Occupational Health Guideline for Chlorine

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: Cl₂
- Synonyms: None
- Appearance and odor: Amber liquid or greenishyellow gas with a characteristic irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorine is a ceiling level of 1 part of chlorine per million parts of air (ppm) averaged over a 15-minute period (Federal Register, Vol. 43, No. 237, pp. 57601-03, 8 December 1978). This may also be expressed as 3 milligrams of chlorine per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 0.5 ppm (1.5 mg/m³) measured over a 15-minute period. The NIOSH Criteria Document for Chlorine should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

Routes of exposure

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

Effects of overexposure

1. Short-term Exposure: Chlorine gas may cause severe irritation of the eyes and respiratory tract with tearing, runny nose, sneezing, coughing, choking, and chest pain. Severe breathing difficulties may occur which may be delayed in onset. Pneumonia may result. Severe exposures may be fatal. In high concentrations chlorine may irritate the skin and cause sensations of burning and

prickling, inflammation, and blister formation. Liquid chlorine may cause eye and skin burns on contact.

- 2. Long-term Exposure: Repeated or prolonged exposure to chlorine may cause corrosion of the teeth and skin irritation.
- 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.

Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to chlorine at potentially hazardous levels:

- —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, cardiac status, and teeth should be stressed. The skin should be examined for evidence of chronic disorders. Simple tests of olfactory ability should be carried out.
- —14" x 17" chest roentgenogram: Chlorine causes human lung damage. Surveillance of the lungs is indicated.
- —FVC and FEV (1 sec): Chlorine 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 above medical examinations are to 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

Chlorine gas is a severe irritant of the eyes, mucous membranes, and skin. The odor threshold for chlorine has been reported at various concentrations and appears to be between 0.02 and 0.2 ppm for most subjects. Nasal irritation and coughing occur at about 0.5 ppm. There is evidence that olfactory fatigue develops at these low concentrations and that some tolerance is built up in

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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chronic industrial exposures. An accidental exposure of humans to unmeasured but high concentrations for a brief period caused burning of the eyes with lacrimation, burning of the nose and mouth with rhinorrhea, cough, choking sensation and substernal pain. These symptoms were frequently accompanied by nausea, vomiting, headache, dizziness, and sometimes syncope. Of 33 of the victims who were hospitalized, all suffered tracheobronchitis, 23 progressed to pulmonary edema, and of those, 14 to pneumonitis. Respiratory distress and substernal pain generally subsided within the first 72 hours; cough increased in frequency and severity after 2 to 3 days and became productive of thick mucopurulent sputum; cough disappeared by the end of 14 days. Prolonged or repeated exposure to 5 ppm may cause respiratory complaints, corrosion of the teeth, and inflammation of the mucous membranes of the nose. It has been reported that chronic exposure may increase susceptibility to respiratory infections. In high concentrations, chlorine irritates the skin and causes sensations of burning and pricking, inflammation, and vesicle formation. Liquid chlorine causes eye and skin burns on contact.

CHEMICAL AND PHYSICAL PROPERTIES

Physical data

- 1. Molecular weight: 70.9
- 2. Boiling point (760 mm Hg): -34.1 C (-29.3 F)
- 3. Specific gravity (water = 1): 1.41 (liquid)
- 4. Vapor density (air = 1 at boiling point of chlorine): 2.5
 - 5. Melting point: -101 C (-149 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): 0.7
- 8. Evaporation rate (butyl acetate = 1): Not applicable

Reactivity

- 1. Conditions contributing to instability: Elevated temperatures may cause cylinders to burst.
- 2. Incompatibilities: Contact with combustible substances (such as gasoline and petroleum products, turpentine, alcohols, acetylene, hydrogen, ammonia, and sulfur) and finely divided metals may cause fires and explosions.
 - 3. Hazardous decomposition products: None.
- 4. Special precautions: Chlorine will attack some forms of plastics, rubber, and coatings.
- Flammability
 - 1. Not combustible, but is a strong oxidizer.
- 2. Compressed gas cylinders containing chlorine should be stored in accordance with 29 CFR 1910.101.
- Warning properties
- 1. Odor Threshold: The odor threshold for chlorine has been reported by several authors to be 0.01 ppm (Summer, May, and Stern).
 - 2. Eye Irritation Level: Grant states that "exposure

to concentrations of chlorine gas as low as 3 to 6 ppm in air causes sensation of stinging and burning of the eyes of some individuals, with associated blepharospasm, redness, and watering, but on continued exposure sensitivity may decrease and signs and symptoms diminish."

The ILO states that eye irritation may occur at 1 to 3 nom.

- 3. Other Information: Patty states that "exposures to low concentrations, 10 to 20 mg/m³ or 3 to 6 ppm, cause a stinging or burning sensation in the eyes, nose and throat, and sometimes headache due to irritation of the accessory nasal sinuses. There may be redness and watering of the eyes, sneezing, coughing, and huskiness or loss of the voice. Bleeding of the nose may occur, and sputum from the pharynx and trachea may be blood-tinged. There is little or no chest pain other than the muscular soreness associated with excessive coughing."
- 4. Evaluation of Warning Properties: Through its odor, chlorine can be detected below the permissible exposure limit, and through its irritant effects, chlorine can be detected within several times of the permissible exposure limit. For the purposes of this guideline, therefore, chlorine is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chlorine. 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

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure chlorine may be used. An analytical method for chlorine is in the NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

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

2 Chlorine September 1978

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, and to prevent the skin from becoming frozen from contact with vessels containing liquid chlorine.
- Where there is any possibility of exposure of an employee's body to liquid chlorine, 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 should be removed immediately and not reworn until the chlorine 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 contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid chlorine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation

Use as chlorinating and oxidizing agent in organic synthesis, manufacture of solvents, automotive antifreeze and antiknock compounds, plastics, resins, elastomers, pesticides, refrigerants, bleaching, and inorganic chemicals

Process enclosure; local exhaust ventilation; personal protective equipment

Controls

Use as fluxing, purification, and extraction agent in metallurgy Process enclosure; local exhaust ventilation

Use as bacteriostat, disinfectant, odor control, and demulsifier in treatment of water and sewage Process enclosure; local exhaust ventilation

Use as a chlorinating agent in the rubber and coatings industry

Process enclosure; local exhaust ventilation

Use as bleaching agent, cleaning agent, and disinfectant in laundries, dishwashers, cleaning powders, cleaning dairy equipment, and bleaching cellulose

Process enclosure; local exhaust ventilation; general dilution 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 or high concentrations of chlorine 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 chlorine or high concentrations of chlorine gas get on the skin, immediately flush the contaminated skin with water. If liquid chlorine or high concentrations of chlorine gas penetrate through the clothing, remove the clothing and immediately flush the skin with water. If irritation is present after washing, get medical attention.

Breathing

If a person breathes in large amounts of chlorine, 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 chlorine 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 inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty through a reducing agent, such as sodium bisulfide and sodium bicarbonate.
- Waste disposal method:

Chlorine may be disposed of by allowing gas to disperse at a safe location.

REFERENCES

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4 Chiorine September 1978

RESPIRATORY PROTECTION FOR CHLORINE

Condition	Minimum Respiratory Protection* Required Above 1 ppm			
Gas Concentration				
25 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against chlorine.**			
	A gas mask with a chin-style or a front- or back-mounted canister providing protection against chlorine.**			
	Any supplied-air respirator with a full facepiece, helmet, or hood.			
	Any self-contained breathing apparatus with a full facepiece.			
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 press demand or other positive pressure mode.			
Escape	Any full-facepiece gas mask providing protection against chlorine.**			
	Any escape self-contained breathing apparatus with a full facepiece.			

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

^{**}Chlorine is a strong oxidizer and should not come in contact with oxidizable materials.

^{***}Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorine; 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.