OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR ACRYLONITRILE

POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about acrylonitrile for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

- **Formula:** C_3H_3N
- **Structure:** $CH_2=CH-C\equiv N$
- **Synonyms:** Acrylon, AN, carbacryl, cyanoethylene, fumigrain, propenenitrile, VCN, ventox, vinyl cyanide
- **Identifiers:** CAS 107-31-1; RTECS AT5250000; DOT 1093, label required: "Flammable Liquid, Poison"
- **Appearance and odor:** Pale yellow liquid with an unpleasant odor similar to pyridine

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 53.07
2. Boiling point (at 760 mmHg): 77.3°C (171°F)
3. Specific gravity at 20°C (68°C) (water = 1): 0.81
4. Vapor density (air = 1 at boiling point of acrylonitrile): 1.83
5. Melting point: -83°C (-117°F)
6. Vapor pressure at 20°C (68°F): 83 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 7.35
8. Evaporation rate (butyl acetate = 1): 4.54
9. Saturation concentration in air (approximate) at 20°C (68°F): 10.9% (109,000 ppm)
10. Ionization potential: 10.91 eV

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers, especially bromine, and strong bases may cause fires and explosions. Contact with copper, copper alloys, ammonia, or amines may cause decomposition. Acrylonitrile will polymerize when hot, and the additional heat liberated by the polymerization may generate high internal pressure and cause containers to explode. Inhibitors are added to the commercial product to prevent self-polymerization.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen cyanide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving acrylonitrile.
3. Caution: Acrylonitrile will attack some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: -1°C (30°F) (closed cup)
2. Autoignition temperature: 481°C (898°F)
3. Flammable limits in air, % by volume: Lower, 3; Upper, 17
4. Extinguishant: Alcohol foam, carbon dioxide, and dry chemical
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)

- **Warning properties**

1. Odor threshold: Approximately 20 ppm
2. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrylonitrile is 2 parts of acrylonitrile per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the OSHA ceiling concentration which shall at no time be exceeded is 10 ppm as determined in any 15-minute sampling period (Skin). The notation for "Skin" refers to the potential contribution to overall exposure by the cutaneous route including the mucous membranes and eyes. The National Institute for Occupational Safety and Health (NIOSH) recommends that acrylonitrile be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 1 ppm as a TWA for up to an 8-hour workshift, 40-hour workweek; the NIOSH ceiling concentration is 10 ppm as determined in any 15-minute sampling period (Skin). The American Conference of Governmental In-

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
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dustrial Hygienists (ACGIH) has designated acrylonitrile as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 2 ppm [4.5 milligrams of acrylonitrile per cubic meter of air (4.5 mg/m³)] as a TWA for a normal 8-hour workday and a 40-hour workweek (Skin) (Table 1).

Table 1.—Occupational Exposure Limits for acrylonitrile

	Exposure limits ppm	mg/m³
OSHA PEL TWA (Skin)*	2	—
Ceiling (15 min) (Skin)	10	—
NIOSH REL TWA (Skin) (Ca)†	1	—
Ceiling (15 min) (Skin)	10	—
ACGIH TLV® TWA (Skin) (A2)§	2	4.5

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.
† (Ca): NIOSH recommends treating as a potential human carcinogen.
§ (A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure
Acrylonitrile may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology
1. *Effects on animals:* In rats, guinea pigs, or dogs, acute inhalation or oral administration of acrylonitrile caused signs of toxicity including decreased water and food consumption, decreased weight gain, histologic changes in the brain resembling anoxia, or damage to the lungs, liver, or kidneys. In rats, chronic inhalation or oral administration of acrylonitrile produced tumors of the brain, stomach, ear canal, and mammary glands, and cancer of the Zymbal gland. Oral administration of acrylonitrile to pregnant rats caused embryotoxic and teratogenic effects.
2. *Effects on humans:* Two separate studies of workers who were potentially exposed to acrylonitrile and who were observed over an 18- or 20-year period showed increased incidences of lung and colon cancers. In addition, at least two deaths from accidental inhalation or skin absorption of acrylonitrile have occurred.

• Signs and symptoms of exposure
1. *Short-term (acute):* Exposure to acrylonitrile can cause eye irritation, headache, sneezing, nausea, vomiting, weakness, light-headedness, and asphyxia.
2. *Long-term (chronic):* Skin contact with acrylonitrile can cause burns, blisters, and dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program
Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation
Prior to placing a worker in a job with a potential for exposure to acrylonitrile, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, gastrointestinal tract, and respiratory, reproductive, and central nervous systems. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to acrylonitrile at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of chronic skin disease or concurrent dermatitis, and a history of reproductive dysfunction. In addition to the medical interview and physical examination, the means to identify these conditions may include an evaluation of fertility.

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker develop symptoms that may be attributed to exposure to acrylonitrile. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the skin, gastrointestinal tract, and respiratory, reproductive, and central nervous systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination.**
The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to acrylonitrile may cause adverse reproductive effects and diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**
Acute SHE's include: Contact and/or allergic dermatitis.

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**
Measurements to determine worker exposure to acrylonitrile should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Ceiling concentration evaluation**
Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of acrylonitrile. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone should consist of a 15-minute sample or a series of consecutive samples that total 15 minutes. A minimum of three measurements should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**
Sampling and analysis may be performed by collecting acrylonitrile vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure acrylonitrile may also be used if available. A detailed sampling and analytical method for acrylonitrile may be found in the *NIOSH Manual of Analytical Methods* (method number 1604).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with acrylonitrile.

SANITATION

Clothing which is contaminated with acrylonitrile should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of acrylonitrile from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of acrylonitrile's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with acrylonitrile should be promptly washed with soap and water.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or smoking of tobacco or other materials, or the storage or use of products for chewing should be prohibited in work areas.

Workers who handle acrylonitrile should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to acrylonitrile may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for acrylonitrile

Operations	Controls
During use in the manufacture of ABS resin, SAN resin, plastic, or surface coating materials	Total enclosure
During the manufacture and transfer of monomer to other reaction vessels or to tank cars.	Total enclosure, local exhaust ventilation, personal protective equipment
During use as a chemical intermediate; during use in the cyanoethylation of cotton	Local exhaust ventilation, personal protective equipment
During use in surface coating applications	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• **Eye exposure**

Where there is any possibility of a worker's eyes being exposed to acrylonitrile, an eye-wash fountain should be provided within the immediate work area for emergency use.

If acrylonitrile gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin exposure**

Where there is any possibility of a worker's body being exposed to acrylonitrile, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If acrylonitrile gets on the skin, wash it immediately with soap and water. If acrylonitrile penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• **Rescue**

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If acrylonitrile is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing acrylonitrile, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing acrylonitrile may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing acrylonitrile may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

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Table 3.—Respiratory protection for acrylonitrile

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.