OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLOROBENZENE

INTRODUCTION

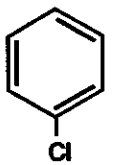
This guideline summarizes pertinent information about chlorobenzene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether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_6H_5Cl

- **Structure**



- **Synonyms**

  Monochlorobenzene, MCB, phenyl chloride, chlorobenzol, benzene chloride

- **Identifiers**

  1. CAS No.: 108-90-7
  2. RTECS No.: CZ0175000
  3. DOT UN: 1134 27
  4. DOT label: Flammable liquid

- **Appearance and odor**

  Chlorobenzene is a colorless to yellowish liquid with a mild, aromatic, almond-like odor. The odor threshold of chlorobenzene is 0.21 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 112.6
  2. Boiling point (760 mm Hg): 131° to 132°C (267.8° to 270°F)
  3. Specific gravity (water = 1): 1.1 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of chlorobenzene): 3.9
  5. Melting point: -45°C (-49°F)

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Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

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Occupational Safety and Health Administration

6. Vapor pressure at 20°C (68°F): 8.8 mm Hg

7. Solubility: Insoluble in water; soluble in alcohol, benzene, chloroform, and ether

8. Evaporation rate (ether = 1): 8.2

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame

2. Incompatibilities: Contact of chlorobenzene with strong oxidizers, dimethyl sulfoxide, powdered sodium, phosphorus trichloride and sodium, or silver perchlorate causes fire, explosion, or a violent reaction.

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

4. Special precautions: None reported

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to chlorobenzene.

1. Flash point: 27.8°C (82°F)

2. Autoignition temperature: 593°C (1,099°F)

3. Flammable limits in air (% by volume): Lower, 1.3; upper, 9.6

4. Extinguishant: Use carbon dioxide, dry chemical, water spray, or standard foam to fight fires involving chlorobenzene.

Fires involving chlorobenzene 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. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of chlorobenzene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorobenzene. Structural firefighters' protective clothing may provide limited protection against fires involving chlorobenzene.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for chlorobenzene is 75 ppm (350 mg/m^3) as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has not issued a recommended exposure limit (REL) for chlorobenzene [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorobenzene a threshold limit value (TLV) of 10 ppm (46 mg/m^3) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

- **Rationale for limits**

The ACGIH limit is based on the risk of liver and other effects associated with exposure to chlorobenzene [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to chlorobenzene can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* Exposure to chlorobenzene causes irritation, narcosis, and liver and kidney damage. In contact with the eyes of rabbits or skin of guinea pigs, chlorobenzene caused a moderate degree of irritation [ACGIH 1991]. Rats, rabbits, and guinea pigs exposed to chlorobenzene at a concentration of 1,000 ppm for 7 hr/day, 5 days/week for 44 days showed signs of lung, liver, and kidney damage; however, exposure to a 475-ppm concentration on the same regimen caused only slight liver damage in one species [Hathaway et al. 1991; ACGIH 1991]. Cats exposed to an 8,000-ppm concentration of chlorobenzene for 30 min showed signs of severe narcosis and died 2 hr after cessation of exposure; however, cats survived exposure to a 660-ppm concentration for 1 hr [Hathaway et al. 1991]. Acutely poisoned animals showed signs of eye and nose irritation and narcosis [Hathaway et al. 1991]. The oral LD_{50} in rats is 2,290 mg/kg, and the lowest lethal concentration in mice is 15 g/m^3 [NIOSH 1993]. In gavage studies of rats and mice administered chlorobenzene 5 days/week for 91 days, dose-dependent necrosis of the liver, degeneration or focal necrosis of the proximal tubules of the kidney, and myeloid or lymphoid depletion of the spleen, bone marrow, and thymus were seen at doses of 250 mg/kg/day or greater in both sexes [Hathaway et al. 1991]. In 2-year gavage studies of male and female rats and mice, male rats administered chlorobenzene doses of 120 mg/kg had a slight but statistically significant increase in neoplastic nodules of the liver. No increase in the incidence of liver tumors was seen in the mice or the female rats [Hathaway et al. 1991].

2. *Effects on Humans:* Exposure to chlorobenzene at a concentration of 200 ppm causes eye and nose irritation, and exposure to higher concentrations causes central nervous system depression. In contact with the skin for brief exposures, liquid chlorobenzene causes only mild irritation; however, prolonged or repeated contact can lead to burns of the skin [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to chlorobenzene may cause redness and inflammation of the eyes and eyelids, runny nose, sore throat, redness and irritation of the skin, headache, dizziness, drowsiness, incoherence, ataxia, loss of consciousness, twitching of the extremities, deep and rapid respiration, and irregular heartbeat. Respiratory arrest may follow.

2. *Chronic exposure:* Long-term exposure to chlorobenzene may cause chronic central nervous system depression: headache, dizziness, and somnolence. Based on effects seen in animals, chronic exposure may cause elevated liver enzymes, enlarged and tender liver, and blood, pus, or protein in the urine. Prolonged or repeated skin contact may cause skin burns.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of chlorobenzene. ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water.

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

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

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

   —Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

   —Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do ***not*** force an unconscious or convulsing person to drink fluid or to vomit.

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, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

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

—Use as a solvent for paints, adhesives, polishes, waxes, and natural rubber, and as a solvent carrier for methylene diisocyanate

—Use as a dry-cleaning agent

—Manufacture of phenol, o- and p-chloronitrobenzene, aniline, DDT, and pharmaceuticals

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

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

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 chlorobenzene, 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, central nervous system, liver, eyes, and skin. 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 chlorobenzene at or below the prescribed exposure limit. The 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 or central nervous system, liver, eyes, or skin.

- **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 chlorobenzene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorobenzene on the respiratory or central nervous system, liver, eyes, or skin. 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. Although chlorobenzene or its metabolites can be detected in the blood or adipose tissue of exposed individuals, no biological monitoring test acceptable for routine use has yet been developed for chlorobenzene.

- **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 chlorobenzene is determined by using a coconut shell solid sorbent tube (100/50-mg sections, 20/40 mesh). Samples are collected at a maximum flow rate of 0.2 liter/min until a maximum air volume of 40 liters is collected. The samples are then desorbed with carbon disulfide to extract the chlorobenzene. Analysis is conducted by gas chromatography using a flame ionization detector. The limit of detection for this procedure is 0.01 mg/sample. This method is described in NIOSH Method No. 1003 of the *NIOSH Manual of Analytical Methods* [NIOSH 1984].

PERSONAL HYGIENE

If chlorobenzene contacts the skin, workers should flush the affected areas immediately with plenty of water, followed by washing with soap and water.

Clothing contaminated with chlorobenzene 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 chlorobenzene, particularly its potential to be irritating to the eyes and skin.

A worker who handles chlorobenzene 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 chlorobenzene or a solution containing chlorobenzene is handled, processed, or stored.

STORAGE

Chlorobenzene 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]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of chlorobenzene should be protected from physical damage and should be stored separately from oxidizers, dimethyl sulfoxide, silver perchlorate, other incompatible chemicals, heat, sparks, and open flame. Only nonsparking tools may be used to handle chlorobenzene. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained chlorobenzene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorobenzene, 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.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. For small dry spills, use a clean, nonsparking shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
7. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the chlorobenzene 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**

Chlorobenzene 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**

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for chlorobenzene is 100 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center ***immediately*** at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

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

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more of chlorobenzene per calendar year or otherwise use 10,000 lb or more of chlorobenzene per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorobenzene 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. Chlorobenzene is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. U037. It is approved for land disposal as long as the concentration of chlorobenzene in the waste or treatment residual does not exceed 5.7 mg/kg. Chlorobenzene also may be disposed of in an

organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

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 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 chlorobenzene 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 clothing (gloves, boots, aprons, and gauntlets, as appropriate) should be worn to prevent skin contact with chlorobenzene. 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. The following material have demonstrated greater than 8 hr of resistance to breakthrough under continuous contact: Viton, Barricade, and Responder. Polyvinyl-alcohol and Teflon have shown resistance to breakthrough between 4 and 8 hr.

If chlorobenzene 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 chlorobenzene 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 chlorobenzene. Contact lenses should not be worn if the potential exists for chlorobenzene exposure.

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