Safetygram #39
Chlorine Trifluoride

Introduction
Chlorine trifluoride (ClF$_3$) is a toxic, corrosive, very reactive liquefied compressed gas packaged in cylinders as a liquid under its own vapor pressure of 1.55 kg/cm$^2$ at 21°C (22 psia at 70°F). ClF$_3$ is a very useful chemical in operations requiring a high-energy fluorinating agent or incendiary material, especially since it can be handled at room temperatures. However, those same factors that make it quite useful also contribute to several high hazard potentials for the product.

Air Products has been the primary manufacturer and distributor of ClF$_3$ in North America for the past 35 years, and the compound represents one of the highest-reactivity products that Air Products currently manufactures or handles worldwide.

Lessons from History
Fluorine (F$_2$) has been recognized as the most powerful oxidizing agent of all known elements. Due to difficulties handling F$_2$ in its most reactive state (liquid), substitutes were evaluated in the late 1920s to find similarly reactive compounds with easier handling. Ruff and Krug successfully isolated ClF$_3$ in 1930 after experimental tests with chlorine monofluoride suggested the presence of a higher fluoride species. Liquid ClF$_3$, is considered more reactive than vapor-phase F$_2$ reactions since more moles of fluorinating agent are present per unit area of reactant surfaces. Also, liquid ClF$_3$ may demonstrate even higher reactivity in certain circumstances than liquid F$_2$ because the F$_2$ liquid temperature is cryogenic, thus reducing its activity potential.

German interest in ClF$_3$ during World War II prompted the first industrial bulk production capability for the material. The Germans produced ClF$_3$ in tonnage quantities for military use in flamethrowers due the liquid’s extreme hypergolic nature with fuels (self-igniting) and as a general incendiary material. Following the war, interest in the use of ClF$_3$ for organic synthesis work increased although the material was eventually considered to be too reactive for practical use and mostly abandoned for these applications. Synthesis reactions proved difficult to control and usually led to a wide variety of reaction by-products that were hazardous.

Many fluorinating compounds were evaluated as potent oxidizers for liquid-fueled rockets in the late 1940s through the early 1950s to overcome the storage and handling disadvantages of liquid F$_2$. ClF$_3$ was first tested in the U.S. in 1948 on a liquid propellant rocket motor using hydrazine as the fuel. Additional testing yielded favorable results. However, all rocket materials of construction (including metals and seals) that could contact ClF$_3$ had to be scrupulously selected, cleaned, and passivated to prevent the components from burning during reaction. ClF$_3$ was also recognized as an extremely hazardous propellant due to its reactivity, toxicity, and toxic by-products of fluorination.

During the liquid rocket propellant era, a major incident involving ClF$_3$ occurred the first time a one-ton steel container was loaded with liquid ClF$_3$ for bulk shipment. The container had been cooled with dry ice to perform the liquid transfer and help make the product safer to handle, since the ClF$_3$ vapor pressure would only be about 0.007 kg/cm$^2$ (0.1 psia) in the subcooled state. However, the dry ice bath embrittled the steel container wall, which split while it was being maneuvered onto a dolly, instantaneously releasing 907 kg (2,000 lb) of cold ClF$_3$ liquid onto the building floor. The ClF$_3$ dissolved the 30 cm (12 inch) thick concrete floor and another 90 cm (36 inches) of gravel underneath the spill. The fumes that were generated (chlorine trifluoride, hydrogen fluoride, chlorine, hydrogen chloride, etc.) severely corroded everything that was exposed. One eyewitness described the incident by stating, “The concrete was on fire!”

Warning: Improper storage, handling or use of chlorine trifluoride can result in serious injury and/or property damage. Use this product in accordance with the Air Products Material Safety Data Sheet (MSDS).
In the 1990s the semiconductor industry began using ClF₃ in the cleaning process for certain chemical vapor deposition (CVD) tool chambers. In situ cleaning of the tool was desirable because the solid residues on the chamber interior were removed from the walls without dismantling the tool or risking personnel exposure to the hazardous residues or cleaning agents. It also yielded quicker turnaround time for the tool to resume wafer processing. The high reactivity of ClF₃ allowed the operation to be accomplished at relatively low temperatures, without requiring plasma or high temperature heating to dissociate it for use during the cleaning process. The use of vapor-phase ClF₃ for CVD chamber cleaning has demonstrated the ability to prolong chamber component life through the lack of high temperature, plasma use, and tool dismantling requirements.

Because the use of ClF₃ in semiconductor applications had increased due to its excellent performance in tool chamber cleaning, Air Products decided to empirically test the reactivity of ClF₃ with materials of construction, personal protective equipment, contaminants commonly found in systems and equipment, and other materials that may come into contact with the product. This Safetygram discusses the results of these tests and provides current recommendations to those who are manufacturing, handling, and performing emergency response with chlorine trifluoride.

### Safety Considerations

#### Health

Chlorine trifluoride is toxic by itself and also reacts with moisture to form a variety of other toxic and corrosive materials, including hydrofluoric acid. When the product escapes into the environment, it hydrolyzes with the moisture in the air or, in the case of human contact, with the moisture in the human body. Direct contact with ClF₃ vapor or liquid can result in a thermal burn in addition to the chemical burns produced by the hydrolysis products. See Figure 1 to see the result of direct product contact with a piece of raw chicken being used to simulate flesh.

Since hydrogen fluoride is the major product of hydrolysis, the health hazards associated with hydrofluoric acid (HF) can be considered as primary health hazards for ClF₃. Medical treatment for hydrofluoric acid exposures is very specialized. Air Products’ Safetygram-29, “Treatment Protocol for Hydrofluoric Acid Burns,” provides detailed information on the health effects and treatment for HF. All users of ClF₃ should use copies of this Safetygram to educate their employees, emergency people and local medical providers so they may know in advance what is required to address these exposures in the way of supplies and treatment. It should be noted that hydrofluoric acid exposure requires immediate specific and specialized medical treatment. Not only can this strong acid cause burns, but also the fluoride ion can be quickly absorbed through the skin, attack underlying tissues, and be absorbed into the bloodstream. If inhaled in high concentrations, HF can cause obstruction of the airway and acute pulmonary edema.

Table 2 gives the exposure levels for chlorine trifluoride and hydrogen fluoride.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical and Chemical Properties</strong></td>
</tr>
<tr>
<td>Molecular Weight</td>
</tr>
<tr>
<td>Boiling Point (1 atm)</td>
</tr>
<tr>
<td>Melting Point</td>
</tr>
<tr>
<td>Gas Density (21.1°C)</td>
</tr>
<tr>
<td>Specific Volume (21.1°C)</td>
</tr>
<tr>
<td>Specific Gravity (air = 1)</td>
</tr>
<tr>
<td>Vapor Pressure (21.1°C)</td>
</tr>
<tr>
<td>Critical Temperature</td>
</tr>
<tr>
<td>Critical Pressure</td>
</tr>
<tr>
<td>Appearance</td>
</tr>
</tbody>
</table>

Odor varies with hydrolysis products; low concentrations are described as bleach-like while higher concentrations are described as acidic or suffocating.

#### Reactivity

Chlorine trifluoride is hypergolic (will initiate the combustion of many materials without an ignition source) with many materials. It is extremely reactive with most inorganic and organic materials. These reactions can be very violent or in some cases explosive. Therefore, all materials that come into contact with chlorine trifluoride must be evaluated.

#### Hydrolysis

Chlorine trifluoride hydrolyzes rapidly with moisture to form mostly hydrogen fluoride along with hydrogen chloride, chlorine monofluoride, and a variety of oxyhalogen compounds. The oxyhalogens may include chlorine dioxide, chlorous acid, chlorine oxyfluoride and oxygen difluoride.
### Table 2

**Exposure Levels for Chlorine Trifluoride**

<table>
<thead>
<tr>
<th>Classification</th>
<th>10-min</th>
<th>30-min</th>
<th>1-hour</th>
<th>4-hour</th>
<th>8-hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC$_{(50)}$</td>
<td>299 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OSHA PEL</td>
<td></td>
<td>0.1 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACGIH TLV</td>
<td></td>
<td>0.1 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NIOSH IDLH</td>
<td></td>
<td>20 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AIHA ERPGs</td>
<td>ERPG-1 = 0.1 ppm</td>
<td>ERPG-2 = 1 ppm</td>
<td>ERPG-3 = 10 ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Proposed AEGL Values for Chlorine Trifluoride**

<table>
<thead>
<tr>
<th>Classification</th>
<th>10-min</th>
<th>30-min</th>
<th>1-hour</th>
<th>4-hour</th>
<th>8-hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEGL-1</td>
<td>0.7 ppm</td>
<td>0.7 ppm</td>
<td>0.35 ppm</td>
<td>0.09 ppm</td>
<td>0.04 ppm</td>
</tr>
<tr>
<td>AEGL-2</td>
<td>6.2 ppm</td>
<td>6.2 ppm</td>
<td>3.1 ppm</td>
<td>0.77 ppm</td>
<td>0.39 ppm</td>
</tr>
<tr>
<td>AEGL-3</td>
<td>81 ppm</td>
<td>27 ppm</td>
<td>14 ppm</td>
<td>3.4 ppm</td>
<td>1.7 ppm</td>
</tr>
</tbody>
</table>

**Exposure Levels for Hydrogen Fluoride**

<table>
<thead>
<tr>
<th>Classification</th>
<th>10-min</th>
<th>30-min</th>
<th>1-hour</th>
<th>4-hour</th>
<th>8-hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC$_{(50)}$</td>
<td>966 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OSHA PEL</td>
<td></td>
<td>3 ppm TWA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACGIH TLV</td>
<td></td>
<td>3 ppm Ceiling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NIOSH IDLH</td>
<td></td>
<td>30 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Proposed AEGL Values for Hydrogen Fluoride**

<table>
<thead>
<tr>
<th>Classification</th>
<th>10-min</th>
<th>30-min</th>
<th>1-hour</th>
<th>4-hour</th>
<th>8-hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEGL-1</td>
<td>2 ppm</td>
<td>2 ppm</td>
<td>2 ppm</td>
<td>1 ppm</td>
<td>1 ppm</td>
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<tr>
<td>AEGL-2</td>
<td>95 ppm</td>
<td>34 ppm</td>
<td>24 ppm</td>
<td>12 ppm</td>
<td>8.6 ppm</td>
</tr>
<tr>
<td>AEGL-3</td>
<td>170 ppm</td>
<td>62 ppm</td>
<td>44 ppm</td>
<td>22 ppm</td>
<td>15 ppm</td>
</tr>
</tbody>
</table>

**Figure 2**

*Vapor ClF$_3$ Exposure to Polyethylene Tubing, Clean and Used*
**Valves and Connections**

**Valves**

Containers in chlorine trifluoride service are equipped with one of several different valves. CP Grade cylinders are valved with an aluminum silica bronze wrench-operated valve while Electronic Grade cylinders are equipped with either a Monel spring-loaded diaphragm valve or a stainless steel pneumatic diaphragm valve designed specifically for chlorine trifluoride service. Cutaway drawings and valve details are available in the Air Products Safetygram-23, “Cylinder Valves,” for the wrench-operated valve. The spring-loaded diaphragm and pneumatic diaphragm valves are of unique designs. Cutaway pictures of these valves appear in Figures 3 and 4.

**Valve Connections**

Valve connections for chlorine trifluoride vary by country. Table 3 lists some of the connection standards used in various countries.

For more information on cylinder valve connections, refer to Air Products’ Safetygram-31, “Cylinder Valve Outlet Connections.”

**Cylinder Storage and Handling**

Cylinders of chlorine trifluoride and other compressed gases should be stored and handled in accordance with Compressed Gas Association Pamphlet P-1, “Safe Handling of Compressed Gases in Containers.” For more information, refer to Air Products’ Safetygram-10, “Handling, Storage, and Use of Compressed Gas Cylinders.”

International or local regulations may require additional safeguards for storage or use. Personnel must know and understand the properties, proper uses, and safety precautions for the specific product before using the product or associated equipment.

**Storage**

Cylinders should be secured in an upright position and stored in a well-ventilated area protected from the weather. The storage area should be secure with limited access. The toxicity, reactivity and corrosivity of ClF₃ requires area monitoring for leakage where the material is stored and used. Storage area temperatures should not exceed 125°F (52°C) and should be free from combustible materials and ignition sources. Storage should be away from heavily traveled areas and emergency exits. Avoid areas where salt or other corrosive materials are present to prevent cylinder deterioration. Valve protection caps and valve outlet seals must remain on cylinders when not connected for use. When returning a cylinder to storage, the valve outlet seal must be installed leak-tight. Separate

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**Table 3**

<table>
<thead>
<tr>
<th>Country</th>
<th>Valve Connection</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>CGA 670 728 Ultra High Integrity (DISS) Connection has been adopted by ISO.</td>
</tr>
<tr>
<td>UK</td>
<td>BS 6</td>
</tr>
<tr>
<td>France</td>
<td>NF P</td>
</tr>
<tr>
<td>Japan</td>
<td>JIS A (22 R)</td>
</tr>
</tbody>
</table>
full and empty cylinders. Avoid excess inventory and storage time. Visually inspect stored cylinders on a routine basis, at least weekly, for any indication of leakage or other problems. Use a first-in, first-out inventory system, and keep up to date inventory records. The use of “FULL,” “IN USE,” and “EMPTY” tags is highly recommended. Some locales require special planning when storage of ClF₃ exceeds a specific amount. Before purchasing ClF₃, contact the local authorities to determine the requirements for the storage of this material. ClF₃ is typically stored in areas specifically designed for ClF₃. Storage areas must be posted with the proper signage, such as NFPA 704 ratings.

**Handling and Use**

Use only in well-ventilated areas designated for ClF₃. Use a suitable handcart designed for cylinder movement. Do not drag, roll or slide cylinders. Never attempt to lift a cylinder by its cap. Secure cylinders at all times during storage, transport and use. Use a pressure-reducing regulator or separate control valve to discharge gas from the cylinder. Never apply flame or local heat to any part of a cylinder. Do not allow any part of the cylinder to exceed 125°F (52°C). High temperature may cause damage to the cylinder. If user experiences any difficulty operating the cylinder valve, discontinue use and contact the supplier. Use an adjustable strap wrench to remove overly tight cylinder caps. To prevent accidental opening of the cylinder valve, never insert anything into the cap holes to assist in cap removal.

Ensure that the cylinder valve is properly closed, the valve outlet seal has been reinstalled leak-tight, and the valve protection cap is installed before returning to storage, moving or shipping the cylinder.

**Disposal**

Return unused product to the supplier for proper disposal. In process applications, gaseous chlorine trifluoride can be disposed of in either liquid or dry scrubbers. Dry scrubbers work well under normal operating conditions for small quantities of ClF₃ but are not recommended for large or emergency releases unless specifically designed. Scrubbers must be designed to withstand the heat generated in the event of a large release. For normal operation, it is recommended an inert gas be used as a diluent prior to product being introduced to scrubber. This will help disperse the heat of reaction. Wet scrubbers typically use caustic solutions, such as potassium or sodium hydroxide, as the scrubbing medium. Wet scrubbers handle the heat of reaction better, as well as neutralize the products of reaction. Disposal of liquid chlorine trifluoride is extremely hazardous and is not recommended.

**System Design, Preparation and Operation**

Chlorine trifluoride is a strongly oxidizing, toxic, corrosive liquefied gas at typical storage temperatures. It is normally packaged in specially cleaned and prepared carbon steel or stainless steel cylinders and is used as a vapor to limit its potential reactivity with system components and other materials. Unless special precautions are taken, ClF₃ should only be removed from cylinders as a vapor. Care must be taken to prevent its condensation in piping or other equipment.

**Materials of Construction**

**Metals**

Most metals are compatible with chlorine trifluoride at ambient pressure and temperatures, provided the metal is oxygen-cleaned and passivated prior to exposure. Passivation allows the formation of a thin metal fluoride surface that is resistant to further reaction with ClF₃, and more importantly, allows a controlled reaction with any remaining contaminants left behind by imperfect cleaning. It is this protective metal fluoride layer that helps determine a metal’s suitability for ClF₃ service. Some metals, such as molybdenum, titanium and tungsten, form fluorides that are relatively volatile. This makes these metals unsuitable for service with this product because the metal fluoride gradually volatilizes off the surface, exposing new metal to the gas. This results in excessive erosion of the metal.

Carbon steel, copper and stainless steel are acceptable at ambient temperatures. Brass is rapidly dezincified by hydrogen fluoride; therefore any moisture contamination or leak of product to the atmosphere will form hydrogen fluoride and rapidly attack the brass. If the potential for elevated temperatures exist, Monel and nickel are the metals of choice. Material selection becomes more critical in systems using ClF₃ in the liquid phase, as more oxidizer is available to contribute to a reaction.

**Elastomers**

Only fluorinated elastomers should be used in chlorine trifluoride systems, and only if a metal cannot be substituted. Cleanliness of these materials is critical, as any contamination can quickly compromise the material. It is recommended that elastomers not be used in service where they will be exposed to the liquid phase, since even these elastomers may deteriorate rapidly and possibly ignite at elevated temperature (130°C). Elastomers are more difficult to clean for oxidizer service because they can absorb the solvents or detergents used to clean them; therefore, all elastomers should be degassed after cleaning in a vacuum oven.

Most non-fluorinated elastomers show little or no resistance to ClF₃. Others like Neoprene™, rubber, polyethylene and PVC have shown resistance during short exposures but are very susceptible to any contamination—the reaction of ClF₃ with the contaminant rapidly propagates to the elastomer.

**Sealants and Lubricants**

TFE tape is the most common sealant used on threaded connections in chlorine trifluoride service. It is important when assembling these connections not to expose the tape directly to the flow path. To avoid this, it is recommended the first thread be left uncovered.

Lubricants of any kind should be avoided, if possible. If a lubricant must be used, a perfluorinated type specially manufactured for use with fluorine products is required. Hydrocarbon-based lubricants must never be used in chlorine trifluoride service, and even approved perfluorinated lubricants must never be exposed to liquid ClF₃.

**System Preparation**

Due to the potential for ignition, systems used for chlorine trifluoride must be very carefully cleaned to remove readily oxidized impurities and scrupulously maintained to prevent contamination. Cleaning agents must be thoroughly removed prior to introducing ClF₃ into systems (normally by extensive purging with high-purity nitrogen or other inert gas), as these agents can also become fuels in the presence of ClF₃. Heating of system components during purging should be considered to ensure removal of low-volatility cleaning agents.

To minimize potential problems, users should avoid excessive use of mechanical connections (to limit potential leakage sites) and elastomers (to limit potential reactivity and contamination) in ClF₃ systems. Similarly, system valves incorporating metal seats should be used if possible to reduce the chance of ignition of elastomer seats. Chlorine trifluoride systems should be passivated before use with increasing concentrations of ClF₃, fluorine, or a fluorine mixture. The system should be observed during passivation for unexpected overheating of any components that would indicate excessive reaction with the components.

**System Operations**

Employees working with ClF₃ should be specially trained to ensure they understand the system requirements and the physical and exposure hazards of ClF₃ and its reaction products. Chlorine trifluoride systems must be kept dry to minimize corrosion and contamination from acids that will form on contact of ClF₃ with moisture.
When not in use, equipment should be depressurized and purged with dry inert gas. For extended out-of-service periods, equipment should be kept sealed under positive pressure with dry inert gas.

As with any hazardous gas cylinder, operators should confirm the cylinder valve is firmly closed before loosening the valve outlet seal to connect a cylinder to the system. The outlet seal should be loosened slowly to limit the release rate of any ClF₃ that may have leaked into the valve outlet. The same procedure should be used to disconnect the cylinder from the system, and the pigtails must be vented and purged thoroughly before loosening the connection.

When connecting new ClF₃ cylinders, care is needed to prevent contamination of the valve outlet connection, especially if a gasketed connection is used. New gaskets must be thoroughly degreased and dried prior to installation unless specially cleaned and packaged gaskets are used directly from the manufacturer. New cleanroom gloves or equally clean alternatives should be used to install replacement gaskets. Similar precautions must be taken when changing other system components to avoid introduction of easily ignited contaminants.

When ClF₃ supply cylinders are initially opened, the operator should always be prepared to quickly reclose the valve should any evidence of reaction, overheating, or leaks develop. If any uncertainty exists about the cleanliness of system components, the cylinder valve should only be opened to introduce a minimal amount of ClF₃ vapor and then immediately closed. This will limit the amount of ClF₃ available to sustain ignition if a problem develops.

It is very important that chlorine trifluoride system pressures be kept well below the ClF₃ vapor pressure at the temperature of the coolest component in the process. This will prevent the condensation of the ClF₃ vapors in the system (see Figure 5). This is primarily to avoid the heightened reactivity of liquid-phase ClF₃ in the system and to allow proper flow control. Use of an absolute pressure regulator is recommended whenever possible to control system pressure below the ClF₃ condensation pressure.

With its relatively high boiling point, chlorine trifluoride vapor pressure is low at typical use temperatures, which can result in unacceptable low system pressure and flow rates, especially from cylinders with little remaining inventory. If the supply cylinder is heated to permit higher flows, it is even more critical to protect against condensation in cooler downstream components. System heating can also be considered to prevent condensation; maintaining uniform heating throughout the system can be difficult.

Prior to any maintenance, including supply cylinder changes, special care must be taken to ensure no hazardous quantity of ClF₃ remains in the equipment. Thorough purging with inert gas should always be done after the ClF₃ cylinder valve is firmly closed. If there is any suspicion of condensed ClF₃ in the system, the process should be heated and (ideally) evacuated to confirm no ClF₃ remains before the system is opened.

**National and Regional Code Requirements**

ClF₃ is a challenging material to properly manage from a code compliance and usage standpoint. This is because ClF₃ possesses both physical hazards (very strong oxidizer and very reactive) and health hazards (toxic and corrosive). The physical hazards of ClF₃ often cause local authorities to require the source containers be positioned remotely from the consumer’s main facility or occupants. However, the low vapor pressure of the product at room temperature provides challenges to distribute the vapor any significant distance.

ClF₃ is classified as a “Hazardous Production Material” (HPM) per regional Code definition based on its NFPA 704 ratings (Figure 6).

An HPM is a solid, liquid, or gas associated with semiconductor manufacturing that has a degree of hazard rating in health, flammability, or reactivity of Class 3 or 4 as ranked by NFPA criteria. Also, an HPM requires that the material be used directly in research, laboratory, or production processes that have as their end product materials that are not hazardous (e.g., integrated circuits).

The physical hazards of ClF₃ often result in the local code authority establishment of low threshold or exempt quantities for the material. However, proper facilitation and usage of ClF₃ does provide a safe supply and distribution system if the hazards and code requirements are adequately addressed. One method to effectively manage ClF₃ hazards is through the use of properly designed and facilitated gas cabinets that are specially engineered to house ClF₃ cylinders and distribution control piping and components.

**Gas Cabinet Supply Safety Considerations**

When chlorine trifluoride is used in microelectronics facilities, consideration should be given to the following gas cabinet system design elements:

- Automatic sprinkler protection is not recommended for ClF₃ gas cabinets due to the potential for violent reaction with leaking ClF₃ (supported in 1997 by a major industrial insurance company’s specific recommendations regarding ClF₃ gas cabinets for the semiconductor industry).

- Pneumatically operated cylinder valves should be considered to allow automatic and immediate supply shutdown should there be a downstream incident.

### Figure 5

**Vapor Pressure of Chlorine Trifluoride**

![Vapor Pressure of Chlorine Trifluoride](image)

### Figure 6

**NFPA Hazard Diamond for Chlorine Trifluoride**

![NFPA Hazard Diamond for Chlorine Trifluoride](image)
A gas detector should be located in the cabinet to monitor and cause an automatic shutdown alarm on either hydrogen fluoride or chlorine dioxide indication.

A heat or smoke detector should be located in the gas cabinet to monitor and cause an automatic shutdown alarm on an internal or external fire condition.

The delivery pipe or tubing should be coaxial (double contained) with a monitoring alarm for loss of primary containment.

**Personal Protective Equipment (PPE)**

**General Rules**

Because PPE may be compromised by the presence of dirt or water, PPE used in normal operations must be clean and free of contamination. In emergency situations where the product is leaking and response time is critical, the PPE must be as clean as possible to prevent reaction with the product. Therefore, only new gloves and acid-splash suits or totally encapsulating suits should be used in emergency situations to minimize the chance of reaction of the product contaminants on PPE. Because the possibility of a reaction exists and the external PPE may melt if exposed to heat, natural fiber clothing should be worn under the PPE to minimize any melted material binding to the skin.

**Cylinder Handling**

Leather gloves, safety glasses with side shields and safety shoes are recommended.

**Operations**

Polycarbonate faceshield over safety glasses, PVC splash suit, inner gloves smooth leather, outer gloves 17-mil nitrile is recommended. All personal protective equipment MUST be clean and dry.

**Emergency Use**

Self-contained breathing apparatus (SCBA), totally encapsulating chemical protective suit (TECP), natural fiber clothing only to be worn under the PPE, smooth leather inner gloves and 17 mil nitrile outer gloves are recommended. Gloves and splash suit MUST be new. Earplugs should also be considered due to the possibility of a loud, vigorous reaction.

**First Aid**

As described under the “Health” section of this Safetygram, chlorine trifluoride is highly toxic and also reacts with moisture to form a variety of toxic and corrosive materials, including hydrofluoric acid. Medical treatment for hydrofluoric acid exposures is very specialized. Air Products’ Safetygram-29, “Treatment Protocol for Hydrofluoric Acid Burns,” provides detailed information on the health effects and treatment for hydrogen fluoride. All users of chlorine trifluoride should use copies of Safetygram-29 to educate their employees, emergency people and local medical providers so they may know in advance what is required to address these exposures in the way of supplies and treatment.

**Emergency Response**

For small vapor leaks, shut off gas flow by closing cylinder valve, using the appropriate PPE. Purge the residual vapor to a scrubber, using an inert gas. Repair the leak. Be sure to thoroughly inspect the area surrounding the leak for any signs of corrosion, which may require replacement of that part of the system. After the repair, the system must again be passivated.

For leaks at the cylinder or through the valve, isolate the cylinder and contact the Air Products Emergency Response System at:

800-523-9374 (in North America)

or

+01-610-481-7711 (all other locations)

In the case of a large vapor release or small liquid spill, immediately evacuate the area. If possible, without risk and while wearing appropriate PPE, stop flow of gas. Do not attempt any remediation! Call the Air Products Emergency Response System immediately.

**Table 4**

<table>
<thead>
<tr>
<th>Transportation Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shipping Name:</strong></td>
</tr>
<tr>
<td><strong>Hazard Class:</strong></td>
</tr>
<tr>
<td><strong>Shipping Label:</strong></td>
</tr>
<tr>
<td><strong>Identification Number:</strong></td>
</tr>
<tr>
<td><strong>Description:</strong></td>
</tr>
</tbody>
</table>

When shipping via common carrier, all cylinders must be secured in an upright position and be located at the rear of the trailer. Never load additional freight on top of the cylinders. For small cylinders, special shipping pallets are mandatory.

- PPE that comes into contact with liquid may ignite.
- Always assume that at least the outer gloves have been exposed to HF; exposure can cause burns.
- Knowing the limitations of PPE in emergency operations, responders should think about how they may come in contact with the material and minimize their exposure.

Figure 7 demonstrates the importance of clean PPE. Upon exposure to a stream of CIF₃ vapor, the new glove exhibits no reaction. The same glove, contaminated with a small amount of oil, instantly bursts into flame.
In the unlikely event of a large liquid spill, evacuate the area and immediately contact the Air Products Emergency Response System. Do not attempt any remediation!

Warning: Any attempt to neutralize a liquid spill may result in an explosion.


**Emergency Response System**

- Call: +1-800-523-9374 (Continental U.S. and Puerto Rico)
- Call: +1-610-481-7711 (other locations)
- 24 hours a day, 7 days a week
- For assistance involving Air Products and Chemicals, Inc. products

**Product Safety Information**

- For MSDS, Safetygrams, and Product Safety Information
  - www.airproducts.com/productsafety

**Technical Information Center**

- Call: +1-800-752-1597 (U.S.)
- Call: +1-610-481-8565 (other locations)
- Fax: +1-610-481-8690
- E-mail: gasinfo@apci.com
- Monday–Friday, 8:00 a.m.–5:00 p.m. EST

**Information Sources**

- Compressed Gas Association (CGA)
  - www.cganet.com
- European Industrial Gases Association (EIGA)
  - www.eiga.org
- Japanese Industrial Gases Association (JIGA)
  - www.jiga.gr.jp/english
- American Chemistry Council
  - www.americanchemistry.com

**For More Information**

**Corporate Headquarters**

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