

Occupational Health Guideline for Perchloryl Fluoride

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_2F
- Synonyms: None
- Appearance and odor: Colorless gas with a characteristic sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for perchloryl fluoride is 3 parts of perchloryl fluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 13.5 milligrams of perchloryl fluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

Perchloryl fluoride can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

• Effects of overexposure

Perchloryl fluoride may cause respiratory irritation. The liquid, if allowed to remain in contact with the skin, may cause a burn. Animal exposures have produced severe breathing difficulties which have sometimes been delayed in onset. Also in animals, perchloryl fluoride can affect the ability of the blood to carry oxygen by forming methemoglobin. In man, methemoglobin formation may cause a bluish discoloration of the skin, drowsiness, dizziness, rapid heart beat, nausea, headache, 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 perchloryl fluoride.

• Recommended medical surveillance

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

—A complete blood count: Perchloryl fluoride has been shown to cause methemoglobinemia in animals. 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.

—14" x 17" chest roentgenogram: Perchloryl fluoride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Perchloryl fluoride 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 other signs and symptoms of respiratory disease occur. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

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

• Summary of toxicology

Perchloryl fluoride gas is a respiratory irritant in humans and in animals causes the formation of methemoglobin. Dogs exposed to 450 ppm or 620 ppm for 4 hours developed hyperpnea, cyanosis, incoordination, and convulsions; methemoglobin levels were 29% and 71%, respectively. In dogs which died from exposure, there was lung damage consisting of alveolar collapse and hemorrhage; pigment deposition in the liver, spleen, and bone marrow was observed. Repeated exposure of three species of animals to 185 ppm for 7 weeks caused the death of more than half of them, guinea pigs being the most susceptible; all of the animals developed dyspnea, cyanosis, methemoglobinemia, alveolar edema, and pneumonitis. With similar repeated exposure of animals to 104 ppm for 6 weeks, the fluoride levels were increased by a factor of 20 to 30 in the blood, 5 to 8 in the urine, and 12 in the rat femur. One report states that workers suffered symptoms of upper respiratory irritation from brief exposure to unspecified concentrations. Perchloryl fluoride has the potential to form methemoglobin in man; the effects of methemoglobinemia are due to anoxia and include cyanosis, evident especially in the lips, nose, and earlobes; other effects are weakness, dizziness, and severe headache. The liquid is reported to produce moderately severe burns with prolonged skin contact.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 102.5
2. Boiling point (760 mm Hg): -46.7 C (-52 F)
3. Specific gravity (water = 1): 1.41 (liquid at 25 C)
4. Vapor density (air = 1 at boiling point of perchloryl fluoride): 3.5
5. Melting point: -146 C (-231 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): 0.06
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: Containers may explode when heated above 500 C (932 F).
2. Incompatibilities: Contact with combustible materials, strong bases, amines, and finely divided metals may cause fires and explosions. Contact with readily oxidizable materials such as hydrogen sulfide, charcoal, sawdust, lampblack, etc. yields explosive products.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride and chlorine) may be released when perchloryl fluoride decomposes.
4. Special precautions: Perchloryl fluoride will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Not combustible by itself, but is a strong oxidizing agent

2. See 29 CFR 1910.101 for special regulations on storage of compressed gas cylinders.

• Warning properties

1. Odor Threshold: Sax states that the odor of perchloryl fluoride "can be detected as low as 10 ppm, although this cannot be relied upon as an indication of toxic concentrations in air."

2. Eye Irritation Level: Grant states that in industry "irritation of the eyes and nose has been reported when fluoride concentration has reached 5 mg/m³ of air." Perchloryl fluoride is not specifically known to be an eye irritant.

3. Evaluation of Warning Properties: Since Sax notes that the odor "cannot be relied upon as an indication of toxic concentrations in air," and since there is no other quantitative information relating warning properties to air concentrations of perchloryl fluoride, this substance is treated like a material with poor 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 perchloryl fluoride 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 the skin from becoming frozen from contact with liquid perchloryl fluoride or vessels containing liquid perchloryl fluoride.
- Non-impervious clothing which becomes contaminated with liquid perchloryl fluoride should be removed immediately and not reworn until the perchloryl fluoride has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid perchloryl fluoride may contact the eyes.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as a liquid oxidizer in rocket fuels, fuels used in cutting and welding, torches and chemical machinery	Process enclosure or adequate safety shields; local exhaust ventilation; personal protective equipment
Use in chemical synthesis in oxidation, ammonolysis, fluorination, perchlorylation, and etherification	Process enclosure or adequate safety shields; local exhaust ventilation; personal protective equipment
Use in flame photometry for analysis of different elements; miscellaneous uses for manufacture of fuel cells, gaseous dielectric for transformers, explosives, and metal processing	Process enclosure or adequate safety shields; 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.

• Skin Exposure

If liquid perchloryl fluoride gets on the skin, immediately flush the perchloryl fluoride from the contaminated skin. If liquid perchloryl fluoride penetrates through the clothing, remove the clothing immediately and flush the skin with water. If irritation or burns are present after washing, get medical attention.

• Breathing

If a person breathes in large amounts of perchloryl fluoride, 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.

• 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.

LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If perchloryl fluoride is leaked, the following steps should be taken:
 1. Ventilate area of leak to disperse gas.
 2. 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.

REFERENCES

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RESPIRATORY PROTECTION FOR PERCHLORYL FLUORIDE

Condition	Minimum Respiratory Protection* Required Above 3 ppm
Vapor Concentration	
30 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
150 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
400 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode and containing non-combustible sorbents.
Greater than 400 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-combustible sorbents and providing protection against perchloryl fluoride. Any escape self-contained breathing apparatus.

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