

Occupational Health Guideline for Fluorine

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: F_2
- Synonyms: None
- Appearance and odor: Pale yellow gas.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for fluorine is 0.1 part of fluorine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.2 milligram of fluorine per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for fluorine a Threshold Limit Value of 1 ppm.

HEALTH HAZARD INFORMATION

• Routes of exposure

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

• Effects of overexposure

Exposure to fluorine gas may cause irritation of the eyes, nose, throat, lungs, and skin. It may cause severe breathing difficulties which may be delayed in onset. At high concentrations, as when coming directly from a gas cylinder, fluorine may cause severe burns of the eyes and skin. In animal experiments, exposure to fluorine has produced kidney and liver damage.

• 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 fluorine.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to fluorine 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 eyes, respiratory tract, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

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

—FVC and FEC (1 sec): Fluorine 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 by signs and symptoms of respiratory disease.

• Summary of toxicology

Fluorine gas is a severe irritant of the eyes, mucous membranes, and skin. It reacts with water to produce ozone and hydrofluoric acid. The LC50 in mice for 60 minutes was 150 ppm; effects were irritation of the eyes and nose and the delayed onset of dyspnea and lethargy; autopsy findings included marked pulmonary congestion and hemorrhage. Mice exposed to sublethal concentrations had pulmonary irritation and delayed development of focal necrosis in the liver and kidneys. In humans the inhalation of high concentrations causes laryngeal spasm and bronchospasm, followed by the delayed onset of pulmonary edema; there may also be

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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gastrointestinal disturbances. Two human subjects found momentary exposure to 50 ppm intolerable; 25 ppm was tolerated briefly, but both subjects developed sore throat and chest pain which persisted for 6 hours. A blast of fluorine gas on the shaved skin of a rabbit caused a second-degree burn; lower concentrations cause severe burns of insidious onset resulting in ulceration, similar to those produced by hydrogen fluoride.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 38
2. Boiling point (760 mm Hg): $-188\text{ C } (-307\text{ F})$
3. Specific gravity (water = 1): (Liquid) 1.5 at boiling point
4. Vapor density (air = 1 at boiling point of fluorine): 1.3
5. Melting point: $-219\text{ C } (-363\text{ F})$
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):

Reacts

8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: Elevated temperatures may cause cylinders to burst.
2. Incompatibilities: Fluorine is a dangerously reactive gas. Contact with water causes formation of toxic hydrogen fluoride gas. It reacts vigorously with most oxidizable materials at room temperature, frequently with ignition. It reacts with nitric acid to form fluorine nitrate, which is an explosive gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride) may be released when fluorine decomposes.
4. Special precautions: Fluorine will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Not combustible, but strong oxidizer.
2. Compressed gas cylinders containing fluorine should be stored in accordance with 29 CFR 1910.101.

• Warning properties

1. Odor Threshold: The *Hygienic Information Guide* for fluorine of the Commonwealth of Pennsylvania Division of Occupational Health states that fluorine "can be detected by odor in concentrations of only a few parts per million." Deichmann and Gerarde note that the odor is "sharp, penetrating, and characteristic."
2. Eye Irritation Level: Grant states that "exposure of human volunteers to fluorine in air showed that, although it caused very little irritation up to 25 ppm, it caused much irritation of the eyes and nose at 100 ppm. However, there were no aftereffects from exposure of the eyes to 100 ppm for one-half minute. Contact with high concentrations of fluorine gas or liquefied fluorine would presumably be extremely destructive."
3. Evaluation of Warning Properties: Since the odor

and irritation thresholds are not within three times the permissible exposure limit, fluorine is treated as 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 fluorine 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 fluorine, and to prevent skin from becoming frozen from contact with vessels containing liquid fluorine.
- Where there is any possibility of exposure of an employee's body to liquid fluorine, 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 liquid fluorine should be removed immedi-

ately and not reworn until the fluorine 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 fluorine contacting the eyes.

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

SANITATION

- Skin that becomes contaminated with liquid fluorine should be immediately washed or showered to remove any fluorine.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use during organic and inorganic synthesis in the production of fluorine compounds, refrigerants, plastics, incendiary devices, and electrolytic solvents	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a rocket fuel oxidizer for ammonia, hydrazine, hydrogen, JP-4, and diborane fuels at laboratories and test sites	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 fluorine or high concentrations of fluorine gas 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 fluorine or high concentrations of fluorine gas get on the skin, immediately flush the contaminated skin with water. If liquid fluorine or high concentrations of fluorine gas penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• Breathing

If a person breathes in large amounts of fluorine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affect-

ed 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 fluorine 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.

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RESPIRATORY PROTECTION FOR FLUORINE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
1 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
25 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 25 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-oxidizable sorbents and providing protection against fluorine. Any escape self-contained breathing apparatus.

*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 fluorine; 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 25 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.