their salts (Miller and Villaume, 1978). The generalized reaction can be written:

$$CH_2{=}CHCN + AH \longrightarrow ACH_2CH_2CN$$

The cyanoethylation of pseudouridine, inosine, and 4-thiouridine by acrylonitrile has been studied as a model for the cyanoethylation of intact tRNA (Miller and Villaume, 1978).

3.6 CHARACTERISTICS OF THE CHEMICAL PRODUCT

Technical grade acrylonitrile is a highly purified product with greater than 99% purity. The major impurity is water, which is usually present at a maximum of about 0.5%. The water improves the stability of the product. Other possible trace contaminants include acetone, acetonitrile, acetaldehyde, iron, peroxides, and hydrogen cyanide. Highly pure acrylonitrile may polymerize spontaneously. To prevent this, methylhydroquinone (35-50 ppm) is added to the commercial product. Yellowing upon exposure to light indicates photoalteration to saturated derivatives.

3.7 CONCLUSION

Acrylonitrile is moderately soluble in water. Because acrylonitrile does not appreciably dissociate in water, hydrogen cyanide is not expected to be a product of hydrolysis. Because the vapor pressure of acrylonitrile is appreciably high, most atmospheric emissions from its manufacture and use should occur as vapor. The evaporation rate of acrylonitrile from water is appreciable. Therefore, evaporation from contaminated water surfaces can be expected to occur. The atmospheric photoreactivity of acrylonitrile is such that a reasonable aerial transport can be expected from airborne acrylonitrile.

4. SAMPLING AND ANALYTICAL METHODS

The level of acrylonitrile has been determined in a number of environmental media of interest. These include: (1) air; (2) water; (3) waste water; (4) soil and sediment; (5) residue in polymers and the extent of monomer migration in food-simulating solvents; and (6) various other media. All these media can directly or indirectly affect the environmental level or human intake of acrylonitrile.

The sampling method is generally dependent on the medium intended to be monitored. The analysis of samples can be divided into two steps, namely, pretreatment or clean-up procedure(s), when necessary, and quantification procedures. The selection of a particular identification and quantification method is dictated by the accuracy, reproducibility, detection limit, and the possible interference(s) of the method. The sampling and analysis of acrylonitrile in the individual media are discussed below.

4.1 AIR

4.1.1 Sampling

The collection of acrylonitrile from air has been done by two methods. The first method consists of direct collection of samples without preconcentration. The second method employs the concentration of acrylonitrile in a collection medium during sampling.

In direct sample collection, the air is drawn into plastic bags (Keresztesy et al., 1977) via a two-way valve by means of a sampling pump. The samples are then transported to the laboratory for analysis.

The disadvantage with direct collection is that it does not allow any concentration of the sample and may cause additional problems during transport and storage of samples. Therefore, the detection limit of the method is not satisfactory for ambient air samples, even with the most sensitive method of

detection available presently. The advantage of direct collection is that the samples can be analyzed without any pretreatment, thereby reducing analysis time and avoiding any sample losses. It also provides a method for continuous area monitoring of acrylonitrile.

In the preconcentration method for sample collection, the air containing acrylonitrile is passed through either a solid sorbent or a trapping liquid medium. Table 4-1 lists the different sorbents and trapping media used for collection of acrylonitrile in air. Activated carbon, silica, and porous polymers have been used as solid sorbents. The sampling unit usually consists of a battery operated pump and a rotometer that indicates the sample flow rate through the sorbent. A tube that contains the solid sorbent is held vertically at a height of 1.5 m from the ground and is connected to the rotometer and the pump unit. Air is drawn through the sorbent tube at a certain flow rate for a specified length of time. At the end of sample collection, the tube is closed with caps and shipped to the laboratory for analysis.

In addition to the error that could be made in measuring the air volume (calibrated pumps may not maintain constant air flow over the entire sampling period), another disadvantage of the solid sorbent method is that sample loss will occur if the breakthrough capacity for the sorbent is exceeded. Therefore, the breakthrough capacity of acrylonitrile through the sorbent should be determined experimentally. The breakthrough capacity is dependent on the relative humidity of air sampled and the presence of other interferences in the air. The concentration of the compound being collected, however, affects the breakthrough volume only slightly. A pollutant present at 20 ppm will break through at only a slightly smaller volume than when present at 1 ppm (Russell, 1975).

For air nearly saturated with moisture, the breakthrough volume for acrylonitrile in Porapax N (4" x 1/4" tube) was determined to be 3 to 5 liters.

Table 4-1. Various Sorbents and Trapping Media for Collection of Acrylonitrile in Air

Sample	Sorbent	Sampling Condition	Desorption Method	Analysis Technique	Confirmation Technique	Detection Limit	Reference
---	SiO_2	0.5 lpm[a] for 4-6 l	Water	Colorimetric	None	---	Krynska, 1970
Plastic producing plant	Silochrom-2 at -50°C	---	Thermal at 200°C	GC-FID[b]	None	---	Korzhova et al., 1974
Acrylic fiber factory	Silica gel	Personnel sampler for 100 min.	Water	GC-FID	None	0.1 ppm	Sakurai et al., 1978
Simulated air	Activated carbon	15 l in gas bag	2% acetone in CS_2	GC-FID	None	0.25-0.5 ppm	Gagnon & Posner, 1979
Plastic processing plant	Activated carbon	0.2 lpm for 8 hr.	2% acetone in CS_2	GC-FID	None	0.03-0.31 ppm	Marra et al., 1978
Eleven production plants	Activated carbon	1.0 lpm for ≈24 hr.	CS_2	GC-FID	None	< 0.3 $\mu g/m^3$	Going et al., 1979
Simulated air	Porapak N	0.1 lpm for 3-5 l	Thermal at 200°C	GC-FID	None	< 1 ppb	Russell, 1975
Simulated air	Porapak N	0.1-0.15 lpm for 3-8 l	Thermal	GC-FID	None	< 0.26 ppm	Campbell & Moore, 1979
Settling pond in acrylonitrile plant	Porous polymer Tenax GC(?)	≈0.07 m^3/hr. for 5-30 min.	Thermal	GC-FID	None	10 ng	Hughes & Horn, 1977
Occupational air	Activated carbon	0.2 lpm for 20 l max	CH_3OH	GC-FID	None	Range 5-135 mg/m^3	NIOSH, 1977
Occupational air	Carbosieve B	1 lpm for 10-20 l	CH_3OH	GC-FID	None	Range 40-750 mg/m^3	Barrett, 1974
--	95% ethanol	1 lpm	---	Polarographic	None	0.5-5 mg/50 ml	Rogaczewska, 1964
Grain fumigant air	Chilled water	0.03-0.33 lpm	---	Polarographic	None	1.08×10^{-5} M	Berck, 1962
---	Water	0.015 lpm for 1.5-3 l	---	Colorimetric	None	---	Mazarova & Nakrap 1978
---	Water	---	---	Colorimetric	None	0.5 mg/m^3	Rogaczewska, 1976
Occupational air	Chilled water	1 lpm for 20-60 l	---	u.v.	None	Range 10-100 ppm	Brieger et al., 1952
Acrylonitrile plant	Chilled water	1 lpm	---	GC-FID	None	50 ppb	Hughes & Horn, 1977
---	Water	---	---	Colorimetric	None	1.0 $\mu g/ml$	Rusakikh, 1973
---	H_2SO_4 & glass beads	0.4 lpm	---	Titrimetric	None	20-300 $\mu g/ml$	Gunther & Blum, 1955
Rubber plant	1% H_2SO_4	---	---	Colorimetric	None	< 0.85 $\mu g/l$	Babanov, 1960
---	1% H_2SO_4	---	---	Colorimetric	None	---	Arato & Bittera, 1972
SAN plant	DMF	0.1-0.3 lpm	---	GC-FID	None	0.5 mg/m^3	Babina, 1979
---	25% methanol at -15°C	---	---	GC-FID	None	---	Fasitta & Licciardello, 1977

[a] lpm = liters per minute

[b] GC-FID = gas chromatography-flame ionization detectors

Breakthrough volumes can be increased by using longer sampling tubes. These tubes, however, will result in increasing the back pressure in the tube.

Activated carbon is the most widely used sorbent for the collection of acrylonitrile in air. The adsorption parameters for activated carbon will vary depending on the nature of the carbon and the treatment it received. With 6-10 mesh BC-AC granular carbon, Sansone et al. (1979) determined the adsorption capacity and adsorption rate constant for acrylonitrile to be 0.404 g/g and 116.0 $min.^{-1}$, respectively. With acrylonitrile that contained 50% relative humidity, Nelson and Harder (1974) determined the adsorption capacity to be 0.174 g/g. The breakthrough times for 1%, 10%, and 99% passage from a 58 g charcoal in a respirator cartridge were determined to be 48.5 min., 61.1 min., and 168 min., respectively (Nelson and Harder, 1974). The types of activated carbon used in the above experiments were different.

The effect of humidity on sample recovery by 1.5 g activated carbon was studied in detail by Going et al. (1979). He observed that introducing a Drierite drying tube to absorb moisture did not significantly improve recoveries at relative humidities equal to or exceeding 70%; however, the average recovery for acrylonitrile with air volumes of 750 liters/g or greater remained acceptable at 75 $\pm$ 9.4% at relative humidities up to 60%, with or without the drying tube.

NIOSH (1977b) determined that the maximum amounts of acrylonitrile that could be collected with a sorbent tube (8 cm x 5 mm) from 100 ppm acrylonitrile in air were 6 mg, 15 mg, and 22 mg when the relative humidities greater than 95%, equal to 50%, and less than 5%, respectively.

Segmentation of the carbon tubes into a front and back section remains the most widely used method for the determination of breakthrough capacity limit during sample collection. If the second tube retains more than a certain

predetermined percentage of acrylonitrile, it indicates that the breakthrough limit has been exceeded.

It is important to determine the stability of acrylonitrile in the sample tubes during transportation and storage. Marrs et al. (1978) showed that acrylonitrile would remain stable on the carbon tubes at room temperature for a minimum of 5 days. Going et al. (1979) demonstrated that acrylonitrile would remain stable up to 8 days on charcoal tubes stored at -17°C and up to 24 days on tubes stored at -78°C.

The collection of acrylonitrile in air by liquid trapping media has been used rarely in recent years because of the inconvenience in handling and transporting the impingers and the need for cooling the trapping media during sample collection. The collection efficiencies and the storage stabilities of acrylonitrile in these media are not always known. The collection efficiency of chilled water as a trapping medium was determined to be over 98% (Berck, 1962; Brieger, 1952). Virtually no data are available regarding the storage stability of acrylonitrile in this trapping medium, but it is expected to be reasonably stable in water and 1% H_2SO_4, particularly since Going et al. (1979) demonstrated that acrylonitrile was stable for about 23 days in neutral distilled water and at a pH of 4. Acrylonitrile collected in aqueous methanol and ethanol and stored at 3°C can be expected to be fairly stable, based on the evidence of Going et al. (1979), who demonstrated that acrylonitrile in carbon disulfide remained stable for over 12 days when stored at 3°C.

4.1.2 Analysis

4.1.2.1 Pretreatment

Acrylonitrile collected on solid sorbents requires a desorption procedure before identification and quantification. Thermal desorption and solvent desorption are two commonly used methods. Thermal desorption normally uses gas

chromatographic methods for identification and quantification. In this procedure, the sorbent tube is heated between 100°C and 200°C in the injection port of a gas chromatograph. To avoid peak broadening, the position of the sample tube in the gas chromatograph injection port should be in the reverse order as that used during sampling. The thermal desorption method is appropriate for use with porous polymers, particularly with Porapak N. Several investigators have used this technique (Campbell and Moore, 1979; Russell, 1975; Hughes and Horn, 1977). The advantages of thermal desorption are that it avoids manual sample pretreatment and the recovery of acrylonitrile is almost quantitative (Campbell and Moore, 1979; Russell, 1975). The method also has a higher sensitivity than the solvent desorption method, where only a fraction of the eluted acrylonitrile can be injected into the gas chromatograph. The disadvantages of the thermal desorption method include its inability to afford replicate analysis and its tendency to cause other gas chromatography separation problems such as shortening retention time and broadening eluted peak due to the presence of adsorbed moisture on the sorbent column (Russell, 1975).

The solvents that have been used for desorption of acrylonitrile from activated carbon are acetone, methanol, carbon disulfide, and 2% acetone in carbon disulfide. The selection of the desorption sorbent is dictated by two considerations, namely, the sorbent desorption efficiency and its compatibility with gas chromatography. For example, if column separation is not adequate, methanol that has a high response on flame ionization detectors (FID) will produce a large peak shadowing the acrylonitrile peak; therefore, it is not very compatible with flame ionization detectors. Although carbon disulfide appears to be compatible with flame ionization detectors, it is a poor solvent for nitrogen/phosphorous detectors. Acetone is the solvent of choice in the latter case.

The recovery efficiencies of acrylonitrile from activated carbon with various solvents are given in Table 4-2.

Table 4-2. Recovery of Acrylonitrile from Various Solvents

Solvent	% Recovery	Reference
Methanol	ca. 50%	Going et al., 1979
Acetone	73.5 ± 5.3%	Marano et al., 1978
2% acetone in CS_2	95.5 ± 7.9%	Gagnon and Posner, 1979
2% acetone in CS_2	94%	Silverstein, 1977
CS_2 (2 ml)	58%	Silverstein, 1977
CS_2 (4 ml)	75%	Silverstein, 1977

It should be recognized that the recovery of acrylonitrile is dependent on the nature of the activated carbon and the extent of loading. Using three different activated carbons and a variable loading of 2 µg to 200 µg acrylonitrile, Going et al. (1979) determined that the CS_2 desorption efficiency varied from 53% to almost 100%. It would appear from Table 4-2 that a 2% acetone in CS_2 is the best solvent for elution of acrylonitrile from activated carbon in terms of both recovery and GC-FID compatibility.

When the acrylonitrile is collected in liquid trapping media, the samples usually do not require any pretreatment prior to the detection and quantification procedures.

4.1.2.2 Identification and Quantification

The methods utilized for the identification and quantification of acrylonitrile collected by sorbent or trapping techniques are shown in Table 4-1 (see 4.1.1). The methods for the analysis of acrylonitrile collected without preconcentration appear in Table 4-3. The infrared techniques are used exclusively for samples that need no preconcentration. Although a number of methods including

Table 4-3. Direct Analysis of Acrylonitrile

Sample	Sample Introduction into Detector Unit	Analysis Technique	Comfirmation Technique	Detection Limit	References
Simulated occupational air	Sample probe & pump	IR-microcomputer	None	0.2 ppm	Jacobs & Syrjala, 1978
Occupational air	Introduction of air from gas bag into evacuated cell	IR	None	0.5 ppm	AIHA, 1970
Acrylonitrile in N_2	Introduction to a vacuum cell at 8 torr	IR lasers	None	0.03 ppm	Sweger & Travis, 1979
Simulated air	Pump & rotometer	Detector tube	None	Range 1-120 ppm	Kobayashi, 1956
Gases generated by heating ABS plastic	Forced air	Detector tube	GC-MS	---	Grote et al., 1978
Occupational air	Passive diffusion	Abcor GASBADGE™	None	Range 0.8-19 ppm	Silverstein, 1977
Simulated air	Direct injection	GC-NPD	MS	100 ppb	Marano et al., 1978
Occupational air	Direct injection	GC-FID	None	0.5 ppm	AIHA, 1970

GC-MS = gas chromatography-mass spectrometry
GC-NPD = gas chromatography-nitrogen/phosphorus detectors
MS = mass spectrometry
GC-FID = gas chromatography-flame ionization detectors

colorimetric, titrimetric, and polarographic were used for the analysis of acrylonitrile in the past, the GC method is most extensively used at the present time. The reason for this is the lower interference and higher sensitivity of detection obtained from GC-flame ionization detection (FID) and GC-nitrogen/phosphorous detection (NPD). The chromatographic columns found to be most appropriate for use with thermally desorbed acrylonitrile were Porapak N (Russell, 1975) and Porapak Q (Campbell and Moore, 1979). In the case of solvent desorption, the columns that were found to be suitable were Durapak OPN/ Poracil C (Going et al., 1979), SP-2100 (Grote et al., 1979) for carbon disulfide; SP-1000 (Marano et al., 1978) for acetone; and SP-1000 (Gagnon and Posner, 1979) and TCEP (Marrs et al., 1978) for methanol. The details of other chromatographic columns are given in subsection 4.7.

4.1.3 Conclusions

The detectors available at present often do not have sufficient sensitivity to allow the detection of acrylonitrile in ambient atmospheric samples, if these samples have been collected without preconcentration. The low level of acrylonitrile in atmospheric samples virtually mandates the use of a preconcentration device during sample collection. Of the two preconcentration methods presently available, namely, solid sorbents and trapping media, the former method is preferable to the latter. The collection of acrylonitrile by solid sorbents affords convenience in handling, shipping, and storage of the samples.

Activated carbon and porous polymer Porapak N are the two best sorbents available for the collection of acrylonitrile in air. The breakthrough capacity for Porapak N (3-5 liters) is lower than that for activated carbon (over 1000 liters). Consequently, Porapak N cannot be used for 24 hour sampling. Even with much lower sample volume, Porapak N will afford a detection limit comparable to that obtained from a larger volume of air collected by activated carbon, for

the following reasons. The efficiency of thermal desorption for acrylonitrile from Porapak N is quantitative, while it is poor with activated carbon; therefore, activated carbon requires solvent desorption. Whereas the entire sample can be injected into the quantitative gas chromatography column in the case of thermal desorption, in the case of solvent desorption, only a fraction of the total sample can be injected.

With activated carbon, 2% acetone in carbon disulfide is the best desorption solvent, since it gives the maximum recovery. This solvent system is compatible with flame ionization detectors. Carbon disulfide, however, is unsuitable when the more sensitive nitrogen/phosphorus detectors are used. Acetone is the most suitable solvent in this case. A number of columns including SP-2100 (Gagnon and Posner, 1979) and Durapak OPN/Poracil C (Going et al., 1979) have been used as the quantitative column when carbon disulfide or 2% acetone in carbon disulfide was the solvent. For acetone solvent, SP-1000 was found to be a suitable quantitative column (Marano et al., 1978).

4.2 WATER

In this section, only water samples obtained from either surface water or treated drinking water will be discussed. Wastewaters will be discussed in subsection 4.3.

4.2.1 Sampling

Water samples have been collected almost exclusively by the grab technique (Kopfler et al., 1976; Wronski and Zbigniew, 1974; Going et al., 1979). In a few instances, multiple grab samples were composited for analysis (Going et al., 1979). It is suggested that the samples should be collected in brown glass bottles with Teflon-lined caps and acidified at the site to a pH $\leq$ 4 (Going et al., 1979). The samples should be maintained at 0 to 4°C by ice or an ice substitute during transportation (Going et al., 1979; Kopfler et al., 1976).

In one instance (Going et al., 1979), an attempt was made to collect acrylonitrile from water by the use of solid sorbents. Four different sorbents, namely, activated carbon, Porapak N, Chromosorb 101, and Chromosorb 104, were tried. Water spiked with acrylonitrile was passed through the sorbents at a rate of 4 ml/min. The sorbents were then eluted with 25 ml methanol at a rate of 5 ml/min. The recoveries of acrylonitrile were poor; with activated carbon, the recovery was 30-35 percent and the porous polymers showed zero percent recovery.

4.2.2 Analysis

4.2.2.1 Sample Treatment

Some water samples were analyzed without any pretreatment. Water samples containing low levels of acrylonitrile were pretreated in order to concentrate the acrylonitrile. Two available methods for concentration are purge-trap (Kopfler et al., 1976; Going et al., 1979) and azeotropic distillation (Going et al., 1979) techniques.

Acrylonitrile can be purged from water at elevated temperatures by passing an inert gas through it. The acrylonitrile contained in the purged gas is then trapped in chromatographic media for subsequent analysis. The details of the purging system were described by Going et al. (1979) and Kopfler et al. (1976). The system used by Kopfler et al. (1976) appears to be preferable to the system used by Going et al. (1979), because the former allows purging of 140 ml of water compared to 10 ml water in the latter case; however, the purge-trap efficiency for acrylonitrile was not studied in detail in the Kopfler et al. (1976) system.

The purging conditions were studied in detail by Going et al. (1979), who found an almost quantitative recovery when helium was passed at a rate of 20 ml/min through water heated to 85°C for 30 minutes. The effect of different trapping systems were also studied by Going et al. (1979). It was established that, under thermal desorption conditions, both Porapak N and Chromosorb 104 gave

quantitative desorption. The recovery from Tenax GC, however, was found to be poor (Going et al., 1979).

In the azeotropic distillation technique, water containing acrylonitrile is distilled with methanol, and a small volume of the azeotropic distillate containing acrylonitrile in methanol is collected for further analysis. This technique serves as a simultaneous clean-up and concentration device for acrylonitrile in water samples. The description of the distillation apparatus was given by Going et al. (1979), who obtained maximum recovery under the following conditions.

A 500 ml water sample was added to the distillation flask along with 25 ml methanol and 5 ml 18 N H_2SO_4 and the content was distilled at a rate of 1 ml/min. The first 10 ml of the distillate were collected for subsequent analysis. The percent recovery was about 90% for the combined first and second 10 ml aliquot of the distillate.

4.2.2.2 Detection and Quantification

With the exception of one case in which a titrimetric method was used (Wronski and Zbigniew, 1974), the rest of the studies reviewed utilized GC separation and GC retention data for the identification of acrylonitrile from water samples. For direct aqueous injection, both Chromosorb 101 (Going et al., 1979) and Chromosorb 102 (Marano et al., 1978) were used, although Going et al. (1979) reported better separability with Chromosorb 101. The same column (Chromosorb 101) was used for acrylonitrile determination by the purge-trap and azeotropic distillation techniques (Going et al., 1979; Kopfler et al., 1976; Federal Register, 1979). An aliquot of the distillate from azeotropic distillation was injected directly into the GC column. In the purge-trap technique, the acrylonitrile from the trapping column was thermally desorbed onto the separating column. A summary of water analysis techniques is given in Table 4-4.

Table 4-4. Analyses of Acrylonitrile in Water

Sample	Collection Method	Analysis Technique	Confirmatory Technique	Detection Limit	Reference
Spiked water	---	Direct injection, GC-NPD	MS	10 ppb	Marano et al., 1978
Drinking water	Grab	Purge-trap (Tenax GC), GC-MS	None	Qualitative	Kopfler et al., 1976
Surface water	Grab	Titrimetric with mercaptoethanol & Na_2SO_3	None	0.5-0.05 ppm	Wronski & Zbigniew, 1974
Surface water	Grab	Direct injection, GC-FID	MS	1 ppm	Going et al., 1979
Surface water	Grab	Purge-trap, GC-FID, & GC-Hall	MS	0.1 ppb	Going et al., 1979
Surface water	Grab	Azeotropic distillation, GC-Hall	MS	0.1-1.3 ppb	Going et al., 1979
Spiked water	Sorbent adsorption	Methanol desorption, GC-Hall	None	Showed poor desorption efficiency & method abandoned	Going et al., 1979

MS = mass spectrometry
GC-NPD = gas chromatography-nitrogen/phosphorus detectors
GC-MS = gas chromatography-mass spectrometry
GC-FID = gas chromatography-flame ionization detectors
GC-Hall = gas chromatography-Hall detector

Although nitrogen/phosphorus detectors (including the Hall detector) and flame ionization detectors were used for quantification, mass spectrometry was employed in a few cases for confirmation.

4.2.3 Conclusions

The two best available methods for the determination of acrylonitrile in water are the purge-trap and the azeotropic distillation techniques. Both methods gave almost quantitative recovery of acrylonitrile in water. The detection limit for acrylonitrile by the purge-trap method was lower than that for the azeotropic distillation method; however, this advantage of the purge-trap technique is somewhat offset by the experimental complexity of the method and its inability to perform replicate analysis on the same water sample.

4.3 WASTEWATER

4.3.1 Sampling

No details regarding the sampling of wastewaters is available. Grab samples may be suitable in certain cases. To monitor the discharges that are dependent on process operation stages, a 24-hour composite sample is preferable.

4.3.2 Analysis

4.3.2.1 Pretreatment

Azeotropic distillation with methanol is a method used frequently for wastewater. This technique allows concentration of acrylonitrile and reduces the possibility of interference. In one case, solvent extractions using benzene, ether, and isobutyl acetate were used (Ponomarev et al., 1974). The recovery of acrylonitrile after three extractions was not quantitative but was reproducible.

The various pretreatment methods used for acrylonitrile determination in waste water are shown in Table 4-5. Table 4-5 also lists the different detection and quantification methods and their detection limits where available. The principles of the detection methods are discussed in subsections 4.2.2.2 and 4.7.

Table 4-5. Analysis of Acrylonitrile in Wastewaters

Sample	Pretreatment	Analysis Technique	Detection Limit	Reference
---	---	Polarographic	10 ppm	Sevest'yanova et al., 1966
---	Solvent extraction	Polarographic	3-5 ppm	Ponomarev et al., 1974
---	Azeotropic distillation	Polarographic	< 0.1 ppm	Daues & Hamner, 1957
---	Azeotropic distillation	Titrimetric	< 2 ppm	Stefanescu & Ursu, 1973
---	None	Colorimetric	< 0.5 ppm	Lawniczak, 1977
---	Azeotropic distillation	Titrimetric	---	Covic-Horvat et al., 1970
From polymerization process	None	GC-FID	0.1 ppm	Deur-Siftar & Svob, 1976

GC-FID = gas chromatography-flame ionization detectors

4.3.3 Conclusions

Although the analysis of acrylonitrile in wastewater by the purge-trap technique has not been reported, it is a potentially appropriate method for wastewater analysis. The usefulness of the method can be enhanced by fractional purging at different temperatures (Kopfler et al., 1976). A better method for acrylonitrile analysis in wastewater is the azeotropic distillation technique. The detection and quantification can be best achieved by either the GC-FID or the GC-NPD technique. The chromatographic columns used for water analysis should be suitable for wastewater analysis.

4.4 SOIL AND SEDIMENT

Only one reference could be found in the literature for the analysis of acrylonitrile in these media. The following discussion in this section is based on the work of Going et al. (1979).

4.4.1 Sampling

Soil from the top 12 cm was removed and placed in glass bottles and stored over dry ice until analyzed. Sediment samples were collected with a dredge and the samples were kept on dry ice until analyzed.

4.4.2 Analysis

4.4.2.1 Pretreatment

The pretreatment of the sediment samples after the removal of excess water was the same as that used for soil samples. The samples were extracted with water using ultrasonic agitation and the mixtures were centrifuged. The supernatants were withdrawn and filtered, and the aqueous extracts were directly used for analysis. A few samples were concentrated by the purge-trap technique already discussed in subsection 4.2.2.1. It should be mentioned that the overall recovery of acrylonitrile from the soil and sediment samples either by direct extraction or by the subsequent purge-trap technique was not determined.

4.4.2.2 Detection and Quantification

Gas chromatography with a Chromosorb 101 column and a Hall detector was used for detection and quantification. The detection limit for direct aqueous injection ranged from 50 to 400 µg/kg. For the purge-trap technique, the detection limit was ca. 0.5 µg/kg.

4.4.3 Conclusions

The desorption efficiency of acrylonitrile from soil and sediment samples by ultrasonic agitation has yet to be determined. Although azeotropic distillation was not used, both this method and the purge-trap technique should be suitable for the determination of low levels of acrylonitrile in these samples.

4.5 RESIDUE IN POLYMERS AND THE EXTENT OF MONOMER MIGRATION IN FOOD-SIMULATING SOLVENTS

Several polymers of acrylonitrile are presently used in the United States as food packaging materials. Until recently, many containers for carbonated beverages had nitrile barrier resins as components; however, the use of nitrile barrier resins in beverage containers in the United States is presently banned by FDA. The ABS resins (terpolymer of acrylonitrile, butadiene, and styrene), however, are currently used for such food packages as margarine tubs, fruit juice containers, and vegetable oil bottles. In this section, the analysis of acrylonitrile residue in both polymers used for food packaging and their migration to food-simulating solvents kept in contact with the polymer will be discussed.

4.5.1 Analysis

4.5.1.1 Pretreatment

4.5.1.1.1 Pretreatment for Polymers

Three methods are available for the pretreatment of polymers prior to quantification. In one method, the sample is dissolved in a suitable solvent and an aliquot of this solution is used for analysis. The solvents used for different polymers are shown in Table 4-6. The disadvantage of direct injection of the

Table 4-6. Analysis of Acrylonitrile Residue in Polymers and Food-Simulating Solvents

Sample	Pretreatment	Analysis Technique	Confirmation Technique	Detection Limit	Reference
Plastic	Pyrolysis & solvent trapping	Polarographic	None	100 ppm	Uhde & Koehler, 1967
Plastic	Dissolved in benzene	Titrimetric	None	< 6 ppm	Roy, 1977
Residue in food-simulating solvent	Direct	GC-FID	None	---	Markelov & Semenenko, 1976
Polymer	(a) Pyrolysis GC (b) Dissolution in dimethyl formamide (c) Dissolution in ether	GC-FID	None	10-100 ppm	Reichle & Tengler, 1968
Residue in food-simulating solvent	Head-space equilibration	GC-FID	None	---	Chudy & Crosby, 1977
Residue in food-simulating solvent	Azeotropic distillation	GC-NPD	MS	< 0.01 ppm	McNeal et al., 1979
Residue in food-simulating solvent	Direct	GC-NPD	None	0.04 ppm	Brown et al., 1978
Polymer	Dissolved in N,N-dimethylacetamide	GC-NPD	None	0.5 ppm	Brown et al., 1978
Residue in food-simulating solvent	Azeotropic distillation	GC-NPD	None	50 ppb	Hartshorn, 1975
ABS resin	Dissolved in dimethyl formamide or dimethyl sulfoxide and head-space equilibration	GC-FID & GC-NPD	None	0.3 ppm	DiPasquale et al., 1978
Residue in food-simulating solvent	Head-space equilibration	GC-NPD	None	30 ppb	DiPasquale et al., 1978
Polymer	Dissolved in o-dichloro-benzene & head-space equilibration	GC-FID	None	0.5 ppm	Steinchen, 1976
Plastic	Dissolved in propylene carbonate and head-space equilibration	GC-NPD	None	0.1 ppm	Gawell, 1979
Residue in beverages	Head-space equilibration	GC-NPD	None	5 ppb	Gawell, 1979

GC-FID = gas chromatography-flame ionization detectors
GC-NPD = gas chromatography-nitrogen/phosphorus detectors

solution is that it accelerates the deterioration of the separating column when GC is used for identification. The polymer build-up in the gas chromatograph injection port can be prevented by addition of water or methanol to precipitate the polymer and the supernatant can be injected into the gas chromatograph. The detection limit of this method, however, is not satisfactory and was determined to be about 10 ppm (Steinchen, 1976).

To avoid column contamination, reduce the interference arising from large amounts of solvent, and increase the sensitivity of detection, the second method, known as the head-space analysis, is presently used for the determination of residual monomer in polymers.

Two approaches to the head-space analysis have been used: solid and solution. The solid approach involves the equilibration of a solid polymer sample in the sealed tube at a constant elevated temperature. The advantage of the solid approach is that it has tenfold more sensitivity than the solution approach (Steinchen, 1976). The disadvantages of this approach are: (a) equilibration with the head-space may take a long time, and (b) since polymer standards of known monomer content are not readily available, the head-space monomer concentration must be related to the original concentration in the polymer either by assuming 100% diffusion of the monomer into the head-space or through determination of equilibrium concentration using Henry's law and the appropriate partition coefficient.

The solution head-space approach has been used with a much wider range of samples (Steinchen, 1976; Gawell, 1979; DiPasquale et al., 1978). In this case, the polymer has been dissolved in a suitable solvent and allowed to equilibrate in a sealed vial at a constant temperature (60-90°C). Sometimes water has been added to the solvent to enhance the equilibrium monomer concentration (Steinchen, 1976). The advantages of this approach are: (a) head-space equili

bration is rapid, (b) calibration procedure is simplified, and (c) the head-space gas/solution partitioning of the constituents is not appreciably affected by changes in the solvent phase.

The third method, which is rarely used at the present time, consists of passing nitrogen gas through the heated polymers and trapping the volatile components in dimethyl formamide (Uhde and Koehler, 1967). The dimethyl formamide solution is subsequently analyzed for acrylonitrile. A variation of this method called the pyrolysis GC technique has also been used (Reichle and Tengler, 1968).

4.5.1.1.2 Pretreatment of Food-Simulating Solvent Containing Monomer Residue

The pretreatment of food-simulating solvents for the determination of monomer content as a result of migration from the polymer has been done in three ways. The first method that has been used is the direct analysis of the solvent left in contact with the polymer for a predetermined time and temperature (Markelov and Semenenko, 1976; Brown et al., 1978). The disadvantage of this method was that it had a poor sensitivity and the large amount of solvent interfered with the small amount of acrylonitrile during the detection and quantification stage (Brown et al., 1978; Hartshorn, 1975).

To avoid the solvent interference and to enhance the sensitivity of detection, either the second or the third method, namely, azeotropic distillation or head-space analysis, is presently employed.

In the azeotropic distillation technique, the solvent is distilled with methanol and the azeotrope containing methanol and acrylonitrile is collected for further analysis. When water or 8% ethanol was used as the food-simulating solvent, the distillation was done by adding methanol directly to the solvent (McNeal et al., 1979). When 3% acetic acid was used as the food-simulating solvent, the solution was neutralized with sodium hydroxide before distillation with methanol (McNeal et al., 1979). When heptane was used as the food-

simulating solvent, it was extracted with water and the water extract was distilled with methanol (McNeal et al., 1979). The average recovery of acrylonitrile from the azeotropic distillation of all the extracts varied between 29.7 ± 2.6% and 32.6 ± 2.8% (McNeal et al., 1979).

The third method employs the principle of the head-space equilibration technique. The solvent was introduced in a sealed vial and allowed to equilibrate at a predetermined temperature for a certain length of time (Chudy and Crosby, 1977; DiPasquale et al., 1978; Gawell, 1979).

4.5.1.2 Detection and Quantification

Although a polarographic (Uhde and Koehler, 1967) and a titrimetric method (Roy, 1977) have been used for the determination of monomer in polymers, these methods lacked adequate sensitivity for the determination of low levels of acrylonitrile. The method used almost exclusively at the present time is gas chromatography, either with flame ionization detectors or with nitrogen/phosphorus detectors. The sensitivity and selectivity of NPD makes it a preferable method over FID.

4.5.2 Conclusions

The best available method for the determination of monomer residue in polymers seems to be the solution head-space and GC analysis. For the determination of the extent of monomer migration in food-simulating solvents, both azeotropic distillation and solution head-space equilibration with subsequent GC analysis are the preferred methods. The preferred stationary phases that have been used for non-aqueous injections are Carbowax-20M and Carbowax-1500 (Chudy and Crosby, 1977; DiPasquale et al., 1978; Steinchen, 1976; Gawell, 1979). For aqueous injections, gas-solid chromatography with porous polymer packings such as Chromosorb-102 (DiPasquale et al., 1978), Chromosorb-101 and -108 (McNeal et al., 1979) and Porapak-QS and -S (Brown et al., 1978) have been used.

4.6 OTHER MEDIA

Acrylonitrile has been determined in many other media such as tobacco, production streams, and foods and grains consumed by humans. Since acrylonitrile-containing pesticides have been voluntarily withdrawn from the market and the other media have no direct bearing on general population exposure, acrylonitrile analysis in these media will not be discussed.

4.7 GENERAL METHODS FOR THE ANALYSIS OF ACRYLONITRILE

This section presents the general methods available for detection and quantification of acrylonitrile without regard to the medium in which it is present. Many of the methods have been applied for analysis of acrylonitrile present in more than one medium. This approach has been adopted so that replication of discussion of the same method from medium to medium is avoided.

The identification and quantification methods can be divided into two categories: one based upon the chemical reactivities of the functional groups in acrylonitrile and the other based upon instrumental techniques.

The chemical techniques that have proved useful are based on (a) hydrolysis of the nitrile group and (b) additions to the double bond. In the hydrolysis method, acrylonitrile is hydrolyzed to ammonia and acrylate ion by a strong base. The resulting ammonia can be determined colorimetrically by the Nessler's method (Aarato and Bittera, 1972; AIHA, 1970) or by NaOCl and Na-salicylate in the presence of Na-nitroferricyanide (Rogaczewska, 1976). Alternatively, the liberated ammonia can be determined by titrimetric method (Gunther and Blinn, 1955).

Colorimetric, titrimetric, and thin layer chromatographic procedures have been developed based upon the addition reaction of acrylonitrile. In one colorimetric procedure, acrylonitrile is brominated with (Krynska, 1960; Russkikh, 1971; Lawniczak, 1977) or without (Russkikh, 1973; Nazarova and Nakrap, 1978)

u.v. light. The excess bromine is neutralized and the cyanogen bromide that is formed is allowed to react with a benzidine-pyridine solution to form a colored complex (Nazarova and Nakrap, 1978). In another method, the acrylonitrile complex that is formed with pyridine in the presence of a basic hypochlorite solution at 60-65°C is measured at 411 nm (Hall and Stevens, 1977).

The titrimetric procedures have been used following the reaction of acrylonitrile with excess Na_2SO_3 (Burkart et al., 1961; Terent'ev and Obtemperanskaya, 1956; Taubinger, 1969), thioglycolic acid (Stefonescu and Ursu, 1973; Covic-Horvat et al., 1970), $NaHSO_3$ (Kostin and Vidanova, 1957), dodecanethiol (Roy, 1977), or lauryl mercaptan (Berck, 1975). The excess reagent is then back-titrated with the appropriate titrant in the presence of an indicator or by the potentiometric method.

A method based on the interaction of acrylonitrile with alkaline $KMnO_4$ solution, which produces a change in the permanganate color, has been used to determine the concentration of acrylonitrile. In this method, the concentration was determined by comparison of the color from a calibration curve (Gisclard et al., 1958).

In the thin layer chromatography (TLC) procedure, the mercuric acetate adduct of acrylonitrile was separated by TLC on silica gel. The solvent system used was described by Braun and Vorendohre (1963). In a recent method (Plieninger and Sharma, 1978), the indole adduct of acrylonitrile was separated by TLC procedure.

The instrumental techniques for identification and quantification have used gas chromatography, polarography, infrared and u.v. spectroscopy, and mass spectrometry.

The vast majority of GC procedures have relied on flame ionization detection (FID). Electron capture detection resulted in one-fifth the sensitivity of FID

(Barrett, 1974, cited in Going et al., 1978). The use of nitrogen/phosphorous detectors (NPD) has resulted in a dramatic increase in the sensitivity of detection. The insensitivity of this detector toward compounds that do not contain nitrogen and phosphorous eliminates interferences from many compounds (DiPasquale et al., 1978). Neither carbon disulfide nor N-containing solvents are suitable for NPD.

The selection of column packing materials for the separation of acrylonitrile from interferences depends on the source of the sample. Numerous packing materials have been used in the past. Based on their chemical characteristics, the stationary liquid or solid phases that have been used for the analysis of acrylonitrile can be summarized as follows:

Polyglycol: (a) Carbowax-1500 (Babina, 1979; DiPasquale et al., 1978; Steinchen, 1976; Gawell, 1979) (b) Carbowax-1540 (Chudy and Crosby, 1977) (c) Carbowax-400 (Lysyj, 1960; DiLorenzo and Russo, 1969) (d) Carbowax-20M (Chudy and Crosby, 1977; DiPasquale et al., 1978; Gawell, 1979) (e) SP-1000 (Marano et al., 1978; Gagnon and Posner, 1979) and (f) Di-glycerol (Ustinovskaya et al., 1977)

Hydrocarbon: (a) Apiezon (Babina, 1979) (b) Tween-80 (Chopra et al., 1978)

Esters and Polyesters: (a) Polyethylene glycol adipate (Panova et al., 1969; Kleshcheva et al., 1971; Markelov and Semenenko, 1976) (b) Neopentyl glycol succinate (Kleshcheva et al., 1971; Korzhova et al., 1974) (c) Triethylene glycol butyrate (Pokrovskaya and Frolova, 1969) (d) Polyethelene glycol succinate (Lysyj, 1960) (e) Dioctyl phthalate (Nestler and Berger, 1965)

beta-beta'-oxydipoprionitrile (Pokrovskaya and Frolova, 1969; Reichle and Tengler, 1968; DiLorenzo and Russo, 1969)

Silica gel ASK (Ivanenko and Lukashevaskaya, 1976)

Porous Polymers: (a) Porapak Q (Balak et al., 1977; Campbell and Moore, 1979) (b) Porapak QS (Brown et al., 1978) (c) Porapak N (Russell, 1975; Tanaka et al., 1975) (d) Porapak S (Brown et al., 1978) (e) Chromosorb 101 (McNeal et al., 1979; Brown et al., 1978) (f) Chromosorb 102 (Marano et al., 1978; DiPasquale et al., 1978) (g) Chromosorb 104 (Going et al., 1979) (h) Chromosorb 108 (McNeal et al., 1979)

Methylsilicone: (a) SE 30 (Berck, 1965) (b) DC-200 (Beaumont and Garrido, 1979)

Aminoalcohol: THEED (Hughes and Horn, 1977)

Tetracyanoethyl: Pentaerytritol (Ustinovskaya et al., 1977; Deur-Siftar and Svob, 1976; Marrs et al., 1978)

The polarographic method was used most extensively in the past for the determination of acrylonitrile. Tetramethyl ammonium iodide (Sevest'yanova and Tomilov, 1963; Gorokhovskaya and Geller, 1962; Uhde and Koehler, 1967; Chao and Ch'en, 1966; Deus and Hamner, 1957; Lezovic and Singliar, 1977; Mekhtiev et al., 1968; Klyaev et al., 1966; Rogaczewska, 1964), tetramethyl ammonium hydroxide (Berck, 1962; Sevast'yanova et al., 1966), and LiCl (Sevest'yanova and Tomilov, 1963; Bogaczek and Joworski, 1970) have been used as the supporting electrolyte for the dropping mercury electrode. Both standard calomel and silver were used as the reference electrode. A continuous polarographic method has been used for the determination of acrylonitrile in industrial streams (Bogaczek and Jaworski, 1970).

Spectroscopic methods using both infrared and ultraviolet techniques have been used for the detection and quantification of acrylonitrile. The sensitivity of acrylonitrile determination by the earlier IR methods was rather poor (Scheddel, 1958; Karaenev et al., 1974). In recent years, however, the use of multiple reflection, which, in essence, has the effect of increasing the cell path-length, has increased the sensitivity significantly (Kurapov et al., 1977; AIHA, 1970; Beaumont and Garrido, 1979). The same principle has been applied for the continuous monitoring of acrylonitrile at 10.5 nm with a portable infrared analyzer (Jacobs and Syrjala, 1978).

An infrared laser technique, called laser stark spectroscopy, that applies electric fields to perturb the molecular rotational energy levels has been used to enhance and modulate the absorption of acrylonitrile. Using the P(28) line from a CO_2 laser and a 40 cm IR cell, the method was shown to detect 0.03 ppm of acrylonitrile in air (Sweger and Travis, 1979).

Acrylonitrile in solution has been determined by u.v. absorption at 195 nm (Petrova et al., 1978) and at 210 nm (Brieger et al., 1952).

Mass spectrometry alone is rarely employed for the quantification of acrylonitrile. It is usually used as a confirmatory technique. In one study, however, it was used for monitoring acrylonitrile concentration in process streams (Thomson, 1974). In combination with GC, mass spectrometry was used for confirmatory identification (Grote et al., 1978; Marano et al., 1978; Tanaka et al., 1975; Going et al., 1979; McNeal et al., 1979). The use of multiple ion monitoring mode increases the detection limit five-fold over full mass scan mode (McNeal et al., 1979).

Finally, detector tubes for area monitoring (Kobayashi, 1956) and gas badges for personnel monitoring (Silverstein, 1977) of acrylonitrile have been proposed.

5. SOURCES IN THE ENVIRONMENT

5.1 PRODUCTION PROCESSES

Acrylonitrile can be produced by the following methods:

(a) Oxidation of propylene in the presence of ammonia (ammoxidation of propylene) using either a bismuth phosphomolybdate or uranium-base catalyst;

(b) Addition of hydrogen cyanide to acetylene using a cuprous chloride catalyst;

(c) Catalytic reaction of propylene with nitrous oxide;

(d) Reaction of ethylene oxide with hydrogen cyanide, followed by catalytic dehydrogenation of ethylene cyanohydrin; and

(e) Ammoxidation of propane.

Processes (a) through (d) have been used for the commercial production of acrylonitrile. The ammoxidation of propane has been studied on a pilot scale (Hughes and Horn, 1977). Since 1971, however, the ammoxidation of propylene is the only process that has been used commercially in the United States. The process is patented by the Standard Oil Company (SOHIO) and is known as the SOHIO process.

5.2 ACRYLONITRILE PRODUCERS

The producers of acrylonitrile monomer in the United States are given in Table 5-1.

Table 5-1. Producers of Acrylonitrile in the United States (Anonymous, 1980)

Producer	Capacity, MT x 10^3
American Cyanimid, Fortier, LA	120
DuPont, Beaumont TX	159
DuPont, Memphis, TN	122
Monsanto, Chocolate Bayou, TX	209
Monsanto, Texas City, TX	209
Vistron, Lima, OH	181
TOTAL	1,000

MT = metric ton

It is anticipated from the demand of acrylonitrile that 862 thousand metric tons (86.2% of total capacity) of acrylonitrile will be produced in the United States in 1980 (Anonymous, 1980). The distribution figures obtained from the same source (Anonymous, 1980) are given in Table 5-2.

Table 5-2. Distribution of Acrylonitrile in 1980 and Future Growth Through 1984 (Anonymous, 1980)

Distribution	Acrylonitrile (MT x 10^3)	Projected Annual Growth
Consumption	664	4%
Imports	Negligible	--
Exports	198	Decline

MT = metric ton

5.3 ACRYLONITRILE USES

Acrylonitrile is used primarily as a raw material in the synthesis of acrylic and modacrylic fibers, ABS and SAN resins, nitrile rubbers, adiponitrile, acrylamide, barrier resins, and other miscellaneous uses. The miscellaneous uses include the production of fatty amines and their derivatives, cyanoethylation of various alcohols and amines, fumigant formulations, and as an absorbent.

A flow diagram summarizing direct and indirect uses of acrylonitrile is given in Figure 5-1. The primary uses of the compounds that contain acrylonitrile are presented in Table 5-3.

The use of nitrile barrier resins in beverage containers has been banned by the FDA because of their suspected carcinogenicity; however, SAN resins and ABS resins are permissible for use in food containers. The ABS resins are also currently used for such food packages as margarine tubs, fruit juice containers, and vegetable oil bottles. Nitrile barrier resins have application in non-beverage packings, including containers for glue, nail polish, correction fluid,

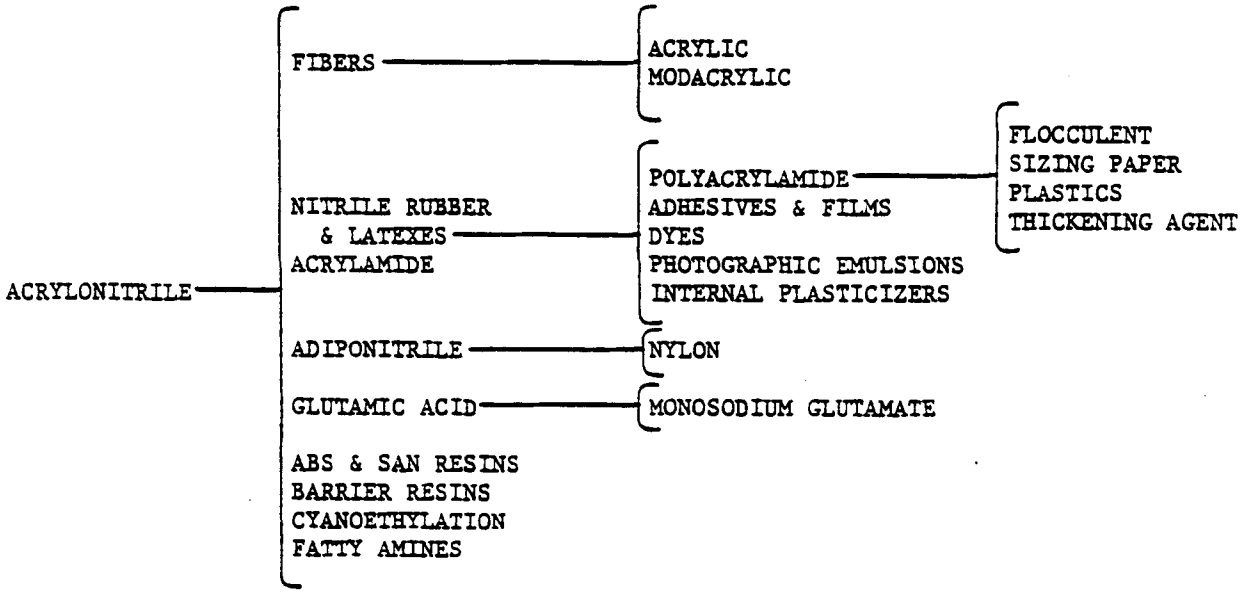


Figure 5-1. Flow Diagram for Acrylonitrile Usage (NIOSH, 1977c)

Table 5-3. Primary Uses of Acrylonitrile-Containing Compounds (Suta, 1979)

Compound	Uses
Acrylic and Modacrylic Fibers	More than 60% of these fibers is used in apparel. Carpeting is the second largest use. Home furnishing uses include blankets, draperies, and upholstery. Industrial uses include sandbags, filter cloths, tents, and tarpaulins. The fibers are also used in synthetic hair wigs.
ABS Resin	Its major markets are pipes and pipe fittings, and automotive components. Other important markets are large appliances, housing for business machines and telephones, recreational vehicle components, toys, sporting goods, and sheeting material for luggage.
SAN Resin	Its primary uses are for drinking tumblers and other houseware items, for automobile instrument panels, and instrument lenses.
Nitrile Elastomers	Its major uses are in rubber hose, seals, gaskets, latex, adhesives, polyvinyl chloride blending, paper coatings, and pigment binders.
Adiponitrile	It is hydrogenated to hexamethylenediamine, which is used to produce nylon.
Acrylamide	Its largest use is in the production of polyacrylamides for waste and water treatment flocculants. Other acrylamide products are used to aid sewage dewatering, and for papermaking strengtheners and retention aids.
Nitrile Barrier Resins	They are used in the manufacture of non-beverage containers for glue, nail polish, correction fluid, air freshener, contact lenses, tooth brushes, and combs (Miller and Villaume, 1978).

air freshener, contact lenses, tooth brushes, and combs (Miller and Villaume, 1978). Fumigant formulations for grain that contain acrylonitrile have been voluntarily withdrawn from the market. Another minor use of acrylonitrile is as an anti-stall automotive additive (Miller and Villaume, 1978).

5.4 CONSUMPTION OF ACRYLONITRILE BY USERS

The breakdown of consumption figures in 1980 and the annual decline or growth through 1984 are given in Table 5-4. For comparison, the estimated consumption figures for 1977 and the projected annual growth percent until 1982 are also given in Table 5-4.

Table 5-4. Consumption and Growth of Acrylonitrile Usage

Product	1980 Consumption[a] (MT x 10^3)	Growth or Decline Through 1984	1977 Consumption[b] (MT x 10^3)	Projected Annual Growth (%)
Acrylic and Modacrylic Fibers	344.8	No Significant Growth	331	5
ABS and SAN Resins	172.4	Growth	142	8.5
Other Miscellaneous	146.5	Decline	163	--
Nitrile Rubbers			24	2.5
Adiponitrile			73	11.5
Acrylamide			24	9
Barrier Resins			9	12
Other			33	5
TOTAL	663.7		636	

[a] Anonymous, 1980

[b] Suta, 1979

MT = metric ton

The users of acrylonitrile for manufacturing different categories of products are given in Tables 5-5 through 5-8.

The only producer of adiponitrile (See Table 5-4) in the United States is Monsanto, Co.; in their facility at Decatur, Alabama, Monsanto produces 87 x 10^3 metric tons per year of adiponitrile (Suta, 1979).

Table 5-5. Producers of Acrylic and Modacrylic Fibers (Suta, 1979)

Producer	Capacity (MT x 10^3)	Trade Name
American Cyanamid		
Pensacola, FL	49	Creslan
Dow Badische		
Williamsburg, VA	28	Zepan II
DuPont		
Camden, SC	68	Orlon
Waynesboro, VA	57	Verel
Kodak		
Kingsport, TN	7	Acrilan
Monsanto		
Decatur, AL	131	Dynel

MT = metric ton

Table 5-6. Producers of SAN and ABS Resins (Suta, 1979)

Producer	Capacity (MT x 10^3)
ABTEC	
Louisville, KY	8
Borg-Warner	
Ottawa, IL	28
Washington, WV	39
Mobil	
Joliet, IL	9
Dow	
Gales Ferry, CT	8
Midland, MI	9
Riverside, MO	19
Torrance, CA	9
Irontown, OH	8
Monsanto	
Addyston, OH	45
Muscatine, IA	15
Springfield, MA	4
Uniroyal	
Scotts Bluff, LA	24

MT = metric ton

Table 5-7. Producers of Nitrile Rubbers and Elastomers (Suta, 1979)

Producer	Capacity (MT x 10^3)	Trade Name
Copolymer Rubber		
Baton Rouge, LA	2	Ny Syn
B.F. Goodrich		
Akron, OH	5	Hycar
Louisville, KY	10	Hycar
Goodyear		
Akron, OH	1	Chemigum
Houston, TX	5	Chemigum
Uniroyal		
Painesville, OH	5	Paracrid

MT = metric ton

Table 5-8. Producers of Acrylamide (Suta, 1979)

Producers	Capacity (MT x 10^3)
American Cyanamid	
Linden, NJ	21
West Wego, LA	7
Dow	
Midland, MI	18
Nalco	
Garysville, LA	4

MT = metric ton

5.5 SOURCES OF EMISSIONS

The sources of acrylonitrile emissions are during: (1) monomer production; (2) polymer production; (3) transportation; and (4) end product usage. Each of these sources is discussed individually below.

5.5.1 Monomer Production and Related Facilities

In order to evaluate the sources of acrylonitrile emissions, it is necessary to understand the industrial operations during monomer production. For a detailed description of industrial operations, the reader is referred to the Monsanto report authored by Hughes and Horn (1977).

Acrylonitrile monomer can enter the ambient atmosphere during its production, waste handling, loading, and storage. The two main sources of air emission during acrylonitrile production are absorber vent and fugitive emission. Hughes and Horn (1977) list the following materials found in atmospheric emissions from acrylonitrile plants: CO, nitrogen oxides, sulfur oxides, hydrocarbons, acetaldehyde, methanol, benzene, toluene, acrylonitrile, hydrogen cyanide, fumaronitrile, pyridine, propionaldehyde, furan, ammonia, and allyl alcohol. The three methods of handling the wastes are incinerator, flare, and treatment in deep well pond. Both flare and incinerator stacks give rise to gaseous emissions of acrylonitrile. The liquid-waste handling facility consists of wastewater treatment in deep well ponds. The concentration of various constituents in the wastewater is given in Table 5-9. The deep well ponds produce three kinds of emission, namely, gaseous, liquid, and solid. The gaseous emission may contain acrylonitrile and may enter into the atmosphere. The liquid run-off from the deep well pond, which contains approximately 175 ppm acrylonitrile, is disposed of by deep well injection to reduce the possibility of contamination of ground water (Miller and Villaume, 1978). A part of the wastewater that contains approximately 120 ppm acrylonitrile is sent to the biopond for biological

Table 5-9. Results of Analysis of Acrylonitrile Plant Wastewater (Hughes and Horn, 1977)

Material Discharged	Concentration (mg/l)	Effluent Factor (g/kg)
Raw wastewater	[a]	4,470
Biological oxygen demand	8,620	38.7
Chemical oxygen demand	32,800	133
Total organic carbon	14,400	57.5
Total solids	36,700 to 57,800	163 to 182
Total suspended solids	184 to 630	0.915 to 1.78
Total dissolved solids	36,500 to 57,200	161 to 181
Oil and grease	135 to 168	0.475 to 0.657
Total nitrogen (as N_2)	4,040 to 22,000	16.9 to 62.1
Ammonia nitrogen (as N_2)	2,600 to 13,600	10.3 to 38.3
Nitrile nitrogen (as N_2)	197 to 270	0.755 to 0.97
Phosphate	0.152 to 6.15	0.0004 to 0.0298
Phenol	0.165 to 2.28	0.0007 to 0.0064
Sulfate	2,700 to 5,309	64.1 to 74.3
Zinc	0.052 to 2.1	0.00002 to 0.0092
Chloride	125 to 858	0.616 to 2.42
Iron	3.13 to 4.24	0.0088 to 0.0182
Copper	$\leq$ 0.5	$\leq$ 0.00024
Chromium	$\leq$ 0.05	$\leq$ 0.00014
Cadmium	$\leq$ 0.05	$\leq$ 0.00024

Other compounds which have been qualitatively identified include:

Acetaldehyde	Methacrylonitrile	Ammonium acetate
Acrolein	trans-Crotonitrile	Ammonium methacrylate
Hydrogen cyanide	cis-Crontonitrile	Ammonium acrylate
Acetic acid	Allyl cyanide	Succinonitrile
Fumaronitrile	Benzonitrile	Acetone
Acrylic acid	Nicotinonitrile	Acetaldehyde cyanohydrin
Acrylamide	Malononitrile	Acetone cyanohydrin
Acrylonitrile	Furonitrile	Acrolein cyanohydrin
Acetonitrile	Ticoline	Pyrazole
Maleonitrile	Lutidine compounds	Methyl pyrazine
Organic polymers	Benzene	Cyanopyrazine
Propionitrile	Toluene	Pyrazine
Ammonium formate		

[a] Not applicable.

treatment (Miller and Villaume, 1978). Eventually, the treated wastewater, which may contain some acrylonitrile, is discharged to surface waters. The solid wastes that are collected from the deep well pond are disposed of by a regulated, EPA-approved landfill operator (Hughes and Horn, 1977).

The mode of acrylonitrile entry into the atmosphere from the loading and storage operations is gaseous emission. Table 5-10 shows the air emission factors from each of the above sources. It can be seen from Table 5-10 that the air emission factors from flare stack, fugitive emission, and deep well pond may have been underestimated by Hughes and Horn (1977). The results of emission measurements by the Engineering Department at Vistron tend to confirm this (Miller and Villaume, 1978).

From the emission factors given in Table 5-10, the total atmospheric emissions of acrylonitrile from monomer production facilities (per year) has been estimated. These values, given in Table 5-11, are somewhat higher since they are derived from the production capacity and not the actual usage of the monomer.

In a recent document, U.S. EPA (1980) has estimated the annual emissions of acrylonitrile from the monomer production facilities. The two overall emission factors used in this document are:

uncontrolled (0% control) : 7.07 g/kg

controlled (93% control) : 0.49 g/kg

In assessing annual emissions, U.S. EPA (1980) assumed an overall control of 85% which would correspond to an emission factor of 1.07. With this emission factor and the 1980 production data, U.S. EPA (1980) estimates the emissions of acrylonitrile from monomer production facilities for the year 1980 at 1080 MT. This value compares favorably with the emission range of 890 MT/yr.-2348 MT/yr. estimated in this document.

Table 5-10. Acrylonitrile Air Emission Factors for Monomer Production

Source of Emission	Air Emission Factor (g/kg)	Reference
Absorber Vent		
Controlled	< 0.002	Hughes and Horn, 1977
Uncontrolled	0.04	Hughes and Horn, 1977
	0.04[a]	Suta, 1979
Uncontrolled Flare Stack	0.04	Hughes and Horn, 1977
	0.5	Suta, 1979
Uncontrolled Fugitive Emission	0.0004	Hughes and Horn, 1977
	0.26	Suta, 1979
Controlled Incinerator Stack	< 0.0015	Hughes and Horn, 1977
Deep Well Pond		
Controlled	None	Hughes and Horn, 1977
Uncontrolled	None	Hughes and Horn, 1977
	0.10	Suta, 1979
Uncontrolled Storage Tank	0.802	Hughes and Horn, 1977
	0.81	Suta, 1979
Loading		
Controlled	0.0065	Hughes and Horn, 1977
Uncontrolled	0.14	Suta, 1979
TOTAL	0.89	Hughes and Horn, 1977
	1.85	Suta, 1979

[a]The absorber vent emission factor is much higher for American Cyanamid, West Wego (3.0 g/kg) and DuPont, Memphis (1.2 g/kg) (Suta, 1979).

Table 5-11. Estimated Atmospheric Emissions of Acrylonitrile from Monomer Production Facilities

Producer	Capacity (MT x 10^3)	Air Emission[a] (MT/year)	Air Emission[b] (MT/year)
American Cyanamid			
West Wego, LA	120	107	578[c]
DuPont			
Beaumont, TX	159	141	294
Memphis, TN	122	109	367[d]
Monsanto			
Chocolate Bayou, TX	209	186	387
Texas City, TX	209	186	387
Vistron			
Lima, OH	181	161	335
TOTAL	1,000	890	2,348

MT = metric ton

[a]Estimated values with an emission factor of 0.89 g/kg (Hughes & Horn, 1977).

[b]Estimated values with an emission factor of 1.85 g/kg (Suta, 1979).

[c]Estimated value with an emission factor of 3.0 g/kg (Suta, 1979).

[d]Estimated value with an emission factor of 4.8 g/kg (Suta, 1979).

5.5.2 Polymer Production Facilities

The emission rates of acrylonitrile from the production of ABS-SAN resins, acrylic and modacrylic fibers, adiponitrile, and nitrile elastomers were estimated by Suta (1979) from data supplied by the United States Environmental Protection Agency. These values are given in Tables 5-12 through 5-15. The emissions from acrylamide production were estimated to be negligible (Suta, 1979).

5.5.3 Emissions During Transportation

Acrylonitrile is shipped primarily by tank cars (40.4%), tank trucks (56.5%), and barges (1.7%) (Miller and Villaume, 1978). For the details of the spills that may occur during transportation, the reader is referred to the study of Miller and Villaume (1978). It has been calculated that the number of accidents causing release of cargo to the atmosphere can be broken down as follows: barge, 0.0117 accidents/yr.; truck, 0.063 accidents/yr.; and rail, 0.17 accidents/yr. (Miller and Villaume, 1978). The details of the magnitude of accidental spills and their impact were also estimated and are shown in Table 5-16.

It should be pointed out that the spill data were vastly underestimated. The reasons for this are twofold. First, the model used for determining the spill was based on the shipment of 80,000 tons per year between two specified destinations. In actuality, more than 300,000 tons of acrylonitrile were sold in the United States during 1976 and most were presumably shipped to the major user sites located throughout the United States. Second, the incorporation of imprecise data for both the past accident rates and the number of trips in the calculation will provide erroneous results.

Some data on actual acrylonitrile spills reported to the Oil and Hazardous Materials Spill Information Retrieval System (OHM-SIRS) of the EPA do exist.

Table 5-12. Estimated Acrylonitrile Emission Rates from ABS-SAN Resin Production (Suta, 1979)

Producer	Acrylonitrile Emissions (MT/year)
ABTEC	
Louisville, KY	125.2
Borg Wagner	
Washington, WV	1,769.0
Ottawa, IL	387.4
Dow	
Torrance, CA	9.1
Midland, MI	15.4
Riverside, MD	5.4
Allyn's Point, CT	8.2
Ironton, OH	8.2
Mobile	
Joliet, IL	49.9
Monsanto	
Addyston, OH	163.3
Muscatine, IA	362.9
Springfield, MA	27.2
Uniroyal	
Scotts Bluff, LA	154.2
TOTAL	3,085.0

MT = metric ton

Table 5-13. Estimated Acrylonitrile Emission Rates from Acrylic and Modacrylic Fiber Production (Suta, 1979)

Producer	Acrylonitrile Emissions (MT/year)
American Cyanamid	
Pensacola, FL	90.7
Dow Badische	
Williamsburg, VA	725.7[a]
DuPont	
Camden, SC	479.9
Waynesboro, VA	338.4
Monsanto	
Decatur, AL	2,993.7[a]
Kodak	
Kingsport, TN	69.4
TOTAL	4,697.8

MT = metric ton

[a]These plants are installing emission controls that should reduce acrylonitrile emissions by about 80% (Suta, 1979).

Table 5-14. Estimated Acrylonitrile Emission Rate from Adiponitrile Production (Suta, 1979)

Producer	Acrylonitrile Emissions (MT/year)
Monsanto	
Decatur, AL	90.7

MT = metric ton

Table 5-15. Estimated Acrylonitrile Emission Rates from Nitrile Elastomer Production (Suta, 1979)

Producer	Acrylonitrile Emissions (MT/year)
Copolymer Rubber	
Baton Rouge, LA	0.9
B.F. Goodrich	
Akron, OH	123.4
Louisville, KY	303.0
Goodyear	
Akron, OH	90.7
Houston, TX	78.9
Uniroyal	
Plainsville, OH	52.6
TOTAL	649.5

MT = metric ton

Table 5-16. Hazards of Acrylonitrile Transportation[a] (A.D. Little, Inc., 1974 as cited in Miller & Villaume, 1978)

Hazard Parameter	Barge	Truck	Rail
Spill Pool Radius (Feet)	200	56	104
Hazard Radius (Feet)	400	126	224
Hazard Area (Acres)	11.53[b] 1.35[d]	1.1[c]	3.3[c]
Relative Exposure (%) Urban/Rural	8/92	23/77	27/73
Expected Number of Annual Spills	0.0117	0.063	0.17
Probability of Ignition Following Spill	0.30	0.25	0.40
Expected Annual Number of People Exposed[e] Urban/Rural	0.008/0.004	0.010/0.002	0.16/0.016
Expected Annual Property Damage ($)[e] Urban/Rural	129/55	160/20	2423/252
Recurrence Interval[f] (Years)	85.5	15.8	5.8

[a] Calculations are based upon the assumption that each mode of transportation handles 100 percent of the quantity shipped.

[b] Area affected by spills into water which ignite. Assumes entire spill quantity contributes to burning pool.

[c] Area affected by spills on land which ignite. If no ignition occurs the exposed land area is equivalent to the pool spill area (πR^2 spill).

[d] For spills into water which do not ignite. The water toxicity hazard distance (feet) measured downstream from spill location for a 500 feet wide, 10 feet deep river flowing at 2.3 feet per second. Assumes vertical dispersion rate at 1.0 feet per minute until uniform mixing is achieved throughout the entire depth of the river. Thereafter, plug flow is assumed with no synergistic or antagonistic reaction between the pollutant and the receiving body of water. For this situation the entire spill quantity contributes to water.

[e] Expected number of people exposed annually and property damage is based upon ignition of the flammable pool for both land and water based spills.

[f] Average number of years between accidents.

From August 1970 to July 1975, 12 acrylonitrile spills were reported to OHM-SIRS, 10 of which occurred during transport. Of these 10 spills, 7 occurred from tank cars, 2 from barges, and 1 from a tank truck. However, OHM-SIRS cautions that only 10-20% of all spills are ever reported (Miller and Villaume, 1978). The Intergovernmental Maritime Consultative Organization estimated 41 tons of acrylonitrile were discharged into the sea from transport and handling in 1970 (NAS, 1975, cited in Miller and Villaume, 1978).

5.5.4 Emissions from End-Product Usage

Another source of environmental contamination is from residual monomer release during end-product usage. The monomer residues in the end-products are given in Table 5-17. The level of acrylonitrile in fibers is so low that handling of the fibers is not a likely source of acrylonitrile exposure. This has been experimentally confirmed by Finkel et al. (1979). Even if the product were heated, it would not result in a significant release of acrylonitrile (Federal Register, 1978a). Acrylonitrile may possibly be leached from fabrics during laundering; however, there has been no study in this area.

Although no study has been made, it is likely that some acrylonitrile will be released from automobile tires, since the rubber polymers contain the maximum amounts of monomer residue. It has been determined by A.T. Kearney, Inc. (Kearney, 1978) that in non-food contact, ABS/SAN containers will not release any acrylonitrile under normal use; in contact with foods, however, these ABS/SAN containers may release acrylonitrile into the foods. It was determined that SAN bottles (7 ppm residual monomer content) kept in contact with 3% acetic acid at 49°C for 1 month would release 0.013 ppm of acrylonitrile to the acetic acid (Brown et al., 1978). The ABS resin (24 ppm residual monomer content) under the same conditions released 0.283 ppm acrylonitrile (Brown et al., 1978).

Table 5-17. Monomer Residue in End-Products of Acrylonitrile

Product Name	Usage	Monomer Residue (ppm)	Reference
Acrylic and Modacrylic Fiber	Fabric	< 1	Miller & Villaume, 1978
Hycar	Rubber	0-100	Miller & Villaume, 1978
Kralastic and Paracril	Resin	50	Miller & Villaume, 1978
UCAR-380	Latex	250	Miller & Villaume, 1978
UCAR-4358	Latex	750	Miller & Villaume, 1978
Acrylamide Monomer	See Figure 5-1	50-100	Miller & Villaume, 1978
Polyacrylamide	See Figure 5-1	1	Kearney, 1978
ABS Resin	Packaging	24	Brown et al., 1978
SAN Resin	Containers	3-7	McNeal et al., 1979
SAN Resin	Containers	2-5	Gawell, 1979

Another possible source of acrylonitrile contamination is from acrylamide products; for example, acrylonitrile (present as impurity) solubilized into aquatic systems from acrylamide during use as a flocculant in water treatment (Miller and Villaume, 1978). Acrylamide used as a soil consolidating agent may contain volatile acrylonitrile (Miller and Villaume, 1978). This might be another source of acrylonitrile in the atmosphere.

Residual acrylonitrile can also result from its use in fumigants. Fumigant formulations containing acrylonitrile are used as pest control for residential buildings (Davis et al., 1973), tobacco, grains, and nuts. Recently, fumigants containing acrylonitrile for grain pest control have been voluntarily withdrawn from the market.

5.5.5 Conclusions

The major sources of acrylonitrile emissions are monomer and polymer production facilities using acrylonitrile, transportation, end product usage, and disposal (incineration or burial). Of these, production and transportation may be the sources of acrylonitrile in all four environmental media--air, water, soil, and sediment.

The major primary sources of acrylonitrile in air are from the monomer and polymer production facilities. The estimated acrylonitrile emissions from different production facilities are shown below:

Production facility	Amount produced (MT/yr)
Monomer	2348
ABS-SAN resin	3085
Acrylic and modacrylic fiber	4698
Adiponitrile	91
Nitrile elastomer	650

Thus, the acrylonitrile emissions from these facilities have been estimated to be 10,872 metric tons per year. The relative importance of the various sources of acrylonitrile in other environmental media is difficult to assess.

6. ENVIRONMENTAL FATE, TRANSPORT, AND DISTRIBUTION

The environmental fate of acrylonitrile in air, water, and soil, is discussed in the following sections. The discussion is based on only a few studies that have been conducted in the field.

6.1 ATMOSPHERIC FATE, PERSISTENCE, AND TRANSPORT

Very few studies have been conducted to investigate the fate of acrylonitrile under atmospheric conditions. Based on the similarity of the physical and chemical properties of acrylonitrile and the olefins, however, it is possible to predict the atmospheric fate of acrylonitrile from what is known about that class of compounds. Like other olefins, acrylonitrile is expected to undergo both chemical and photochemical reactions in the atmosphere. These reactions are discussed individually in the following sections.

6.1.1 Atmospheric Chemical Reactions

Although no specific references are available, atmospheric oxidation reactions typical of olefins may take place with acrylonitrile. For example, oxygen atoms formed as a result of the photolysis of nitrogen dioxide in the atmosphere usually add to the olefinic double bond. Oxygen atoms react with olefins more rapidly than with other unsaturated aromatic and acetylinic hydrocarbons. This addition reaction forms an excited epoxide that subsequently decomposes to alkyl and acyl radicals (U.S. EPA, 1979).

Hydroxyl radicals, formed as a result of atmospheric photolysis of nitrous acid and degradation of other free radicals, add to the double bond of the olefins. The rate constant for this addition reaction is about 10 times greater than for the atomic oxygen olefin reaction (Morris and Niki, 1971).

Atmospheric ozone is formed in significant quantities when nitrogen dioxide levels in the atmosphere are about 25 times greater than nitrogen monoxide

levels. Ozone, while not as strong an oxidizing agent as O• or •OH radicals, reacts with olefins at appreciable rates when ozone concentrations reach or exceed 0.25 ppm. Ozone adds to the olefinic double bond forming an aldehyde and a diradical. The diradical may further decompose or may participate in reactions with O_2, NO_2, and NO.

6.1.2 Photochemical Reactions

The photochemistry of acrylonitrile vapor at 213.9 nm was studied by Gandini and Hackett (1978). The photolysis was shown to proceed via two molecular elimination pathways, one yielding acetylene and hydrogen cyanide and the other yielding cyanoacetylene and hydrogen. The quantum yields for the two processes were determined to be 0.50 and 0.31, respectively. In the presence of such photosensitizers as xanthene, triphenylene, benzophenone, acetophenone, fluorenone, and dibromoanthracene, the major product of photolysis of acrylonitrile in solution was shown to be 1,2-dicyanocyclobutane (Gale, 1971; Hosaka and Wakamatsu, 1968). The dicyanocyclobutane is not very stable, however, and it is unlikely that the reaction will proceed in the gas phase.

6.1.3 Atmospheric Persistence and Transport

Only one study that experimentally investigated the atmospheric persistence of acrylonitrile is available. Joshi (1977, cited in Suta, 1979) estimated the atmospheric half-life of acrylonitrile to be 9 to 10 hours. An atmospheric half-life of 9-10 hours is sufficiently long for aerial transport to play a significant role in the distribution of acrylonitrile in the neighborhood of emission sources. It has been calculated by Suta (1979) that when the average wind speed is 4 meters/second, 86% of the emitted acrylonitrile will survive at 30 km downwind from the source, and 78% will survive at 50 km downwind.

6.2 FATE, PERSISTENCE, TRANSPORT, AND BIOACCUMULATION IN AQUEOUS MEDIA

6.2.1 Chemical Reactivity in Water

The chemical stability of acrylonitrile in water at different pH's was studied by Going et al. (1979). He spiked distilled water and Mississippi River water with 10 ppm acrylonitrile. Prior to spiking, the pH was adjusted to 4 or 10 or left unadjusted. All samples were stored at room temperature in Teflon-capped vials for 1, 6, and 23 days. There was no indication of sample decomposition in distilled water even after 23 days at any of the tested pH values. The samples in river water showed decomposition on storage. The sample with unaltered pH showed complete decomposition after 6 days. The sample stored at pH 10 showed little decomposition after 6 days but completely decomposed after 23 days. The pH 4 sample showed even less decomposition after 6 days and only 23% decomposition after 23 days. It is not certain whether the decomposition of acrylonitrile is at least partly due to microbial effect. If so, the extremes of pH may have an inhibitory effect on the microorganisms in the river water. Spiking sterilized water with acrylonitrile and monitoring sample decomposition may provide an answer.

Acrylonitrile, if present in surface waters that are used as sources of drinking water, may react with chlorine or hypochlorite during the chlorination step of the treatment process. It has been suggested that the reaction products could be a mixture of $OHCH_2CHClCN$ and $ClCH_2CHOHCN$ (Kondratenko et al., 1971). The presence of detectable levels of acrylonitrile in previously aerated surface water (used as a source of drinking water), however, is not very likely because of rapid volatilization.

6.2.2 Photochemical Reaction in Water

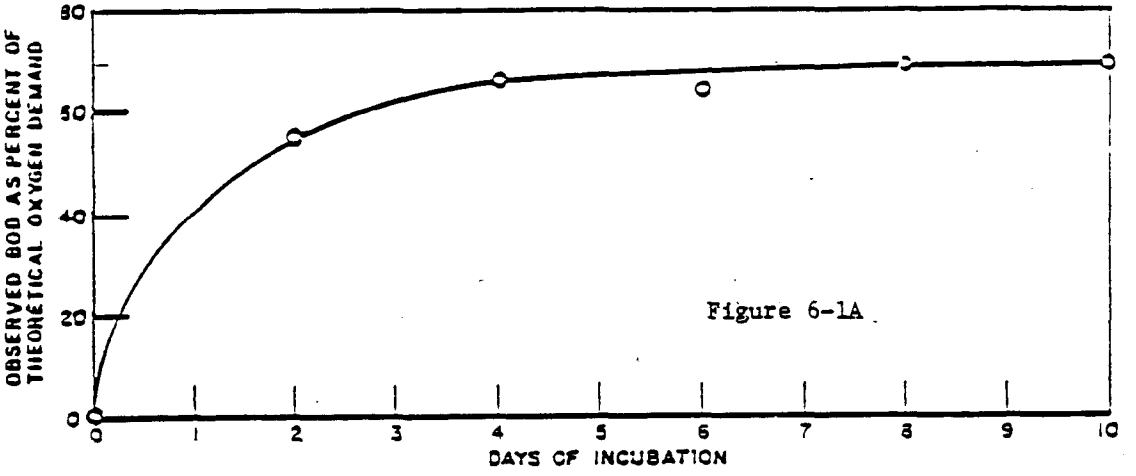
Another mode of acrylonitrile degradation may be photochemical reaction in water; however, little is known regarding the photochemistry of acrylonitrile in water in the concentration region likely to be present in natural water bodies.

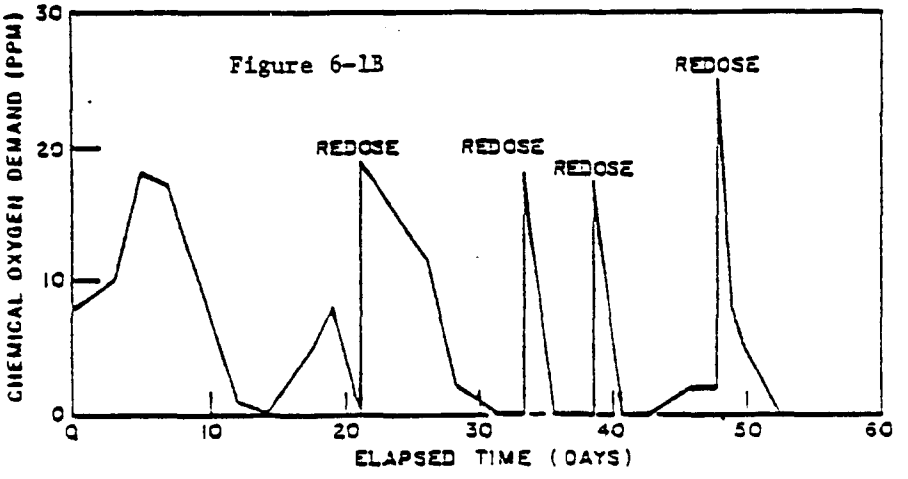
6.2.3 Degradation of Acrylonitrile by Microorganisms

Limited data suggest that loss of acrylonitrile from water systems via biological degradation can be expected. Both aerobic and anaerobic microorganisms are capable of degrading acrylonitrile, especially acclimated microorganisms. The breakdown products of aerobic microorganisms may include ammonia and acrylic acid (Mills and Stack, 1955), followed by nitrification of ammonia (Chekhovskaya et al., 1966). The latter authors found that acrylonitrile at concentrations of 50 ppm or higher may inhibit nitrification.

Mills and Stack (1955) suggested a mechanism for the biological oxidation of acrylonitrile. Using microorganisms from the Kanawha River (WV) that had been acclimated with acrylonitrile for 27 days, the Biological Oxygen Demand (BOD) of acrylonitrile was measured. The rate of aerobic oxidation was quite rapid and reached completion in five days. As shown in Figure 6-1A, about 70% of the acrylonitrile was degraded. From the nitrogen balance data, the authors suggested that the biological oxidation of acrylonitrile proceeds by an enzyme-catalyzed hydrolysis of the nitrile group to acrylic acid and ammonia.

The microbial fate of acrylonitrile in natural water was studied by Cherry et al. (1956). Acrylonitrile (10 ppm) was added to filtered aerated water from the Hackensack River (NJ). Nitrogen and phosphorus nutrients were added to the water. The complete disappearance of acrylonitrile from water took about 20 days. Subsequent redosing with acrylonitrile reduced the degradation time. These results are shown in Figure 6-1B. Similar results were obtained at 25 and





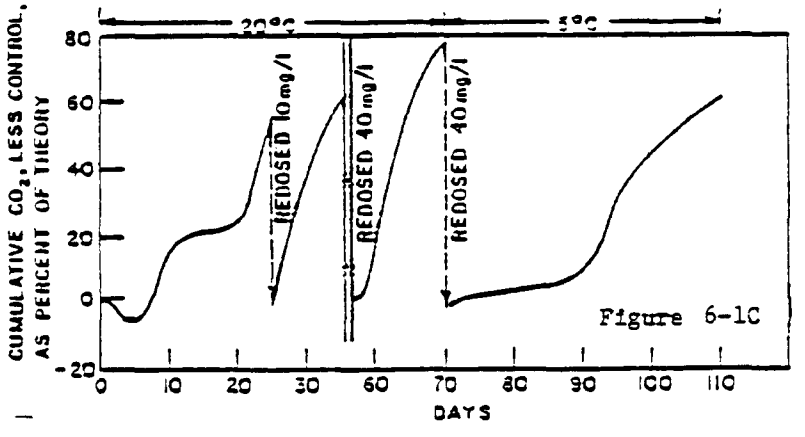


Figure 6-1. Biological Oxidation of Acrylonitrile in Aqueous Systems
A (Mills and Stack, 1955)
B (Cherry et al., 1956)
C (Ludzack et al., 1958)

50 ppm acrylonitrile; that is, the acclimated microorganisms degraded the acrylonitrile more rapidly than did the unacclimated microorganisms.

Ludzack et al. (1958) also found similar results. These authors spiked Ohio River water with 10 ppm acrylonitrile at 20°C. As shown in Figure 6-1C, there was a lag period of about a week, followed by several days of rapid degradation after which a plateau was reached. By day 22, another period of activity occurred. Redosing this water with acrylonitrile produced no lag period and plateau but produced rapid degradation of acrylonitrile by the already acclimated microorganisms. Evidently the degradation rate was temperature dependent; when a sample was redosed at 5°C, the degradation rate was found to be slower than that seen in the sample redosed at 20°C.

Ludzack et al. (1958) noted that acrylonitrile was degraded more rapidly by microorganisms in Ohio River water than by microorganisms in aged sewage. They also found that acrylonitrile was more resistant to biological degradation than aceto-, adipo-, benzo-, and lacto-nitriles.

The aerobic degradation of acrylonitrile in water can also proceed via activated sludge. Experiments conducted by Dow Chemical Company (NAS, 1975, cited in Miller and Villaume, 1978) indicated almost complete degradation of acrylonitrile to ammonia in 20 days. The effectiveness of acclimated activated sludge for the rapid degradation of acrylonitrile in water was also shown by Ludzack et al. (1961).

Kato and Yamamura (1976) discovered that aerobic microorganisms of the genus Nocardia were capable of degradation of cyanides and nitriles. More than 90% of the acrylonitrile was degraded by these microorganisms.

The preceeding studies show that acrylonitrile can be degraded aerobically. Ludzack et al. (1961), Lank (1969, cited in Miller and Villaume, 1978), and Hovious et al. (1973, cited in Miller and Villaume, 1978) studied acrylonitrile

degradation under anaerobic conditions. Lank (1969, cited in Miller and Villaume, 1978) found that acrylonitrile at a concentration of 10 ppm could be treated by anaerobic digestion. Hovious et al. (1973, cited in Miller and Villaume, 1978), however, determined that, even at a concentration of 50 ppm, acrylonitrile was inhibitory to some anaerobes. The inhibition was not complete, so some residual activity remained. Acrylonitrile's inhibition of anaerobic digestion by microorganisms was also confirmed by Ludzack et al. (1961). These authors recommended that the anaerobic digestion should not be used for treatment of acrylonitrile-containing water.

6.2.4 Bioaccumulation in Water

A bioconcentration factor (BCF) relates the concentration of a chemical in water to the concentration in aquatic organisms. It is important to determine the BCF for acrylonitrile in aquatic organisms in order to evaluate the levels of human intake of acrylonitrile from this source and also to assess ecological effects. There are a number of theoretical correlation equations that have been established to relate BCF to either the octanol-water partition coefficient or the water solubility of the chemical. These equations are given below:

$$\log BCF = 0.76 \log K_{ow} - 0.23 \quad \text{(Veith et al., 1979)}$$

$$\log BCF = 0.542 \log K_{ow} + 0.124 \quad \text{(Neely et al., 1974)}$$

$$\log BCF = -0.508 \log S + 3.41 \quad \text{(Chiou et al., 1977)}$$

where K_{ow} = partition coefficient of the chemical between octanol and water, and S = water solubility of the chemical expressed in μmol/l.

The above equation of Veith et al. (1979) is applicable for the whole fish; whereas the equations of Neely et al. (1974) and Chiou et al. (1977) are applicable for fish muscle only.

If the values for K_{ow} and S for acrylonitrile are assumed to be 0.12 (Leo et al., 1971) and 1.385×10^6 μmol/l (Groet, 1978), respectively, the theoretical

values for BCF can be calculated to be 0.1 (equation of Veith et al., 1979) for the whole fish and 0.4 (equation of Neely et al., 1974) and 2.0 (equation of Chiou et al., 1977) for fish muscle.

U.S. EPA (1978a) experimentally measured the steady-state BCF for acrylonitrile in bluegills containing about 4.8% lipids. The experimental value was 48. The BCF for lipid-soluble compounds is proportional to percent lipids (U.S. EPA, 1979). The weighted average lipid content in all the aquatic foods consumed by an individual in the United States was calculated to be 3.0% (U.S. EPA, 1979). An adjustment factor of 3.0/4.8 = 0.625 was used to adjust the measured BCF from the 4.8% lipid of the bluegill to the 3.0% lipids that is the weighted average for consumed fish and shellfish. Thus, the weighted average bioconcentration factor for acrylonitrile in the edible portion of all aquatic organisms consumed by an individual in the United States was calculated to be 48 x 0.625 = 30 (U.S. EPA, 1980).

It can be concluded from the above discussions that the experimental BCF for acrylonitrile in consumable aquatic foods is about two orders of magnitude higher than the calculated value.

6.2.5 Persistence and Transport in Water

Few studies are available that investigate persistence and transport of acrylonitrile in water other than the river water studies discussed previously. The partial vapor pressure of acrylonitrile in its water azeotrope is 80 mm Hg at 20°C (Miller and Villaume, 1978); this pressure is significant enough to cause evaporation of acrylonitrile from water. Using the method of Dilling (1977), the half-life of evaporation of acrylonitrile from water with an assumed depth of 1 meter can be calculated to be 795 minutes. It should be mentioned, however, that no experimental data are available to demonstrate this transport possibility.

The observations from the two studies of accidental spills of acrylonitrile can be used to provide further insight into the persistence and transport of acrylonitrile in water (see Section 7.3.4).

Both these spill incidents show that it is possible to transport acrylonitrile from contaminated land to surface waters (since the medium of land to water transfer was percolated water). In the absence of evaporative effect, acrylonitrile can be expected to have a long persistence in water. The bacterial decomposition of acrylonitrile in soil will probably be of little importance in cases of spills because the toxic effect of the large spills on the bacteria. If the spill occurs during winter, the low temperature of soil will further decrease the influence of biodegradation.

6.3 FATE, PERSISTENCE, AND TRANSPORT IN SOIL

Few data are available on this subject. Acrylonitrile can be degraded by soil fungi (Giacin et al., 1973). Fungi capable of acrylonitrile biodegradation included Penicillium, Aspergillus, and Cladosporium species (Giacin et al., 1973). The products of decomposition were probably carbon dioxide and ammonia. Although other microorganisms slowly degraded acrylonitrile, best results were obtained with soil fungi. The microbe Nocardia rhodochrous LL100-21 slowly degraded acrylonitrile, but the rate of degradation increased with added acetate (DiGeronimo and Antoine, 1976).

7. ENVIRONMENTAL LEVELS AND EXPOSURE

7.1 ENVIRONMENTAL LEVELS

Although acrylonitrile levels in occupational atmospheres (Marrs et al., 1978; Sakurai et al., 1978; Martin, 1978) and in industrial point sources (Hughes and Horn, 1977; Hollingsed, 1978, cited in Miller and Villaume, 1978; Suta, 1979) have been determined, only one study conducted by Midwest Research Institute (Going et al., 1979) has determined environmental levels of acrylonitrile. This study was designed to determine the levels of acrylonitrile in ambient air samples, surface waters, and soils and sediments around acrylonitrile and acrylonitrile polymer manufacturing facilities. Data for acrylonitrile levels in atmospheric samples obtained away from manufacturing facilities or from sites without the manufacturing facilities are not available.

7.1.1 Atmospheric Levels of Acrylonitrile Around Its Major Production and Usage Facilities

The atmospheric levels of acrylonitrile around manufacturing facilities are given in Table 7-1. The samples were collected by passing the air through activated carbon over a period of approximately 24 hours for all stations, except Monsanto in Decatur, Alabama, where two 24-hour samples were collected. The acrylonitrile from the activated carbon was desorbed by carbon disulfide and analyzed by gas chromatography with a flame ionization detector. The average recovery of acrylonitrile determined with spiked samples was 63% (Going et al., 1979).

The values for maximal average concentrations given in Table 7-1 have been derived in the following manner: The sum of all the determined concentrations has been divided by the number of determinations. When the determined concentrations were less than the detection limit, the data used for averaging are the values at the detection limit.

Table 7-1. Atmospheric Monitoring Data for Acrylonitrile (Going et al., 1979)

Site	Product	Distance (km) of Collection from Plant[a]	No. of Samples Collected[b]	Concentration of Acrylonitrile ($\mu g/m^3$)		
				High	Low	Maximal Average[c]
American Cyanamid, New Orleans, LA	Acrylonitrile	0.6-1.8	5	13.6	< 0.1	2.6
American Cyanamid, Linden, NJ	Acrylonitrile	0.5-1.8	6	15.9	< 0.1	3.2
Monsanto, Texas City, TX	Acrylonitrile	0.7-2.6	7	8.9	< 0.3	3.2
Monsanto, Decatur, AL	Acrylic and Modacrylic Fibers	1.3-5.0	5	4.2	< 0.1	1.2
DuPont, Lugoff, SC	Acrylic Fibers	0.7-2.2	8	1.1	< 0.1	0.3
DuPont, Waynesboro, VA	Acrylic and Modacrylic Fibers	0.3-0.9	6	7.0	< 0.2	1.3
Borg-Warner, Washington, WV	ABS/SAN Resins	0.5-1.3	4	325.0	< 0.2	84.0
Goodrich, Louisville, KY	Nitrile Elastomers & ABS/SAN Resin	0.4-3.0	4	4.3	< 0.2	1.2
Monsanto, Addyston, OH	ABS/SAN Resins	0.3-1.0	5	1.1	< 0.2	0.5
Uniroyal, Painesville, OH	Nitrile Elastomers	0.3-0.9	5	3.1	< 0.1	1.0
Vistron, Lima, OH	Acrylonitrile & Acrylamide	0.2-0.6	5	148.0	< 0.2	34.4

[a] The distances of sample collection points are obtained from Suta, 1979.

[b] Sometimes replicate samples were collected from the same sampling point.

[c] See text for explanation.

The highest individual concentration from this monitoring data was 325 $\mu g/m^3$ and the lowest was < 0.1 $\mu g/m^3$ (Going et al., 1979). The recorded concentrations depend greatly on the meteorological conditions, the production stage within the plant at the time of sampling, and the presence of emission control devices in the plant. This is reflected in the high maximal average acrylonitrile level (84 $\mu g/m^3$) in one plant and a low level (0.5 $\mu g/m^3$) in another plant, even though both produced ABS/SAN resins. Such high and low atmospheric levels of acrylonitrile are also reflected in the data for other plant emissions, all manufacturing the same acrylonitrile (see Table 7-1). A comparison of the experimental monitoring data (Going et al., 1979) with the dispersion modeling data of Suta (1979) is given in Table 7-2.

A comparison of the dispersion modeling data (Suta, 1979) with the actual monitoring data (Going et al., 1979) shows that, although the difference between the experimental concentrations and the concentrations derived from dispersion modeling (Suta, 1979), on the average, was about 20%, 90% of the individual values had much higher variations. In many instances, the agreement between the two were poor. Therefore, the need for more experimental monitoring data cannot be overemphasized.

It is interesting to note that the atmospheric acrylonitrile level near the American Cyanamid Plant in Linden, New Jersey, which produces only acrylamide, is comparable to that near plants that manufacture other products derived from acrylonitrile. In deriving the sources of emissions (see Section 5.5.2), Suta (1979) made the assumption that acrylamide production is a negligible source of acrylonitrile emission.

7.1.2 Acrylonitrile Levels in Surface Waters

The acrylonitrile monitoring data for surface waters is given in Table 7-3. These data were obtained by Going et al. (1979). Whenever possible, grab samples

Table 7-2. Comparison of Monitoring and Dispersion Modeling Data (Suta, 1979)

Plant/Location	Distances (km)	Acrylonitrile Concentration (ug/m^3)	
		Monitoring[b]	Dispersion Modeling[c]
American Cyanamid New Orleans, LA	0.50-0.99	4.3	4.3
	1.00-1.49	0.1	2.5
	1.50-1.99	0.1	1.9
American Cyanamid Linden, NJ	0.50-0.99	0.5	d
	1.00-1.49	6.0	d
	1.50-1.99	0.7	d
Monsanto Texas City, TX	0.50-0.99	2.4	6.5
	1.00-1.49	nd	-
	1.50-1.99	3.8	2.5
	2.00-2.49	0.9	1.8
	2.50-2.99	5.2	1.3
Monsanto Decatur, AL	1.00-1.49	1.2	21.0
	1.50-1.99	2.3	9.3
	2.00-2.49	0.8	7.2
	2.50-4.99	nd	-
	5.00-5.49	0.2	3.1
DuPont-May Camden, NJ	0.50-0.99	0.7	7.4
	1.00-1.49	0.3	2.3
	1.50-1.99	0.1	1.3
	2.00-2.49	0.2	1.1
DuPont Waynesboro, VA	0.30-0.49	3.6	5.2
	0.50-0.99	0.2	3.4
Borg-Wagner Washington, WV	0.50-0.99	157.6	42.1
	1.00-1.49	0.3	30.4
B.F. Goodrich Louisville, KY	0.30-0.49	2.3	7.2
	0.50-1.99	nd	-
	2.00-2.49	0.2	1.7
	2.50-2.99	nd	-
	3.00-3.49	0.2	1.0
Monsanto Addyston, OH	0.30-0.49	0.2	5.9
	0.50-0.99	0.4	3.9
	1.00-1.49	1.1	2.8
Uniroyal Plainsville, OH	0.30-0.49	1.3	1.2
	0.50-0.99	0.7	0.9
Vistron Lima, OH	0.30-0.49	43.4	10.6
	0.50-0.99	0.2	5.2

nd = no data

[a] Estimated distance from the acrylonitrile production within the plant.

[b] Average of all monitoring stations within the indicated distances.

[c] Estimated concentrations at the midpoint of the distances.

[d] Dispersion modeling estimates were not made for acrylamide plants.

Table 7-3. Acrylonitrile Monitoring Data for Surface Waters (Going et al., 1979)

Site	Product	Concentration in water, µg/l	
		High	Low
Mississippi River near American Cyanamid, New Orleans, LA	Acrylonitrile	n.d.[a]	< 0.1
Arthur Hill near American Cyanamid, Linden, NJ	Acrylamide	0.8	n.d.
Texas City Ship Channel near Monsanto, Texas City, TX	Acrylonitrile	0.4	< 0.1
Tennessee River near Monsanto, Decatur, AL	Acrylic and modacrylic fibers	3500	< 0.1
Wateree River near DuPont, Lugoff, SC	Acrylic fibers	19.7	< 0.1
South River and Discharge Point at DuPont, Waynesboro, VA	Acrylic and modacylic fibers	n.d.	< 1.3
Ohio River near Borg-Warner, Washington, WV	ABS/SAN resins	1.9	1.4
Ohio River near B.F. Goodrich, Louisville, KY	Nitrile elastomers and ABS/SAN resins	2.0	< 1.4
Ohio River near Monsanto, Addyston, OH	ABS/SAN resins	8.0	< 1.4
Influent and effluent from treatment facilities from wastewater at Uniroyal, Painesville, OH	Nitrile elastomers	4300	9.3
Discharge point at Ottawa River at Vistron, Lima, OH	Acrylonitrile and acrylamide	n.d.	< 1.3

[a] n.d. = not determined

were collected upstream and downstream of the plant discharge points. In some instances, discharged wastewater from the plants were collected for analysis.

Two complementary techniques, azeotropic distillation and purge-trap, were used for reducing interference and concentrating acrylonitrile in the samples. The method used for quantification was GC with a Hall nitrogen-selective detector. Samples that appeared to contain acrylonitrile were confirmed by GC-MS analysis. Analytical quality assurance was done by spiking and analyzing field samples (Going et al., 1979).

The two highest levels of acrylonitrile shown in Table 7-3 were obtained from the Monsanto plant in Decatur, Alabama, and the Uniroyal plant in Painesville, Ohio. These values were high, however, because these samples represent discharged wastewater prior to adequate dilution in surface water. The high acrylonitrile content in the discharged wastewaters is an indication that an effective control of these wastewaters is necessary to minimize the pollution of surface waters.

7.2 ACRYLONITRILE LEVELS IN SOILS AND SEDIMENTS

The environmental levels of acrylonitrile in a few soil and sediment samples are shown in Tables 7-4 and 7-5. These data were obtained from the investigations of Going et al. (1979).

The soil samples were collected from the air sampling locations. The collection of sediment samples was restricted by the accessibility of the sediments from the waterbody. The methods of analyses were the same for both soil and sediment samples. The sediments free from excess water and the soil samples were ultrasonically agitated with water. In most analyses, the water extracts were directly injected into the gas chromatograph equipped with a Hall nitrogen-selective detector. One sample each from soil and sediment was further purified

Table 7-4. Acrylonitrile Monitoring Data for Sediments (Going et al., 1979)

Site	Concentration (µg/kg)[a]
Mississippi River near American Cyanamid, New Orleans, LA	< 0.5
Tennessee River near Monsanto, Decatur, AL	< 50
Wateree River near DuPont, Lugoff, SC	< 50
South River near DuPont, Waynesboro, WV	< 50

[a]These figures were the lowest detection limit

Table 7-5. Acrylonitrile Monitoring Data for Soils (Going et al., 1979)

Site	Concentration (µg/kg)[a]
American Cyanamid, New Orleans, LA	≈ 0.5
American Cyanamid, Linden, NJ	< 50
Monsanto, Texas City, TX	< 100
Monsanto, Decatur, AL	< 50
DuPont, Lugoff, SC	< 50
DuPont, Waynesboro, VA	< 50
Borg-Werner, Washington, WV	< 50
B.F. Goodrich, Louisville, KY	< 400
Monsanto, Addyston, OH	< 400
Uniroyal, Painesville, OH	< 400
Vistron, Lima, OH	< 100

[a]These figures were the lowest detection limit

and concentrated by the purge-trap technique before GC injection. The recoveries of acrylonitrile from the samples were not determined.

It is obvious from Tables 7-4 and 7-5 that, with the exception of one soil sample, the level of acrylonitrile in all other samples was below the detection limit of the method used. This may be expected in view of the relatively high water solubility and high volatility of acrylonitrile. The detection limit, however, could have been lowered either with the purge-trap or azeotropic distillation of the water extract.

7.3 ENVIRONMENTAL EXPOSURE

Population exposure from environmental acrylonitrile emissions can take place through four principal sources: (1) industrial emissions in air; (2) drinking water; (3) consumed foods; and (4) spillage during transportation. The exposure from each of these sources is discussed below.

7.3.1 Exposure From Air Polluted by Industrial Sources

The total number of people expected to be exposed to different levels of acrylonitrile concentrations from different industrial sources was calculated by Suta (1979) and is given in Table 7-6.

The estimated values were derived on the basis of a dispersion modeling from the emitted acrylonitrile concentration values and estimated population density around the plants. The estimated exposure values were determined for people residing within 10 concentric rings (of various radii ranging from 0 to 30 km) about each plant.

The estimated exposures in Table 7-6 are somewhat underestimated for two reasons. First, the exposures beyond 30 km were not included in all the calculations. Second, the exposure from acrylamide plant emissions was ignored, even though the experimental data from Going et al. (1979) indicated such exposures might be significant.

Table 7-6. Estimated Population Exposure to Atmospheric Acrylonitrile from Specific Emission Sources (Suta, 1979)

Annual Average Acrylonitrile Concentration ($\mu g/m^3$)	Estimated Population Exposure					
	Distance from Source (km)	Acrylonitrile Monomer	ABS/SAN Resins	Acrylic and Modacrylic Fibers	Nitrile Elastomer	Adiponitrile
15.0-19.9	0.3-0.5		2,700			
10.0-14.9	0.5-1	50	--			
5.0-9.9	1-2	240	850	4,700	1,800	
1.0-4.9	2-3	64,000	73,000	52,000	22,000	
0.50-0.99	3-4	140,000	79,000	70,000	81,000	
0.10-0.49	4-6	1,800,000	680,000	370,000	650,000	22,000
0.050-0.099	6-10	600,000[b]	1,200,000	190,000	690,000	32,000
0.010-0.049	10-15	0[b]	1,400,000[b]	260,000[b]	2,700,000[b]	65,000
0.005-0.009	15-20	0[b]	510,000[b]	0[b]	5,100[b]	0[b]
0.001-0.004	20-30	0[b]	790,000[b]	0[b]	93,000[b]	0[b]
Total people exposed		2,600,000	4,700,000	950,000	4,200,000	120,000

[a] To convert from $\mu g/m^3$ to ppb, multiply concentrations by 0.46.

[b] Exposures in these ranges are underestimated because calculations were made only for exposures within 30 km of each plant.

7.3.2 Exposure From Drinking Water

Trace amounts of acrylonitrile have been detected in drinking water (Kopfler et al., 1976), although the amount was not quantitated. In the absence of such data, it is impossible to evaluate the human intake from this source.

7.3.3 Exposure From Foods

The three possible sources of acrylonitrile exposure from foods are: (a) fish and shellfish; (b) food containers and packaging materials; and (c) foods fumigated with acrylonitrile-containing fumigants.

Edible aquatic organisms may bioconcentrate acrylonitrile from contaminated waters. The weighted average bioconcentration factor for acrylonitrile in the edible portion of all aquatic organisms consumed by Americans has been calculated to be 30 (U.S. EPA, 1980).

The polymers and copolymers containing residual acrylonitrile monomer could migrate from the food-contact items to the food itself. The amount of migration depends on the residual monomer content in the polymer or copolymer, the time of storage, and the temperature of storage. The effects of these factors on acrylonitrile migration are shown in Table 7-7.

Since the monomer migration is substantial from ABS/SAN resins to ethanol, the FDA currently does not permit the use of these containers for alcohol and carbonated beverages. Gawell (1979), using SAN bottles containing 3 to 5 ppm residual monomer, showed, however, that the migration in some samples of beer and soft drinks amounted to < 0.005 mg/kg. The author did not specify the storage conditions. FDA has determined that the migration of monomer from SAN resin containers (3.3 ppm residual acrylonitrile) to the beverages could be as high as 14 ppb (Flood, 1980) after 96 days contact at 120°F.

Under FDA regulations, copolymers of acrylonitrile listed in Table 7-8 are permitted in food-contact applications including food packaging, such as for

Table 7-7. Acrylonitrile Migration Under Different Storage Conditions

Migrating Solvent	Nature of Plastic	Residual Monomer Content of Plastic (ppm)	Time of Storage (months)	Temp. of Storage (°C)	Acrylo-nitrile Found (ppm)	Reference
3% acetic acid	SAN	7	1	49	0.013	Brown et al., 1978
			2	49	0.017	Brown et al., 1978
			3	49	0.022	Brown et al., 1978
			4	49	0.028	McNeal et al., 1979
			5	49	0.038	Brown et al., 1978
3% acetic acid	SAN	3	2	49	0.012	McNeal et al., 1979
			2	66	0.023	McNeal et al., 1979
3% acetic acid	ABS	24	1	49	0.283	Brown et al., 1978
			2	49	0.557	Brown et al., 1978
			3	49	0.723	Brown et al., 1978
			5	49	0.920	Brown et al., 1978
8% ethanol	SAN	10	?	49	0.078	McNeal et al., 1979
		25	?	49	0.126	McNeal et al., 1979

Table 7-8. Amounts of Various Acrylonitrile Copolymers Used in Food-Contact Applications (Troxell, 1980)

Copolymer	Use[a]	Amount used in 1977 (millions of pounds)
ABS Resins	Refrigerator/freezer linings	125
ABS Resins	Small appliances (motor housings, bases for blenders and can openers, etc.)	10-15
ABS Resins	Packaging (sheet and film for blister packs)	15
ABS Resins	Margarine tubs	< 1
SAN Resins	Drinking tumblers, blenders, jars, components of appliances, etc.	≈50
Nitrile Elastomers/ Latexes	Hoses and paper coating	7-14
High Nitrile Resins	Mostly vegetable oil bottles	< 10
Polyvinylidine chloride - Acrylonitrile Resin	Cellophane & paperboard	≈20

[a] Some of the applications may result in incidental food contact.

luncheon meats, peanut butter, margarines, fruit juices, and vegetable oils. Some acrylonitrile exposure may result from these sources, although it is difficult to quantify the amount. FDA has determined that the migration of the monomer from the containers to vegetable oil and margarine could be as high as 37 ppb (Flood, 1980).

Foods that have been fumigated with acrylonitrile-containing fumigants present a risk of acrylonitrile exposure. Fumigants containing acrylonitrile for grain pest control have been voluntarily withdrawn from the market. Other foods, such as walnuts, are no longer fumigated with acrylonitrile-containing fumigants. The residue level of acrylonitrile in walnuts that have been fumigated may range from 7.5-17.5 ppm after 2 days to 0-8.5 ppm after 38 days (Berck, 1960). Finally, acrylonitrile has been used as a fumigant for stored tobacco. Guerin et al. (1974) have qualitatively determined the presence of acrylonitrile in tobacco smoke, and, the amount has been determined to be 1-2 mg per U.S. cigarette smoked (IARC, 1979). It is not clear whether the source of acrylonitrile is from fumigation of the tobacco or from the combustion process itself.

7.3.4 Exposure From Spillage during Transportation

The expected numbers of people in urban/rural areas exposed annually from spills during transportation of acrylonitrile by three modes of transportation were calculated as follows: barge, 0.008/0.004; truck, 0.010/0.002; and rail, 0.16/0.016 (Miller and Villaume, 1978). These figures represent the cases in which the entire commodity is transported by one mode. It can be concluded that transportation of acrylonitrile by rail (40.4% of overall shipment) poses the greatest hazard and by barge (1.7% of the overall shipment) the least hazard.

The preceding estimate was based on exposure due to ignition of the spilled area and toxic exposure from contaminated surface water due to spill (see Section 5.5.3). However, contamination of the ground water and the subsequent

exposure from usage of the water as a source of drinking water was not considered in the calculation.

Two recent cases of accidental spills leading to ground water contamination show the possibility of population exposure from this source. A spill of 36,000 gallons of acrylonitrile onto farmland (Gilford, Inc., 2/22/77) caused contamination of the nearby groundwater and a creek (Miller and Villaume, 1978). Evidently, the acrylonitrile percolated through the soil into the groundwater and the creek. For several months after the spill, the concentration of acrylonitrile in the groundwater increased after it rained (Miller and Villaume, 1978).

Another spill of 20,000 gallons of acrylonitrile (near Mapleton, IL, 12/23/77) caused similar contamination of the groundwater and creeks located near the spill (Miller and Villaume, 1978). Monitoring data from five wells, all located within 100 feet from the spill site, showed high levels of acrylonitrile in the water (46 mg/l to 3520 mg/l) at the end of 108 days (Miller and Villaume, 1978). Acrylonitrile levels started decreasing about 170 days after the spill, but acrylonitrile had not completely disappeared from the well water even after 351 days. Nine additional wells, located at an average distance of about 1000 feet from the spill site, showed no trace of acrylonitrile. Tap water at six nearby residences (an average distance of 1150 feet from the spill site) contained no acrylonitrile. A little Marsh Creek located about 750 feet from the site of the spill showed 32 mg/l of acrylonitrile at the end of 58 days after the spill, but acrylonitrile finally disappeared after about 108 days.

7.3.5 Exposure From Thermal Degradation

Thermal decomposition of polymers containing acrylonitrile is another source of acrylonitrile in the atmosphere. Pyrolysis of the following polymers--polyacrylonitrile (Tsuchiya and Sumi, 1977; Guyot et al., 1978), ABS/SAN resins (Chaigneau and LeMoan, 1974), acrylonitrile-methacrylate copolymers (Guyot

et al., 1978), vinyl chloride-acrylonitrile copolymers (Tanaka et al., 1975)--produces hydrogen cyanide and acrylonitrile.

The composition of the gases evolved during pyrolysis and combustion of polymers and copolymers of acrylonitrile depends on a number of factors, including the nature of the polymer, gas composition, gas flow rate, and heating rate of the flame (Sarofim et al., 1973). Pyrolysis prevails at lower temperature and decomposition requires higher temperature (Sarofim et al., 1973). The pyrolysis of SAN bottles with He and air at a flow rate of 1 to 3 l/min and heated at a rate of 5°C/min to 48000°C/min produced the following major nitrogen components (Sarofim et al., 1973).

HNC: 5.4 to 14.3% of total nitrogen in SAN
Acrylonitrile: 7.5 to 38.0% of total nitrogen in SAN

The combustion of SAN bottles under a variety of conditions was studied in detail by Kaiser and Bergman (1973). Their results are summarized below:

The combustion of SAN bottles alone with 83% excess air produced smoke, odor, and toxic gases in appreciable amounts. The concentrations of two major nitrogen components and hydrogen cyanide in the flue gases were the following:

Acrylonitrile: 270 ppm of total gases
Methacrylonitrile: 34 ppm of total gases
HCN: 1 ppm of total gases

From these results, the authors concluded that the burning of SAN bottles in campfires, fireplaces, and outdoor trash burners could be hazardous.

Mixed with household refuse or the usual commercial or industrial plant wastes, a few percent (2 to 4%) of SAN containers will burn in large incinerators (about 1 ton/hr) without producing any detectable level of HCN or acrylonitrile. As a matter of fact, other than a slight increase in NO production, the SAN addition to household and commercial refuse will produce less harmful gases than the burning of refuse without SAN. This is probably due to the fact that SAN in refuse aids in the completion of combustion of the refuse.

As the size of the incinerator decreases, combustion of SAN with other refuse will increase production of smoke, particulate matter, acrolein, acid gases, HCN, NO_x, and total hydrocarbons.

Preliminary estimates of ambient concentrations and exposure levels of acrylonitrile may be obtained from the modeling of the dispersion of acrylonitrile as a result of pyrolysis and combustion. However, in the absence of any such dispersion modeling data, it is difficult to estimate the exposure level from this source.

7.4 CONCLUSIONS

Most acrylonitrile exposures result from ABS/SAN resin and nitrile elastomer production. The risk for population exposure from the acrylonitrile sources is dependent on a number of factors, including the height of the release point source; that is, the higher release point will result in greater dilution of the pollutants at ground level and also spreads it over a larger area. In general, for the same amount of emission and topography, acrylonitrile emission points with lower elevation will result in higher ground level concentrations than elevated acrylonitrile emission points. On the basis of the elevation and other relevant factors, monomer and ABS/SAN resin production results in the highest estimated total risk in terms of exposed population and exposure concentration.

8. BIOLOGICAL EFFECTS ON MICROORGANISMS

Loveless et al. (1954) studied the effect of acrylonitrile on growth and cell division of yeast (Saccharomyces cerevisiae) and bacteria (Escherichia coli), as measured by dry weights and cell counts during the logarithmic growth phase. Treatment with 1000 mg/l reduced the growth of E. coli but had no effect on cell size; this concentration inhibited growth and division in S. cerevisiae. Treated cells were 170% larger than control cells and weighed 52% more.

Acrylonitrile was not toxic to the bacterium Nocardia rhodochrous at a concentration of 10,000 mg/l in both (DiGeronimo and Antoine, 1976). This concentration of acrylonitrile supported growth of these bacteria as a sole source of nitrogen, but not as a source of carbon.

Acrylonitrile has been shown to be inhibitory to anaerobic bacteria. Ludzack et al. (1961) reported that acrylonitrile inhibited gas production by anaerobic digester cultures which were dosed repeatedly with 10 to 40 mg/l acrylonitrile. Hovious et al. (1973, cited in Miller and Villaume, 1979) found that 50 to 100 mg/l acrylonitrile inhibited gas production by anaerobic methanogenic bacteria in proportion to dose.

Acrylonitrile was used as a fumigant to control mold growth on packaged papads, an Indian bread (Narasimhan et al., 1972). Papads with 18 or 20% moisture content were sealed in polyethylene bags, fumigated for 48 hours with 32 or 64 mg/l acrylonitrile, and checked for mold growth after one month. The higher dose prevented mold growth at both moisture levels, whereas the lower dose prevented mold growth only in the 18% moisture papads. The species of molds were not identified.

Some limited information concerning the effects of acrylonitrile on aquatic microorganisms was provided by Cherry et al. (1956). Nutrient-enriched and aerated river water was dosed with 10, 25, or 50 mg/l acrylonitrile. Balanced

populations of bacteria, diatoms, algae, protozoa, and rotifers developed at 10 and 25 mg/l, whereas fungal species predominated at 50 mg/l.

9. BIOLOGICAL EFFECTS ON PLANTS

There is limited information concerning the effects of acrylonitrile on plants.

Garrison (1978) studied the effects of acrylonitrile on cultured seagrass (Ruppia maritima). Acrylonitrile was added to the water column to give concentrations ranging from 10 µg/l to 10 g/l. Concentrations greater than 100 mg/l totally inhibited photosynthesis and respiration, as measured by dissolved oxygen changes. Lower concentrations had no effect on these processes. Although all concentrations reduced the growth rate of shoots, the growth rate of roots was stimulated at concentrations below 1 mg/l acrylonitrile.

The effect of acrylonitrile on pea seedlings (Pisum sativum) was studied by Burg and Burg (1967), who reported that 0.17 mM (ca. 9 ppm) acrylonitrile was "toxic" (undefined effect) and that lower levels showed no effect on seedling elongation.

Fumigant mixtures of 1:1 acrylonitrile:carbon tetrachloride had no adverse effects on seed germination of beans, beets, corn, peas, lettuce, onions, tomatoes, wheat, and oats when seeds were fumigated for 24 to 48 hours at concentrations ranging from 1 to 25 pounds per 1000 cubic feet (Glass and Crosier, 1949, cited in Miller and Villaume, 1978).

Smith (1975) investigated the effects of acetone vapor on net photosynthesis of Ilex aquifolum leaves in illuminated growth cabinets. Net photosynthesis of leaves exposed to an air stream containing 0.01 mg acetone per ml air (10 ppm) for 15 minutes was only 40% of control net photosynthesis.

When acrylonitrile was added to aerated, nutrient-enriched river water, balanced growth of bacteria, diatoms, algae, protozoa, and rotifers occurred at 10 to 25 mg/l acrylonitrile (Cherry et al., 1956). At 50 mg/l, however, fungal growth predominated.

Kihlman (1961) reported that 1 mM (53 ppm) acrylonitrile was not mutagenic to broad bean root tips (Vicia faba). The details of this study are given in Section 13.4.

10. BIOLOGICAL EFFECTS ON DOMESTIC ANIMALS

No information was found concerning the effects of acrylonitrile on domestic animals other than dogs and cats. The effects of acrylonitrile on these animals are discussed in Section 13.

11. BIOLOGICAL EFFECTS ON WILDLIFE

No information was found on the toxicity of acrylonitrile to wildlife other than insects.

11.1 INSECTS

Judson et al. (1962) studied the ovicidal effects of acrylonitrile and other chemicals on the eggs of the yellow-fever mosquito (Aedes aegypti). Mature eggs were exposed for 24 hours to the vapor of 5 or 10 µl added acrylonitrile in sealed one quart jars (21-32°C, 100% humidity) and then placed in deoxygenated water to determine hatchability. The percent mortality at the two treatment levels (4.2 or 8.4 mg/l, by calculation) was 60 percent and 92 percent, respectively.

Bond (1963) exposed adult granary weevils (Sitophilus granarius) and cadelle larvae (Tenebroides mauritanicus) to a series of acrylonitrile fumigant concentrations for an unspecified period. The exposed insects were then divided into three groups, which were kept for 48 hours in an atmosphere of nitrogen, oxygen, or air and then placed in air for five days. The dosage (expressed as the product of concentration and exposure time) required to kill 50 percent of the insects kept in air was 23.0 for T. mauritanicus and 5.4 for S. granarius. The median lethal concentration cannot be calculated from these values because Bond did not specify the duration of exposure to the fumigant. The results did indicate, however, that oxygen enhanced the toxicity of acrylonitrile and most of the other chemicals tested.

Lindgren et al. (1954) fumigated eight species of insects with a series of acrylonitrile concentrations for two or six hours. Mortalities were counted four days after fumigation. The LD50 and LD95 values are given in Table 11-1.

Similar toxicity studies were conducted with acrylonitrile by Bond and Buckland (1976, 1978) with several insect species. The duration of exposure,

Table II-1 Lethal Dose Values for Insects Exposed to Acrylonitrile Fumigation

Species	Length of Exposure (hours)	Length of Test (days)	LD50 (mg/l)	LD95 (mg/l)	LD99 (mg/l)	Reference
Granary Weevil	8	7	0.7	-	1.2	Bond & Buckland, 1976
(Sitophilus granaria	6	4	2.0	2.9	-	Lindgren et al., 1954
	5	7	1.4	-	2.2	Bond & Buckland, 1978
	2	4	4.5	8.0	-	Lindgren et al., 1954
Rice Weevil	6	4	1.0	1.8	-	Lindgren et al., 1954
(Sitophilus oryza)	2	4	2.5	6.5	-	Lindgren et al., 1954
	24	7	0.40	0.78	-	Rajendran & Muthu, 1976
Mexican Bean Weevil	6	4	1.4	2.1	-	Lindgren et al., 1954
(Zabrotes pectoralis	2	4	2.0	4.0	-	Lindgren et al., 1954
Bean Weevil	6	4	1.1	2.0	-	Lindgren et al., 1954
(Acanthoscelides ob tus)	2	4	3.0	5.5	-	Lindgren et al., 1954
Drug-store Beetle	6	4	1.7	2.5	-	Lindgren et al., 1954
(Stegobium paniceum)	2	4	3.0	7.0	-	Lindgren et al., 1954
Confused Flour Beetl	8	7	1.9	-	2.5	Bond & Buckland, 1976
(Tribolium confusum)	6	4	3.0	4.9	-	Lindgren et al., 1954
	2	4	6.5	11.0	-	Lindgren et al., 1954
Pulse Beetle	24	2	0.43	0.56	-	Rajendran & Muthu, 1976
(Callosobruchus chin is)						
Red Flour Beetle	5	7	2.6	-	4.3	Bond & Buckland, 1978
(Tribolium castaneum	24	7	1.05	1.32	-	Rajendran & Muthu, 1976
Saw-toothed Grain Be e	6	4	1.1	2.0	-	Lindgren et al., 1954
(Oryzaephilus surina ais)	2	4	3.5	6.5	-	Lindgren et al., 1954
	24	7	0.76	1.27	-	Rajendran & Muthu, 1976
Lesser Grain Borer	6	4	0.8	1.4	-	Lindgren et al., 1954
(Rhyzopertha dominic	2	4	2.5	4.0	-	Lindgren et al., 1954
	24	7	0.76	1.08	-	Rajendran & Muthu, 1976
Cadelle	8	7	2.8	-	6.0	Bond & Buckland, 1976
(Tenebroides maurita us)	5	7	3.8	-	8.4	Bond & Buckland, 1976

time at which mortalities were counted, and the LD50 and LD99 values are given in Table 11-1. Bond and Buckland (1976) found that acrylonitrile alone was more toxic than methyl bromide alone or mixtures of both compounds. Although acrylonitrile is too flammable for use as a fumigant alone, it does enhance the toxicity of non-flammable methyl bromide, especially at low temperatures. Bond and Buckland (1978) showed that fumigation with acrylonitrile and methyl bromide:acrylonitrile mixtures was more effective in atmospheres of 20-50% carbon dioxide than in air.

Rajendran and Muthu (1976) also conducted fumigation bioassays with six species of stored product insects. As shown in Table 11-1, the longer exposure period (24 hours) resulted in LD50 and LD95 values that were lower than those reported for the same species by the previously cited workers.

The results presented in Table 11-1 indicate that the concentration of acrylonitrile required to kill 95% or more of test groups of insects is between about 0.5 and 10 mg/l, depending on species and exposure time. This concentration is between 1.3 and 2.6 times the LD50 concentration.

The only other information found concerning effects of acrylonitrile in insects was by Benes and Sram (1969), who found that acrylonitrile was not mutagenic in fruit flies (Drosophila melanogaster).

12. BIOLOGICAL EFFECTS ON AQUATIC ORGANISMS

12.1 ACUTE TOXICITY

The acute toxicity of acrylonitrile has been determined for several species of marine and freshwater fish and invertebrates.

12.1.1 Freshwater Fish

The majority of information concerning the acute toxicity of acrylonitrile to aquatic organisms has been developed with freshwater fish. The most comprehensive study is that of Henderson et al. (1961), who reported median lethal concentration (LC50) values for fathead minnows (Pimephales promelas), bluegill sunfish (Lepomis macrochirus) and guppies (Poecilia reticulata = Lebistes reticulatus). Each bioassay utilized 5 acrylonitrile concentrations in a geometric series and 10 fish per concentration. The test solutions were not renewed during the 96-hour exposure period. LC50 values were calculated by graphical interpolation from mortality data at 24, 48, and 96 hours of exposure. These and other values are presented in Table 12-1.

The 96-hour LC50 values ranged between 11.8 mg/l for the most sensitive species (bluegills) and 33.5 mg/l for the least sensitive species (guppies). The LC50 value decreased by a factor of about 2 between 24 and 96 hours in most tests, indicating that toxicity increased with exposure time. In contrast, toxicity tests with other organic nitriles (lactonitrile, benzonitrile, acetonitrile, adiponitrile, oxydipropionitrile) showed relatively little or no increase in the toxicity of these compounds with longer exposure time. Acrylonitrile LC50 values for fathead minnows were slightly lower in hard water (320 mg/l hardness) than in soft water (20 mg/l hardness), which indicates that acrylonitrile toxicity may increase with higher water hardness. Because confidence intervals for these LC50 values cannot be calculated from the reported data, it is unknown whether the

Table 12-1. Median Lethal Concentration (LC50) Values for Fish Exposed to Acrylonitrile

Species	Temp. (1°C)	Type Test	Dilution Water	LC50 (mg/l) 24 hr	48 hr	72 hr	96 hr	Reference
Fathead Minnows[a] (Pimephales promelas)	25	S	FW(hard)[f]	32.7	16.7	-	14.3	Henderson et al., 1961
Fathead Minnows[a] (Pimephales promelas)	25	S	FW(soft)[g]	34.3	21.5	20.5	18.1	Henderson et al., 1961
Fathead Minnows[a] (Pimephales promelas)	25	F	FW(soft)[g]	33.5	14.8	11.1	10.1	Henderson et al., 1961
Bluegill Sunfish[b] (Lepomis macrochirus)	25	S	FW(soft)[g]	25.5	14.3	-	11.8	Henderson et al., 1961
Guppies[c] (Poecilia reticulata)	25	S	FW(soft)[g]	44.6	33.5	-	33.5	Henderson et al., 1961
Goldfish (Carassius auratus)	NR	S	FW	-	-	40	-	Paulet and Vidal, 1975
Zebrafish (Brachydanio rerio)	20	F	FW	-	15	-	-	Slooff, 1978
Minnow (Phoxinus phoxinus)	NR	NR	FW	38.2	17.6	-	-	Marconi and Ionescu, 1974
Carp (Cyprinus carpio)	NR	NR	FW	37.4	24.0	-	-	Marconi and Ionescu, 1974
Rainbow Trout (Salmo gairdneri)	NR	NR	FW(hard)	-	70	-	-	Jackson and Brown, 1970
Golden Ide[d] (Leuciscus idus melanotus)	20	S	FW[h]	-	13,28	-	-	Junnke and Luedemann, 1978
Pinfish[e] (Lagodon rhomboides)	13.7-20.4	S	SW	24.5	-	-	-	Daugherty and Garrett, 1951

[a] length 50.3-63.5 mm (2-2.5 inches); weight =1.5 g

[b] length 38.1-50.8 mm (1.5-2 inches); weight =2 g

[c] length 25.4 mm (1 inch); weight =0.1 g

[d] length 50-70 mm; weight 1.5 ± 0.3 g

[e] standard length 57-113 mm

[f] hardwater - pH 8.2, alkalinity 320 mg/l; acidity 0 mg/l; hardness 380 mg/l

[g] soft water - pH 7.4, alkalinity 16 mg/l; acidity 2 mg/l; hardness 20 mg/l

[h] pH 7-8; degree of water hardness 15 ± 3° (German "Hartegrad")

S = static exposure
F = flow through exposure
FW= freshwater
SW= seawater
NR= not reported

difference is statistically significant. It can be concluded, however, that water hardness has little effect on acrylonitrile toxicity.

Henderson et al. (1961) also conducted continuous-flow acrylonitrile bioassays with fathead minnows in soft water. The exposure conditions are described in Section 12.2 and the 24, 48, 72, and 96 hour LC50 values are given in Table 12-1. Comparison of static and continuous-flow LC50 values shows that toxicity is equal at 24 hours, but is greater under continuous-flow conditions after 48 hours. Lower toxicity under static conditions may indicate that acrylonitrile was lost from water through adsorption, volatility, chemical change, fish uptake, or biodegradation.

Renn (1955) exposed bluegill sunfish under static and continuous-flow exposure conditions to 0.38-3.79 mg/l acrylonitrile and found no mortality during a 24-hour exposure period. White crappies (Pomoxis annularis) exposed to 4 acrylonitrile concentrations under continuous-flow conditions began dying after about 2 hours in 90.9 mg/l and after about 8 hours in 68.2 mg/l. No mortality occurred during 24-hour exposure to 37.9 or 22.7 mg/l. The concentrations given here were calculated from Renn's concentration data, which were reported in mg/l nitrogen as acrylonitrile.

The 48-hour LC50 of acrylonitrile to zebrafish (Brachydanio rerio) was determined to be 15 mg/l by Slooff (1978). This bioassay was conducted with 10 fish per concentration in closed 10-liter aquaria under flow-through (6 l/hr) conditions.

Paulet and Vidal (1975) determined a 72-hour LC50 of 40 mg/l for goldfish (Carassius auratus). This bioassay was conducted under static conditions in 12-liter aquaria. No other information was provided.

Bandt (1953) provided some limited information concerning the static toxicity of acrylonitrile to two freshwater fish species, bleak (Ablurnus

alburnus) and roach (Rutilus rutilus). Bleak and roach were exposed in groups of one or two fish to 20 to 100 mg/l acrylonitrile for up to 20 days. Although concentrations of 25 mg/l and greater were eventually lethal, the only bleak exposed to 20 mg/l showed no effect after 20 days of exposure. Renn concluded from this limited information that the threshold concentration for prolonged exposure would be about 20 to 25 mg/l. As seen in Section 12.2, this value is much too high.

Juhnke and Luedemann (1978) reported acute toxicity levels of acrylonitrile to golden ide (Leuciscus idus melanotus) that had been determined by using the identical protocol in two different laboratories. The 48-hour LC0, LC50, and LC100 (0, 50, 100% mortality) values determined at each laboratory are given below:

	48 Hour Lethal Concentration Values (mg/l)		
	LC0	LC50	LC100
Laboratory 1	16	28	48
Laboratory 2	8	13	20

Although these tests presumably were conducted under identical conditions (see Table 12-1), the values reported by laboratory 1 are about twice as high as those reported by laboratory 2. The authors did not discuss the reasons for the different results.

12.1.2 Marine Fish

The only report of acrylonitrile toxicity to marine fish is by Daugherty and Garrett (1951). Groups of eight pinfish (Lagodon rhomboides) were acclimated for 22-24 hours in 30 liters of aerated seawater at 13.7 to 20.4°C. Acrylonitrile was then added to give 16 concentrations ranging from 0.25 to 60 mg/l. No deaths occurred at 20 mg/l or less, or in controls. All fish died at 30 mg/l, which was the next higher concentration tested. The 24-hour LC50, as determined by

graphical interpolation, was 24.5 mg/l. This value is about the same as the 24-hour LC50 values reported for freshwater fish (Table 12-1).

12.1.3 Freshwater Invertebrates

Bandt (1953) provided some limited information concerning the static acute toxicity of acrylonitrile to scuds (Gammarus sp., a freshwater crustacean). Groups of ten scuds were exposed to 25, 50, or 100 mg/l acrylonitrile for up to 72 hours. All animals exposed to 50 and 100 mg/l were dead by 48 hours. There was no mortality in the group exposed to 25 mg/l for 3 days.

Acrylonitrile may be more toxic to Daphnia magna, another species of freshwater crustacea (LeBlanc, 1980). The 24 and 48-hour LC50 values (and 95% confidence interval values) for this species tested under static conditions were 13 (11-15) and 7.6 (6.2-9.2) mg/l, respectively. The "no discernible effect concentration" was 0.78 mg/l.

Randall and Knopp (1980) determined the static 48-hour EC50 (median effective concentration) of acrylonitrile for D. magna. This value (and its 95% confidence interval) was 10.95 (9.54-12.56) mg/l, which is in reasonably good agreement with the 48-hour LC50 value reported by LeBlanc (1980). Both of these studies utilized young (< 24 hours old) D. magna, and water of similar mean hardness (155-173 mg/l as $CaCO_3$) and temperature (22°C).

12.1.4 Marine Invertebrates

Portmann and Wilson (1971, cited in Miller and Villaume, 1978) exposed groups of 8 to 25 brown shrimp (Crangon crangon) to serial dilutions of acrylonitrile in aquaria containing 10 gallons (37.85 l) seawater at 15°C. The reported LC50 was 10-33 mg/l.

12.2 SUBCHRONIC TOXICITY

There is information concerning the subchronic toxicity of acrylonitrile to several species of freshwater fish and one species of freshwater invertebrate. No information was found for marine fish or invertebrates.

12.2.1 Freshwater Fish

Henderson et al. (1961) conducted five replicate subchronic bioassays with fathead minnows under continuous-flow exposure conditions. Groups of 50 fish were exposed to each of 7 acrylonitrile concentrations or to control water (20 mg/l hardness, 25°C) for up to 30 days. Controlled amounts of test solutions were pumped into glass bottles containing 10 fish and 10 liters of water so that a renewal time of 100 minutes was obtained. The fish were fed daily. The mean LC50 values determined for the five replicate bioassays are given below:

Exposure Time (Days)	1	2	3	4	5	10	15	20	25	30
LC50 (mg/l)	33.5	14.8	11.1	10.1	8.1	6.9	5.2	4.2	3.5	2.6

The LC50 decreased linearly with exposure time between 15 and 30 days, indicating that the lethal threshold concentration had not been determined at the 30 day mark and that mortalities would have continued to occur at concentrations well below 2.6 mg/l after 30 days.

Cumulative subchronic toxicity was also found by Jackson and Brown (1970, cited in Miller and Villaume, 1978), who exposed rainbow trout to 2 to 200 mg/l acrylonitrile for time periods as long as 100 days. Although the LC50 after 48-hour exposure was 70 mg/l, exposure to 2.2 mg/l for 100 days resulted in 50% mortality.

Very little is known about the mechanisms of acrylonitrile toxicity in fish. Henderson et al. (1961) noted that the first sign of acrylonitrile toxicity in fathead minnows was extreme darkening of the skin, followed in 1 to 3 days by death. They found no cyanide, formed from acrylonitrile, in the exposure water.

In contrast, the more rapid, non-cumulative toxicity of lactonitrile was attributed to the formation of cyanide, which was measured in the exposure water. It is not known whether metabolic formation of cyanide from acrylonitrile occurs in fish, although cyanide or thiocyanate formation has been reported in mammals (Section 13). Toxic action in mammals is attributed primarily to direct effects of acrylonitrile and secondarily to cyanide toxicity. Slooff (1978) studied the effect of acrylonitrile and other chemicals on respiratory activity of rainbow trout. The frequency of respiratory movements was significantly increased after 24-hour exposure to 5 mg/l acrylonitrile under flow-through conditions. This effect was preceded by a temporary, but significant, decrease in breathing rate. The concentration at which this sublethal effect occurred (5 mg/l) was three times lower than the 48-hour LC50 for zebrafish (15 mg/l), determined under similar flow-through exposure conditions.

12.2.2 Freshwater Invertebrates

The only information concerning subchronic toxicity of acrylonitrile to aquatic invertebrates was developed with Daphnia magna (U.S. EPA, 1978). No adverse effects were found when this invertebrate was exposed over its entire life cycle to as much as 3.6 mg/l acrylonitrile. As mentioned previously (12.1.3), the 48-hour EC50 reported for this species was 7.55 mg/l, which is only about twice as high as the chronic no-observed-effect concentration. In contrast, the 48-hour LC50 was about 32 times higher than the 100-day LC50 for rainbow trout (Jackson and Brown, 1970, cited in Miller and Villaume, 1978) and about six times higher than the 30-day LC50 for fathead minnows (Henderson et al., 1961). Although the chronic no-observed-effect concentration has not been determined with any fish species, it is probable that it would be considerably lower than 2 mg/l.