

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROPICRIN

INTRODUCTION

This guideline summarizes pertinent information about chloropicrin for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

• Formula



• Synonyms

Nitrotrichloromethane, trichloronitromethane, nitrochloroform, Chlor-o-pic, Acquinite, Microlysin, Pic-fume, Profume A, Dolochlor, Larvacide 100

• Identifiers

1. CAS No.: 76-06-2
2. RTECS No.: PB6300000
3. DOT UN: 1580 56 (liquid chloropicrin)
4. DOT label: Poison B

• Appearance and odor

At room temperature, chloropicrin is a noncombustible, oily, colorless liquid with an intense and penetrating

odor. The odor threshold reported for chloropicrin is 1.1 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 164.4
2. Boiling point (760 mm Hg): 112°C (234°F)
3. Specific gravity (water = 1): 1.66 at 20°C (68°F)
4. Vapor density (air = 1 at boiling point of chloropicrin): 5.7
5. Melting point: -64°C (-83°F) (solidifies)
6. Vapor pressure at 20°C (68°F): 20 mm Hg
7. Solubility: Nearly insoluble in water; soluble in ether, benzene, absolute alcohol, acetic acid, carbon tetrachloride, acetone, methyl alcohol, and carbon disulfide.
8. Evaporation rate: Data not available

• Reactivity

1. Conditions contributing to instability: Heat, friction, or strong impact may cause chloropicrin to detonate.
2. Incompatibilities: Contact of chloropicrin with strong oxidizers may cause fires or explosions. Chloropicrin also reacts violently with aniline in the presence of heat, alcoholic sodium hydroxide, sodium methoxide, and propargyl bromide.

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Public Health Service
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National Institute for Occupational Safety and Health
Education and Information Division

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3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen, chlorine, and carbon monoxide) may be released when chloropicrin is heated to decomposition.

4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to chloropicrin; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire.

Fires involving chloropicrin should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloropicrin may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloropicrin. Chemical protective clothing that is specifically recommended for chloropicrin may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chloropicrin.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for chloropicrin is 0.1 ppm (0.7 mg/m³) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.7 mg/m³) as a TWA for up to a 10-hr workday and a 40-hr workweek for chloropicrin [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloropicrin a threshold limit value (TLV) of 0.1 ppm (0.67 mg/m³) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of severe eye, skin, and respiratory irritation with chloropicrin exposure [NIOSH 1992]. The ACGIH limit is based on the risk of severe eye and pulmonary effects associated with exposure to chloropicrin [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloropicrin can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Chloropicrin is a severe eye, mucous membrane, and lung irritant; it is particularly injurious to the small and medium-size bronchi. The oral LD₅₀ in rats is 250 mg/kg, and the LC₅₀ in the same species is 14.4 ppm for 4 hours [NIOSH 1993]. Acute poisoning causes pulmonary congestion, hemorrhage, edema, and tissue infiltration [ACGIH 1991]. Rats inhaling chloropicrin for longer test periods (duration unspecified) developed kidney, liver, and muscle damage [ACGIH 1991]. In mice, exposure to a 9-ppm concentration of chloropicrin in air caused a 50-percent decrease in respiratory rate (with ulceration and necrosis of the respiratory tract lining) and moderate lung damage [Hathaway et al. 1991]. A National Cancer Institute bioassay for carcinogenicity in rats and mice administered chloropicrin by gavage yielded inconclusive results [Clayton

and Clayton 1981]. Chloropicrin is weakly mutagenic in bacterial test systems [Hayes and Laws 1991].

2. *Effects on Humans:* Chloropicrin is a lacrimator and a severe irritant of the respiratory system in humans; it also causes severe skin irritation on contact. Chloropicrin was formerly used as a war gas; the gastrointestinal effects associated with exposure caused it to be called "vomiting gas" [Genium 1990]. Splashed into the eye, chloropicrin has caused corneal edema and liquification of the cornea [NLM 1993]. Exposure to a chloropicrin concentration of 15 ppm cannot be tolerated for more than 1 minute, and exposure to 4 ppm for a few seconds is temporarily disabling because it causes severe eye and respiratory irritation [Hathaway et al. 1991]. Exposure to 0.3 to 0.37 ppm chloropicrin for 3 to 30 seconds causes tearing and eye pain, and this substance is also a severe skin irritant [ACGIH 1991; Clayton and Clayton 1981]. Exposure to a 15-ppm concentration of chloropicrin for a few seconds causes respiratory tract injury [Clayton and Clayton 1981]. In humans, exposure to 119 ppm in air for 30 minutes is lethal; death is caused by pulmonary edema [Hathaway et al. 1991]. Twenty-seven workers in a cellulose factory who were exposed to a high (not further specified) concentration of chloropicrin for 3 minutes developed pneumonitis after 3 to 12 hours of irritating coughing and difficulty in breathing; they subsequently developed pulmonary edema and one died [NLM 1993]. Exposure to chloropicrin apparently increases an individual's susceptibility to chloropicrin intoxication on subsequent exposure [Hathaway et al. 1991; Clayton and Clayton 1981]. Sublethal exposures may cause delayed-onset pulmonary edema, and late deaths may occur from secondary infection [Clayton and Clayton 1981].

• **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to chloropicrin include severe pain and tearing of the eyes and corneal burns and opacification; burns and redness of the skin; cough, difficulty breathing, and pulmonary edema; and vertigo, nausea, and vomiting.
2. *Chronic exposure:* The signs and symptoms of repeated exposure to chloropicrin include increased susceptibility to the acute effects of this substance and damage to the lungs. Based on effects seen in animals, chronic exposure to chloropicrin may cause

enlarged and tender liver, jaundice, elevated liver enzymes, and pus, blood, or protein in the urine.

• **Emergency procedures**

WARNING!
Exposed victims may die!
Transport victims immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. *Immediately* initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists or aerosols of chloropicrin! *Immediately but gently* flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.
2. *Skin exposure:* Severe burns and skin corrosion may result! *Immediately* remove all contaminated clothing! *Immediately, continuously, and gently* wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.
3. *Inhalation exposure:* Move the victim to fresh air *immediately*. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chloropicrin or any material containing it is ingested:

—Do *not* induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and *no more*.

—Do *not* permit the victim to drink milk or carbonated beverages!

—Do *not* permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloropicrin and lead to worker exposures to this substance:

- Use as a fumigant on stored grains, cereals, fruits, nuts, vegetables, tobacco, floral crops, lawns, turf, and ornamentals
- Use as a soil fumigant, disinfectant, and sterilizer for the control of fungi, nematodes, and other injurious organisms
- Use as a chemical intermediate in organic synthesis of dyes (methyl violet) and as an oxidizing agent
- Use as an additive to impart a warning odor to odorless fumigants and gases
- Restricted use as a rodenticide and pesticide
- Formerly, use as a tear gas and as a chemical warfare agent

The following methods are effective in controlling worker exposures to chloropicrin, depending on the feasibility of implementation:

- Process enclosure
- Local exhaust ventilation
- General dilution ventilation
- Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. *Industrial ventilation—a manual of recommended practice*. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. *Industrial ventilation—a self study companion*. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. *Design of industrial ventilation systems*. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. *Engineering design for control of workplace hazards*. New York, NY: McGraw-Hill.
5. Plog BA [1988]. *Fundamentals of industrial hygiene*. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and con-

trol work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chloropicrin, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system and skin. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloropicrin at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system and skin.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloropicrin exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloropicrin on the respiratory system or skin. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to

a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloropicrin.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne chloropicrin is made using a midget fritted glass bubbler containing 10 milliliters of isopropanol. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 120 liters is collected. Analysis is conducted by high performance liquid chromatography with an ultraviolet detector or by gas chromatography using an electron capture detector. The limit of detection for this procedure is not known. This method is described in the OSHA Laboratory In-House Methods File [1989].

PERSONAL HYGIENE

If chloropicrin contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 minutes, and then wash with soap and water.

Clothing contaminated with chloropicrin should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of chloropicrin, particularly its potential to cause severe eye and skin irritation.

A worker who handles chloropicrin should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chloropicrin is handled, processed, or stored.

STORAGE

Chloropicrin should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Containers of chloropicrin should be protected from physical damage or shock and should be stored separately from strong oxidizers and other incompatible materials. Because containers that formerly contained chloropicrin may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chloropicrin, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Ventilate atmosphere to reduce concentrations.
4. Water spray may be used to reduce vapors.
5. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
6. For large liquid spills, build dikes far ahead of the spill to contain the chloropicrin for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

• Emergency planning requirements

Chloropicrin is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

• Reportable quantity requirements for hazardous releases

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloropicrin; there is no reportable quantity for this substance.

• Community right-to-know requirements

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of chloropicrin emitted or released from their facility annually.

• Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although chloropicrin is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

• Conditions for respirator use

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloropicrin exceeds prescribed exposure limits. Respirators

may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and gauntlets) should be worn to prevent skin contact with chloropicrin. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. The following material has been recommended for use against permeation by chloropicrin and provides protection for periods greater than 8 hours: Responder. Teflon withstands permeation by chloropicrin for greater than 4 hr but less than 8 hr.

If chloropicrin is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chloropicrin might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within

the immediate work area whenever the potential exists for eye or skin contact with chloropicrin. Contact lenses should not be worn if the potential exists for chloropicrin exposure.

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