

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND  
SUPPORTING DOCUMENTATION FOR

\*\*\* METHYLENE CHLORIDE \*\*\*

NIOSH/OSHA Draft Technical Standard  
and Supporting Documentation for METHYLENE CHLORIDE

basic text of this document contains the draft technical standard developed by the Joint Review Committee of the NIOSH/OSHA Standards Revision Program and the supporting documentation for the substance METHYLENE CHLORIDE.

SCP draft technical standards are recommendations to the Department of Health and Safety for its consideration in rulemaking and have no legal status until final rules have been promulgated by that agency. This draft standard is provided for your information only.

References and Sources, Respirator Table Documentation and Use/Exposure Control Documentation are the working documents used by the various SCP working groups during the development of the draft technical standard and serve as the technical foundation for the standard. The classification for the substance and the regulatory statements were derived following a decision logic established for the various sections of the standard.

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Definitions. (1) "Permissible exposure" means exposure of employees to airborne concentrations of methylene chloride not in excess of 500 parts per million (ppm) averaged over an eight-hour work shift (time weighted average) and not in excess of 1,000 parts per million (ppm) at any time during an eight-hour work shift except that an exposure not in excess of 1,000 parts per million (ppm) at any aggregate of 5 minutes in any 2 hours may be permitted as stated in 29 CFR 1910.1000, Table Z-2.

"Action level" means one half of the permissible exposure for methylene chloride for an eight-hour work shift.

Exposure determination and measurement. (1) Each employer who has a place of employment in which methylene chloride is released into the workplace air shall determine if any employee may be exposed to airborne concentrations of methylene chloride at or above the action level. The determination shall be made each time there is a change in production, process, or control measures which could result in an increase in airborne concentrations of methylene chloride.

A written record of the determination shall be made and it shall contain at least the following information:

Any information, observations, or calculations which may indicate employee exposure to methylene chloride;

(b) Any measurements of methylene chloride taken;

(c) Any employee complaints of symptoms which may be attributable to exposure to methylene chloride; and

(d) Date of determination, work being performed at the time, location of work site, name, and social security number of each employee considered.

If the employer determines that any employee may be exposed to methylene chloride at or above the action level, the exposure of the employee in each work operation who is believed to have the greatest exposure shall be measured. The exposure measurement shall be representative of the maximum eight-hour time weighted average exposure of the employee.

If the exposure measurement taken pursuant to paragraph (b)(3) of this section reveals employee exposure to methylene chloride at or above the action level, the employer shall:

(1) Identify all employees who may be exposed at or above the action level; and

(2) Measure the exposure of the employees so identified.

If an employee exposure measurement reveals that an employee is exposed to methylene chloride at or above the action level, but not above the permissible exposure, the exposure of that employee shall be measured at least every two months.

If an employee exposure measurement reveals that an employee is exposed to methylene chloride above the permissible exposure, the employer shall:

(1) Measure the exposure monthly of the employee so exposed; and

(2) Institute control measures as required by paragraph (d) of this section.

(3) Individually notify, in writing, within five days, every employee found to be exposed to methylene chloride above the permissible exposure. The employee shall also be notified of the corrective action taken to reduce the exposure to at or below the permissible exposure.

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If two consecutive employee exposure measurements taken at least one apart reveal that the employee is exposed to methylene chloride below action level, the employer may terminate measurement for the employee. For purposes of this paragraph, employee exposure is that which would be if the employee were not using a respirator.

Methods of measurement. (1) An employee's exposure shall be obtained by a combination of long term or short term samples which represents the employee's actual exposure averaged over the time periods appropriate to the permissible exposure (See Appendix B (iv) of this section).

The method of measurement shall have an accuracy, to a confidence of 95 percent, of not less than that given in Table 1.

Table 1

Concentration	Required Accuracy
at or below the permissible exposure	± 25%
above the permissible exposure but below the action level	± 35%
above the action level	± 50%

Compliance. (1) No employee shall be exposed to methylene chloride above the permissible exposure as defined in paragraph (a)(1) of this section.

Employee exposures to airborne concentrations of methylene chloride shall be controlled to at or below the permissible exposure by engineering and work practice controls:

Engineering and work practice controls shall be instituted to reduce exposures to at or below the permissible exposure, except to the extent such controls are not technically feasible.

Wherever engineering and work practice controls are not sufficient to reduce exposures to at or below the permissible exposure, they shall nevertheless be used to reduce exposure to the lowest level feasible and shall be supplemented by respirators in accordance with paragraph (d)(4) of this section.

Engineering controls. (i) When mechanical ventilation is used to control exposure, measurements which demonstrate system effectiveness, for example, air velocity, static pressure, or air volume, shall be made at least every three months. Measurements of system effectiveness shall also be made within five days of any change in production, process, or control which might result in an increase in airborne concentrations of methylene chloride.

(j) In the design of open surface tank ventilation for the purposes of paragraph (d), operations involving methylene chloride shall be classified as Class I at 70 degrees F.

Compliance with the permissible exposure shall not be achieved by the use of respirators except:

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- During the time period necessary to install or implement engineering work practice controls; or
- ) In work situations in which engineering and work practice controls are technically not feasible; or
  - i) To supplement engineering and work practice controls when such controls fail to reduce airborne concentrations of methylene chloride to at or below the permissible exposure; or
  - ) In emergencies.

Where respirators are needed and permitted under this paragraph to reduce employee exposure, the employer shall select and provide the appropriate respirator from Table 2 and shall ensure that the employee uses the respirator provided.

TABLE 2 RESPIRATORY PROTECTION FOR METHYLENE CHLORIDE

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION
<b>Concentration</b>	
100 ppm or less	Any supplied-air respirator with a full facepiece, helmet or hood. ----- Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm or entry into escape from high 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.
Firefighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Emergency escape	Any gas mask providing protection against organic vapors. ----- Any escape self-contained breathing apparatus.

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Respirators shall be approved by the Mining Enforcement and Safety Administration (formerly Bureau of Mines) or by the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part 11.

The employer shall institute a respiratory protection program in accordance with § 1910.134(b), (d), (e), and (f).

Fire and safety. (1) The employer shall familiarize himself with information contained in the Substance Technical Guidelines (Appendix B in this section) for methylene chloride.

For the purpose of compliance with § 1910.309, locations classified as hazardous locations due to the presence of methylene chloride shall be in I, Group D.

For the purpose of compliance with § 1910.157, methylene chloride is classified as a Class B fire hazard.

For the purpose of compliance with § 1910.178, locations classified as hazardous locations due to the presence of methylene chloride shall be in I, Group D.

Spray finishing operations shall be performed in accordance with §§ 1910.107 and 1910.94(c).

Dip tank operations shall be performed in accordance with §§ 1910.108 and 1910.94(d).

Where a fan is located in ductwork and where methylene chloride is present in the ductwork in concentrations greater than 30,000 ppm (approximately 25 percent of the lower flammable limit), the fan rotating element shall be of nonsparking material or the casing shall consist of, or be lined with, nonsparking material. There shall be sufficient clearance between the fan rotating element and the fan casing so as to prevent contact.

Sources of ignition such as smoking or open flames are prohibited where methylene chloride presents a fire or explosion hazard.

Methylene chloride shall be stored so as not to come in contact with strong oxidizers, strong caustics and chemically active metals.

Personal protective equipment. (1) Employers shall provide and ensure that employees use impervious clothing, gloves, face shields (1/4-inch minimum) and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylene chloride. Face shields shall comply with § 1910.133(a)(2), (a)(4), (a)(5) and (a)(6).

Employers shall ensure that non-impervious clothing which becomes contaminated with liquid methylene chloride be removed promptly and not be reworn until the methylene chloride is removed from the clothing.

Employers shall provide and ensure that employees use splash-proof safety goggles (cup-cover type dust and splash safety goggles) which comply with § 1910.133 (a)(2)-(a)(6) where liquid methylene chloride may contact the eyes.

Spills and disposal. In the event that liquid methylene chloride is spilled the employer shall immediately provide available ventilation and clean up the spill.

Sanitation. Employers shall ensure that employees whose skin becomes wet with liquid methylene chloride promptly wash or shower with soap or mild detergent and water to remove any methylene chloride from the skin.

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Training and information. (1) Each employer who has a workplace in methylene chloride is present shall keep a copy of this regulation Appendixes A, B and C at the workplace. This material shall be made available to affected employees.

Each employer who has employees exposed to methylene chloride above action level or employees who may have skin or eye contact with liquid methylene chloride, or employees who work where a spill of methylene chloride may occur, shall annually:

Inform affected employees of the information contained in the Hazardance Safety Data Sheet for methylene chloride (Appendix A of this section);

Advise affected employees as to the signs and symptoms of exposure to methylene chloride.

Instruct affected employees to advise the employer of the development of signs and symptoms of exposure to methylene chloride which are listed in Appendix A of the section;

Instruct affected employees to inform the employer if they develop any of the medical conditions listed in paragraph (j)(2) of this section;

Provide training to ensure that employees understand the precautions for the use, emergency procedures, and the correct use of protective equipment relative to methylene chloride.

Medical Surveillance. (1) The employer shall provide medical procedures as required by this paragraph. All medical procedures shall be performed by or under the supervision of a physician at no cost to the employee.

The employer shall obtain from each employee who is exposed, or will be exposed, to liquid methylene chloride or airborne concentrations of methylene chloride at or above the action level, without regard to the use of respirators, information as to whether such employee has a history of any of the following medical conditions:

- Kidney disease
- Liver disease
- Skin disease
- Heart disease

The employer shall provide a medical examination for the employee if:

The employee provides a history of any of the medical conditions listed in paragraph (j)(2) of this section; or

The employee informs the employer of the development of any of the medical conditions listed in paragraph (j)(2) of this section or any of the signs or symptoms of exposure to methylene chloride which are listed in Appendix A which the employee suspects are caused by exposure to methylene chloride.

The employer shall provide to the examining physician the following information:

A copy of this regulation with Appendixes A, B and C for methylene chloride;

A description of the affected employee's duties as they relate to exposure to methylene chloride;

A description of any personal protective equipment including respirators required to be used;

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) The results of any measurements which may indicate the affected employee's exposure;

The affected employee's anticipated exposure; and

) Upon request of the physician, any available information from previous medical examinations of the affected employee.

Where a medical examination is required by paragraph (j)(3) of this section, following such examination the employer shall obtain a written opinion from the examining physician which conforms with paragraph (j)(6) of this section.

(i) The physician's written opinion shall be a signed statement by the examining physician specifically stating: (A) Whether the employee has any undetected medical condition which would place the employee at increased risk of material impairment of the employee's health from exposure to methylene chloride or would directly or indirectly aggravate any detected medical condition;

Any recommended limitations upon the employee's exposure to methylene chloride including limitations upon the use of personal protective equipment and respirators;

That the employee has been informed by the physician of any detected medical conditions which require further medical examination or treatment.

) The physician's written opinion shall not reveal specific medical findings or diagnoses unrelated to exposure to methylene chloride.

i) The employer shall provide the employee with a copy of the physician's written opinion.

No employee shall be exposed to liquid methylene chloride or airborne concentrations of methylene chloride in such a way as would put the employee at increased risk of material impairment of his health from such exposure. This determination may be based on the physician's written opinion.

The employer shall provide emergency and follow up medical attention and treatment for any employee injured through exposure to methylene chloride.

If an employee refuses any required medical examination, the employer shall inform the employee of the possible health consequences of such refusal and obtain a signed statement from the employee indicating that the employee understands the risk involved by refusal to be examined.

) No medical procedure which would be performed pursuant to this section need be performed if records of a previous such procedure performed in the past six months are acceptable to the examining physician.

Recordkeeping. (1) Exposure determination. (i) The employer shall maintain an accurate record of all determinations required to be made pursuant to paragraph (b)(1) of this section.

) The record shall include the written determination required in paragraph (b)(2) of this section.

i) This record shall be maintained until replaced by a more recent determination.

Exposure measurements. (i) The employer shall keep an accurate record of all measurements taken to determine employee exposure to methylene chloride.

) This record shall include:

The date of measurement;

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Operations involving exposure to methylene chloride which are being monitored;

Sampling and analytical methods used and evidence of their accuracy, including the method, results and date of calibration of sampling equipment;

Number, duration, and results of samples taken; and

Name, social security number and exposure of the employee monitored.

i) This record shall be maintained until replaced by a more recent record but in no event for less than one year.

Mechanical ventilation. (i) When mechanical ventilation is used as engineering control, the employer shall maintain an accurate record of measurements demonstrating the effectiveness of such ventilation required by paragraph (d)(3) of this section.

) This record shall include:

Date of measurement;

Type of measurement taken;

Result of measurement.

i) These records shall be maintained for at least one year.

Employee training and information. (i) The employer shall keep an accurate record of all employee training and information required by paragraph (i) of this section.

) This record shall include:

Date of training;

Name and social security number of employee trained;

Content or scope of training provided.

i) This record shall be maintained until replaced by a more recent record.

Medical surveillance. (i) The employer shall keep an accurate record of employee medical surveillance required by paragraph (j) of this section.

) The record shall include:

Information concerning medical conditions obtained from the employee pursuant to paragraph (j)(2) of this section;

Any employee medical complaints relative to exposure to methylene chloride;

A copy of information provided to the physician pursuant to paragraph (ii), (iii), (iv), (v), and (vi) of this section.

Physician's written opinion; and

A signed statement of any refusal to be examined.

i) This record shall be maintained for the duration of the employment of the affected employee.

Access to records. (i) All records required to be maintained by this section shall be made available upon request to authorized representatives of the Assistant Secretary of Labor for Occupational Safety and Health and the Director of the National Institute for Occupational Safety and Health.

) Employee exposure determination and exposure measurement records required to be maintained by this section shall be made available to employees and former employees and their designated representatives.

i) Employee medical records required to be maintained by this section shall be made available upon written request to a physician designated by the employee or former employee.

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Employee observation of measurement. (1) The employer shall give  
ted employees or their representatives an opportunity to observe any  
ement of employee exposure to methylene chloride which is conducted  
ant to this section.

When observation of measurement of employee exposure to methylene  
ide requires entry into an area where the use of personal protective  
es, including respirators, is required, the observer shall be provided  
and required to use such equipment and comply with all other  
cable safety procedures.

Without interfering with the measurement, observers shall be entitled

Receive an explanation of the measurement procedure.

- ) Visually observe all steps related to the measurement of the  
rne concentration of methylene chloride that are being performed at  
lace of exposure; and
- i) Record the results obtained.

E: The information contained in the following appendixes is advisory  
ture and is not intended, by itself, to create any additional  
ations not otherwise imposed or detract from any existing obligation.

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APPENDIX A

SUBSTANCE SAFETY DATA SHEET  
FOR METHYLENE CHLORIDE

SUBSTANCE IDENTIFICATION

- A. Substance: Methylene chloride
- B. Permissible Exposure: 500 parts of methylene chloride per million parts of air (ppm) averaged over an eight-hour work shift. Also, 1000 ppm shall not be exceeded during an eight-hour workshift except that a peak of 2000 is permitted for 5 minutes in any 2 hours during the work shift.
- C. Appearance and Odor: Colorless liquid with an odor like chloroform.

HEALTH HAZARD DATA

- A. Ways in Which the Chemical Affects Your Body: Methylene chloride can affect your body if you inhale it or if it comes in contact with your eyes or skin. It may also affect your body if you swallow it.
- B. Effects of Overexposure:
  - 1. Short-Term Exposure: Methylene chloride is an anesthetic. Inhaling the vapor may cause mental confusion, lightheadedness, nausea, vomiting and headache. Continued exposure may cause increased lightheadedness, staggering, unconsciousness and death. High vapor concentrations may also cause irritation of the eyes and respiratory tract. Exposure to this chemical may make the symptoms of angina worse. Skin exposure to the liquid may cause irritation. If the liquid is held in contact with the skin it may cause skin burns. Splashes of the liquid into the eyes may cause irritation.
  - 2. Long-Term Exposure: Prolonged or repeated exposure to methylene chloride may cause irritation of the skin.
  - 3. Reporting Signs and Symptoms: You should inform your employer if you develop any signs or symptoms and suspect that they are caused by exposure to methylene chloride.

EMERGENCY FIRST AID PROCEDURES

- A. Eye Exposure: If methylene chloride gets into your eyes, wash the eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.
- B. Skin Exposure: If methylene chloride gets on your skin, promptly wash the contaminated skin using soap or a mild detergent if the methylene chloride has not already evaporated. If methylene chloride soaks through your clothing, remove the clothing promptly and wash the skin

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using soap or a mild detergent. If irritation persists after washing, get medical attention.

- C. Breathing: If you or any other person breathes in large amounts of methylene chloride 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.
- D. Swallowing: When methylene chloride has been swallowed get medical attention immediately. If medical attention is not immediately available, get the person to vomit by having him touch the back of the throat with his finger or by giving him large amounts (one pint or more) of warm salt water (two tablespoons of salt per pint of water). Do not make an unconscious person vomit.
- E. Rescue: Move 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 yourself. Understand your emergency rescue procedures and know the locations of the equipment before the need arises.

RESPIRATORS AND PROTECTIVE CLOTHING

- A. Respirators: Respirators are not the best way to control exposure to methylene chloride. You can only be required to wear them for routine use if your employer is in the process of installing controls or control measures prove inadequate. You may be required to wear respirators for non-routine activities or in emergencies. If respirators are worn, they must have a Mining Enforcement and Safety Administration (MESA) or National Institute for Occupational Safety and Health (NIOSH) approval label. (Older respirators may have a Bureau of Mines approval label.) For effective protection, respirators must fit your face and head snugly. Respirators should not be loosened or removed in work situations where there use is required. If you can smell methylene chloride while wearing a respirator, the respirator is not working correctly; go immediately to fresh air. If you experience difficulty breathing while wearing a respirator, tell your employer.
- B. Protective Clothing: You must wear impervious clothing, gloves, face shield or other appropriate protective clothing to prevent repeated or prolonged skin contact with liquid methylene chloride. Replace or repair impervious protective clothing that has developed leaks.
- C. Eye Protection: You must wear splash-proof safety goggles (cup-cover type dust and splash safety goggles) where eye contact to liquid methylene chloride may occur.

PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

- A. Methylene chloride vapors, at elevated temperatures, can form explosive mixtures with air.
- B. Methylene chloride must be stored in tightly closed containers in a cool, dry, well ventilated area away from

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heat, sparks, flames, strong oxidizers, strong caustics, and chemically active metals.

- C. Sources of ignition such as smoking and open flames are prohibited wherever methylene chloride is handled, used or stored in a manner that could create a potential fire or explosion hazard.
- D. If your skin becomes wet with liquid methylene chloride, you must promptly wash or shower with soap or mild detergent and water to remove any methylene chloride from the skin.
- E. You must promptly remove any non-impervious clothing that becomes wet with liquid methylene chloride and this clothing must not be reworn until the methylene chloride is removed from the clothing.
- F. Fire extinguishers, where provided, must be readily available and you should know where they are and how to operate them.
- G. Ask your supervisor where methylene chloride is used in your work area and for any additional plant safety and health rules.

ACCESS TO INFORMATION

- A. Each year your employer is required to inform you of the information contained in this Substance Safety Data Sheet for methylene chloride. In addition, your employer must instruct you in the safe use of methylene chloride, emergency procedures, and the correct use of protective equipment.
- B. Your employer is required to determine whether you are being exposed to methylene chloride. You or your representative have the right to observe employee exposure measurements and to record the results obtained. If your employer determines that you are being overexposed, he is required to inform you of the exposure and of the actions which are being taken to reduce your exposure.
- C. Your employer is required to keep records of exposure determinations, exposure measurements, and medical surveillance. Your employer is required to make records of exposure determinations and your exposure measurements available to you or your representative upon your request. Your employer is required to release your medical records to your physician upon your written request.

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APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES  
FOR METHYLENE CHLORIDE

PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: Dichloromethane; methylene dichloride
2. Formula:  $\text{CH}_2\text{Cl}_2$
3. Molecular weight: 84.9

B. Physical Data

1. Boiling point (760 mm Hg): 39.8 C (104 F).
2. Specific gravity (Water = 1): 1.3
3. Vapor density (air = 1 at boiling point of methylene chloride): 2.9
4. Melting point: -97 C (-142 F)
5. Vapor pressure at 20 C (68 F): 350 mm Hg
6. Solubility in water, % by weight at 20 C (68 F): 1.32
7. Evaporation rate (butyl acetate = 1): 27.5
8. Appearance and odor: Colorless liquid with an odor like chloroform

FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: None with normal test method.
2. Autoignition temperature: 556 C (1033 F)
3. Flammable limits in air, % by volume: (at elevated temperatures) Lower: 12; Upper: 19
4. Extinguishing media: Dry chemical, carbon dioxide, foam.
5. Special fire-fighting procedures: Do not use a solid stream of water since a stream will scatter and spread the fire. Use water spray to cool containers exposed to a fire.
6. Unusual fire and explosion hazards: Methylene chloride vapors, at elevated temperatures, can form explosive mixtures with air. All ignition sources must be controlled where methylene chloride is used, handled or stored in a manner that could create a potential fire or explosion hazard.
7. Above 30,000 ppm, one-fourth of the lower flammable limit, is one situation in which methylene chloride is considered to be a potential fire and explosion hazard.
8. For purposes of compliance with 29 CFR 1910.309, the classification of hazardous locations as described in Article 500 of the National Electric Code for methylene chloride shall be Class I Group D.

B. Reactivity

1. Conditions contributing to instability: Heat and

ire.

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2. Incompatibilities: Contact with strong oxidizers, strong caustics, and chemically active metals such as aluminum or magnesium powder, sodium and potassium may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene and carbon monoxide) may be released in a fire involving methylene chloride.
4. Special precautions: Liquid methylene chloride will attack some forms of plastics, rubber and coatings.

SPILL AND LEAK PROCEDURES

- A. If methylene chloride is spilled or leaked, the following steps should be taken:
  1. Remove all ignition sources.
  2. Ventilate area of spill or leak.
  3. Collect for reclamation or absorb in vermiculite, dry sand, earth or a similar material.
- B. Persons not wearing protective equipment should be restricted from areas of spills or leaks until cleanup has been completed.

MONITORING AND MEASUREMENT PROCEDURES

- A. Exposure Above the Action Level:
  1. Eight hour exposure evaluation: Measurements taken for the purpose of determining employee exposure under this section are best taken such that the average eight-hour exposure may be determined from a single sample or two (2) four-hour samples. Short term samples (up to 30 minutes) may also be used to determine average exposure level if a minimum of five (5) measurements are taken in a random manner over the eight-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random equal duration samples taken on one (1) work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).
  2. Ceiling Evaluation: Measurements taken for the purpose of determining employee exposure under this section must be taken during periods of maximum expected airborne concentrations of methylene chloride in the employee's breathing zone. A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.
  3. Peak Above Ceiling Evaluation: Measurements taken for the purpose of determining employee exposure under this section must be taken during periods of maximum expected airborne concentration of methylene chloride. Each measurement should consist of a 5-minute sample or series of consecutive samples totaling five (5) minutes

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in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

4. Monitoring Techniques: The sampling and analyses under this section may be performed by instruments such as: detector tubes certified by NIOSH under 42 CFR Part 84, portable direct-reading instruments, dosimeters, or gas and vapor adsorption tubes with subsequent chemical analyses. The method of measurement must determine the concentration of methylene chloride to plus or minus 35%.

B. Exposure Above the Permissible Exposure: The monitoring and measurements under this section should be essentially the same described under paragraph (IV)(A). When sampling for peak exposure evaluations, more than three (3) measurements should be taken during the work shift so that increased confidence may be placed in the judgement that the employee has or has not, in fact, been exposed in excess of the permissible limit. Laboratories performing chemical analyses should be accredited in Industrial Hygiene Chemistry by the American Industrial Hygiene Association. The method of measurement must determine the concentration of methylene chloride to plus or minus 25%.

C. Methods: Methods meeting the above accuracy requirements are available from NIOSH.

D. Qualified Persons: Since many of the duties relating to employee protection are dependent on the results of monitoring and measuring procedures, employers should assure that the evaluation of employee exposures is performed by a competent industrial hygienist or other technically qualified person.

#### MISCELLANEOUS PRECAUTIONS

- A. Store methylene chloride in tightly closed containers in a cool, dry, well ventilated area.
- B. High exposures to methylene chloride can occur when transferring the liquid from one container to another.
- C. Employers should advise employees of all areas and operations where exposure to methylene chloride could occur.

#### COMMON OPERATIONS

Common operations in which exposure to methylene chloride is likely to occur are: during its production and its use as a solvent in paint and varnish removers, cold and ultrasonic cleaning, in the manufacture of cellulose acetate, in extraction and in paints, lacquers and varnishes; as a degreaser; as a refrigerant; as an ingredient in aerosol formulations, and in plastics processing; and in the manufacture of bromochloromethane.

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APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

ROUTE OF ENTRY

alation.

TOXICOLOGY

ethylene chloride vapor is a mild narcotic. Exposure of animals to 1000 ppm for 7 hours was fatal; cats repeatedly exposed to 7200 ppm for weeks developed kidney and liver damage. Animals repeatedly exposed to 1000 ppm for 6 months showed no histologic abnormalities. Cardiac arrhythmias attributed to sensitization of the myocardium have been observed following exposure to high concentrations of some chlorinated hydrocarbons, but dogs exposed to 10,000 and 20,000 ppm of methylene chloride did not show this phenomenon. In human experiments, inhalation of 500 to 1000 ppm for 1 to 2 hours resulted in lightheadedness; there was a sustained elevation of carboxyhemoglobin level. A chemist exposed repeatedly to concentrations ranging from 500 to 3600 ppm developed signs of toxic encephalopathy. A healthy young worker engaged in degreasing metal parts had a brief exposure to an undetermined but very high concentration of vapor. He complained of excessive fatigue, weakness, dizziness, lightheadedness, chills, and nausea; pulmonary edema developed after several hours, but all signs and symptoms had cleared within 18 hours of terminating the exposure. Liquid methylene chloride is irritating to the skin on repeated contact. Splashed in the eye, it is painfully irritating, but is not likely to cause serious injury.

SIGNS AND SYMPTOMS

fatigue, weakness, sleepiness, lightheadedness, numbness and tingling of the limbs; nausea; irritation of the eyes and skin from liquid splashes.

SPECIAL TESTS

Carboxyhemoglobin levels may be a useful measure of biochemical effect.

TREATMENT

Remove the person from exposure. Flush eyes with water and wash skin with soap and water. If swallowed and the person is conscious, induce vomiting. Give artificial resuscitation if indicated. Recovery is usually rapid and complete.

SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

GENERAL

In animals at high doses, methylene chloride causes narcosis. It is also reported that methylene chloride metabolism causes an increase in CO levels. Persons with pre-existing heart disease may be at

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increased risk. It has poor warning properties because humans adapt readily to it. It is important that the physician become familiar with plant operating conditions in which exposure to methylene chloride occurs. Those with skin disease may not tolerate the wearing of protective clothing and those with chronic respiratory disease may not tolerate the wearing of negative pressure respirators.

#### PREPLACEMENT

Routine medical histories and physical examination are not required. However, the employer must screen employees for history of certain medical conditions (listed below) which might place the employee at increased risk from methylene chloride exposure. Only those giving a positive history of these conditions must be referred for further medical examinations.

1. Skin disease -- Methylene chloride can cause dermatitis on prolonged exposure. Persons with preexisting skin disorders may be more susceptible to the effects of this agent.
2. Liver disease -- Methylene chloride causes liver damage in animals and this justifies consideration before exposing persons with impaired liver function.
3. Kidney disease -- Methylene chloride causes kidney disease in animals and this justifies special consideration before exposing persons with impaired renal function.
4. Cardiovascular Disease -- Because of reports of excessive carbon monoxide levels following exposure to methylene chloride, persons with cardiac disease may be at increased risk.

#### PERIODIC EXAMINATIONS

Routine periodic examinations are not required. However, if the employer becomes aware of an employee with the above-listed conditions, he must refer such employee for further medical examination.

ences

American Conference of Governmental Industrial Hygienists: "Methylene Chloride (Dichloromethane)," Documentation of the Threshold Values for Substances in Workroom Air (3d ed., 2d printing); Cincinnati, 1974, pp. 338-339.

Hygienic Guide Series: "Dichloromethane," American Industrial Hygiene Association Journal, 26:633-636, 1965.

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Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II -  
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pp. 1257-1259.

Hughes, J. P.: "Hazardous Exposure to Some So-Called Safe Solvents,"  
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Stewart, R. D., et al: "Experimental Human Exposure to Methylene  
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Reinhardt, C. F., et al: "Epinephrine-Induced Cardiac Arrhythmia  
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REFERENCES AND SOURCES  
METHYLENE CHLORIDE  
1910.93

Compliance - Open surface tank classification based on  
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Fire and Safety  
Electrical - Classification based on "Fire Hazard Classifica-  
tion of Chemical Vapors Relative to Explosion-proof Electrical  
Equipment," H. Carhart et al., National Academy of Sciences,  
1973, report to U. S. Coast Guard, report no. CG-D-92-74, p. 17.  
Personal Protective Equipment, and, (h) Sanitation  
s: Patty, "Industrial Hygiene and Toxicology;" Grant, "Toxicology  
of the Eye"  
n: "Methylene Chloride," Manufacturing Chemists Association, Inc.,  
Chemical Safety Data Sheet; "Methylene Chloride," Commonwealth  
of Pennsylvania, Dept. of Environmental Resources (Occupational  
Health); Patty, "Industrial Hygiene and Toxicology;" Stewart et al.,  
"Absorption of Carbon Tetrachloride, Trichloroethylene,  
Tetrachloroethylene, Methylene Chloride and 1,1,1-Trichloroethane  
Through the Human Skin," AIHA Journal, Sept. - Oct. 1964, p. 439  
estation: Sax, "Dangerous Properties of Industrial Materials;"  
Stecher, "The Merck Index"

MENTS

Eye - Classification: 2

Output statement numbers: 10

Exceptions: None

Patty states that "direct contact with the liquid will be  
painful and irritating, but it is not likely to cause  
serious injury." Grant reports that methylene chloride  
"presents no particular hazard to the eyes."

Skin - Classification: 2

Output statement number: 2, 16g, 16i

Exceptions: See below

The Commonwealth of Pennsylvania reports that "repeated skin  
contact can cause a dry, scaling and fissured dermatitis."  
Patty notes, "the problem may be accentuated by the chemical  
being sealed to the skin by shoes or tight clothing. The  
situation is most severe with paint remover formulations  
that form a 'skin' or film." In a human subject experiment,  
Stewart et al reported "within two minutes following  
immersion of the thumbs in (methylene chloride) all subjects  
experienced an intense burning sensation on the dorsum of  
their thumbs." Following ten minutes of immersion, any  
movement "triggered waves of searing pain." After removal  
from the exposure, the thumbs reportedly felt "numb and  
cold, as if asleep." The slight erythema and parathesia  
subsided in one hour. Stewart examined alveolar air for  
evidence of skin absorption and found a maximum concentra-  
tion 20 minutes after exposure (1.1 - 6.6 ppm). After  
5 hours less than 0.1 ppm was still detectable. A classi-  
fication of 2 is concluded to be sufficient for the  
substance. Statements

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7 and 20 are not used because of its high vapor pressure at 20 C of 350 mm Hg. It does not have a flashpoint.

The NFPA Handbook considers it to be "practically non-flammable."

Ingestion - Classification: 0

Output statement numbers: None

Exceptions: None

An oral MLD for dogs of 3000 mg/kg is recorded in the Merck Index. Acute local and acute systemic effects are reported as moderate by Sax, while chronic systemic effects are considered slight. The vapor pressure of the substance is so high that ingestion of harmful amounts is concluded not to present a problem in industry.

SUBSTANCE TECHNICAL GUIDELINES

References cited for this document include:

National Fire Protection Association, "Fire Protection Guide on Hazardous Materials," 5th edition, 1973 (NFPA)

Manufacturing Chemists Association, Chemical Safety Data Sheet SD-86 (MCA)

Stauffer Chemical Co., "Stauffer Chlorinated Hydrocarbons" (Stauffer)  
Chemical USA, "Dow Methylene Chloride" (Dow)

As of data items used:

- A. 1. Synonyms: NFPA-325M; NFPA-49; MCA
2. Formula: NFPA-325M
3. Molecular weight: Stauffer
1. Boiling point: NFPA-325M/ MCA
2. Specific gravity: NFPA-325M; MCA
3. Vapor density: NFPA-325M; MCA
4. Melting point: MCA; Dow; Stauffer
5. Vapor pressure: MCA; Stauffer
6. Solubility in water: Stauffer
7. Evaporation rate: Stauffer
8. Appearance and odor: NFPA-49
- A. 1. Flash point: NFPA-49
2. Autoignition temperature: NFPA-49
3. Flammable limits: MCA; NFPA-49
4. Extinguishing media: ADL
5. Special fire fighting procedures: NFPA-49; MCA
6. Unusual fire and explosion hazards: ADL
1. Conditions contributing to instability: ADL
2. Incompatibilities: ADL
3. Hazardous decomposition products: NFPA-49; ADL
4. Special precautions: ADL
- A. Steps if released or spilled: ADL

Waste disposal method: MCA; ADL

Miscellaneous precautions: NFPA-49

USE/EXPOSURE AND CONTROL DOCUMENT

References used in the preparation of this document include:

Chemical Abstracts, "78, 79 (1973), 80 (1974), Chemical Abstracts Service (CA)  
Chemical Engineering," June 24, 1974, p. 149 (Chem Eng)

Conline, D. M., "Chemical and Process Technology Encyclopedia," McGraw  
Hill, 1974 (Considine)

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SH HSM-99-73-62 (HPI)  
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2 (MCA)  
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Occup. Med. 6(2), 116 - 20 (1952) (Moskowitz)  
n, M. S., "Methylene Chloride: New Problems?," Michigan Dept.  
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- Riestra, J. F., "Food Processing with Chlorinated Solvents,"  
d Technology 28(2), 25 - 32 (1974) (Valle - Riestra)  
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Considine, Safety Council, Moskowitz, ILO, HPI, Dow Chem Eng,  
na #98, Guide, Profile  
Sciarra, CA, Safety Council, Chem Eng, HPI, Dow, Guide, SRI, Profile  
Chem Eng, Safety Council, Dow HPI, ILO, Penna #98, NIOSH 11852,  
file, SRI  
Chem Eng, Dow, ILO, HPI, Penna #98, Safety Council, Profile, SRI  
ILO, SRI, Faith, Chem Eng, HPI, SRI  
Considine, HPI, ILO, Chem Eng, Dow SRI, Faith, Safety Council  
Dow, SRI, CA, Safety Council, Considine, HPI, Patty, Chem Eng.  
owitz, Valle - Riestra  
Dow, Guide, CA, Considine, SRI, Safety Council, HPI, Patty, Chem Eng,  
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CA, Sciarra, Chem Eng, Dow  
Chem Eng  
SRI, Moskowitz, Chem Eng, Dow, Safety Council  
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owitz were the references used for all of the Specific Control  
ods.

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RESPIRATOR TABLE DOCUMENTATION

ance: Methylene chloride

L. Standard: 500 ppm, where 1000 ppm shall not be exceeded except  
t a peak is permitted of 2000 ppm for 5 minutes in any 2 hours.

NG PROPERTIES:

r Threshold: Different authors have reported varying odor thresholds  
for methylene chloride. Summer and Staub both report 150 ppm;  
Kirk-Othmer and Sax both report 25 - 50 ppm; Spector reports  
320 ppm. Patty, however, states that since one can become adapted  
to the odor, odor cannot be considered an adequate warning  
property.

Irritation Level: Grant reports that methylene chloride "presents  
no particular hazard to the eyes." Kirk-Othmer, however, reports  
that "methylene chloride vapor is seriously damaging to the  
eyes." Sax agrees with Kirk-Othmer's statement.

The Documentation of TLV's states that irritation of the  
eyes has been observed in workers who had been exposed to concen-  
trations up to 5000 ppm, but that neurasthenic disorders were  
found in 50%, and digestive disturbances in 30% of the persons  
exposed.

ar Information: Gleason reports that methylene chloride may be  
"irritating to the respiratory tract and may produce pulmonary  
edema," but Gleason gives no quantitative information. The  
Documentation of TLV's reports that in one investigation,  
irritation of the respiratory passages was observed in workers who  
had been exposed to concentrations up to 5000 ppm.

luation of Warning Properties: Since there is no detailed inform-  
ation available relating the irritant effects of methylene  
chloride to air concentrations and since adaptation to the odor  
occurs, methylene chloride is treated as a material with poor  
warning properties. Gas sorbent respiratory equipment is not  
permitted.

5000 ppm

is for IDLH Value: Spector states that a 10 minute exposure to  
methylene chloride at 2330 ppm produces vertigo in man. On the  
other hand, Sax states that at 2300 ppm there was no feeling of  
dizziness during one-hour exposures. Thienes and Haley in  
Clinical Toxicology page 117 state that no dizziness, but  
slight nausea, is caused by exposure to a concentration of 2300  
ppm for one hour and state that "at a concentration of 25,000  
ppm methylene chloride is not lethal. The proposed threshold  
limit value for methylene chloride has been reduced from 500 ppm  
to 100 ppm which would have limited the use of other than self-  
contained breathing apparatus to 5000 ppm based on protection  
factor considerations had the 100 ppm been set as the standard.  
Considering the above information an IDLH of 5000 ppm is used  
for this substance.

ar Toxicological Information: Methylene dichloride is highly  
volatile and, therefore, in poorly ventilated areas high concen-  
trations may develop.

Patty reports that the principal physiological response  
to an exposure to methylene chloride is narcosis. "It does not

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cause significant organic injury." Exposures to high concentrations may cause loss of consciousness rapidly. Other "symptoms of excessive exposure may be dizziness, nausea, tingling or numbness of the extremities, sense of fullness in the head, sense of heat, stupor, or dullness, lethargy, and drunkenness."

Patty reports a mouse 8-hour LC50 of 15,000 ppm. All animals survived a concentrations of 11,000 ppm for the same period.

The Documentation of TLV's notes that Lehmann and Flury observed that "slight narcosis occurs at 4000 to 6100 ppm in several species of animals," and that many investigators have determined lethal concentrations of approximately 15,000 ppm for a 7-hour exposure.

120,000 ppm

PRESSURE: 350 mm Hg at 20 deg. C.

440 mm Hg at 25 deg. C

ATED CONCENTRATIONS AT: 20 deg. C.: Approximately 460,500 ppm  
25 deg. C.: Approximately 579,000 ppm

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USE/EXPOSURE AND CONTROL DOCUMENT  
METHYLENE CHLORIDE

Use/Exposure	Principal Route of Entry	Currently Used Control Methods
Inhalation of vapor and skin contact with liquid during use as a solvent in paint and varnish removers	A,B,D	General dilution ventilation; local exhaust ventilation; personal protective equipment (goggles, gloves, protective clothing)
Inhalation of vapor and skin contact with liquid during manufacture and use of aerosols (used as solvent and vapor pressure depressant for insecticides, polishes, paints, hair sprays, room deodorants, oven cleaners, fire extinguishing agents)	A,B,D	General dilution ventilation; local exhaust ventilation; personal protective equipment (goggles, gloves, protective clothing)
Inhalation of vapor and skin contact with liquid during use as solvent in cold cleaning and ultrasonic cleaning (for electrical and electronic equipment, automotive equipment, office and plant maintenance, textiles, apparel, leather goods, metal and metal fabrication industries, aerospace, nuclear, and precision industries, machinery and molds for plastics manufacture, brush cleaners, carbon removers; used with other industrial cleaning solvents to reduce flammability)	A,B,D	General dilution ventilation; local exhaust ventilation; personal protective equipment (goggles, gloves, protective clothing)
Inhalation of vapor and skin contact with liquid during use as solvent in vapor degreasing (thermal switches, thermometers)	A,B,D	Process enclosure; local exhaust ventilation
Inhalation of vapor and	A,B,D	Process enclosure; local

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skin contact with liquid during manufacture and distribution of methylene chloride		exhaust ventilation; personal protective equipment (goggles, respiratory protective devices)
Inhalation of vapor and skin contact with liquid during use as cooling solvent in the manufacture of cellulose acetate (used for manufacture of fibers, lacquers, protective coatings, photographic film, thermoplastic molding compositions, cigarette filters, magnetic tape)	A,B,D	Process enclosure; local exhaust ventilation
Inhalation of vapor and skin contact with liquid during use in plastics processing (solvent for manufacture of resins and plastics (methyl methacrylate and epoxy resins), blowing agent for flexible foams, mold release agent, solvent for manufacture of synthetic fibers (rayon and PVC), solvent in processing of photographic film)	A,B,D	Process enclosure; local exhaust ventilation
Inhalation of vapor and skin contact with liquid during use as an extraction solvent (for edible fats, cocoa, butter, beer flavoring in hops, decaffeinated coffee, oleoresin manufacture for furniture processing), oils, waxes, perfumes, flavorings, drugs)	A,B,D	General dilution ventilation; local exhaust ventilation; personal protective equipment (goggles, gloves, protective clothing)
Inhalation of vapor and skin contact with liquid during wide use as solvent for paints, lacquers, varnishes, enamels, adhesives, rubber cements, in	A,B,D	General dilution ventilation; local exhaust ventilation; personal protective equipment (goggles, gloves, protective clothing)

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manufacture of printed  
circuit boards, for  
organic synthesis, as  
carrier for pharmaceutical  
tablet coatings, for  
shrink-fitting of synthetic  
rubber covers, in dyeing of  
synthetic fibers)

Inhalation of vapor and  
skin contact with liquid  
during use in organic  
synthesis (preparation  
of bromochloromethane)

A,B,D

Process enclosure; local  
exhaust ventilation

Inhalation of vapor and  
skin contact with liquid  
during use as a secondary  
refrigerant (in air  
conditioning, for  
scientific testing)

A,B,D

General dilution ventila-  
tion; local exhaust venti-  
lation; personal protec-  
tive equipment (goggles,  
gloves, protective  
clothing)

- A -- Inhalation
- B -- Skin and eye contact resulting in  
localized irritation
- C -- Ingestion
- D -- Skin contact resulting in  
absorption and subsequent  
systemic poisoning