Occupational Health Guideline for Hydrogen Cyanide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: HCN
- Synonyms: Hydrocyanic acid; prussic acid; formonitrile
- Appearance and odor: Colorless or pale blue liquid or gas with a bitter almond odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen cyanide is 10 parts of hydrogen cyanide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 11 milligrams of hydrogen cyanide per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 5 mg cyanide/m³ averaged over a 10-minute period. The NIOSH Criteria Document for Hydrogen Cyanide and Cyanide Salts should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Hydrogen cyanide can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation, ingestion, or skin absorption of hydrogen cyanide may be rapidly fatal. Larger doses may cause the person to rapidly lose consciousness, stop breathing, and die. At lower levels of exposure, a person may experience weakness, headache, confusion, nausea, and vomiting. These symptoms may be followed by unconsciousness and death. Hydrogen cyanide liquid may irritate the eyes.

2. Long-term Exposure: Effects from chronic exposure to hydrogen cyanide are non-specific and rare.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hydrogen cyanide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to hydrogen cyanide at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of fainting spells, such as occur in various types of cardiovascular and nervous disorders, and and those who are unusually susceptible to effects of anoxia or with anemia would be expected to be at increased risk from exposure. Examination of the cardiovascular, nervous, and upper respiratory systems, and thyroid should be stressed.

—Cardiovascular disease: Persons with cardiac disease may be at increased risk. An electrocardiogram should be performed on workers over 40 years of age and where indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

3. First Aid Kits: First aid kits should be immediately available in workplaces where there is a potential for the release of hydrogen cyanide. These kits should contain a minimum of 48 ampules, each of 0.3 ml amyl nitrate, and complete instructions for use. In addition, 2 physician's kits should be immediately available to trained medical personnel. These kits should contain the above quantity of amyl nitrate as well as sterile sodium

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nitrite solution (3%) and sterile sodium thiosulfate solution (25%). All of the above drugs should be replaced at least biannually to ensure their potency.

• **Summary of toxicology**

Hydrogen cyanide (HCN) vapor, a source of cyanide ion, is an asphyxiant due to an inhibitory action on metabolic enzyme systems and can be rapidly fatal. Cyanide exerts this effect because it inactivates certain enzymes by forming very stable complexes with the metal in them. Cytochrome oxidase is probably the most important of these since it occupies a fundamental position in the respiratory process and is involved in the ultimate electron transfer to molecular oxygen. Since cytochrome oxidase is present in practically all cells that function under aerobic conditions, and since the cyanide ion diffuses easily to all parts of the body, it is capable of suddenly bringing to a halt practically all cellular respiration. A few inhalations of high concentrations of HCN may be followed by almost instantaneous collapse and cessation of respiration; 270 ppm HCN is immediately fatal to humans, 181 ppm is fatal after 10 minutes, 135 ppm after 30 minutes, and 110 ppm may be fatal in 1 hour. At lower levels of exposure to HCN, the earliest symptoms of intoxication may include weakness, headache, confusion, and occasionally nausea and vomiting; respiratory rate and depth usually increase initially and at later stages become slow and gasping; if cyanosis is present, it usually indicates that respiration has either ceased or has been very inadequate for a few minutes. Humans tolerate 45 to 54 ppm for ½ to 1 hour without immediate or delayed effects, while 18 to 36 ppm may result in some symptoms after an exposure of several hours. The ingestion by humans of 50 to 100 mg of HCN may also be fatal. Eye contact with liquid HCN may cause irritation. Cyanide is one of the few toxic substances for which an antidote exists, and it functions as follows. First, amyl nitrite (inhalation) and sodium nitrite (intravenously) are administered to form methemoglobin, which binds firmly with free cyanide ions. This traps any circulating cyanide ions. The formation of 10 to 20% methemoglobin usually does not involve appreciable risk, yet provides a large amount of cyanide-binding substance. Second, sodium thiosulfate is administered intravenously to increase the rate of conversion of cyanide to the less toxic thiocyanate. Methylene blue should not be administered, because it is a poor methemoglobin former and, moreover, promotes the conversion of methemoglobin back to hemoglobin.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 27
2. Boiling point (760 mm Hg): 26 C (79 F)
3. Specific gravity (water = 1): 0.7
4. Vapor density (air = 1 at boiling point of hydrogen cyanide): 0.93
5. Melting point: −14.4 to −16.8 C (7 to 2 F)
6. Vapor pressure at 20 C (68 F): 620 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

• **Reactivity**

1. Conditions contributing to instability: Older samples may polymerize and explode unless acid stabilizer is maintained at proper concentration. Samples containing more than 2− 5% of water are less stable than dry material. Samples stored more than 90 days are hazardous.
2. Incompatibilities: Contact with bases such as caustics and amines may cause violent polymerization and explosion.
3. Hazardous decomposition products: None more toxic than hydrogen cyanide.
4. Special precautions: Liquid hydrogen cyanide will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: −17.8 C (0 F) (closed cup)
2. Autoignition temperature: 538 C (1000 F)
3. Flammable limits in air, % by volume: Lower: 5.6; Upper: 40
4. Extinguishant: Dry chemical, carbon dioxide, alcohol foam

• **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "the odor of HCN is usually described as 'sweet'; trained persons describe the odor as that of bitter almonds and can detect it at about one ppm." The Manufacturing Chemists Association (MCA) states that "although hydrocyanic acid has a characteristic odor, its toxic action at hazardous concentrations is so rapid that it is of no value as a warning."
2. Eye Irritation Level: Grant states that "only occasionally has reference been made to an irritation of the eye, conjunctivitis, or superficial keratitis developing after chronic exposure to hydrogen cyanide gas."
3. Evaluation of Warning Properties: For the purposes of this guideline, hydrogen cyanide has been treated as a material with poor warning properties. Although the odor threshold appears to be below the permissible exposure limit, Patty states that "the sense of smell is . . . easily fatigued; and there is wide individual variation in the minimum odor threshold."

MONITORING AND MEASUREMENT PROCEDURES

• **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of hydrogen cyanide. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Hydrogen cyanide may be monitored by collection in midget impingers containing sodium hydroxide, followed by analysis with an ion specific electrode. An analytical method for hydrogen cyanide is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid hydrogen cyanide.

• Where there is any possibility of exposure of an employee's body to liquid hydrogen cyanide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Any clothing which becomes wet with, or non-impervious clothing which becomes contaminated with, liquid hydrogen cyanide should be removed immediately and not reworn until the hydrogen cyanide is removed from the clothing.

• Clothing wet with hydrogen cyanide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydrogen cyanide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hydrogen cyanide, the person performing the operation should be informed of hydrogen cyanide's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid hydrogen cyanide contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to hydrogen cyanide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with hydrogen cyanide should be immediately washed or showered to remove any hydrogen cyanide.

• Employees who handle hydrogen cyanide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen cyanide may occur and control methods which may be effective in each case:

Operation	Controls
Use in fumigation of structures and agricultural crops	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use of cyanide salts or solutions in metal treatment operations, blast furnace and coke oven operations, metal ore processing, and photoengraving operations	Process enclosure; local exhaust ventilation; personal protective equipment
Use in production of intermediates in synthesis of acrylic plastics, nylon 66, chelating agents, dyes, pharmaceuticals, and specialty chemicals	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquid hydrogen cyanide gets into the eyes, wash 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.

• **Skin Exposure**

If liquid hydrogen cyanide gets on the skin, immediately flush the contaminated skin with water. If liquid hydrogen cyanide soaks through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of hydrogen cyanide, 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.

• **Swallowing**

When hydrogen cyanide has been swallowed and the person is conscious, 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.

• **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 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.

SPILL, LEAK, AND DISPOSAL PROCEDURES

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

• If hydrogen cyanide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Hydrogen cyanide should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of hydrogen cyanide vapors are permitted.

• Waste disposal method:

Liquid hydrogen cyanide may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR HYDROGEN CYANIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
50 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 50 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against hydrogen cyanide. Any escape self-contained breathing apparatus.

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

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of hydrogen cyanide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 50 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.