

Occupational Health Guideline for Chlorine 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: ClO_2
- Synonyms: None
- Appearance and odor: Yellow-green to orange gas or liquid with a pungent, sharp odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorine dioxide is 0.1 part of chlorine dioxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.3 milligram of chlorine dioxide per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

Chlorine 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

1. *Short-term Exposure:* Chlorine dioxide may cause irritation of the eyes, nose, throat, and lungs. It may produce coughing, wheezing, and severe breathing difficulties which may be delayed in onset.

2. *Long-term Exposure:* Repeated exposure to chlorine dioxide may cause chronic bronchitis.

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 chlorine dioxide.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to chlorine 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 system and eyes should be stressed.

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

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

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.

• Summary of toxicology

Chlorine dioxide gas is a severe respiratory and eye irritant. Delayed deaths occurred in animals after exposure to 150 to 200 ppm for less than 1 hour. Rats repeatedly exposed to 10 ppm died after 10 to 13 days of exposure; there was nasal and ocular discharge and dyspnea; autopsy revealed purulent bronchitis. Exposure of a worker to 19 ppm for an unspecified time period was fatal. Repeated acute exposure of workers to undetermined concentrations is stated to have caused eye and throat irritation, nasal discharge, cough, wheezing, bronchitis, and delayed onset of pulmonary edema. Repeated exposure may cause chronic bronchitis.

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

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 67.5
2. Boiling point (760 mm Hg): 11 C (52 F)
3. Specific gravity (water = 1): 1.6 (Liquid at boiling point)
4. Vapor density (air = 1 at boiling point of chlorine dioxide): 2.3
5. Melting point: -59 C (-74 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 0.8 (commercial solutions)
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: Temperatures above 130 C (266 F) cause rapid decomposition of gas. It will detonate if heated rapidly to 100 C (212 F).
2. Incompatibilities: Contact with dust and other combustible materials such as organic matter and sulfur may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine gas) may be released when chlorine dioxide decomposes.
4. Special precautions: Chlorine dioxide will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: Not applicable
2. Self-accelerating decomposition temperature: 130 C (266 F)
3. Explosive limits in air: Concentrations over 40 percent in air will sustain a decomposition wave set off by an electric spark. Gas is explosive at concentrations over 10 percent and can be ignited by almost any form of energy such as sunlight, heat, or sparks.
4. Extinguishant: None known

• Warning properties

1. Odor Threshold: May reports an odor threshold for chlorine dioxide of 0.1 ppm.
2. Eye Irritation Level: Grant states that "chlorine dioxide is a reddish yellow, poisonous gas which is very irritating to the respiratory tract. Industrially, men exposed to low concentrations of the gas in air have been noted occasionally to suffer from irritation of the eyes and to see haloes about lights, but these effects have been minor compared to respiratory irritation. The corneas of workers seeing haloes have not been examined to determine whether epithelial edema is present and responsible for this symptom." The *Documentation of TLVs* notes that "Elkins stated that a concentration of chlorine dioxide (ClO₂) of 5 ppm was definitely irritating."
3. Evaluation of Warning Properties: Since the odor threshold of chlorine dioxide is at the permissible exposure limit, this substance could be treated as a material with good warning properties.

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

At the time of publication of this guideline, no measurement method for chlorine dioxide had been published by NIOSH.

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 chlorine dioxide.
- Where there is any possibility of exposure of an employee's body to liquid chlorine 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 chlorine dioxide and any clothing which becomes wet with liquid chlorine dioxide should be removed immediately and not rework until the chlorine 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 chlorine dioxide contacting the eyes.

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

SANITATION

- Skin that becomes contaminated with chlorine dioxide should be immediately washed or showered with soap or mild detergent and water to remove any chlorine dioxide.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as bleaching agent for wood pulp and paper and textiles	Process enclosure; local exhaust ventilation; personal protective equipment
Use in water treatment to remove tastes and odors by oxidation; use in bleaching fats and oils, and to improve product, and leather dressing	Process enclosure; local exhaust ventilation; personal protective equipment
Use as bleaching and maturing agent in flour for baking; use as bleaching, cleaning, and unhairing agent in leather manufacture	Process enclosure; local exhaust ventilation; personal protective equipment
Use in chemical synthesis as oxidizing agent; use in control of microorganisms in fruit and vegetable processing as oxidizing agent; and as bacteria and algae control in aquariums and packaged pharmaceuticals	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 chlorine dioxide or strong concentrations of chlorine dioxide vapor 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 immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid chlorine dioxide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid chlorine dioxide penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation or burns are present after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chlorine 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**

If liquid chlorine dioxide has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the chlorine dioxide. Do not induce vomiting. 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 chlorine dioxide 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 the liquid form, evacuate persons not wearing protective equipment from spill area. Allow chlorine dioxide to evaporate while providing all available ventilation.

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RESPIRATORY PROTECTION FOR CHLORINE DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration 5 ppm or less	<p>A chemical cartridge respirator with a full facepiece and cartridge(s) containing non-combustible sorbents and providing protection against chlorine dioxide.</p> <p>A gas mask with a chin-style or a front- or back-mounted canister containing non-combustible sorbents and providing protection against chlorine dioxide.</p> <p>Any supplied-air respirator with a full facepiece, helmet, or hood.</p> <p>Any self-contained breathing apparatus with a full facepiece.</p>
10 ppm or less	<p>A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.</p>
Greater than 10 ppm or entry and escape from unknown concentrations	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p> <p>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.</p>
Fire Fighting	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p>
Escape	<p>Any gas mask containing non-combustible sorbents and providing protection against chlorine dioxide.</p> <p>Any escape self-contained breathing apparatus.</p>

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