



## A Recommended Standard for Occupational Exposure to . . . .

### Acrylonitrile

The National Institute for Occupational Safety and Health (NIOSH) recommends that employee exposure to acrylonitrile in the workplace be controlled so that no worker will be exposed to acrylonitrile in excess of 4 ppm (8.7 mg/cu m) in air as determined by a 4-hour sample collected at 0.2 liter/minute. Because it is not possible at present to establish a safe exposure level for a carcinogen, the NIOSH recommendation is to restrict exposure to very low levels that can still be reliably measured in the workplace. The recommended exposure limit of 4 ppm is the lowest level at which a reliable estimate of occupational exposure to acrylonitrile can be determined at this time because of a limitation in the air measurement technique. Short-term studies are presently underway within the Institute to resolve those problems causing the limitation. If the studies bear positive results, the Institute will forward a recommendation to reduce the permissible exposure limit to some value less than 4 ppm. The present Federal Standard is 20 ppm, determined as a time-weighted average (TWA) concentration for up to an 8-hour work shift in a 40-hour workweek. In addition, the standard contains recommendations for medical surveillance, informing employees of hazards, sanitation, work practices, labeling and posting, personal protective clothing and equipment, monitoring, and recordkeeping.

The recommended standard is designed to protect the health and provide for the safety of employees for up to a 10-hour work shift, 40-hour workweek, over a working lifetime. Compliance with all sections of the standard should, at the minimum, substantially reduce the risk of acrylonitrile-induced cancer and prevent other adverse effects of exposure to acrylonitrile in the workplace. The employer should regard the recommended workplace environmental limit as the upper boundary for exposure and make every effort to keep the exposure as low as possible.

The acute toxic effects of acrylonitrile are similar to those from cyanide poisoning. Toxic effects of acrylonitrile inhalation which have been noted in animals include damage to the central nervous system, lungs, liver, and kidneys. Embryotoxic effects in mice have also been reported. However, the more recent evidence of acrylonitriles chronic toxicity has caused a reassessment of the hazard of workers of

acrylonitrile. In April 1977, the Manufacturing Chemists Association reported interim results of two-year feeding and inhalation studies (conducted by the Dow Chemical Company) of acrylonitrile in laboratory rats. By both routes of administration, acrylonitrile caused the development of central nervous system tumors and Zymbal gland carcinomas; no such tumors were seen in control animals. Exposure to 80 ppm of acrylonitrile also revealed an increased incidence of mammary region masses.

A preliminary epidemiologic study conducted by the E.I. DuPont de Nemours & Company, Inc. of a cohort of 470 acrylonitrile polymerization workers from the company's Camden, South Carolina, textile fibers plant indicates an excess risk of lung and colon cancer among workers with potential acrylonitrile exposure. A total of 16 cancer cases occurred by between 1969 and 1975 among the cohort first exposed between 1950 and 1955; only 5.8 cancer cases would have been expected, based on DuPont Company rates (excluding the cohort). Although the epidemiologic findings are preliminary in nature and may not alone provide definitive evidence of the carcinogenicity of acrylonitrile in man, when considered in light of the laboratory experiments demonstrating carcinogenicity in rats, a serious suspicion is raised that acrylonitrile is a human carcinogen. Thus, NIOSH believes that acrylonitrile must be handled in the workplace as a suspect human carcinogen.

Acrylonitrile is an explosive, flammable liquid having a normal boiling point of 77 C and a vapor pressure of 80 mm Hg (20 C). Synonyms for acrylonitrile include acrylon, carbacryl, cyanoethylene, fumigrain, 2-propenenitrile, VCN, ventox, and vinyl cyanide.

Approximately 1.5 billion pounds of acrylonitrile are manufactured each year in the United States by the reaction of propylene with ammonia and oxygen in the presence of a catalyst. The major use of acrylonitrile is in the production of acrylic and modacrylic fibers by copolymerization with methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, or vinylidene chloride. Acrylic fibers are used in the manufacture of apparel, carpeting, blankets, draperies, and upholstery. Some applications of modacrylic fibers are synthetic furs and hair wigs.

Other major uses of acrylonitrile include the manufacture of acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins (used to produce a variety of plastic products), nitrile elastomers and latexes, and other chemicals, such as adiponitrile and acrylamide. Acrylonitrile is also used as a fumigant. NIOSH estimates that approximately 125,000 persons are potentially exposed to acrylonitrile in the workplace.

The recommended standard is part of a continuing series of recommendations developed by

NIOSH in accordance with the Occupational Safety and Health Act of 1970. The recommended standard is being transmitted to the Department of Labor September 29, 1977, for review and consideration in the standard setting process. If research by NIOSH results in the development of improved methods for sampling and analysis of acrylonitrile in air from the occupational environment, information regarding the new methods will be forwarded to the Department of Labor.

## I. RECOMMENDATIONS FOR AN ACRYLONITRILE STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that employee exposure to acrylonitrile in the workplace be controlled by adherence to the following sections. The standard is designed to protect the health and provide for the safety of employees for up to a 10-hour work shift, 40-hour workweek, over a working lifetime. Compliance with all sections of the standard should, at the minimum, substantially reduce the risk of acrylonitrile-induced cancer and prevent other adverse effects of exposure to acrylonitrile in the workplace. The employer should regard the recommended workplace environmental limit as the upper boundary for exposure and make every effort to keep the exposure as low as possible. The criteria and standard will be subject to review and revision as necessary.

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Thus, NIOSH believes that acrylonitrile must be handled in the workplace as a suspect human carcinogen.

"Occupational exposure to acrylonitrile" refers to any workplace situation in which acrylonitrile is manufactured, polymerized, used, handled, or stored. All sections of the standard shall apply where there is occupational exposure to acrylonitrile.

### Section 1 - Environmental (Workplace Air)

#### (a) Concentration

Acrylonitrile shall be controlled in the workplace so that the concentration of airborne acrylonitrile, sampled and analyzed according to the procedures in Appendix I, is not greater than 4 ppm (approximately 8.7 mg/cu m) of breathing zone air.

#### (b) Sampling and Analytical Methods

The environmental limit represents the lowest reliably detectable concentration of acrylonitrile measurable by the recommended sampling and analytical methods. Procedures for the collection and analysis of acrylonitrile in air shall be as provided in Appendix I or by any methods shown to

be equivalent in accuracy, precision, and sensitivity to the methods specified.

## Section 2 - Medical

Medical surveillance shall be made available as specified below for all workers occupationally exposed to acrylonitrile.

(a) Preplacement initial, and annual medical examinations shall include:

(1) An initial or interim medical and work history with special attention to skin, respiratory and gastrointestinal systems, and those non-specific symptoms, such as headache, nausea, vomiting, dizziness, weakness, or other central nervous system dysfunctions that may be associated with chronic exposure.

(2) A physical examination giving particular attention to the skin, thyroid, respiratory system, and central nervous system.

(3) A 14" x 17" posteroanterior chest X-ray.

(4) Further tests of the intestinal tract, such as proctosigmoidoscopy, on all workers over the age of 40 and all other workers who, in the opinion of the responsible physician, show appropriate indications.

(5) A judgment of the worker's ability to use positive pressure respirators.

(b) Initial medical examinations shall be made available to presently employed workers as soon as possible after the promulgation of a standard based on these recommendations.

(c) The employer shall ensure that employees trained in first-aid measures are on duty whenever there is occupational exposure to acrylonitrile.

(d) Two physician's-treatment kits shall be immediately available to trained medical personnel at each plant where there is a potential for the release of, or for contact with, acrylonitrile. These kits should contain, as a minimum:

1. Two (2) boxes (2 dozen) ampules; each ampule containing 0.3 ml of amyl nitrite. Ampules shall be replaced biannually or sooner if needed to ensure their potency.

2. Two (2) ampules of sterile sodium nitrite solution (10 ml of a 3% solution in each).

3. Two (2) ampules of sterile sodium thiosulfate solution (50 ml of a 25% solution in each).

4. 2 sterile 10-ml syringes with intravenous needles.

5. 1 sterile 50-ml syringe with intravenous needle.

6. 1 tourniquet.

7. 1 gastric tube (rubber).

8. 1 non-sterile 100-ml syringe.

One kit should be portable in order that it may be carried by medical personnel while accompanying a patient to the hospital. The other kit should be kept under lock and key to assure that it is intact and available when and if needed. The key should be readily available at all times to the work supervisor on duty and the storage place should be of such construction as to allow access in the event of loss of the key.

(e) First-aid kits shall be immediately available at workplaces where there is a potential for the release, accidental or otherwise, of acrylonitrile. This kit shall contain as a minimum two (2) boxes of ampules (2 dozen), each containing 0.3 ml of amyl nitrite. Ampules shall be replaced biannually or sooner if needed to ensure their potency. The amyl nitrite ampules should be protected from high temperatures. In all cases, the contents of the physician's-treatment and first-aid kits shall be replaced before the manufacturer's assigned expiration dates.

(f) Appropriate medical services shall be made available to any employee with adverse health effects from acrylonitrile in the workplace.

(g) Medical records shall be maintained for all workers occupationally exposed to acrylonitrile. Pertinent medical records shall be maintained for 30 years following the last occupational exposure to acrylonitrile. These records shall be made available to the designated medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employer, and of the employee or former employee.

## Section 3 - Labeling and Posting

A label shall be placed on each shipping and storage container of acrylonitrile and all areas where there is occupational exposure to acrylonitrile shall be posted.

All warning signs shall be printed both in English and in the predominant language of non-English-reading workers. Illiterate workers and workers reading languages other than those used on labels and posted signs shall receive verbally disseminated information regarding hazardous areas and shall be informed of the instructions printed on labels and signs.

(a) Labeling

Each container of acrylonitrile shall carry in a readily visible location a label stating:

## ACRYLONITRILE

(Trademark, Common Name, or Chemical Name)

**DANGER!**  
**MAY CAUSE CANCER**  
**INHALATION IS HAZARDOUS AND MAY CAUSE UNCONSCIOUSNESS AND RESPIRATORY FAILURE**  
**SKIN CONTACT MAY CAUSE BLISTERS OR BURNS**

Store in a cool, well ventilated area.  
Keep container closed when not using.  
Avoid breathing vapor.  
Use only with adequate ventilation.  
Do not get in eyes, in open wounds, or on skin or clothing.  
In case of contact, immediately flush eyes with plenty of low-pressure flowing water. Call a physician. Flush skin with water.  
Wash clothing before reuse  
Use fresh clothing daily Take showers after work, using plenty of soap

**Special First Aid:** Remove contaminated clothing and wash the skin and eyes immediately Administer artificial respiration immediately if breathing has stopped. If the person is unconscious, amyl nitrite may be used as an antidote by a properly trained individual in accordance with established emergency procedure Obtain medical assistance immediately

### (b) Posting

Warning placards shall be affixed in readily visible locations in or near areas where there is occupational exposure to acrylonitrile. The information shall be arranged as in the following example

### WARNING

**CANCER-SUSPECT AGENT**  
**(ACRYLONITRILE)**  
**USED IN THIS AREA**  
**SKIN CONTACT MAY CAUSE BLISTERS OR BURNS**

### AUTHORIZED PERSONNEL ONLY

Do not get in eyes, in open wounds, or on skin or clothing.

If respiratory protection is required in accordance with Section 4, the following statement in large letters shall be added to the required sign:

## RESPIRATORY PROTECTION REQUIRED IN THIS AREA

### Section 4 - Personal Protective Clothing and Equipment

#### (a) Protective Clothing

(1) Employers shall provide and ensure that employees use gloves, face shields (eight-inch minimum) and other appropriate protective clothing or equipment necessary to prevent skin contact with liquid acrylonitrile. Face shields shall comply with 29 CFR 1910.133(a)(2), (a)(4), (a)(5), and (a)(6).

(2) Where exposure of an employee's body to liquid acrylonitrile may occur, employers shall provide facilities for quick drenching of the body within the immediate work area for emergency use.

(3) Employers shall ensure that any pervious clothing which becomes wet with, or impervious clothing which becomes grossly contaminated with, acrylonitrile is removed immediately and not reworn until the acrylonitrile has been removed from the clothing.

(4) Employers shall ensure that clothing wet with liquid acrylonitrile is placed in closed containers for storage until it can be discarded or until acrylonitrile is removed from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the acrylonitrile, the employer shall inform the person(s) performing the operation of the hazardous properties of acrylonitrile Work clothing shall not be taken home by employees.

(5) Eye protection shall be provided by the employer and used by the employees where eye contact with liquid acrylonitrile is likely. Selection, use, and maintenance of eye protective equipment shall be in accordance with the provisions of the American National Standard Practice for Occupational and Educational Eye and Face Protection, ANSI Z87 1-1968. Unless eye protection is afforded by a respirator hood or facepiece, protective goggles [splash-proof safety goggles (cup-cover type dust and splash safety goggles) which comply with 29 CFR 1910.133-(a)(2)-(a)(6)] or a face shield shall be worn at operations where there is danger of contact of the eyes with liquid acrylonitrile because of spills or splashes. If there is danger of liquid acrylonitrile striking the eyes from underneath, or around the sides of the face shield, safety goggles shall be worn as added protection.

(6) The employer shall ensure that all personal protective devices are inspected regularly and maintained in clean and satisfactory working condition

#### (b) Respiratory Protection

(1) Engineering controls shall be used when feasible to keep concentrations of airborne

acrylonitrile at or below the recommended environmental limit. Respiratory protective equipment may only be used in the following circumstances:

(A) During the time necessary to install or test the required engineering controls.

(B) For operations such as nonroutine maintenance and repair activities in which brief exposure at concentrations in excess of the recommended environmental limit may occur.

(C) During emergencies when concentrations of airborne acrylonitrile might exceed the recommended environmental limit.

(2) When a respirator is permitted by paragraph (b)(1) of this section, it shall be selected and used in accordance with the following requirements:

(A) The employer shall establish and enforce a respiratory protective program. The requirements for such a program are listed in 29 CFR 1910.134.

(B) The employer shall provide respirators in accordance with Table I-1 and shall ensure that employees use the respirators in a proper manner when the concentration of airborne acrylonitrile exceeds the recommended environmental limit. The respirators shall be those approved by NIOSH or the Mining Enforcement and Safety Administration. The standard for approval is specified in 30 CFR 11. The employer shall ensure that respirators are properly cleaned, maintained, and stored when not in use.

### Section 5 - Informing Employees of Hazards from Acrylonitrile

(a) The employer shall ensure that each employee assigned to work in an area where there is occupational exposure to acrylonitrile is informed of the hazards and relevant symptoms of exposure to acrylonitrile, and of proper condi-

tions and precautions for the handling and use of acrylonitrile. Workers shall be advised that skin exposure to liquid acrylonitrile may cause blister formation and burns and that exposure to airborne acrylonitrile may have an immediate effect of causing unconsciousness or respiratory failure and, on a long-term basis, may increase the risk of developing cancer, particularly of the lungs and large intestine. Information shall be given to employees at the beginning of employment and at least twice a year thereafter.

(b) The employer shall institute a continuing education program, conducted by instructors qualified by experience or training, to ensure that all employees have current knowledge of job hazards, proper maintenance and cleanup methods, and proper respirator use. The instructional program shall include a description of the environmental and medical surveillance procedures and of the advantages to the employee of participating in these procedures. Instruction shall include the information specified in the "Material Safety Data Sheet," which shall be kept on file and readily accessible to employees at all places of employment where there is occupational exposure to acrylonitrile. Workers engaged in maintenance and repair shall be included in these training programs.

(c) Required information shall be recorded on the "Material Safety Data Sheet" or on a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

### Section 6 - Work Practices

(a) Control of Airborne Acrylonitrile

Engineering controls, such as process enclosure or local exhaust ventilation, shall be used to keep concentrations of airborne acrylonitrile at or below the recommended environmental limit. If

**TABLE I-1  
RESPIRATOR SELECTION GUIDE**

Concentration of Acrylonitrile	Respirator Type Approved under Provisions of 30 CFR 11
Greater than 2 mg/cu m or Emergency (entry into area of unknown concentration for emergency purposes)	(1) Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive pressure mode  (2) Combination Type C supplied-air respirator with full facepiece operated in pressure-demand mode and auxiliary self-contained air supply

used, ventilation systems shall be so designed and operated as to prevent accumulation or recirculation of airborne acrylonitrile in the workplace environment and to effectively remove acrylonitrile from the breathing zone of employees. Exhaust ventilation systems discharging to outside air must conform to applicable local, state, and federal regulations and must not constitute hazards to employees or to the general population. Before maintenance work on control equipment begins, sources of airborne acrylonitrile shall be eliminated to the extent feasible.

Enclosures, exhaust hoods, and ductwork shall be kept in good repair so that design airflows are maintained. Airflow at each hood shall be measured at least semiannually and preferably monthly. Continuous airflow indicators are recommended, such as water or oil manometers properly mounted at the juncture of fume hood and duct throat (marked to indicate acceptable airflow). A log shall be kept showing design airflow and results of semiannual or monthly inspections.

Whenever feasible, operations involving acrylonitrile should be placed in an isolated area, in combination with other engineering controls, to reduce exposure of employees not directly concerned with the acrylonitrile operations.

**(b) Regulated Areas**

Regulated areas shall be established and maintained where there is occupational exposure to acrylonitrile, and access to these areas shall be limited to authorized persons who have been properly informed of the potential hazards of acrylonitrile and proper control measures. A daily roster shall be made of all persons who enter regulated areas.

**(c) Cleanup of Spills**

Solutions containing acrylonitrile shall be removed from work areas by vacuum cleaning, or another method, which does not increase the concentration of airborne acrylonitrile.

**(d) Emergency Procedures**

Procedures for emergencies, including fires, shall be established to meet foreseeable events. Necessary emergency equipment shall be kept in readily accessible locations.

**(e) Fire and Safety**

(1) Acrylonitrile shall be stored so it will not come in contact with strong oxidizers (especially bromine), strong bases, copper, copper alloys, ammonia, and amines. Acrylonitrile monomer shall be checked at least weekly to determine inhibitor content.

(2) For the purpose of compliance with 29 CFR 1910.309, locations classified as hazardous locations due to the presence of acrylonitrile shall be Class I, Group D.

(3) For the purpose of compliance with 29 CFR 1910.157, acrylonitrile is classified as a Class B fire hazard.

(4) For the purpose of compliance with 29 CFR 1910.106, liquid acrylonitrile is classified as a Class IB flammable liquid.

(5) Where a fan is located in ductwork and where acrylonitrile is present in the ductwork in concentrations greater than 7,500 ppm (approximately 25 percent of the lower flammable limit), the rotating element of the fan shall be of non-sparking material or the casing shall consist of, or be lined with, nonsparking material. There shall be sufficient clearance between the rotating element of the fan and the fan casing to prevent contact between the rotating element and the casing.

(6) Sources of ignition, such as smoking or open flames, are prohibited where acrylonitrile presents a fire or explosion hazard.

**(f) Disposal of Waste**

Waste material shall be disposed of in a manner that is not hazardous to employees or to the general population. Spills of acrylonitrile and flushing of such spills shall be channeled for appropriate treatment or collection for disposal. They shall not be channeled directly into the sanitary sewer system. Acrylonitrile wastes shall be appropriately marked and any operations generating airborne acrylonitrile shall be enclosed. In selecting the method of waste disposal, applicable local, state, and federal regulations should be consulted.

**(g) Storage**

Containers of acrylonitrile shall be kept tightly closed when not in use. Containers shall be stored in a safe manner to minimize the possibility of accidental breakage or spills.

**(h) General Work Practices**

(1) Good housekeeping practices shall be observed to prevent contamination of areas and equipment with liquid acrylonitrile and to prevent buildup of such contamination.

(2) Good personal hygiene practices should be encouraged. Employees shall be required to wash all exposed areas of the body upon exiting from regulated areas. Employees occupationally exposed to acrylonitrile shall be required to shower at the end of the workshift.

**(i) Work Clothing/Protective Clothing**

(1) Coveralls or similar full-body protective clothing and head, leg, and shoe coverings shall be worn by each employee entering a regulated area. Upon exiting from a regulated area, the protective clothing shall be left at the point of exit. With the last exit of the day, the protective clothing shall be placed in a suitably marked and closed container for disposal or laundering.

(2) Such clothing shall be changed as soon as possible if accidentally contaminated with liquid acrylonitrile

(3) The employer shall provide for the laundering of this clothing and shall ensure that soiled work clothing is not taken home by the employee. Precautions shall be taken to protect personnel who handle and launder soiled clothing. These workers shall be advised of the hazards of and means of preventing exposure to acrylonitrile

## Section 7 - Sanitation

(a) Emergency showers and eye-flushing fountains with adequate pressure of cool water shall be provided and be quickly accessible in areas where there is potential of skin or eye contact with acrylonitrile. This equipment shall be frequently inspected and maintained in good working condition.

(b) Locker-room facilities, including showers and washbasins, located in nonexposure areas, shall be provided for employees required to change clothes before and after each work shift. The facilities shall provide for storage of street clothing and clean work clothing separately from soiled work clothing. Covered containers shall be provided for work clothing removed at the end of the work shift or after a contamination incident. The clothing shall be held in these containers until it is removed for decontamination or disposal

(c) Food preparation, dispensing (including vending machines), and eating shall be prohibited in areas where there is occupational exposure to acrylonitrile. Eating facilities provided for employees shall be located in nonexposure areas. Washing facilities should be accessible nearby.

(d) Smoking and carrying smoking or chewing materials shall be prohibited in work areas where there is occupational exposure to acrylonitrile.

## Section 8 - Monitoring and Recordkeeping Requirements

### (a) Monitoring

(1) As soon as possible after promulgation of a standard based on these recommendations, each employer who has a place of employment in which acrylonitrile is manufactured, polymerized, handled, stored, or otherwise used shall determine by an industrial hygiene survey the extent of exposure to acrylonitrile. Surveys shall be repeated at least once every year and within 30 days of any process change likely to result in occupational exposure to acrylonitrile. Records of these surveys, including the basis for

any conclusion that there is no occupational exposure to acrylonitrile, shall be retained until the next survey has been completed.

(2) If there is occupational exposure to acrylonitrile a program of personal monitoring shall be instituted to measure or permit calculation of the exposure of all employees.

(A) In all personal monitoring, samples representative of the breathing zones of the employees shall be collected.

(B) For each environmental determination, a sufficient number of samples shall be taken to characterize the employees' exposures during each work shift. Variations in work and production schedules and in employees' locations and job functions shall be considered in choosing sampling times, locations, and frequencies.

(C) Each operation in each work area shall be sampled at least once every 3 months.

(3) If an employee is found to be exposed to acrylonitrile in excess of the recommended environmental limit, the exposure of that employee shall be measured at least once a week, control measures shall be initiated, and the employee shall be notified of the extent of the exposure and of the control measures being implemented. Such monitoring shall continue until two consecutive determinations, 1 week apart, indicate that the employee's exposure no longer exceeds the recommended environmental limit. Routine monitoring may then be resumed.

### (b) Recordkeeping

Environmental monitoring records shall be maintained for at least 30 years after the employee's last occupational exposure to acrylonitrile. These records shall include the dates and times of measurements, job function and location of employees within the worksite, methods of sampling and analysis used, types of respiratory protection in use at the time of sampling, environmental concentrations found, and identification of exposed employees. Each employee shall be able to obtain information on that employee's own environmental exposures. Daily rosters of authorized persons who enter regulated areas shall be retained for 30 years. Environmental monitoring records and entry rosters shall be made available to designated representatives of the Secretary of Labor and of the Secretary of Health, Education, and Welfare.

Pertinent medical records for each employee shall be retained for 30 years after the employee's last occupational exposure to acrylonitrile. Records of environmental exposures applicable to an employee should be included in that employee's medical records. These medical records shall be made available to the designated medical representatives of the Secretary of Labor,



of the Secretary of Health, Education, and Welfare, of the employer, and of the employee or former employee

(c) Employee Observation of Measurement

(1) The employer shall give affected employees or their representatives an opportunity to observe any measurement made pursuant to the standard of employee exposure to acrylonitrile.

(2) When observation of measurement of employee exposure to acrylonitrile requires entry into an area where the use of personal protective devices, including respirators, is required, the ob-

server shall be provided with and required to use such equipment and comply with all other applicable safety procedures.

(3) Without interfering with the measurement, observers shall be entitled to.

(i) Receive an explanation of the measurement procedure.

(ii) Observe all steps related to the measurement of the concentration of airborne acrylonitrile that are being performed at the place of exposure; and

(iii) Record the results obtained.

## APPENDIX I

### PREFACE TO NIOSH METHOD NO. S156 (ACRYLONITRILE)

NIOSH Method No S156 (copy attached), with slight modifications, is recommended for sampling and analysis of acrylonitrile in air. Method S156 utilizes a charcoal tube for collection of the sample and analysis by gas-chromatography.

Data from the Standards Completion Program (SCP) indicates that at lower loadings than about 400 micrograms on the charcoal tube, the desorption efficiency may not be adequate, thus, the analysis would be questionable.

In addition, since the breakthrough studies of the SCP were not carried out beyond 48 liters [0.2 liter/minute for 4 hours at 92.0 mg

acrylonitrile/cu m (42.4 ppm)] and since the effects of humidity on breakthrough are unknown, it cannot be presently assumed that sampling for 8 hours can be accomplished without breakthrough.

Therefore, based upon the best available data, the Institute has determined that 4 ppm of acrylonitrile is the lowest concentration measurable at the present time by a reliable sampling/analytical method.

To determine the workplace air concentration of acrylonitrile, collect a 4-hour sample at a flow rate of 0.2 liter/minute.

9/22/77

#### Acrylonitrile

Analyte:	Acrylonitrile	Method No. S156
Matrix:	Air	Range. 17.5-70.0 mg/cu m
OSHA Standard:	20 ppm (45 mg/cu m)-skin	Precision ( $\overline{CV}_T$ ) 0.073
Procedure:	Adsorption on charcoal, desorption with methanol, GC	Validation Date. 7/4/75

#### 1. Principle of the Method (Reference 11.1)

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with methanole.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained for standards.

#### 2. Range and Sensitivity

2.1 This method was validated over the range of 17.5-70.0 mg/cu m at an atmospheric

temperature and pressure of 22°C and 760 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 4.5-135 mg/cu m. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of acrylonitrile and other substances in the air. The first section of the charcoal tube was found to hold at least 3.97 mg of acrylonitrile when a test atmosphere containing 92.0 mg/cu m of acrylonitrile in air was sampled at 0.18 liter per minute for 240 minutes, at that time the concentration of acrylonitrile in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of ac-

tivated charcoal separated by a section of urethane foam. See Section 6.2) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

### 3. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

### 4. Precision and Accuracy

4.1 The Coefficient of Variation ( $\overline{CV}_T$ ) for the total analytical and sampling method in the range of 17.5-70.0 mg/cu m was 0.073. This value corresponds to a 3.3 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.0% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in Section 10.5.

### 5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

### 6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within  $\pm 5\%$  at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft x 1/4-in stainless steel) packed with 50/80 mesh Porapak, Type Q.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with

glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes 10-microliter, and other convenient sizes for making standards

6.8 Pipets 1.0-ml delivery pipets.

6.9 Volumetric flasks 10-ml or convenient sizes for making standard solutions

## 7 Reagents

7.1 Chromatographic quality methanol.

7.2 Acrylonitrile, reagent grade.

7.3 Hexane, reagent grade

7.4 Purified nitrogen

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

## 8 Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water

8.2 Calibration of Personal Pumps Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected

### 8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm)

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 20 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least  $\pm 5\%$ .

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 With each batch of ten samples submit one tube from the same lot of tubes which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

## 8.4 Analysis of Samples

8.4.1 Preparation of Samples In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately

8.4.2 Desorption of Samples Prior to analysis, 1.0 ml of methanol is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow

2. 65 ml/min (24 psig) hydrogen gas flow to detector

3. 500 ml/min (50 psig) air flow to detector

4. 235°C injector temperature

5. 255°C manifold temperature (detector)

6. 155°C column temperature

**8.4.4 Injection.** The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

**8.4.5 Measurement of area.** The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

## 8.5 Determination of Desorption Efficiency

**8.5.1 Importance of determination.** The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is

necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

**8.5.2 Procedure for determining desorption efficiency.** Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution of acrylonitrile containing 0.239 g/ml is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

The amount injected is equivalent to that present in a 20-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of methanol with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

## 9 Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml methanol. The

density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

## 10 Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml methanol and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections

10.3 Add the weights found in the front and backup sections to get the total weight in the sample

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount

found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{D \cdot E}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{M.W} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where

- P = pressure (mm Hg) of air sampled
- T = temperature (°C) of air sampled
- 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
- M.W = molecular weight (g/mole) of analyte
- 760 = standard pressure (mm Hg)
- 298 = standard temperature (°K)

## 11 References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind Hyg Assoc J, 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

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CENTER FOR DISEASE CONTROL  
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