



DEPARTMENT OF LICENSING AND REGULATORY AFFAIRS

DIRECTOR'S OFFICE

OCCUPATIONAL HEALTH STANDARDS

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(By authority conferred on the director of the department of licensing and regulatory affairs
by sections 14 and 24 of 1974 PA 154, MCL 408.1014 and 408.1024
and Executive Reorganization Order Nos. 1996-2, 2003-1, 2008-4,
and 2011-4, MCL 445.2001, 445.2011, 445.2025, and 445.2030)

R 325.51501, R 325.51502, R 325.51505, R 325.51507, R 325.51508, R 325.51509, R 325.51510, R 325.51511,
R 325.51513, R 325.51516, R 325.51517, R 325.51519, R 325.51520, R 325.51521, R 325.51522, R 325.51523,
R 325.51524, R 325.51525, and R 325.51526 of the Michigan Administrative Code are amended,
R 325.51501a and R 325.51519a are added,
R 325.51504 and R 325.51527 are rescinded, as follows:

PART 307. ACRYLONITRILE

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R 325.51501. Scope and application.

Rule 501. (1) The rules in this part apply to all occupational exposures to acrylonitrile (AN), chemical abstracts service registry no. 000107131, except as provided in subrules (2) and (3) of this rule.

(2) The rules in this part do not apply to exposures that result solely from the processing, use, and handling of the following materials:

(a) Acrylonitrile-butadiene-styrene (ABS) resins, Styreneacrylonitrile (SAN) resins, nitrile barrier resins, solid nitrile elastomers, and acrylic and modacrylic fibers in the form of finished polymers, including products fabricated from such finished polymers.

(b) Materials made from or containing AN, or both, for which objective data is reasonably relied upon to demonstrate that the material is not capable of releasing AN in airborne concentrations of more than 1 part per million (ppm) as an 8-hour, time-weighted average under the expected conditions of processing, use, and handling which cause the greatest possible release.

(c) Solid materials made from or containing AN, or both, which will not be heated above 170 degrees Fahrenheit during handling, use, or processing.

(3) An employer who relies on the exemption in subrule (2)(b) of this rule shall maintain records of the objective data supporting that exemption and of the basis of the employer's reliance on the data, as provided in R 325.51521.

R 325.51501a. Referenced standards.

Rule 1a. (1) The following Michigan occupational safety and health standards are referenced in these rules. Up to 5 copies of these standards may be obtained at no charge from the Michigan Department of Licensing and Regulatory Affairs, MIOSHA Regulatory Services Section, 7150 Harris Drive, P.O. Box 30643, Lansing, Michigan 48909-8143, or via the internet at website:

www.michigan.gov/mioshastandards. For quantities greater than 5, the cost, at the time of adoption of these rules, is 4 cents per page.

(a) General Industry Safety Standard Part 33 "Personal Protective Equipment," R 408.13301 to R 408.13398.

(b) Occupational Health Standard Part 430 "Hazard Communication," R 325.77001 to R 325.77003.

(c) Occupational Health Standard Part 433 "Personal Protective Equipment," R 325.60001 to R 325.60013.

(d) Occupational Health Standard Part 451 "Respiratory Protection," R 325.60051 to R 325.60052.

(e) Occupational Health Standard Part 470 "Employee Medical Records and Trade Secrets," R 325.3451 to R 325.3476.

(f) Occupational Health Standard Part 474 "Sanitation," R 325.47401 to R 325.47427.

(2) Appendices A, B, C, and D to these rules are informational only and are not intended to create any additional obligations or requirements not otherwise imposed by these rules or to detract from any established obligations or requirements.

R 325.51502 Definitions.

Rule 502. As used in these rules:

(1) "Acrylonitrile" or "AN" means acrylonitrile monomer, chemical formula CH₂=CHCN.

(2) "Act" means 1974 PA 154, MCL 408.1001 to MCL 408.1094.

(3) "Action level" means a concentration of AN of 1 ppm as an 8-hour, time-weighted average.

(4) "Authorized person" means any person specifically authorized by the employer whose duties require the person to enter a regulated area, or any person entering such an area as a designated representative of employees for the purpose of exercising the opportunity to observe monitoring procedures under R 325.51526.

(5) "Decontamination" means the treating of materials and surfaces by water washdown, ventilation, or other means to assure that the materials will not expose an employee to airborne concentrations of AN of more than 1 ppm.

(6) "Director" means the director of the Michigan department of licensing and regulatory affairs or his or her designee.

(7) "Emergency" means any occurrence, such as, equipment failure, rupture of containers, or failure of control equipment, which results in an unexpected massive release of AN.

(8) "Liquid AN" means AN monomer in liquid form and liquid or semiliquid polymer intermediates, including slurries, suspensions, emulsions, and solutions which are produced during the polymerization of AN.

R 325.51503 Airborne concentrations; permissible employee exposure limits.

Rule 503. (1) With respect to airborne concentrations, the following limits apply:

(a) An employer shall assure that an employee is not exposed to an airborne concentration of acrylonitrile of more than 2 ppm as an 8-hour, time-weighted average.

(b) An employer shall assure that any employee is not exposed to an airborne concentration of acrylonitrile of more than 10 ppm as averaged over any 15-minute period during the working day.

(2) An employer shall assure that an employee is not exposed to skin contact or eye contact with liquid AN.

R 325.51504. Rescinded.

R 325.51505. Employee exposure; determination of airborne exposure levels; employer monitoring of airborne concentrations; monitoring exposure below action level; monitoring exposure at or above action level; monitoring exposure of more than permissible limits; additional monitoring; written notice to employee of exposure level; measurement accuracy.

Rule 505. (1) For the purposes of these rules, employee exposure is that exposure which would occur if the employee were not using a respirator.

(2) Determinations of airborne exposure levels shall be made from air samples that are representative of each employee's exposure to AN over an 8-hour period.

(3) An employer who has a place of employment in which AN is present shall monitor each such workplace and work operation to accurately determine the airborne concentrations of AN to which an employee may be exposed.

(4) If the monitoring required by these rules reveals that employee exposure is below the action level, an employer may discontinue monitoring for that employee.

(5) If the monitoring required by these rules reveals that employee exposure is at or above the action level but below the permissible exposure limits, an employer shall repeat such monitoring for each affected employee at least once every 6 months. An employer shall continue these measurements every 6 months until not less than 2 consecutive measurements, taken not less than 7 days apart, are below the action level, and thereafter the employer may discontinue monitoring for that employee.

(6) If the monitoring required by these rules reveals that employee exposure is in excess of the permissible exposure limits, an employer shall repeat these determinations for each such employee at least quarterly. An employer shall continue these quarterly measurements until not less than 2 consecutive measurements, taken not less than 7 days apart, are below the permissible exposure limits, and thereafter an employer shall monitor at least once every 6 months.

(7) If there is a production, process, control, or personnel change which may result in new or additional exposures to AN, additional monitoring that complies with these rules shall be conducted.

(8) Within 15 working days after the receipt of the results of monitoring required by these rules, an employer shall notify each employee in writing of the results of these rules which represent that employee's exposure.

(9) If the results indicate that the representative employee exposure exceeds the permissible exposure limits, an employer shall include in the written notice a statement that the permissible exposure limits were exceeded and a description of the corrective action being taken to reduce exposure to or below the permissible exposure limits.

(10) The method of measurement of employee exposure shall be accurate to a confidence level of 95% to within plus or minus 35% for concentrations of AN at or above the permissible exposure limits, and plus or minus 50% for concentrations of AN below the permissible exposure limits.

R 325.51506 Regulated areas; establishment, demarcation and segregation; access; prohibited activities.

Rule 506. (1) An employer shall establish a regulated area where AN concentrations are in excess of the permissible exposure limits.

(2) A regulated area shall be demarcated and segregated from the rest of the workplace in a manner that minimizes the number of persons who will be exposed to AN.

(3) Access to a regulated area shall be limited to authorized persons or to persons who are otherwise authorized by the act or rules promulgated pursuant thereto.

(4) An employer shall assure that neither food nor beverages are present or consumed, that tobacco products are not present or used, and that cosmetics are not applied, in the regulated area.

R 325.51507 Engineering and work practice controls to control employee exposure.

Rule 507. (1) An employer shall institute engineering and work practice controls to reduce and maintain employee exposures to AN at or below the permissible exposure limits, except to the extent that an employer establishes that such controls are not feasible.

(2) If the engineering and work practice controls that can be instituted are not sufficient to reduce employee exposures to or below the permissible exposure limits, an employer shall nonetheless use them to reduce exposures to the lowest levels achievable by these controls and shall supplement the controls by the use of respiratory protection that complies with the requirements of R 325.51509.

R 325.51508. Employee exposure; written program to reduce exposure by means of engineering and work practice controls required; content; completion of program; availability; revision and update.

Rule 508. (1) An employer shall establish and implement a written program to reduce employee exposures to or below the permissible exposure limits solely by means of engineering and work practice controls, as required by R 325.51507.

(2) A written program shall include, at a minimum, all of the following:

(a) A description of each operation or process resulting in employee exposure to AN above the permissible exposure limits.

(b) An outline of the nature of the engineering controls and work practices to be applied to the operation or process in question.

(c) A report of the technology considered for meeting the permissible exposure limit.

(d) Other relevant information.

(3) An employer shall complete the steps set forth in the written program by the dates in the schedule.

(4) A written program shall be submitted to the director upon request and shall be available at the worksite for examination and copying by the director or any affected employee or representative.

(5) The written program required by this rule shall be revised and updated at least annually to reflect the current status of the program.

R 325.51509 Respiratory protection.

Rule 509. (1) For employees who use respirators required by these rules, the employer shall select and provide each employee an appropriate respirator that complies with the requirements of these rules. An employer shall ensure that employees use respirators during all of the following:

(a) Periods necessary to install or implement feasible engineering and work practice controls.

(b) Work operations, such as maintenance and repair activities or reactor cleaning, for which the employer establishes that engineering and work practice controls are not feasible.

(c) Work situations for which feasible engineering and work practice controls are not yet sufficient to reduce an employee's exposure to or below the permissible exposure limits.

(d) Emergencies.

(2) For escape, the employer shall provide employees with any organic vapor respirator or any self-contained breathing apparatus permitted for use by these rules.

(3) The employer shall implement a respiratory protection program in accordance with Occupational Health Standard Part 451 "Respiratory Protection," as referenced in R 325.51501a, which covers each employee required by these rules to use a respirator.

(4) If air-purifying respirators (chemical-cartridge or chemical canister types) are used, then both of the following apply:

(a) The air-purifying canister or cartridge must be replaced prior to the expiration of its service life or at the completion of each shift, whichever occurs first.

(b) A label must be attached to the cartridge or canister to indicate the date and time at which it is first installed on the respirator.

R 325.51510 Emergency situations; written plans; alarms.

Rule 510. (1) An employer shall develop written plan for emergency situations for each workplace where liquid AN is present. Appropriate portions of the plan shall be implemented in the event of an emergency.

(2) The plan shall specifically provide that an employee who is engaged in correcting an emergency condition shall be equipped as required in R 325.51509 until the emergency has abated.

(3) An employee who is not engaged in correcting the emergency shall be evacuated from the area and shall not be permitted to return until the emergency has abated.

(4) If the possibility of employee exposure to AN in excess of the ceiling limit exists, the employer shall install a general alarm and use it to promptly alert employees of such occurrences.

R 325.51511 Protective clothing and equipment; provision and use.

Rule 511. Where eye or skin contact with liquid AN might occur, an employer shall provide, at no cost to the employee, and shall assure that employees wear, impermeable protective clothing or other equipment to protect any area of the body that may come in contact with liquid AN. The employer shall comply with General Industry Safety Standard Part 33 "Personal Protective Equipment," as referenced in R 325.51501a.

R 325.51512 Protective clothing and equipment; cleaning and replacement; decontamination; notice to laundering or cleaning persons of potentially harmful effects of exposure to AN.

Rule 512. (1) An employer shall clean, launder, maintain, or replace protective clothing and equipment required by these rules as needed to maintain their effectiveness.

(2) An employer shall assure that impermeable protective clothing that contacts or is likely to have contacted liquid AN is decontaminated before being removed by the employee.

(3) An employer shall assure that an employee whose permeable clothing becomes wetted with liquid AN immediately removes the contaminated clothing and showers. The clothing shall be decontaminated before it is removed from the regulated area.

(4) An employer shall assure that protective clothing or equipment is not removed from the change room, except for the purposes of laundering, maintenance, or disposal.

(5) An employer shall inform any person in writing who launders or cleans protective clothing or equipment of the potentially harmful effects of exposure to AN.

R 325.51513 Hygiene facilities and practices; change rooms; showers.

Rule 513. (1) All surfaces shall be maintained of visible accumulations of liquid AN.

(2) An employer shall institute a program for detecting leaks and spills of liquid AN, including regular visual inspections, for operations involving liquid AN.

(3) If a spill of liquid AN is detected, an employer shall assure that surfaces contacted by the liquid AN are decontaminated. An employee who is not engaged in decontamination activities shall leave the area of the spill and shall not be permitted in the area until decontamination is completed.

(4) AN waste, scrap, debris, bags, containers, or equipment shall be decontaminated before being incorporated in the general waste disposal system.

(5) If an employee is exposed to an airborne concentration of AN above the permissible exposure limit, or if an employee is required to wear protective clothing or equipment pursuant to R 325.51511, the facilities required by Occupational Health Standard Part 474 "Sanitation," as referenced in R 325.51501a, including clean change rooms and shower facilities, shall be provided by an employer for use by such employees, and the employer shall assure that the employees use the facilities provided.

(6) An employer shall assure that an employee who wears protective clothing or equipment for protection from skin contact with liquid AN showers at the end of the work shift.

(7) An employer shall assure that, in the event of skin or eye exposure to liquid AN, an affected employee showers immediately to minimize the danger of skin absorption.

(8) An employer shall assure that an employee working in the regulated area washes his or her hands and face before eating.

R 325.51514 Medical surveillance program generally.

Rule 514. (1) An employer shall institute a program of medical surveillance for each employee who is or will be exposed to AN at or above the action level, without regard to the use of respirators, and shall provide each such employee with an opportunity for medical examinations and tests pursuant to these rules at the employer's cost.

(2) An employer shall assure that all medical examinations and procedures are performed by or under the supervision of a licensed physician.

R 325.51515 Medical surveillance program; initial examinations.

Rule 515. At the time of initial assignment, or upon institution of the medical surveillance program, an employer shall provide each affected employee with an opportunity for a medical examination, including, at a minimum, all of the following elements:

(a) A work history and medical history with special attention to skin, respiratory, and gastrointestinal systems, and those nonspecific symptoms, such as headache, nausea, vomiting, dizziness, weakness, or other central nervous system dysfunctions, which may be associated with acute or chronic exposure to AN.

(b) A complete physical examination with special attention to the peripheral and central nervous system, gastrointestinal system, respiratory system, skin, and thyroid.

(c) A 14-inch by 17-inch posterior-anterior chest x ray.

(d) Further tests of the intestinal tract, including fecal occult blood screening, for all workers 40 years of age or older and other affected employees for whom, in the opinion of the physician, such testing is appropriate.

R 325.51516 Medical surveillance program; periodic and additional examinations.

Rule 516. (1) An employer shall provide the examinations specified in R 325.51515 at least annually for all employees specified in R 325.51514.

(2) If an employee has not had the examination specified in R 325.51515 within 6 months preceding termination of employment, an employer shall make such examination available to the employee before termination.

(3) If for any reason an employee develops signs or symptoms which may be associated with exposure to AN, an employer shall provide an appropriate examination and emergency medical treatment.

R 325.51517 Medical surveillance program; information provided to physician by employer.

Rule 517. An employer shall provide all of the following information to the examining physician:

(a) A copy of these rules and related appendices which may be obtained from the department of licensing and regulatory affairs.

(b) A description of an affected employee's duties as they relate to the employee's exposure.

(c) The employee's representative exposure level.

(d) The employee's anticipated or estimated exposure level for preplacement examinations or for cases of exposure due to an emergency.

(e) A description of any personal protective equipment used or to be used.

(f) Information from previous medical examinations of the affected employee which is not otherwise available to the examining physician.

R 325.51518 Medical surveillance program; physician's written opinion.

Rule 518. (1) An employer shall obtain a written opinion from the examining physician which shall include all of the following:

(a) The results of the medical examination and tests performed.

(b) The physician's opinion as to whether an employee has any detected medical condition or conditions which would subject the employee to an increased risk of material health impairment from exposure to AN.

(c) Any recommended limitations upon the employee's exposure to AN or upon the use of protective clothing and equipment such as a respirator.

(d) A statement that the employee has been informed by the physician of the results of the medical examination and any medical conditions which require further examination or treatment.

(2) An employer shall instruct the physician not to reveal specific findings or diagnoses unrelated to occupational exposure to AN in the written opinion.

(3) An employer shall provide a copy of the written opinion to the affected employee.

R 325.51519 Employee information and training program; applicability; provision of information to employees; availability of rules and other materials to employees and director.

Rule 519. (1) An employer shall institute a training and information program and ensure the participation of all employees in the program, as follows:

(a) Each employee exposed to AN above the action level.

(b) Each employee whose exposures are maintained below the action level by engineering and work practice controls.

(c) Each employee subject to potential skin or eye contact with liquid AN. All training shall be in accordance with the requirements of these rules.

(2) Training shall be provided at the time of initial assignment or upon institution of the training program and at least once annually thereafter.

(3) The employer shall assure that each employee is informed of all of the following:

(a) The information contained in appendices A and B of these rules. Appendices A and B are available from the department of licensing and regulatory affairs.

(b) The quantity, location, manner of use, release, or storage of AN, and the specific nature of operations which could result in exposure to AN, as well as any necessary protective steps.

(c) The purpose, proper use, and limitations of respirators and protective clothing.

(d) The purpose and a description of the medical surveillance program required by these rules.

(e) The emergency procedures developed, as required by R 325.51510.

(f) Engineering and work practice controls, their function, and an employee's relationship to these controls.

(g) A review of these rules.

(4) An employer shall make a copy of these rules and appendices readily available to all affected employees.

(5) Upon request, an employer shall provide all materials relating to the employee information and training program to the director.

R 325.51519a Hazard communication--general.

Rule 519a. (1) Chemical manufacturers, importers, distributors and employers shall comply with all requirements of the Occupational Health Standard Part 430 "Hazard Communication," as referenced in R 325.51501a, for AN and AN-based materials not exempted under R 325.51501(1).

(2) In classifying the hazards of AN and AN-based materials at least all of the following hazards must be addressed:

(a) Cancer.

(b) Central nervous system effects.

(c) Liver effects.

(d) Skin sensitization.

(e) Skin, respiratory, and eye irritation.

(f) Acute toxicity effects.

(g) Flammability.

(3) An employer shall include AN and AN-based materials in the hazard communication program established to comply with the Occupational Health Standard Part 430 "Hazard Communication." An employer shall ensure that each employee has access to labels on containers of AN and AN-based materials and to safety data sheets. An employer shall ensure that each employee is trained in accordance with the requirements of R 325.51519 and Occupational Health Standard Part 430 "Hazard Communication," as referenced in R 325.51501a.

(4) The employer shall ensure that no statement appears on or near any sign or label required by these rules that contradicts or detracts from the required sign or label.

R 325.51520. Signs and labels.

Rule 520. (1) An employer shall post signs to clearly indicate all workplaces where AN concentrations exceed the permissible exposure limits. The signs shall bear the following legend:

DANGER
ACRYLONITRILE (AN)
MAY CAUSE CANCER
RESPIRATORY PROTECTION MAY BE REQUIRED
IN THIS AREA
AUTHORIZED PERSONNEL ONLY

(2) Prior to June 1, 2016, an employer may use the following legend in lieu of that specified in subrule (1) of this rule.

DANGER
ACRYLONITRILE (AN)
CANCER HAZARD
AUTHORIZED PERSONNEL ONLY
RESPIRATORS MAY BE REQUIRED

(3) An employer shall ensure that signs required by this rule are illuminated and cleaned as necessary so that the legend is readily visible.

(4) An employer shall ensure that precautionary labels are in compliance with R 325.51519a(1) and are affixed to all containers of liquid AN and AN-based materials which are not exempted under R 325.51501. The employer shall ensure that the labels remain affixed when the materials are sold, distributed, or otherwise leave the employer's workplace.

(5) Prior to June 1, 2015, an employer may include the following information on precautionary labels required by subrule (4) of this rule in lieu of the labeling requirements in R 325.51519a:

DANGER
CONTAINS ACRYLONITRILE (AN)
CANCER HAZARD

(6) An employer shall ensure that the precautionary labels required by these rules are readily visible and legible.

(7) An employer shall ensure that statements do not appear on or near any sign or label required by this rule which contradict or detract from the required sign or label.

(8) An employer may use labels or signs required by other statutes, rules, or ordinances in addition to, or in combination with, signs and labels required by this rule.

R 325.51521 Operations exempted under R 325.51501; records of objective data required; maintenance.

Rule 521. (1) If the processing, use, and handling of materials made from or containing AN are exempted pursuant to R 325.51501, an employer shall establish and maintain an accurate record of the objective data reasonably relied upon in support of the exemption which shall include, at a minimum, all of the following information:

- (a) The material qualifying for exemption.
- (b) The source of the objective data.
- (c) The testing protocol and the results of the testing or an analysis of the material, or both, for the release of AN.
- (d) A description of the operation exempted and how the data supports the exemption.

(e) Other data relevant to the operations, materials, and processing covered by the exemption.

(2) An employer shall maintain the record for the duration of the employer's reliance upon such objective data.

R 325.51522 Monitoring of exposure; records; maintenance.

Rule 522. (1) An employer shall establish and maintain an accurate record of all monitoring required by R 325.51505. The exposure monitoring record shall include all of the following:

(a) The dates, number, duration, and results of each of the samples taken, including a description of the sampling procedure used to determine representative employee exposure.

(b) A description of the sampling and analytical methods used and the data relied upon to establish that the methods used meet the accuracy and precision requirements of R 325.51505(10).

(c) Type of respiratory protective devices worn, if any.

(d) Name, social security number, and job classification of the employee monitored and of all other employees whose exposure the measurement is intended to represent.

(2) An employer shall maintain the record for not less than 40 years or for the duration of employment plus 20 years, whichever is longer.

R 325.51523 Medical surveillance records; maintenance.

Rule 523. (1) An employer shall establish and maintain an accurate record for each employee subject to medical surveillance as required by R 325.51514 to R 325.51516. The medical surveillance record shall include all of the following:

(a) A copy of the physician's written opinion.

(b) Any employee medical complaints related to exposure to AN.

(c) A copy of the information provided to the physician as required by R 325.51517.

(d) A copy of the employee's medical and work history.

(2) An employer shall assure that the record is maintained for not less than 40 years or the duration of employment plus 20 years, whichever is longer.

R 325.51524 Availability of records.

Rule 524. (1) Upon request, an employer shall make all records that are required to be maintained by these rules available to the director for examination and copying.

(2) Upon request, an employer shall make records that are required to be maintained by R 325.51521 to R 325.51523 available to affected employees, former employees, or their designated representatives for examination and copying in accordance with the provisions of Occupational Health Standard Part 470 "Employee Medical Records and Trade Secrets," as referenced in R 325.51501a.

(3) Records that are required pursuant to the provisions of R 325.51521 shall be provided in the same manner as exposure monitoring records.

R 325.51525 Retention and disposal of records; successor employer; transmittal and notice to director.

Rule 525. (1) If an employer ceases to do business, then the successor employer shall receive and retain all records that are required to be maintained by these rules for the prescribed period.

(2) The transfer of records and notification to employees shall be accomplished in accordance with the provisions of Occupational Health Standard Part 470 "Employee Medical Records and Trade Secrets," as referenced in R 325.51501a.

R 325.51526 Exposure monitoring; employee observation.

Rule 526. (1) An employer shall provide affected employees or their designated representatives with an opportunity to observe any monitoring of employee exposure to AN which is conducted pursuant to R 325.51505.

(2) If the observation of the monitoring of employee exposure to AN requires entry into an area where the use of protective clothing or personal protective clothing and equipment required to be worn by employees working in the area, the employer shall assure the use of such clothing and equipment, and shall require the observer to comply with all other applicable safety and health procedures.

(3) If the monitoring is not interfered with, observers shall be entitled to all of the following:

(a) To receive an explanation of the measurement procedures.

(b) To observe all steps related to the measurement of airborne concentrations of AN performed at the place of exposure.

(c) To record the results obtained.

R 325.51527. Rescinded.

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APPENDIX A - SUBSTANCE SAFETY DATA SHEET FOR ACRYLONITRILE

I. SUBSTANCE IDENTIFICATION

- A. Substance: Acrylonitrile (CH₂CHCN).
- B. Synonyms: Propenenitrile; vinyl cyanide; cyanoethylene; AN; VCN; acylon; carbacryl; fumigian; ventox.
- C. Acrylonitrile can be found as a liquid or vapor, and can also be found in polymer resins, rubbers, plastics, polyols, and other polymers having acrylonitrile as a raw or intermediate material.
- D. AN is used in the manufacture of acrylic and modiacrylic fibers, acrylic plastics and resins, speciality polymers, nitrile rubbers, and other organic chemicals. It has also been used as a fumigant.
- E. Appearance and odor: Colorless to pale yellow liquid with a pungent odor which can only be detected at concentrations above the permissible exposure level, in a range of 13-19 parts AN per million parts of air (13-19 ppm).
- F. Permissible exposure: Exposure may not exceed either:
 - 1. Two parts AN per million parts of air (2 ppm) averaged over the 8-hour workday; or
 - 2. Ten parts AN per million parts of air (10 ppm) averaged over any 15-minute period in the workday.
 - 3. In addition, skin and eye contact with liquid AN is prohibited.

II. HEALTH HAZARD DATA

- A. Acrylonitrile can affect your body if you inhale the vapor (breathing), if it comes in contact with your eyes or skin, or if you swallow it. It may enter your body through your skin.
- B. Effects of overexposure:
 - 1. Short-term exposure: Acrylonitrile can cause eye irritation, nausea, vomiting, headache, sneezing, weakness, and lightheadedness. At high concentrations, the effects of exposure may go on to loss of consciousness and death. When acrylonitrile is held in contact with the skin after being absorbed into shoe leather or clothing, it may produce blisters following several hours of no apparent effect. Unless the shoes or clothing are removed immediately and the area washed, blistering will occur. Usually there is no pain or inflammation associated with blister formation.
 - 2. Long-term exposure: Acrylonitrile has been shown to cause cancer in laboratory animals and has been associated with higher incidences of cancer in humans. Repeated or prolonged exposure of the skin to acrylonitrile may produce irritation and dermatitis.
 - 3. Reporting signs and symptoms: You should inform your employer if you develop any signs or symptoms and suspect they are caused by exposure to acrylonitrile.

III. EMERGENCY FIRST AID PROCEDURES

- A. Eye exposure: If acrylonitrile gets into your eyes, wash your eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.
- B. Skin exposure: If acrylonitrile gets on your skin, immediately wash the contaminated skin with water. If acrylonitrile soaks through your clothing, especially your shoes, remove the clothing immediately and wash the skin with water. If symptoms occur after washing, get medical attention immediately. Thoroughly wash the clothing before reusing. Contaminated leather shoes or other leather articles should be discarded.
- C. Inhalation: If you or any other person breathes in large amounts of acrylonitrile, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
- D. Swallowing: When acrylonitrile has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.
- E. Rescue: Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency procedures. Do not become a casualty yourself. Understand your emergency rescue procedures and know the location of the emergency equipment before the need arises.
- F. Special first aid procedures: First aid kits containing an adequate supply (at least two dozen) of amyl nitrite pearls, each containing 0.3 ml, should be maintained at each site where acrylonitrile is used. When a person is suspected of receiving an overexposure to acrylonitrile, immediately remove that person from the contaminated area using established rescue procedures. Contaminated clothing must be removed and the acrylonitrile washed from the skin immediately. Artificial respiration should be started at once 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 procedures. Medical aid should be obtained immediately.

IV. RESPIRATORS AND PROTECTIVE CLOTHING

A. Respirators. You may be required to wear a respirator for nonroutine activities, in emergencies, while your employer is in the process of reducing acrylonitrile exposures through engineering controls, and in areas where engineering controls are not feasible. If respirators are worn, they must have a label issued by the National Institute for Occupational Safety and Health under the provisions of 42 CFR part 84 stating that the respirators have been approved for use with organic vapors. For effective protection, respirators must fit your face and head snugly. Respirators must not be loosened or removed in work situations where their use is required.

B. Supplied-air suits: In some work situations, the wearing of supplied-air suits may be necessary. Your employer must instruct you in their proper use and operation.

C. Protective clothing: You must wear impervious clothing, gloves, face shield, or other appropriate protective clothing to prevent skin contact with liquid acrylonitrile. Where protective clothing is required, your employer is required to provide clean garments to you as necessary to assume that the clothing protects you adequately.

Replace or repair impervious clothing that has developed leaks.

Acrylonitrile should never be allowed to remain on the skin. Clothing and shoes which are not impervious to acrylonitrile should not be allowed to become contaminated with acrylonitrile, and if they do the clothing and shoes should be promptly removed and decontaminated. The clothing should be laundered or discarded after the AN is removed. Once acrylonitrile penetrates shoes or other leather articles, they should not be worn again.

D. Eye protection: You must wear splashproof safety goggles in areas where liquid acrylonitrile may contact your eyes. In addition, contact lenses should not be worn in areas where eye contact with acrylonitrile can occur.

V. PRECAUTIONS FOR SAFE USE, HANDLING, AND STORAGE

A. Acrylonitrile is a flammable liquid, and its vapors can easily form explosive mixtures in air.

B. Acrylonitrile must be stored in tightly closed containers in a cool, well-ventilated area, away from heat, sparks, flames, strong oxidizers (especially bromine), strong bases, copper, copper alloys, ammonia, and amines.

C. Sources of ignition such as smoking and open flames are prohibited wherever acrylonitrile is handled, used, or stored in a manner that could create a potential fire or explosion hazard.

D. You should use non-sparking tools when opening or closing metal containers of acrylonitrile, and containers must be bonded and grounded when pouring or transferring liquid acrylonitrile.

E. You must immediately remove any non-impervious clothing that becomes wetted with acrylonitrile, and this clothing must not be reworn until the acrylonitrile is removed from the clothing.

F. Impervious clothing wet with liquid acrylonitrile can be easily ignited. This clothing must be washed down with water before you remove it.

G. If your skin becomes wet with liquid acrylonitrile, you must promptly and thoroughly wash or shower with soap or mild detergent to remove any acrylonitrile from your skin.

H. You must not keep food, beverages, or smoking materials, nor are you permitted to eat or smoke in regulated areas where acrylonitrile concentrations are above the permissible exposure limits.

I. If you contact liquid acrylonitrile, you must wash your hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

J. Fire extinguishers and quick drenching facilities must be readily available, and you should know where they are and how to operate them.

K. Ask your supervisor where acrylonitrile is used in your work area and for any additional plant safety and health rules.

VI. ACCESS TO INFORMATION

A. Each year, your employer is required to inform you of the information contained in this Substance Safety Data Sheet for acrylonitrile. In addition, your employer must instruct you in the proper work practices for using acrylonitrile, emergency procedures, and the correct use of protective equipment.

B. Your employer is required to determine whether you are being exposed to acrylonitrile. You or your representative has the right to observe employee measurements and to record the results obtained. Your employer is required to inform you of your exposure. If your employer determines that you are being overexposed, he or she is required to inform you of the actions which are being taken to reduce your exposure to within permissible exposure limits.

C. Your employer is required to keep records of your exposures and medical examinations. These records must be kept by the employer for at least forty (40) years or for the period of your employment plus twenty (20) years, whichever is longer.

D. Your employer is required to release your exposure and medical records to you or your representative upon your request.

[63 FR 1152, Jan. 8, 1998]

APPENDIX B - SUBSTANCE TECHNICAL GUIDELINES FOR ACRYLONITRILE

I. PHYSICAL AND CHEMICAL DATA

- A. Substance identification: 1. Synonyms: AN; VCN; vinyl cyanide; propenenitrile; cyanoethylene; Acrylon; Carbacryl; Fumigrain; Ventox.
2. Formula: $\text{CH}_2 = \text{CHCN}$.
 3. Molecular weight: 53.1.
- B. Physical data: 1. Boiling point (760 mm Hg): 77.3 deg. C (171 deg. F);
2. Specific gravity (water = 1): 0.81 (at 20 deg. C or 68 deg. F);
 3. Vapor density (air=1 at boiling point of acrylonitrile): 1.83;
 4. Melting point: -83 deg. C (-117 deg. F);
 5. Vapor pressure (@20 deg. F): 83 mm Hg;
 6. Solubility in water, percent by weight @ 20 deg. C (68 deg. F): 7.35;
 7. Evaporation rate (Butyl Acetate = 1): 4.54; and
 8. Appearance and odor: Colorless to pale yellow liquid with a pungent odor at concentrations above the permissible exposure level. Any detectable odor of acrylonitrile may indicate overexposure.

II. FIRE, EXPLOSION, AND REACTIVITY HAZARD DATA

- A. Fire:
1. Flash point: -1 deg. C (30 deg. F) (closed cup).
 2. Autoignition temperature: 481 deg. C (898 deg. F).
 3. Flammable limits air, percent by volume: Lower: 3, Upper: 17.
 4. Extinguishing media: Alcohol foam, carbon dioxide, and dry chemical.
 5. Special fire-fighting procedures: Do not use a solid stream of water, since the stream will scatter and spread the fire. Use water to cool containers exposed to a fire.
 6. Unusual fire and explosion hazards: Acrylonitrile is a flammable liquid. Its vapors can easily form explosive mixtures with air. All ignition sources must be controlled where acrylonitrile is handled, used, or stored in a manner that could create a potential fire or explosion hazard. Acrylonitrile vapors are heavier than air and may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which acrylonitrile is being handled.
 7. For purposes of compliance with the requirements of 29 CFR 1910.106, acrylonitrile is classified as a class IB flammable liquid. For example, 7,500 ppm, approximately one-fourth of the lower flammable limit, would be considered to pose a potential fire and explosion hazard.
 8. For purposes of compliance with 29 CFR 1910.157, acrylonitrile is classified as a Class B fire hazard.
 9. For purpose of compliance with 29 CFR 1919.309, locations classified as hazardous due to the presence of acrylonitrile shall be Class I, Group D.

B. Reactivity:

1. Conditions contributing to instability: Acrylonitrile will polymerize when hot, and the additional heat liberated by the polymerization may cause containers to explode. Pure AN may self-polymerize, with a rapid build-up of pressure, resulting in an explosion hazard. Inhibitors are added to the commercial product to prevent self-polymerization.
2. Incompatibilities: Contact with strong oxidizers (especially bromine) and strong bases may cause fires and explosions. Contact with copper, copper alloys, ammonia, and amines may start serious decomposition.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen cyanide, oxides of nitrogen, and carbon monoxide) may be released in a fire involving acrylonitrile and certain polymers made from acrylonitrile.
4. Special precautions: Liquid acrylonitrile will attack some forms of plastics, rubbers, and coatings.

III. SPILL, LEAK, AND DISPOSAL PROCEDURES

- A. If acrylonitrile is spilled or leaked, the following steps should be taken:
1. Remove all ignition sources.
 2. The area should be evacuated at once and re-entered only after the area has been thoroughly ventilated and washed down with water.
 3. If liquid acrylonitrile or polymer intermediate, collect for reclamation or absorb in paper, vermiculite, dry sand, earth, or similar material, or wash down with water into process sewer system.
- B. Persons not wearing protective equipment should be restricted from areas of spills or leaks until clean-up has been completed.
- C. Waste disposal methods: 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. In selecting the method of waste disposal, applicable local, State, and Federal regulations should be consulted.

IV. MONITORING AND MEASUREMENT PROCEDURES

A. Exposure above the Permissible Exposure Limit:

1. Eight-hour exposure evaluation: Measurements taken for the purpose of determining employee exposure under this section are best taken so that the average 8-hour exposure may be determined from a single 8-hour sample or two (2) 4-hour samples. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee.)

2. Ceiling evaluation: Measurements taken for the purpose of determining employee exposure under this section must be taken during periods of maximum expected airborne concentrations of acrylonitrile in the employee's breathing zone. A minimum of three (3) measurements should be taken on one work shift. The average of all measurements taken is an estimate of the employee's ceiling exposure.

3. Monitoring techniques: The sampling and analysis under this section may be performed by collecting the acrylonitrile vapor on charcoal adsorption tubes or other composition adsorption tubes, with subsequent chemical analysis. Sampling and analysis may also be performed by instruments such as real-time continuous monitoring systems, portable direct-reading instruments, or passive dosimeters. Analysis of resultant samples should be by gas chromatograph.

Appendix D lists methods of sampling and analysis which have been tested by NIOSH and OSHA for use with acrylonitrile. NIOSH and OSHA have validated modifications of NIOSH Method S-156 (See Appendix D) under laboratory conditions for concentrations below 1 ppm. The employer has the obligation of selecting a monitoring method which meets the accuracy and precision requirements of the standard under his unique field conditions. The standard requires that methods of monitoring must be accurate, to a 95-percent confidence level, to + or - 35-percent for concentrations of AN at or above 2 ppm, and to + or - 50-percent for concentrations below 2ppm. In addition to the methods described in Appendix D, there are numerous other methods available for monitoring for AN in the workplace. Details on these other methods have been submitted by various companies to the rulemaking record, and are available at the OSHA Docket Office.

B. Since many of the duties relating to employee exposure are dependent on the results of monitoring and measuring procedures, employers shall assure that the evaluation of employee exposures is performed by a competent industrial hygienist or other technically qualified person.

V. PROTECTIVE CLOTHING

Employees shall be provided with and required to wear appropriate protective clothing to prevent any possibility of skin contact with liquid AN. Because acrylonitrile is absorbed through the skin, it is important to prevent skin contact with liquid AN. Protective clothing shall include impermeable coveralls or similar full-body work clothing, gloves, head-coverings, as appropriate to protect areas of the body which may come in contact with liquid AN.

Employers should ascertain that the protective garments are impermeable to acrylonitrile. Non-impermeable clothing and shoes should not be allowed to become contaminated with liquid AN. If permeable clothing does become contaminated, it should be promptly removed, placed in a regulated area for removal of the AN, and not worn again until the AN is removed. If leather footwear or other leather garments become wet from acrylonitrile, they should be replaced and not worn again, due to the ability of leather to absorb acrylonitrile and hold it against the skin. Since there is no pain associated with the blistering which may result from skin contact with liquid AN, it is essential that the employee be informed of this hazard so that he or she can be protected.

Any protective clothing which has developed leaks or is otherwise found to be defective shall be repaired or replaced. Clean protective clothing shall be provided to the employee as necessary to assure its protectiveness. Whenever impervious clothing becomes wet with liquid AN, it shall be washed down with water before being removed by the employee. Employees are also required to wear splash-proof safety goggles where there is any possibility of acrylonitrile contacting the eyes.

VI. HOUSEKEEPING AND HYGIENE FACILITIES

For purposes of complying with 29 CFR 1910.141, the following items should be emphasized:

A. The workplace should be kept clean, orderly, and in a sanitary condition. The employer is required to institute a leak and spill detection program for operations involving liquid AN in order to detect sources of fugitive AN emissions.

B. Dry sweeping and the use of compressed air is unsafe for the cleaning of floors and other surfaces where liquid AN may be found.

C. Adequate washing facilities with hot and cold water are to be provided, and maintained in a sanitary condition. Suitable cleansing agents are also to be provided to assure the effective removal of acrylonitrile from the skin.

D. Change or dressing rooms with individual clothes storage facilities must be provided to prevent the contamination of street clothes with acrylonitrile. Because of the hazardous nature of acrylonitrile, contaminated protective clothing should be placed in a regulated area designated by the employer for removal of the AN before the clothing is laundered or disposed of.

VII. MISCELLANEOUS PRECAUTIONS

A. Store acrylonitrile in tightly-closed containers in a cool, well-ventilated area and take necessary precautions to avoid any explosion hazard.

B. High exposures to acrylonitrile can occur when transferring the liquid from one container to another.

C. Non-sparking tools must be used to open and close metal acrylonitrile containers. These containers must be effectively grounded and bonded prior to pouring.

D. Never store uninhibited acrylonitrile.

E. Acrylonitrile vapors are not inhibited. They may form polymers and clog vents of storage tanks.

F. Use of supplied-air suits or other impervious coverings may be necessary to prevent skin contact with and provide respiratory protection from acrylonitrile where the concentration of acrylonitrile is unknown or is above the ceiling limit. Supplied-air suits should be selected, used, and maintained under the immediate supervision of persons knowledgeable in the limitations and potential life-endangering characteristics of supplied-air suits.

G. Employers shall advise employees of all areas and operations where exposure to acrylonitrile could occur.

VIII. COMMON OPERATIONS

Common operations in which exposure to acrylonitrile is likely to occur include the following: Manufacture of the acrylonitrile monomer; synthesis of acrylic fibers, ABS, SAN, and nitrile barrier plastics and resins, nitrile rubber, surface coatings, specialty chemicals, use as a chemical intermediate, use as a fumigant and in the cyanoethylation of cotton.

APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES FOR ACRYLONITRILE

I. ROUTE OF ENTRY

Inhalation; skin absorption; ingestion.

II. TOXICOLOGY

Acrylonitrile vapor is an asphyxiant due to inhibitory action on metabolic enzyme systems. Animals exposed to 75 or 100 ppm for 7 hours have shown signs of anoxia; in some animals which died at the higher level, cyanomethemoglobin was found in the blood. Two human fatalities from accidental poisoning have been reported; one was caused by inhalation of an unknown concentration of the vapor, and the other was thought to be caused by skin absorption or inhalation. Most cases of intoxication from industrial exposure have been mild, with rapid onset of eye irritation, headache, sneezing, and nausea. Weakness, lightheadedness, and vomiting may also occur. Exposure to high concentrations may produce profound weakness, asphyxia, and death. The vapor is a severe eye irritant. Prolonged skin contact with the liquid may result in absorption with systemic effects, and in the formation of large blisters after a latent period of several hours. Although there is usually little or no pain or inflammation, the affected skin resembles a second-degree thermal burn. Solutions spilled on exposed skin, or on areas covered only by a light layer of clothing, evaporate rapidly, leaving no irritation, or, at the most, mild transient redness. Repeated spills on exposed skin may result in dermatitis due to solvent effects.

Results after 1 year of a planned 2-year animal study on the effects of exposure to acrylonitrile have indicated that rats ingesting as little as 35 ppm in their drinking water develop tumors of the central nervous system. The interim results of this study have been supported by a similar study being conducted by the same laboratory, involving exposure of rats by inhalation of acrylonitrile vapor, which has shown similar types of tumors in animals exposed to 80 ppm.

In addition, the preliminary results of an epidemiological study being performed by duPont on a cohort of workers in their Camden, S.C. acrylic fiber plant indicate a statistically significant increase in the incidence of colon and lung cancers among employees exposed to acrylonitrile.

III. SIGNS AND SYMPTOMS OF ACUTE OVEREXPOSURE

Asphyxia and death can occur from exposure to high concentrations of acrylonitrile. Symptoms of overexposure include eye irritation, headache, sneezing, nausea and vomiting, weakness, and lightheadedness. Prolonged skin contact can cause blisters on the skin with appearance of a second-degree burn, but with little or no pain. Repeated skin contact may produce scaling dermatitis.

IV. TREATMENT OF ACUTE OVEREXPOSURE

Remove employee from exposure. Immediately flush eyes with water and wash skin with soap or mild detergent and water. If AN has been swallowed, and person is conscious, induce vomiting. Give artificial resuscitation if indicated. More severe cases, such as those associated with loss of consciousness, may be treated by the intravenous administration of sodium nitrite, followed by sodium thiosulfate, although this is not as effective for acrylonitrile poisoning as for inorganic cyanide poisoning.

V. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. As noted above, exposure to acrylonitrile has been linked to increased incidence of cancers of the colon and lung in employees of the duPont acrylic fiber plant in Camden, S.C. In addition, the animal testing of acrylonitrile has resulted in the development of cancers of the central nervous system in rats exposed by either inhalation or ingestion. The physician should be aware of the findings of these studies in evaluating the health of employees exposed to acrylonitrile.

Most reported acute effects of occupational exposure to acrylonitrile are due to its ability to cause tissue anoxia and asphyxia. The effects are similar to those caused by hydrogen cyanide. Liquid acrylonitrile can be absorbed through the skin upon prolonged contact. The liquid readily penetrates leather, and will produce burns of the feet if footwear contaminated with acrylonitrile is not removed.

It is important for the physician to become familiar with the operating conditions in which exposure to acrylonitrile may occur. Those employees with skin diseases may not tolerate the wearing of whatever protective clothing may be necessary to protect them from exposure. In addition, those with chronic respiratory disease may not tolerate the wearing of negative-pressure respirators.

B. Surveillance and screening. Medical histories and laboratory examinations are required for each employee subject to exposure to acrylonitrile above the action level. The employer must screen employees for history of certain medical conditions which might place the employee at increased risk from exposure.

1. Central nervous system dysfunction. Acute effects of exposure to acrylonitrile generally involve the central nervous system. Symptoms of acrylonitrile exposure include headache, nausea, dizziness, and general weakness. The animal studies cited above suggest possible carcinogenic effects of acrylonitrile on the central nervous system, since rats exposed by either inhalation or ingestion have developed similar CNS tumors.

2. Respiratory disease. The du Pont data indicate an increased risk of lung cancer among employees exposed to acrylonitrile.

3. Gastrointestinal disease. The du Pont data indicate an increased risk of cancer of the colon among employees exposed to acrylonitrile. In addition, the animal studies show possible tumor production in the stomachs of the rats in the ingestion study.

4. Skin disease. Acrylonitrile can cause skin burns when prolonged skin contact with the liquid occurs. In addition, repeated skin contact with the liquid can cause dermatitis.

5. General. The purpose of the medical procedures outlined in the standard is to establish a baseline for future health monitoring. Persons unusually susceptible to the effects of anoxia or those with anemia would be expected to be at increased risk. In addition to emphasis on the CNS, respiratory and gastrointestinal systems, the cardiovascular system, liver, and kidney function should also be stressed.

APPENDIX D - SAMPLING AND ANALYTICAL METHODS FOR ACRYLONITRILE

There are many methods available for monitoring employee exposures to acrylonitrile. Most of these involve the use of charcoal tubes and sampling pumps, with analysis by gas chromatograph. The essential differences between the charcoal tube methods include, among others, the use of different desorbing solvents, the use of different lots of charcoal, and the use of different equipment for analysis of the samples.

Besides charcoal, considerable work has been performed on methods using porous polymer sampling tubes and passive dosimeters. In addition, there are several portable gas analyzers and monitoring units available on the open market.

This appendix contains details for the methods which have been tested at OSHA Analytical Laboratory in Salt Lake City, and NIOSH in Cincinnati. Each is a variation on NIOSH Method S-156, which is also included for reference. This does not indicate that these methods are the only ones which will be satisfactory. There also may be workplace situations in which these methods are not adequate, due to such factors as high humidity. Copies of the other methods available to OSHA are available in the rulemaking record, and may be obtained from the OSHA Docket Office. These include, the Union Carbide, Monsanto, Dow Chemical and Dow Badische methods, as well as NIOSH Method P & CAM 127.

Employers who note problems with sample breakthrough should try larger charcoal tubes. Tubes of larger capacity are available, and are often used for sampling vinyl chloride. In addition, lower flow rates and shorter sampling times should be beneficial in minimizing breakthrough problems.

Whatever method the employer chooses, he must assure himself of the method's accuracy and precision under the unique conditions present in his workplace.

NIOSH METHOD S-156 (UNMODIFIED)

Analyte: Acrylonitrile.

Matrix: Air.

Procedure: Absorption on charcoal, desorption with methanol, GC.

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 methanol.

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 deg. 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 0.18 liter per minute for 240 minutes; at that time the concentration of acrylonitrile in the effluent was less than 5 percent of that in the influent. (The charcoal tube consists of two sections of activated 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. Interference.

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 (CVT) 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 (previous) OSHA standard level (20 ppm). 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 20 ppm level using the overall sampling and analytical method were 6.0 percent 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 percent 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 + or - 5 percent at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: Glass tubes 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 charcoals prepared from coconut shells and is fired at 600 deg. 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 silicated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 1 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-ftX 1/4 -in stainless steel) packed with 50/80 mesh Poropak, 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 flask: 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 backup 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 + or - 5 percent.

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 10 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 deg. C injector temperature.
5. 255 deg. C manifold temperature (detector).
6. 155 deg. 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 blowback 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 percent 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 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 tube.

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 sample. 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

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

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, because samples are desorbed in this amount of 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:
 mg sample = mg found in front section of sample tube.
 mg sample = 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 sec. 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.

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

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

$$\text{mg/cu m} = \text{Corrected mg (section 10.4)} \times \frac{1,000 \text{ (liter/cu m)}}{\text{air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

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

Where:

P	=	Pressure (mm Hg) of air sampled.
T	=	Temperature (deg. C) of air sampled.
24.45	=	Molar volume (liter/mole) at 25 deg. C and 760 mm Hg.
M.W.	=	Molecular weight (g/mole) of analyte.
760	=	Standard pressure (mm Hg).
298	=	Standard temperature (deg. 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.

NIOSH Modification of NIOSH Method S-156

The NIOSH recommended method for low levels for acrylonitrile is a modification of method S-156. It differs in the following respects:

- (1) Samples are desorbed using 1 ml of 1 percent acetone in CS(2) rather than methanol.
- (2) The analytical column and conditions are:

Column: 20 percent SP-1000 on 80/100 Supelcoport 10 feet x 1/8 inch S.S.
Conditions:

- Injector temperature: 200 deg. C.
- Detector temperature: 100 deg. C.
- Column temperature: 85 deg. C.
- Helium flow: 25 ml/min.
- Air flow: 450 ml/min.
- Hydrogen flow: 55 ml/min.

- (3) A 2 ul injection of the desorbed analyte is used.
- (4) A sampling rate of 100 ml/min is recommended.

OSHA Laboratory Modification of NIOSH Method S-156

- Analyte: Acrylonitrile.
- Matrix: Air.
- Procedure: Adsorption on charcoal, desorption with methanol, GC.

1. Principle of the Method (Reference 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 vial, and the analyte is desorbed with methanol.

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. Advantages and disadvantages of the method.

2.1 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.

2.2 This method may not be adequate for the simultaneous analysis of two or more substances.

2.3 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 percent of that found on the front section, the possibility of sample loss exists.

2.4 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.

3. Apparatus.

3.1 A calibrated personal sampling pump whose flow can be determined within + or - (5) percent at the recommended flow rate.

3.2 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 deg. C prior to packing. The adsorbing section contains 100 mg of charcoal, the back-up section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the back-up section. A plug of sintered 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.

3.3 Gas chromatograph equipped with a nitrogen phosphorus detector.

3.4 Column (10-ft x 1/8"-in stainless steel) packed with 100/120 Supelcoport coated with 10 percent SP 1000.

3.5 An electronic integrator or some other suitable method for measuring peak area.

3.6 Two-milliliter sample vials with Teflon-lined caps

3.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

3.8 Pipets: 1.0-ml delivery pipets.

3.9 Volumetric flasks: convenient sizes for making standard solutions.

4. Reagents.

4.1 Chromatographic quality methanol.

4.2 Acrylonitrile, reagent grade.

4.3 Filtered compressed air.

4.4 Purified hydrogen.

4.5 Purified helium.

5. Procedure.

5.1 Cleaning of equipment. All glassware used for the laboratory analysis should be properly cleaned and free of organics which could interfere in the analysis.

5.2 Calibration of personal pumps. Each pump must be calibrated with a representative charcoal tube in the line.

5.3 Collection and shipping of samples.

5.3.1 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).

5.3.2 The smaller section of the charcoal is used as the backup and should be placed nearest the sampling pump.

5.3.3 The charcoal should be placed in a vertical position during sampling to minimize channeling through the charcoal.

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

5.3.5 A sample size of 20 liters is recommended. Sample at a flow rate of approximately 0.2 liters per minute. The flow rate should be known with an accuracy of at least + or - (5) percent.

5.3.6 The temperature and pressure of the atmosphere being sampled should be recorded.

5.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Rubber caps should not be used.

5.3.8 Submit at least one blank tube (a charcoal tube subjected to the same handling procedures, without having any air drawn through it) with each set of samples.

5.3.9. Take necessary shipping and packing precautions to minimize breakage of samples.

5.4 Analysis of samples.

5.4.1 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 vial. The separating section of foam is removed and discarded; the section is transferred to another capped vial. These two sections are analyzed separately.

5.4.2 Desorption of samples. Prior to analysis, 1.0 ml of methanol is pipetted into each sample container. Desorption should be done for 30 minutes in an ultrasonic bath. The sample vials are recapped as soon as the solvent is added.

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

1. 30 ml/min (60 psig) helium carrier gas flow.
2. 3.0 ml/min (30 psig) hydrogen gas flow to detector.
3. 50 ml/min (60 psig) air flow to detector.
4. 200 deg. C injector temperature.
5. 200 deg. C detector temperature.
6. 100 deg. C column temperature.

5.4.4 Injection. Solvent flush technique or equivalent.

5.4.5 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.

5.5 Determination of desorption efficiency.

5.5.1 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.

5.5.2 Procedure for determining desorption efficiency. The reference portion of the charcoal tube is removed. To the remaining portion, amounts representing 0.5X, 1X, and 2X (X represents TLV) based on a 20 l air sample are injected onto several tubes at each level. Dilutions of acrylonitrile with methanol are made to allow injection of measurable quantities. These tubes are then allowed to equilibrate at least overnight. Following equilibration they are analyzed following the same procedure as the samples. A curve of the desorption efficiency amt recovered/amt added is plotted versus amount of analyte found. This curve is used to correct for adsorption losses.

6. Calibration and standards.

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 prepared by plotting concentration 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 NPD response. Multiple injections are necessary.

7. Calculations.

Read the weight, corresponding to each peak area from the standard curve, correct for the blank, correct for the desorption efficiency, and make necessary air volume corrections.

8. Reference. NIOSH Method S-156.

[43 FR 45809, Oct. 3, 1978, as amended at 45 FR 35283, May 23, 1980; 54 FR 24334, June 7, 1989; 61 FR 5507, Feb. 13, 1996]



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