Occupational Health Guideline for Chlorine Trifluoride

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: ClF3
• Synonyms: None
• Appearance and odor: Greenish-yellow, almost colorless liquid or gas with a sweet, but irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)
The current OSHA standard for chlorine trifluoride is a ceiling level of 0.1 part of chlorine trifluoride per million parts of air (ppm). This may also be expressed as 0.4 milligram of chlorine trifluoride per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION
• Routes of exposure
Chlorine trifluoride 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
Effects on humans from exposure to chlorine trifluoride have not been reported. Animal experiments have shown that exposure to this chemical can cause severe irritation of the eyes and respiratory tract. Severe breathing difficulties have occurred. These difficulties may sometimes be delayed in onset. Severe burns of the eyes and skin have been produced in animals from contact with this chemical.
• 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 trifluoride.
• Recommended medical surveillance
The following medical procedures should be made available to each employee who is exposed to chlorine trifluoride 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 should be stressed. The skin and eyes should be examined for evidence of chronic disorders.
     —14" x 17" chest roentgenogram: Chlorine trifluoride causes lung damage in animals. Surveillance of the lungs is indicated.
     —FVC and FEV (1 sec): Chlorine trifluoride is a severe pulmonary irritant in animals. 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 trifluoride gas is an extremely severe irritant of the eyes, respiratory tract, and skin. The injury caused by chlorine trifluoride can be extremely severe and, in part, attributed to its hydrolysis products including chlorine, hydrogen fluoride, and chlorine dioxide. Exposure of rats to 800 ppm for 15 minutes was fatal, but nearly all survived when exposed for 13 minutes. There was severe inflammation of all exposed mucosal surfaces, resulting in lacrimation, corneal ulceration, and burning of exposed areas of skin. In another study, exposure of rats to 480 ppm for 40 minutes or to 96 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.

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Centers for Disease Control
National Institute for Occupational Safety and Health

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

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for 3.7 hours was fatal; in the latter group, there were pulmonary edema and marked irritation of the bronchial mucosa. Effects in humans have not been reported, but exposure may cause some effects; inhalation may be expected to cause pulmonary edema, and contact with eyes or skin may cause severe burns.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data
  1. Molecular weight: 92.5
  2. Boiling point (760 mm Hg): 11.8°C (53°F)
  3. Specific gravity (water = 1): 1.88 (liquid)
  4. Vapor density (air = 1 at boiling point of chlorine trifluoride): 3.14
  5. Melting point: −76.3°C (−105°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): Violent reaction to form chlorine gas and hydrofluoric acid
  8. Evaporation rate (butyl acetate = 1): Not applicable

- Reactivity
  1. Conditions contributing to instability: Chlorine trifluoride decomposes above 220°C (428°F) and may explode container.
  2. Incompatibilities: Chlorine trifluoride will cause most combustible materials to ignite spontaneously. The exceptions are dry, highly fluorinated polymers such as “Teflon” and “Kel-F,” the metals used in storage containers (monel, copper, and stainless steel) or gaskets (teflon), nitrogen gas or air, and the inert gases (neon, etc.). Chlorine trifluoride reacts violently with water, sand, silicon-containing compounds, glass, and asbestos.
  3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine and hydrogen fluoride) may be released when chlorine trifluoride decomposes.
  4. Special precautions: Chlorine trifluoride will attack all forms of plastics, rubber, and resins, except the high fluorinated polymers “Teflon” and Kel-F.”

- Flammability
  1. Not combustible by itself, but is very reactive and may cause fire on contact with organic matter.

- Warning properties
  1. Odor Threshold: Deichmann and Gerarde note that chlorine trifluoride has a “somewhat sweet odor.” No quantitative information is available, however, concerning the odor threshold.
  2. Irritation Level: Grant states that “chlorine trifluoride is an extremely reactive, corrosive and irritating gas which experimentally has been observed to cause a severe reaction in the lungs and in all exposed mucous membranes. It is highly irritating to the skin and eyes, and has caused severe corneal ulcers in dogs.”
  3. Evaluation of Warning Properties: Since no quantitative data are available relating warning properties to air concentrations of chlorine trifluoride, this gas is treated as a material with poor warning properties. In addition, since chlorine trifluoride is a powerful oxidizer, it should not be allowed to contact combustible materials.

MONITORING AND MEASUREMENT PROCEDURES

- Ceiling Evaluation
  Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chlorine trifluoride. 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
  At the time of publication of this guideline, no measurement method for chlorine trifluoride 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 trifluoride.
  1. Where there is any possibility of exposure of an employee’s body to liquid chlorine trifluoride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
  2. Any clothing which becomes contaminated with chlorine trifluoride should be removed immediately and
not worn until the chlorine trifluoride 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 trifluoride contacting the eyes.
• Where there is any possibility that employees' eyes may be exposed to liquid chlorine trifluoride, an eyewash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

<table>
<thead>
<tr>
<th>Operation</th>
<th>Controls</th>
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</thead>
<tbody>
<tr>
<td>Use as a fluorinating agent in organic and inorganic chemical synthesis; use in the separation of uranium isomers</td>
<td>Process enclosure; local exhaust ventilation; personal protective equipment</td>
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<tr>
<td>Use as a cutting agent for well castings in oil well drilling</td>
<td>Process enclosure; local exhaust ventilation; personal protective equipment</td>
</tr>
<tr>
<td>Use as a rocket fuel oxidizer as an igniter and propellant in liquid propellant engines; use as an incendiary</td>
<td>Process enclosure; local exhaust ventilation; personal protective equipment</td>
</tr>
</tbody>
</table>

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 trifluoride or strong concentrations of chlorine trifluoride 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 chlorine trifluoride or strong concentrations of chlorine trifluoride vapor get on the skin, immediately flush the contaminated skin with large quantities of water. If liquid chlorine trifluoride or strong concentrations of chlorine trifluoride vapor penetrate through the clothing, remove the clothing immediately and flush the skin with large amounts of water. Get medical attention immediately.
• Breathing
  If a person breathes in large amounts of chlorine trifluoride, 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 trifluoride has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the chlorine trifluoride. 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 trifluoride is spilled or leaked, the following steps should be taken:
  1. Ventilate area of spill or leak.
  2. 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.
  3. If in the liquid form, evacuate persons not wearing protective equipment from spill area. Allow chlorine trifluoride to evaporate while providing all available ventilation.

REFERENCES

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

### RESPIRATORY PROTECTION FOR CHLORINE TRIFLUORIDE

<table>
<thead>
<tr>
<th>Condition</th>
<th>Minimum Respiratory Protection* Required Above 0.1 ppm</th>
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<tr>
<td>Gas Concentration</td>
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<tr>
<td>5 ppm or less</td>
<td>Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.</td>
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<tr>
<td>20 ppm or less</td>
<td>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.</td>
</tr>
<tr>
<td>Greater than 20 ppm** or entry and escape from unknown concentrations</td>
<td>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</td>
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<tr>
<td></td>
<td>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.</td>
</tr>
<tr>
<td>Fire Fighting</td>
<td>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</td>
</tr>
<tr>
<td>Escape</td>
<td>A gas mask containing non-combustible sorbents and providing protection against chlorine trifluoride. Any escape self-contained breathing apparatus.</td>
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*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 chlorine trifluoride; 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 20 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.