OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROACETYL CHLORIDE

INTRODUCTION

This guideline summarizes pertinent information about chloroacetyl chloride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_2H_2Cl_2O$

- **Structure**

  $ClCH_2COCl$

- **Synonyms**

  Chloroacetic acid chloride; chloroacetic chloride; monochloroacetyl chloride; chloracetyl chloride

- Identifiers

  1. CAS No.: 79-04-9
  2. RTECS No.: AO6475000
  3. DOT UN: 1752 59
  4. DOT label: Corrosive

- **Appearance and odor**

  Chloroacetyl chloride is a colorless to slightly yellow liquid with a strong, pungent odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 112.94
  2. Boiling point (760 mm Hg): 105° to 110°C (221° to 230°F)
  3. Specific gravity (water = 1): 1.42 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of chloroacetyl chloride): Data not available
  5. Melting point (at 760 mm Hg): 106°C (222.8°F)
  6. Freezing point: -22.5°C (-8.5°F)
  7. Vapor pressure at 21°C (69.8°F): 20 mm Hg
  8. Solubility: Insoluble in water; soluble in ether and acetone
  9. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, open flame, and water
  2. Incompatibilities: Contact of chloroacetyl chloride

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with water causes decomposition and the release of hydrogen chloride gas and chloroacetic acid; avoid contact with alcohols, amines, and alkalis.

3. Hazardous decomposition products: Toxic gases (such as hydrogen chloride, phosgene, and chlorine) may be released in a fire involving chloroacetyl chloride.

4. Special precautions: Keep chloroacetyl chloride away from moisture or water.

- **Flammability**

The National Fire Protection Association has assigned a flammability rating of 0 (no fire hazard) to chloroacetyl chloride; this substance is not combustible.

1. Flash point: Not applicable

2. Autoignition temperature: Not applicable

3. Flammable limits in air: Not applicable

4. Extinguishant: Use an extinguishant that is suitable for the materials involved in the surrounding fire. Do not use water.

Fires involving chloroacetyl chloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of chloracetyl chloride should be moved from the fire area if it is possible to do so safely. If this is not possible, cool fire-exposed containers from the sides with water until well after the fire is out. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chloroacetyl chloride. Chemical protective clothing that is specifically recommended for chloroacetyl chloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chloroacetyl chloride.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chloroacetyl chloride [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.05 ppm (0.2 mg/m^3) as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chloroacetyl chloride a threshold limit value (TLV) of 0.05 ppm (0.23 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek and a short-term exposure limit (STEL) of 0.15 ppm (0.69 mg/m^3) for periods not to exceed 15 min. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 minutes. The ACGIH has also assigned a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of skin and respiratory irritation associated with choloracetyl chloride exposure. The ACGIH limits are based on the risk of eye, skin, and respiratory irritation and systemic effects associated with exposure to chloroacetyl chloride.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chloroacetyl chloride can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Chloroacetyl chloride is highly corrosive to tissues; in animals it affects the lungs, eyes, and skin. In rabbits the dermal LD_{50} is 178 mg/kg and the dermal LD_{LO} ranges from 316 to 501 mg/kg [AIHA 1987; NIOSH 1989; ACGIH 1991]. The LC_{50} in the rat is 1,000 ppm for a 4-hr exposure [NIOSH 1989]. A 5 to 10 min exposure to a

concentration of 4 ppm caused respiratory difficulty in rats, but no effect was observed from the inhalation of a 2.5-ppm chloroacetyl chloride concentration for 7 hr [NLM 1992; AIHA 1987]. A 30-day inhalation study with rats, mice, and hamsters showed that these animals develop eye and respiratory irritation at an airborne concentration of 2.5 ppm [NLM 1992]. The oral LD_{50} in the rat is 120 mg/kg; cough and dermatitis were noted before death [NIOSH 1989].

2. *Effects on Humans:* In humans, chloroacetyl chloride is corrosive to the skin and eyes and affects the respiratory system [Sittig 1985]. The effects of acute workplace exposure include mild to moderate skin irritation and burns, lacrimation, mild eye burns, mild to moderate respiratory effects with cough, dyspnea, cyanosis, and mild gastrointestinal effects [ACGIH 1991; AIHA 1987]. Respiratory effects include coughing, difficult breathing, and oxygen insufficiency [ACGIH 1991a]. Workers exposed to peak chloroacetyl chloride concentrations of 140 ppb developed eye irritation and reported experiencing minimal respiratory irritation [NLM 1992]. In an industrial accident, a worker was drenched by a mixture containing chloroacetyl chloride, xylidine, benzene, and sodium carbonate. Although immediately put under a shower, he suffered extensive first- and second-degree burns, developed pulmonary edema, and had three episodes of cardiac arrest during emergency treatment. He went into a coma that lasted several weeks; the ultimate outcome of this case is not reported [ACGIH 1991; NLM 1992]. Workers involved in the rescue of this employee suffered blisters on their hands and complained of tightness of the chest and slight nausea for as long as 2 days after the incident [NLM 1992]. Most of the acute effects experienced by this worker are believed to have been caused by the chloroacetyl chloride.

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute inhalation overexposure to chloroacetyl chloride include pain, redness, and tearing of the eyes, sore throat, pain in the chest, fluid in the lungs, and difficult breathing. Contact with the liquid can cause severe skin or eye burns.

2. *Chronic exposure:* The signs and symptoms of continued low-level exposure to chloroacetyl chloride may include a burning sensation in the upper respiratory tract, wheezing, laryngitis, and shortness of breath.

- **Emergency procedures**

WARNING!

Exposed victims may die!

Transport immediately to emergency medical facility!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of chloroacetyl chloride! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of lethal amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

   If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if chloroacetyl chloride or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

   —Do ***not*** permit the victim to drink milk or carbonated beverages!

   —Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue:* Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve chloroacetyl chloride and may result in worker exposures to this substance:

—Manufacture of herbicides (such as alachlor, allidochlor, butachlor, and others) and tear gas

—Use as an intermediate in the manufacture of chloroacetophenone and other chemicals

—Manufacture of pharmaceuticals, such as chlordiazepoxide hydrochloride, diazepam, lidocaine, and mianserin

The following methods are effective in controlling worker exposures to chloroacetyl chloride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Personal protective equipment and local ventilation are a necessity at chloroacetyl chloride transfer points where leakage can be expected.

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

- **Preplacement medical evaluation**

Before a worker is placed in a job with a potential for exposure to chloroacetyl chloride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chloroacetyl chloride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the respiratory system.

- **Periodic medical examinations and biological monitoring**

  Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chloroacetyl chloride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chloroacetyl chloride on the respiratory tract. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chloroacetyl chloride.

- **Medical examinations recommended at the time of job transfer or termination**

  The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chloroacetyl chloride is determined by using a XAD-2 tube coated with 1- (2-pyridyl)piperazine. Samples are collected at a recommended flow rate of 0.05 liter/min until a recommended air volume of 10 liters is collected. Analysis is conducted by high performance liquid chromatography using an ultraviolet detector. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If chloroacetyl chloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with chloroacetyl chloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of chloroacetyl chloride, particularly its potential to cause eye and skin burns.

A worker who handles choloroacetyl chloride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where chloroacetyl chloride or a solution containing chloroacetyl chloride is handled, processed, or stored.

STORAGE

Chloroacetyl chloride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chloroacetyl chloride should be protected from physical damage and should be stored separately from water, steam, surface moisture, oxidizing agents, strong bases, alcohols, heat, sparks, and open flame. Because containers that formerly contained chloroacetyl chloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chloroacetyl chloride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Notify safety personnel.

3. Remove all sources of heat and ignition.

4. Ventilate the area of the spill or leak.

5. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.

6. For large liquid spills, build dikes far ahead of the spill to contain the chloroacetyl chloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

  Chloroacetyl chloride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of chloroacetyl chloride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

  Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chloroacetyl chloride emitted or released from their facility annually.

- **Hazardous waste management requirements**

  EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although chloroacetyl chloride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

  Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for the waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

  Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chloroacetyl chloride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

  Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of

an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent any skin contact with chloroacetyl chloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to chloroacetyl chloride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to chloroacetyl chloride.

If chloroacetyl chloride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which chloroacetyl chloride might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with chloroacetyl chloride.

REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

ACGIH [1993]. 1993-1994 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

AIHA [1987]. Emergency response planning guidelines: chloroacetyl chloride. Akron, OH: American Industrial Hygiene Association.

ATS [1987]. Standardization of spirometry—1987 update. American Thoracic Society. Am Rev Respir Dis 136:1285-1296.

CFR. Code of Federal regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

DOT [1987]. 1987 Emergency response guidebook, guide 59. Washington, DC: U.S. Department of Transportation, Office of Hazardous Materials Transportation, Research and Special Programs Administration.

Genium [1985]. Material safety data sheet no. 591. Schednectady, NY: Genium Publishing Corporation.

NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

NIOSH [1987b]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

NIOSH [1989]. Registry of toxic effects of chemical substances database: chloroacetyl chloride. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

NLM [1992]. The hazardous substances data bank: chloroacetyl chloride. Bethesda, MD: National Library of Medicine.

OSHA [1989]. OSHA laboratory in-house methods file. Salt Lake City, UT: U.S. Department of Labor, OSHA Analytical Laboratory, P. O. Box 65200, 1781 South 300 West, Salt Lake City, Utah 84165-0200.