

Occupational Health Guideline for Tetranitromethane

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: $C(NO_2)_4$
- Synonyms: Tetan
- Appearance and odor: Colorless to pale yellow liquid or solid. The vapor has a pungent odor and causes tears.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetranitromethane is 1 part of tetranitromethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 8 milligrams of tetranitromethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

Tetranitromethane 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 tetranitromethane may cause irritation of the eyes, upper respiratory tract and skin. It may also cause headaches, fatigue, and drowsiness. After prolonged exposure, the central nervous system and heart may be affected and difficult breathing may occur. Tetranitromethane has been reported to affect the ability of the blood to carry oxygen. This may result in a bluish discoloration of the skin, headache, weakness, irritability, drowsiness, shortness of breath, and unconsciousness.

• 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 tetranitromethane.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to tetranitromethane 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, eyes, blood, central nervous system, and liver should be stressed. The skin should be examined for evidence of chronic disorders.

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

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

—A complete blood count: Tetranitromethane has been shown to cause methemoglobinemia in humans. Persons with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

• Summary of toxicology

Tetranitromethane vapor is a severe irritant of the eyes and respiratory tract. The LC50 for rats was 1230 ppm

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.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

for 36 minutes; effects were lacrimation, rhinorrhea, gasping, and cyanosis; pulmonary edema was present at autopsy. Repeated exposure to 3.65 ppm for 6 months caused the death of 60% of the rats; at autopsy there were signs of lung infection following acute pneumonitis. In three species of animals, intravenous injection caused methemoglobinemia, anemia, damage to the central nervous system, and edema of the lungs and liver. In workers, various studies showed that exposure caused irritation of the eyes, nose, and throat; dizziness, headache; chest pain, dyspnea; and occasionally skin irritation. Methemoglobinemia is stated to be a systemic effect from human exposure; symptoms result from anoxia and include cyanosis, evident especially in the lips, nose, and earlobes; other effects are weakness, dizziness, and severe headache. Concentrations in excess of 1 ppm will cause lacrimation and upper respiratory irritation, while 0.4 ppm may cause mild irritation. The liquid on the skin may cause mild burns.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 196
2. Boiling point (760 mm Hg): 126 C (259 F)
3. Specific gravity (water = 1): 1.64
4. Vapor density (air = 1 at boiling point of tetranitromethane): 6.8
5. Melting point: 14 C (57 F)
6. Vapor pressure at 20 C (68 F): 8.4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Data not available

• Reactivity

1. Conditions contributing to instability: Combustible organic matter wet with tetranitromethane may be highly explosive and susceptible to initiation by rather mild shocks.
2. Incompatibilities: Contact with hydrocarbons, alkalies, and metals may form explosive mixtures.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving tetranitromethane or when tetranitromethane decomposes.
4. Special precautions: Tetranitromethane will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Not combustible by itself, but is considered by some to be a weak explosive.

• Warning properties

1. Odor Threshold: Patty states that "tetranitromethane can be recognized by its characteristic acrid biting odor." No quantitative information is available, however, concerning its odor threshold.
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "the irritant property of tetranitromethane may serve as an index to the degree of exposure which can be tolerated, because concentrations in excess of 1

ppm will cause lacrimation and upper respiratory irritation. Concentrations as low as 0.4 ppm may cause mild irritation." Grant states that "the vapors of tetranitromethane are very irritating to the eyes, nose, and respiratory passages. It has been proposed for use as an irritant war gas. Animals are said to show evidence of irritation of the eyes rather quickly at concentrations from 3.3 to 25.2 ppm in air."

3. Evaluation of Warning Properties: Through its irritant effects, tetranitromethane can be detected below the permissible exposure limit. For the purposes of this guideline, therefore, tetranitromethane is treated as a material with good warning properties. It is a strong oxidizer.

MONITORING AND MEASUREMENT PROCEDURES

• General

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).

• Method

Sampling and analyses may be performed by drawing tetranitromethane through ethyl acetate with subsequent gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure tetranitromethane may be used. An analytical method for tetranitromethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

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 skin contact with solid or liquid tetranitromethane where skin contact may occur.
- Clothing which may have become contaminated with tetranitromethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tetranitromethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tetranitromethane, the person performing the operation should be informed of tetranitromethane's hazardous properties.
- Non-impervious clothing which becomes contaminated with tetranitromethane should be removed promptly and any clothing which becomes wet with liquid tetranitromethane should be removed immediately and not reworn until the tetranitromethane is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid tetranitromethane contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid or liquid tetranitromethane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with tetranitromethane should be promptly washed or showered with soap or mild detergent and water to remove any tetranitromethane.
- Eating and smoking should not be permitted in areas where tetranitromethane is handled, processed, or stored.
- Employees who handle solid or liquid tetranitromethane 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 tetranitromethane may occur and control methods which may be effective in each case:

Operation

Use as an ingredient in manufacture of liquid explosives; use as an octane number improver in diesel fuels

Use as a laboratory analytical reagent as a nitrating agent; use in research in rocket propellants

Controls

Process enclosure; local exhaust ventilation; personal protective equipment

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 solid or liquid tetranitromethane or strong concentrations of tetranitromethane vapors get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention promptly. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If solid or liquid tetranitromethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid tetranitromethane or penetrates through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention immediately.

• Breathing

If a person breathes in large amounts of tetranitromethane, 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 solid or liquid tetranitromethane have 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 tetranitromethane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material. Avoid shock and friction if liquid spills on combustible matter such as wood and paper.

- Waste disposal method:

Liquid tetranitromethane may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill. Solid tetranitromethane may be collected in the most convenient manner and disposed of in a secured sanitary landfill. Care should be taken when disposing, since tetranitromethane is a weak explosive.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Tetranitromethane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

- American Industrial Hygiene Association: "Tetranitromethane," *Hygienic Guide Series*, Detroit, Michigan, 1964.

- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.

- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

- Hager, K. F.: "Tetranitromethane," *Industrial and Engineering Chemistry*, 41:2168-2172, 1949.

- Horn, H. J.: "Inhalation Toxicology of Tetranitromethane," *A.M.A. Archives of Industrial Hygiene and Occupational Medicine*, 10:213-222, 1954.

- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.

- Mangelsdorff, A. F.: "Treatment of Methemoglobinemia," *A.M.A. Archives of Industrial Hygiene and Occupational Medicine*, 14:148-153, 1956.

- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

- Stecher, P. G. (ed.): *The Merck Index* (8th ed.), Merck Co., Inc., Rahway, New Jersey, 1968.

RESPIRATORY PROTECTION FOR TETRANITROMETHANE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
5 ppm or less	Any chemical cartridge respirator with a full facepiece and a cartridge containing non-combustible sorbents and providing protection against tetranitromethane. A gas mask with a chin-style or a front- or back-mounted canister containing non-combustible sorbents and providing protection against tetranitromethane. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5 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	A gas mask containing non-combustible sorbents and providing protection against tetranitromethane. Any escape self-contained breathing apparatus.

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