

Methylene Chloride Workplace Chemical Protection Program

Issue Date: 12/5/2024

Applies to: All laboratories, shops, studios, and work areas where methylene chloride or mixtures containing methylene chloride at 0.1% or greater concentration is handled. This program applies to all employees, students, and visitors, including persons not employed by U-M, with the potential to be exposed (i.e., potentially exposed persons) to methylene chloride at a U-M facility.

Adherence to this Program satisfies the Workplace Chemical Protection Program (WCPP) and Exposure Control Plan requirements of 40 CFR Part 751, Methylene Chloride; Regulation Under the Toxic Substances Control Act.

Appendix A: Operation Specific Exposure Control Plan shall be completed by the end user to detail the specific controls that are in place.

Description

Methylene chloride (CAS # 75-09-2) is a volatile, colorless liquid with a chloroform-like odor. Synonyms include: Dichloromethane; DCM; MeCl & MeCl₂, Methane dichloride; Methylene bichloride; Methylene dichloride. This Program applies to all isotopologues of methylene chloride, including its deuterated form (CAS # 1665-00-5).

Regulatory Information

In April 2024, the <u>EPA finalized prohibitions and workplace protections under the Toxic Substances</u> <u>Control Act (TSCA) for methylene chloride</u> that prohibits most industrial and commercial uses of methylene chloride. Thirteen conditions of use of methylene chloride are not subject to complete prohibition under this rule. This Program pertains to the following two conditions of use permitted by the EPA rule:

Use as a Laboratory Chemical: refers to the industrial or commercial use of methylene chloride in a laboratory process or in specialized laboratory equipment for instrument calibration/maintenance chemical analysis, chemical synthesis, extracting and purifying other chemicals, dissolving other substances, executing research, development, test and evaluation methods, and similar activities, such as use as a solvent, reagent, analytical standard, or other experimental use.

Use as a bonding agent for solvent-welding: refers to the industrial or commercial use of methylene chloride or a solvent blend including methylene chloride to chemically bond polymer substrates including, but not limited to, acrylic or polycarbonate, creating an airtight, waterproof, and in some cases seamless joint.

For these conditions of use, the EPA has mandated that employers institute a Workplace Chemical Protection Plan (WCPP). All other uses of methylene chloride are prohibited.

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<u>Part 313, Methylene Chloride</u> is a general industry standard promulgated by the Michigan Occupational Safety and Health Administration (MIOSHA) to regulate occupational exposure to methylene chloride. Compliance with this Program satisfies requirements of both the EPA rule and, where applicable, MIOSHA Part 313.

Potential Hazards

- Methylene chloride exposure can cause adverse health effects to the central nervous system (CNS), liver, and cardiovascular system including mental confusion, light-headedness, nausea, vomiting, and headache.
- Methylene Chloride is metabolized by the body to carbon monoxide and therefore reduces the blood's ability to transport oxygen. It is also a suspected carcinogen.
- Exposure may also cause eye and respiratory tract irritation.
- Skin exposure to liquid may cause irritation and skin burns after extended exposures.
- Consult the SDS for methylene chloride, U-M's <u>GoldFFX SDS database</u>, as well as the references section for more information.

Occupational Exposure Limits (OELs)

Existing occupational exposure limits Occupational Exposure Limits enacted by the EPA's TSCA regulation are significantly more restrictive than MIOSHA OELs and must be adhered to.

- EPA Existing Chemical Exposure Limit (ECEL): 2 ppm (8 mg/m) as an 8-hour TWA
- EPA Action Level: 1 ppm (4 mg/m) as an 8-hour TWA
- EPA Short-Term Exposure Limit (STEL): 16 ppm (57 mg/m3) as a 15-minute TWA
- MIOSHA Action Level: 12.5 ppm as an 8-hour TWA
- MIOSHA 8-hour Permissible Exposure Limit (PEL): 25 ppm as an 8-hour TWA
- MIOSHA 15-minute STEL: 125 ppm as a 15-minute TWA

Exposure monitoring

Exposure monitoring is mandatory to ensure that all potentially exposed persons are not exposed to methylene chloride above the EPA exposure limits and to ensure regulatory compliance for all persons exposed above the EPA action level. Before commencing any new operations involving methylene chloride at or above 0.1% concentration or altering existing operations in any manner that may present increased exposure potential, users shall notify EHS to perform an exposure assessment.

Exposure monitoring shall be completed by EHS for all new operations and when a change is made to an existing operation that may present an increased exposure. If the initial monitoring results indicate the exposure is below the EPA action level and the EPA STEL, subsequent monitoring shall be conducted at least once every 5 years. Under scenarios where the action level, ECEL, or STEL are exceeded, or the task to be monitored does not occur within the required monitoring period, subsequent monitoring shall be conducted in accordance with 40 CFR 751.109(d)(3).

Exposure monitoring shall be conducted for all potentially exposed persons or for an individual or group of individuals determined to be representative of the exposure group. EHS shall determine when representative samples are appropriate.

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Potentially exposed persons will be notified of monitoring results within 15 business days after receipt of the monitoring results.

EHS shall maintain recordkeeping of all exposure monitoring events for a period of at least 5 years from the monitoring event.

Operation Specific Exposure Control Plan

The supervisor, or a competent representative, of the unit or group that conducts operations involving methylene chloride shall complete and maintain Appendix A: Operation Specific Exposure Control Plan (ECP). The ECP documents exposure control measures used by the unit or group, how the controls are implemented, and why alternative controls were not selected. The supervisor of the unit or group is ultimately responsible for development, implementation, compliance, and maintenance of the ECP within their work areas.

Whenever it is feasible to do so, personnel are required to substitute methylene chloride with a safer alternative or eliminate methylene chloride from operations entirely. If substitution or elimination are not feasible, it shall be documented why these controls are not feasible in the ECP.

Procedures for responding to any change that may reasonably be expected to introduce additional sources of exposure, or otherwise result in increased exposure, including procedures for implementing corrective actions to mitigate exposure to methylene chloride, shall be documented in the ECP. Supervisors, or a competent representative, will review and update the exposure control plan to ensure effectiveness of the exposure controls, identify any necessary updates to the exposure controls, and confirm that all persons are properly implementing the exposure controls.

Engineering Controls

- Work with open containers of methylene chloride should be conducted only in a fume hood, glovebox, or other containment device.
- Operations that involve the handling of methylene chloride outside of a fume hood or glove box must be vetted via exposure monitoring to ensure they do not exceed exposure limits.
- Emergency eyewash and shower facilities must be readily available within the work area for immediate flushing or eyes or skin in the event of personal exposure.

Work Practice Controls

- Designate an area for working with methylene chloride, and label it as such.
- Keep containers closed as much as possible. Handle open containers only in a chemical fume hood.
- Use in the smallest practical quantities for the experiment being performed.
- Purchase smaller unit volumes of stock containers. For example, refilling of kegs for a solvent purification system can be performed in a standard height fume hood if filled from 4L bottles.
- Once work with methylene chloride is complete, wipe down the work area with soap and water solution.
- Keep away from ignition sources. Incompatible with strong oxidizers and metals.
- Wash hands thoroughly after use. Do not eat, drink, or smoke in areas where methylene chloride or other chemicals are used.

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Regulated areas

- As defined by the EPA, A regulated area distinguishes places where airborne concentrations of methylene chloride exceed, or there is a reasonable possibility they may exceed, the applicable ECEL or the EPA STEL.
- Regulated areas must be established within 3 months following receipt of monitoring data that indicates the EPA ECEL or STEL is exceeded.
- A regulated area must be visibly marked from the rest of the workplace in a manner that
 adequately establishes and alerts potentially exposed persons to the boundaries of the area and
 minimizes the number of authorized persons exposed to methylene chloride within the
 regulated area.
- Demarcation of the regulated area will be accomplished by posting of signage that reads
 "Danger: Regulated Area. Methylene chloride, authorized personnel only. Respiratory protection
 and protective clothing required". Barriers, caution tape, or any other highly visible indicator that
 would effectively indicate the boundaries of the area may be used, in addition to the required
 signage.
- Access to the regulated area is restricted to authorized individuals who have received appropriate training and personal protective equipment.
- Respiratory protection is required by all individuals who enter the regulated area while
 operations involving methylene chloride are being conducted. Respiratory protection shall be
 issued and used in compliance with the following section (Personal Protective Equipment).

Personal Protective Equipment

Skin and eye protective equipment

- Methylene chloride readily penetrates through standard nitrile, natural rubber, and polyvinyl chloride laboratory gloves.
- Wear two pairs of gloves when using methylene chloride. Disposable gloves provide minimum
 protection for general laboratory use and should be changed frequently or whenever contamination
 is suspected.
- The <u>inner glove</u> should be made of a laminate of <u>polyethylene (PE)/ethylene vinyl alcohol (EVOH)</u>, e.g., Silvershield®/4H by North or a laminate of <u>Viton®/Butyl rubber</u>, a laminate of <u>polyethylene vinyl alcohol/ethylene vinyl alcohol (PVA/EVA)</u>, <u>Polyvinyl Alcohol (PVA)</u>, or other laminate materials that are resistant to methylene chloride to prevent penetration through to skin.
- Based on work activities, <u>outer gloves</u> made of nitrile or neoprene are also recommended to prevent
 cuts, tears, punctures, or rips to the inner methylene chloride-resistant gloves. [NOTE: Because
 methylene chloride can readily penetrate nitrile and neoprene, wearing just an outer glove of this
 material will not protect your skin from methylene chloride exposure.]
- Do not wear contact lenses while working with methylene chloride.
- Splash goggles should be worn when a splash hazard exists; safety glasses with side shields (both that meet the requirements of ANSI/ISEA Z87.1) are required at a minimum when methylene chloride is used in a closed system.
- A fully buttoned laboratory coat must be worn when working with chemicals. A chemically resistant
 apron should be used if transferring or using large quantities of methylene chloride in open
 containers.

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Also, refer to the EHS <u>Glove Compatibility Chart</u>.

Respiratory Protection

- Respiratory protection is to be used only when all other control measures are exhausted. When
 engineering, substitution, engineering, and administrative controls cannot feasibly reduce
 exposures below the EPA OELs, respiratory protection is mandatory.
- If respiratory protection is needed, supplied-air respirators must be used. Cartridge based air purifying respirators are not permitted.
- All use of respiratory protection must be prescribed by EHS and all users of respiratory
 protection must comply with the <u>U-M Respiratory Protection Program</u>. If prescribed, users will
 receive training on the use, maintenance, and care of the prescribed respirator.
- When prescribed, respirator selection criteria shall comply with 40 CFR 751.109(f)(2).

Transportation and Storage

- Transport methylene chloride in secondary containment, preferably a polyethylene or other non-reactive acid/solvent bottle carrier.
- Keep the container in a cool, well-ventilated area.
- Keep the container tightly closed and sealed until ready for use.
- Store in secondary containment away from moisture, strong oxidizers, strong caustics, plastics, rubber, nitric acid, water + heat, and chemically active metals, such as aluminum and magnesium powder, sodium, potassium, and lithium.
- Avoid storing on the floor.
- Avoid ignition sources.

Medical Surveillance

Medical surveillance will be available for employees who may be exposed above the EPA action level on 30 or more days per year or above the EPA ECEL or EPA STEL on 10 or more days per year. When a medical determination recommends removal because the employee's exposure to methylene chloride may contribute to or aggravate the employee's existing cardiac, hepatic, neurological (including stroke), or skin disease, medical removal protection benefits will be provided. When applicable, medical surveillance services will be provided by U-M Occupational Health Services (OHS).

Personal Exposure and Spill Response

Refer to the <u>Laboratory Emergencies SOP</u> for detailed spill response procedures and treatment facilities.

In case of personal exposure, remove the affected person from the exposure immediately. Flush the affected area for at least 15 minutes with an emergency eyewash or shower, as appropriate. Seek medical attention.

Minor, incidental spills wholly contained by a fume hood or glovebox may be handled by adequately trained personnel. Contain and collect the spilled material with absorbents. Package for hazardous waste disposal. Use care to avoid personal exposure via inhalation or dermal contact.

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Spills or any unintended release outside of a fume hood or glovebox **must be reported** to emergency personnel for response and cleanup. Any volume of methylene chloride released outside of direct containment will almost certainly result in overexposure to not equipped with respiratory protection.

Waste Disposal

Spent, unused, and expired methylene chloride is considered hazardous waste and must be properly disposed of in accordance with state and federal regulations. Contact EHS-HMM at (734) 763-4568 for waste containers, labels, manifests, waste collection, and any questions regarding proper waste disposal. Also, refer to the EHS <u>Hazardous Waste</u> Web page for more information.

Training of Personnel

Training will be provided by the supervisor to potentially exposed persons prior to or at the time of initial assignment to a task involving potential exposure to methylene chloride.

- Availability of this U-M Workplace Chemical Protection Program document
- Presentation of the Operation Specific Exposure Control Plan(s) and acknowledgment of ECP by the trainee
- Requirements and accessibility of the MIOSHA Methylene Chloride Standard and the EPA TSCA Final Rule on Methylene Chloride
- Hazards communication, labeling, and safety data sheets
- Methods and observations to detect the presence of methylene chloride
- Operations where methylene chloride may be present
- Measures individuals must take to protect themselves from hazards associated with methylene chloride. This includes:
 - The proper use of engineering controls
 - When to use PPE
 - Proper donning, doffing, adjustment, and wearing of PPE
 - o PPE limitations
 - Proper care maintenance, useful life, and disposal of PPE

References and additional resources

Regulatory references and additional reading

- US EPA Risk Management for Methylene Chloride
 - https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-methyle ne-chloride
- MIOSHA Part 3131 Methylene Chloride
 - o https://www.michigan.gov/leo/-/media/Project/Websites/leo/Documents/MIOSHA/Standards/C ombined/CS_GI_313/CS_GI_313__03-31-2021.pdf?rev=1f810151c39e44258cd070ff755c9bbb& hash=8E722FCCA850E8FDFBD7E1CE32285BAF
- US OSHA Substance Safety Data Sheet and Technical Guidelines for Methylene Chloride
 - o http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=10095

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- ASTDR -ToxFAQs for Methylene Chloride
 - o https://wwwn.cdc.gov/TSP/ToxFAQs/ToxFAQsDetails.aspx?faqid=233&toxid=42#:~:text=chemicals%20are%20present.-.Highlights,chloride%20can%20result%20in%20burns
- NIOSH Pocket Guide to Chemical Hazards Methylene Chloride
 - o https://www.cdc.gov/niosh/npg/npgd0414.html

Alternative Chemical Selection

- Sigma-Aldrich Greener Solvent Alternatives
 - https://www.sigmaaldrich.com/deepweb/assets/sigmaaldrich/product/documents/115/ 677/greener_solvent_alternatives.pdf
- A convenient guide to help select replacement solvents for dichloromethane in chromatography
 - https://pubs.rsc.org/en/content/articlelanding/2012/gc/c2gc36064k
- ACS Tools for Innovation in Chemistry: Solvent Selection Tool
 - https://www.acsgcipr.org/tools-for-innovation-in-chemistry/

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Major Revisions (Tracking purposes only -- Do not print)

Date	Revision
12/5/2024	Initial Publication