Occupational Health Guideline for Nitrogen Dioxide

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: NO_2 and N_2O_4
- Synonyms: Nitrogen tetroxide; NTO; dinitrogen tetroxide; nitrogen peroxide
- Appearance and odor: Dark brown fuming liquid or gas with a pungent, acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nitrogen dioxide is a ceiling of 5 parts of nitrogen dioxide per million parts of air (ppm) (*Federal Register*, Vol. 43, No. 237, pp. 57601-03, 8 December 1978). This may also be expressed as 9 milligrams of nitrogen dioxide per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 1 ppm (1.8 mg/m^3) averaged over a 15-minute period. The NIOSH Criteria Document for Oxides of Nitrogen should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nitrogen dioxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to nitrogen dioxide may cause severe breathing difficulties which are usually delayed in onset and which may cause death. Recovery may be slow (2 to 3 weeks) with possible relapse and possible permanent lung damage. Pneumonia may occur. Irritation of the eyes, nose, throat, and wet skin may occur with acute exposures.

- **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 nitrogen dioxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nitrogen dioxide 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. Examination of the respiratory tract and cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Nitrogen dioxide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nitrogen dioxide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—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 or as otherwise indicated by the responsible physician.

- **Summary of toxicology**

Nitrogen dioxide gas is a respiratory irritant; it causes pulmonary edema and rarely, among survivors, bronchiolitis obliterans. Brief exposure of humans to concentrations of about 250 ppm causes cough, production of mucoid or frothy sputum, and increasing dyspnea. Within 1 to 2 hours the person may develop pulmonary edema with tachypnea, cyanosis, and fine crackles and wheezes throughout the lungs, and tachycardia. Alter-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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natively, there may be only increasing dyspnea and cough over several hours, the symptoms then gradually subside over a 2- to 3-week period. The condition may then enter a second stage of abruptly increasing severity; fever and chills precede a relapse with increasing dyspnea, cyanosis, and recurring pulmonary edema. Death may occur either in the initial or second stage of the disease; a severe second stage may follow a relatively mild initial stage. The subject who survives the second stage usually recovers over 2 to 3 weeks; however, some do not return to normal, but experience varying degrees of impaired pulmonary function. The radiographic features in the acute initial stage vary from normal to those of typical pulmonary edema; most reports mention a pattern of nodular shadows on the chest film at the outset. The roentgenogram may then clear, only to show miliary mottling as the second stage commences, progressing to the development of a confluent pattern. Results of pulmonary function tests in the acute stage show reduction in lung volume and diffusing capacity; similar findings are recorded in the second stage. Pathologic examination of the acute lesion shows extensive mucosal edema and inflammatory cell exudation. The delayed lesion shows the histologic appearance of bronchiolitis obliterans; small bronchi and bronchioles contain an inflammatory exudate which tends to undergo fibrinous organization, finally obliterating the lumen. The effects expected in humans from exposure to nitrogen dioxide for 60 minutes are: 100 ppm, pulmonary edema and death; 50 ppm, pulmonary edema with possible subacute or chronic lesions in the lungs; 25 ppm, respiratory irritation and chest pain. A concentration of 50 ppm is moderately irritating to the eyes and nose; 25 ppm is irritating to some people.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 46 and 92
2. Boiling point (760 mm Hg): 21 C (70 F)
3. Specific gravity (water = 1): 1.45 (liquid)
4. Vapor density (air = 1 at boiling point of nitrogen dioxide): 2.83
5. Melting point: −11.2 C (11.8 F)
6. Vapor pressure at 20 C (68 F): 720 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions (reacts to form nitric acid and nitric oxide)
8. Evaporation rate (butyl acetate = 1): Much greater than 1

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to explode.
2. Incompatibilities: Contact with all combustible materials, chlorinated hydrocarbons, ammonia, and carbon disulfide may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when nitrogen dioxide decomposes.
4. Special precautions: Nitrogen dioxide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible, but strong oxidizing agent.

- **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* reports an odor threshold of 5 ppm.
2. Eye Irritation Level: According to Grant, "the gas at a concentration in approximately 70 ppm in air causes irritation of the eyes and nose evident in guinea pigs, rabbits, monkeys, and dogs during the first hour of exposure. At this concentration the gas has been lethal to most of the animals if exposed for eight hours, and under these conditions corneal opacities have been produced in the rabbits. The corneas of rabbits that survived such exposures did not improve under observation during twenty days. However, the gas at concentrations up to 20 ppm in air and exposure of four hours has produced no significant effect on the corneas of rabbits . . . . Exposure of the same magnitude repeated daily for more than a month also has not been damaging to the eye." The *Documentation of TLV's* reports that according to Patty, 10-20 ppm "were mildly irritant to the eyes . . . ."
3. Other Information: The AIHA *Hygienic Guide* states that "exposures of relatively short duration to concentrations above 5 ppm produce cough and irritation of the respiratory tract."
4. Evaluation of Warning Properties: Through its odor and irritant effects, nitrogen dioxide can be detected slightly above the recommended permissible exposure limit. For the purposes of this guideline, therefore, nitrogen dioxide is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of nitrogen dioxide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) 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**

Sampling and analyses may be performed by collection of gas in a reagent-filled impinger with a subsequent spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure nitrogen dioxide may be used. An analytical method for nitrogen dioxide 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 nitrogen dioxide.

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

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

• Non-impervious clothing which becomes contaminated with nitrogen dioxide should be removed immediately and not reworn until the nitrogen dioxide is removed from the clothing.

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

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

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use during metal surface treatment with nitric acid; in production of intermediates in manufacture of sulfuric acid, nitric acid, and fertilizers	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation of fumes during engine maintenance, synthesis of dyes, manufacture of nitrocellulose paints, lacquers, and storage of silage in agricultural operations; production and handling of rocket propellants	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation of fumes during detonation of explosives	Personal protective equipment
Use in chemical synthesis during nitration operations	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 nitrogen dioxide or strong concentrations of nitrogen dioxide vapor get 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 nitrogen dioxide or strong concentrations of nitrogen dioxide vapor get on the skin, immediately flush the contaminated skin with water. If liquid nitrogen dioxide or strong concentrations of nitrogen dioxide vapor penetrate 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 nitrogen dioxide, 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 liquid nitrogen dioxide has been swallowed and if the person is conscious, immediately give the person large amounts of water to dilute the nitrogen dioxide. Do not attempt to make the 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 AND LEAK PROCEDURES

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

• If nitrogen dioxide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. If in the liquid form, allow to vaporize.
3. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

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RESPIRATORY PROTECTION FOR NITROGEN DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Gas Concentration	
50 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) containing non-oxidizable sorbents and providing protection against nitrogen dioxide.** A gas mask with a chin-style or a front- or back-mounted canister containing non-oxidizable sorbents and providing protection against nitrogen dioxide. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
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 containing non-oxidizable sorbents and providing protection against nitrogen dioxide. Any escape self-contained breathing apparatus.

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

**Nitrogen dioxide is an oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials, such as activated charcoal, and therefore should not be used to provide protection against nitrogen dioxide. Only non-oxidizable sorbents are allowed.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitrogen dioxide; 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.