

**criteria for a recommended standard . . . . .  
occupational exposure to  
methylene chloride**

**U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE**  
Public Health Service    Center for Disease Control  
National Institute for Occupational Safety and Health

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**OCCUPATIONAL EXPOSURE  
TO  
METHYLENE CHLORIDE**



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## PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers exposed to an ever-increasing number of potential hazards at their workplace. The National Institute for Occupational Safety and Health has projected a formal system of research, with priorities determined on the basis of specified indices, to provide relevant data from which valid criteria for effective standards can be derived. Recommended standards for occupational exposure, which are the result of this work, are based on the health effects of exposure. The Secretary of Labor will weigh these recommendations along with other considerations such as feasibility and means of implementation in developing regulatory standards.

It is intended to present successive reports as research and epidemiologic studies are completed and as sampling and analytical methods are developed. Criteria and standards will be reviewed periodically to ensure continuing protection of the worker.

I am pleased to acknowledge the contributions to this report on methylene chloride by members of my staff and the valuable constructive comments by the Review Consultants on methylene chloride, by the ad hoc committees of the American Industrial Hygiene Association and the American Academy of Occupational Medicine, by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine, and by William M. Pierce on respiratory protection and work practices. The NIOSH recommendations for

standards are not necessarily a consensus of all the consultants and professional societies that reviewed this criteria document on methylene chloride. Lists of the NIOSH Review Committee members and of the Review Consultants appear on the following pages.

*John F. Finklea, M.D.*

John F. Finklea, M.D.  
Director, National Institute for  
Occupational Safety and Health

The Division of Criteria Documentation and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for development of the criteria and recommended standard for methylene chloride. Agatha Corporation developed the basic information for consideration by NIOSH staff and consultants under contract No HSM-99-73-20. Jon R. May, Ph.D., had NIOSH program responsibility. Final preparation of the document was accomplished by Robert W. Mason, Ph.D.

REVIEW COMMITTEE  
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

Elliott S. Harris, Ph.D.  
Director, Division of Biomedical and  
Behavioral Sciences

Richard E. Kupel  
Division of Physical Sciences  
and Engineering

Marshall E. LaNier  
Director, Division of Technical Services

Frank L. Mitchell, D.O.  
Division of Criteria Documentation and  
Standards Development

Department of Labor Liaison:

Robert Manware  
Office of Standards

NIOSH REVIEW CONSULTANTS ON METHYLENE CHLORIDE

Jacqueline Messite, M.D.  
Assistant Director  
Division of Industrial Hygiene  
State Department of Labor  
New York, New York 10013

David A. Padden  
International Union, United Automobile, Aerospace  
& Agricultural Implement Workers of America-UAW  
Detroit, Michigan 48214

Leonard D. Pagnotto  
Division of Occupational Hygiene  
Massachusetts Department of Labor and Industries  
Boston, Massachusetts 02116

Jack E. Peterson, Ph.D.  
Department of Environmental Medicine  
Medical College of Wisconsin  
Milwaukee, Wisconsin 53226

Robert L. Raleigh, M.D.  
Assistant Director  
Health and Safety Laboratory  
Eastman Kodak Company  
Rochester, New York 14650

Lyman K. Skory  
DOW Chemical Company  
Midland, Michigan 48640



CRITERIA DOCUMENT: RECOMMENDATIONS FOR AN  
OCCUPATIONAL EXPOSURE STANDARD FOR METHYLENE CHLORIDE

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## I. RECOMMENDATIONS FOR A METHYLENE CHLORIDE STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that worker exposure to dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), commonly known as methylene chloride, be controlled in the workplace by adherence to the following sections. The standard is designed to protect the health and safety of workers for up to a 10-hour workday, 40-hour workweek over a working lifetime; compliance with all sections of the standard should prevent adverse effects of methylene chloride on the health and safety of workers. The standard is measurable by techniques that are valid, reproducible, and available to industry and governmental agencies. Sufficient technology exists to permit compliance with the recommended standard. The standard will be subject to review and revision as necessary.

"Occupational exposure to methylene chloride" is defined as exposure above one-half the daily time-weighted average (TWA) exposure limit, except when there is also exposure to carbon monoxide (CO) at more than 9 ppm.

Because the toxicities of CO and methylene chloride are additive, the appropriate environmental limit and action level of methylene chloride must be reduced in the presence of CO. When CO levels are more than 9 ppm "occupational exposure to methylene chloride" shall be determined from the following formula:

$$\frac{C(\text{CO})}{L(\text{CO})} + \frac{C(\text{CH}_2\text{Cl}_2)}{L(\text{CH}_2\text{Cl}_2)} \leq 0.5$$

where:

C(CO) = TWA exposure concentration of CO, ppm

L(CO) = the recommended TWA exposure limit of CO = 35 ppm

C(CH<sub>2</sub>Cl<sub>2</sub>) = TWA exposure concentration of methylene chloride, ppm

L(CH<sub>2</sub>Cl<sub>2</sub>) = the recommended TWA exposure limit  
of methylene chloride = 75 ppm

Exposure to methylene chloride below the appropriate "occupational exposure" level as defined above will not require adherence to the following sections, except for Section 4(a)(4), Section 6(d), and Sections 7(a) and (b).

Section 1 - Environmental (Workplace Air)

(a) Concentration

(1) In the absence of occupational exposure to CO above a time-weighted average (TWA) of 9 ppm for up to a 10-hour workday, occupational exposure to methylene chloride shall be controlled so that workers are not exposed to methylene chloride in excess of 75 ppm (261 mg/cu m) determined as a TWA for up to a 10-hour workday, 40-hour workweek.

(2) In the presence of exposure to CO in the work environment at more than 9 ppm determined as a TWA exposure for up to a 10-hour workday, exposure limits of CO, or methylene chloride or both shall be reduced to satisfy the relationship:

$$\frac{C(\text{CO})}{L(\text{CO})} + \frac{C(\text{CH}_2\text{Cl}_2)}{L(\text{CH}_2\text{Cl}_2)} \leq 1$$

where:

C(CO) = TWA exposure concentration of CO, ppm

L(CO) = the recommended TWA exposure limit of CO = 35 ppm

C(CH<sub>2</sub>Cl<sub>2</sub>) = TWA exposure concentration of methylene chloride, ppm

L(CH<sub>2</sub>Cl<sub>2</sub>) = the recommended TWA exposure limit  
of methylene chloride = 75 ppm

(3) Occupational exposure shall be controlled so that workers are not exposed to methylene chloride above a peak concentration of 500 ppm (1,740 mg/cu m) as determined by any 15-minute sampling period.

(b) Sampling and analysis

(1) Procedures for sampling and analysis of workroom air for methylene chloride shall be as provided in Appendices I and II, or by any equivalent methods.

(2) Where required, monitoring of workroom air for CO shall be in accord with the sampling requirements of this and the CO standard. Recommended methods for sampling and analysis of workroom air for CO are given in Criteria for a Recommended Standard...Occupational Exposure to Carbon Monoxide.

Section 2 - Medical

(a) Comprehensive preplacement and annual medical examinations shall be made available to all workers subject to exposure to methylene chloride unless a different frequency is indicated by professional medical judgement based on such factors as emergencies, variations in work periods, and preexisting health status of individual workers.

(b) These examinations shall include, but shall not be limited to:

(1) A comprehensive or interim medical and work history to include but not be limited to occurrence of headache, dizziness, fatigue, pain in the limbs, and irritation of the skin and eyes.

(2) A comprehensive medical examination including at least blood counts (hemoglobin or rbc). In addition, clinical impressions of autonomic and pulmonary function shall be noted and follow-up measurements

shall be made where indicated.

(3) An evaluation of the advisability of the workers using respirators.

(4) Such a medical program could also provide the opportunity for advising the worker of the increased hazards of methylene chloride exposure due to CO from tobacco smoking.

(5) It is recommended that COHb values be determined periodically at the end of the workday. It is further recommended that this sampling and analysis be quarterly and coincide with environmental monitoring. If COHb values in excess of 5% are found, an investigation of the source of COHb shall be instituted, and if appropriate from this investigation, periodic environmental monitoring for CO shall be performed.

(c) Medical records shall be maintained for persons employed one or more years in work involving methylene chloride. All medical records with supporting documents shall be maintained at least 5 years after the individual's employment is terminated. The medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employer, and of the employee or former employee shall have access to all medical records.

### Section 3 - Labeling (Posting)

The following sign shall be affixed in a readily visible location at or near entrances to areas in which there is occupational exposure to methylene chloride:

METHYLENE CHLORIDE

CAUTION: BREATHING VAPOR MAY BE  
HAZARDOUS TO HEALTH.

Use only with adequate ventilation.

Keep containers closed when not in use.

May generate toxic phosgene gas on contact  
with flame or very hot metal surface.

AVOID CONTACT WITH SKIN.

Can be absorbed through skin.

This warning sign shall be printed in English and, unless they are otherwise trained and informed of the hazardous conditions, in the predominant language of non-English-speaking workers. Illiterate workers shall be informed.

Section 4 - Personal Protective Equipment and Clothing

(a) Respiratory Protection

(1) Engineering controls shall be used wherever feasible to maintain methylene chloride concentrations at or below the prescribed limits. Compliance with the permissible exposure limits may be achieved by the use of respirators only:

(A) During the time period necessary to install or test the required engineering controls.

(B) For nonroutine operations such as brief exposure at concentrations in excess of the environmental limit for maintenance or repair activities.

(C) During emergencies when air concentrations of methylene chloride may exceed the permissible limit.

(2) When respirators are permitted by paragraph (1) of this Section, a respirator program meeting the requirements of 29 CFR 1910.134 and 30 CFR 11.2-1 shall be established and enforced by the employer.

(3) Only appropriate respirators as described in Table I-1 shall be used pursuant to the following requirements:

(A) For the purpose of determining the type of respirator to be used, the employer shall measure, when possible, the atmospheric concentration of methylene chloride in the workplace initially and thereafter whenever process, worksite, climate, or control changes occur which are likely to increase the methylene chloride concentration; this requirement shall not apply when only supplied-air, positive pressure respirators will be used.

(B) The respirator and canister used shall be of the appropriate class, as determined on the basis of exposure to methylene chloride. The employer shall ensure that no worker is being exposed to methylene chloride in excess of the standard because of improper respirator selection, fit, use, or maintenance.



TABLE I-1  
 RESPIRATOR SELECTION GUIDE FOR PROTECTION  
 AGAINST METHYLENE CHLORIDE

Maximum Use Concentrations of Methylene Chloride (Multiples of TWA)	Respirator Type
Less than or equal to 750 ppm (10X)	1) Any supplied air respirator.
Less than or equal to 3,750 ppm (50X)	1) Any supplied air respirator, with full facepiece, helmet or hood. 2) Any self-contained breathing apparatus with full facepiece.
3,750 ppm or more	1) Self-contained breathing apparatus, pressure demand mode (positive pressure), in full facepiece. 2) Combination supplied air respira- tor, pressure demand mode, with auxiliary self-contained air supply.
Evacuation or escape (no concentration limit)	1) Any escape-type, self-contained breathing apparatus. 2) Any escape-type gas mask providing protection against methylene chloride

(C) The employer shall provide respirators in accordance with Table I-1 and shall ensure that the employee uses the respirator provided.

(D) Respiratory protective devices described in Table I-1 shall be those approved under provisions of 30 CFR 11.

(E) Respirators specified in Table I-1 for use in higher concentrations of methylene chloride are permitted in atmospheres of lower concentrations.

(F) Industrial size and chin-type canisters shall not be used except for escape.

(G) Chemical cartridge respirators shall not be used with methylene chloride.

(H) The employer shall ensure that respirators are adequately cleaned, maintained, and stored and that employees are instructed on the use of respirators and on how to test for leakage.

(4) Where an emergency may develop which could result in employee injury from overexposure to methylene chloride, the employer shall provide respiratory protection as listed in Table I-1.

(b) Protective Clothing

In any operation where the worker may come into direct contact with liquid methylene chloride, protective clothing shall be worn. The clothing shall be both impervious and resistant to methylene chloride. Gloves, boots, overshoes, and bib-type aprons (at least knee length) shall be provided when necessary. Impervious supplied-air hoods or suits shall be worn when entering confined spaces such as pits or tanks. In situations where heat stress is likely to occur, air-supplied suits shall be used.

All protective clothing shall be well aired and inspected for physical defects prior to reuse.

(c) Eye Protection

Eye protection shall be provided for any employee engaged in an operation where methylene chloride liquid or spray may enter the eye. Chemical-type goggles, safety glasses with splash shields, or plastic face shields made completely of methylene chloride-resistant materials shall be used.

Suitable eye protection shall be in accordance with 29 CFR 1910.133.

Section 5 - Informing Employees of Hazards from Methylene Chloride

(a) All new and present employees in a methylene chloride area shall be kept informed of the hazards, relevant symptoms, effects of over-exposure to, and proper precautions concerning safe use and handling of methylene chloride. The increased hazards of methylene chloride exposure from concomitant exposure to CO in the environment and from hard work and smoking shall be included in the information.

(b) The information explaining hazards of working with methylene chloride shall be kept on file and readily accessible to the worker at all places of employment where methylene chloride is manufactured, used, transported or stored.

(c) Information as required shall be recorded on US Department of Labor Form OSHA-20 "Material Safety Data Sheet," or a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

Section 6 - Work Practices

(a) Handling and Storage

(1) Containers delivered by truck or rail shall not be unloaded until the vehicle in which they arrived has been ventilated. The vehicle shall not be entered if the odor of methylene chloride is perceptible.

(2) Storage containers, piping, and valves shall be periodically checked for leakage.

(3) Storage facilities shall be designed to:

(A) Contain spills.

(B) Prevent contamination of workroom air.

(b) Contaminant Controls

(1) Suitable engineering controls designed to limit exposure to methylene chloride to that prescribed in subsection (a) of Section 1 shall be utilized. Ventilation systems shall be designed to prevent the accumulation or recirculation of methylene chloride in the workroom and to effectively remove methylene chloride from the breathing zones of workers. Ventilation systems shall be subjected to regular preventive maintenance and cleaning to ensure maximum effectiveness, which shall be verified by periodic airflow measurements.

(2) Portable exhaust ventilation or suitable general ventilation shall be provided for operations that require the application of liquid methylene chloride, such as paint removal or machine degreasing.

(c) Equipment Maintenance and Emergency Procedures

Air saturated with methylene chloride is immediately dangerous to life and creates a limited egress situation.

(1) Exits from methylene chloride hazard areas shall be plainly marked. Emergency exit doors shall be conveniently located and shall open to areas which will remain free of contamination in an emergency.

(2) Confined spaces

(A) Entry into confined spaces or into other areas where there may be limited egress shall be controlled by a permit system. Permits shall be signed by an authorized representative of the employer certifying that preparation of the confined space, precautionary measures, personal protective equipment, and procedures to be used are all adequate.

(B) Tanks, pits, tank cars, process vessels, tunnels, sewers, or other confined spaces which have contained methylene chloride shall be thoroughly ventilated, tested for methylene chloride, oxygen, carbon monoxide, flammable gases, and other suspected noxious gases and inspected prior to entry.

(C) Inadvertent infiltration of methylene chloride into the confined space while work is in progress inside shall be prevented by disconnecting and blanking off methylene chloride supply lines.

(D) Confined spaces shall be ventilated to keep any methylene chloride concentration below the standard and to prevent oxygen deficiency.

(E) Personnel entering confined spaces shall be furnished with adequate personal protective equipment and with a lifeline tended by another worker outside the space. The worker on the outside shall also be equipped with approved respiratory, eye, and skin protection, lifeline, and have contact with a third party.

(F) Written operating instructions and emergency medical procedures shall be formulated and posted in conspicuous locations where accidental exposure to anesthetic concentrations of methylene chloride may occur. These instructions and procedures shall be printed in English and, unless they are otherwise trained and informed of the hazardous areas, in the predominant language of non-English-speaking workers, if any. All illiterate workers shall receive such training.

(d) Showers and Eye Wash Fountains

Showers and eye wash fountains shall be provided and so located as to be readily accessible in all areas where skin or eye splash with methylene chloride is likely. If methylene chloride is splashed on the skin, contaminated clothing shall be promptly removed and the skin washed with soap and water. If liquid methylene chloride contacts the eyes, they shall be thoroughly irrigated with clean water. Medical assistance shall be promptly provided in cases of eye splash. Such incidents shall be reported to the immediate supervisor by the affected employee or by a fellow worker.

Section 7 - Monitoring and Recordkeeping

(a) Where it has been determined that the environmental concentrations do not result in TWA workday exposures above one-half the TWA environmental limit, environmental monitoring is not required. However, records which form the basis for concluding that the exposures are below one-half the limit shall be maintained and exposure surveys shall be made when any process change indicates the need for reevaluation or at the discretion of the compliance officer.

(b) Where exposure concentrations have not been determined, they shall be determined within 6 months of the promulgation of a standard incorporating these recommendations.

(c) Where it has been determined that environmental concentrations result in TWA workday exposures above one-half the limit, employers shall maintain records of environmental exposures to methylene chloride based upon the following sampling and recording schedules:

(1) Samples shall be collected at least every 6 months in accordance with Appendix I for the evaluation of the work environment with respect to the recommended standard.

(2) Environmental samples shall be taken when a new process is installed or when process changes are made which may cause an increase in environmental concentrations. Increased production, relocation of existing operations, and increased overtime also requires resampling.

(3) In all monitoring, samples shall be collected which are representative of breathing-zone exposures characteristic of each job or specific operation in each work area. Sufficient numbers of samples shall be collected to express the variability of exposure for the work situation and to estimate TWA workday exposures and peak exposures for every employee.

(4) The minimum number of representative TWA exposure determinations for an operation or process shall be based on variation in exposures and production schedules, considering the number of workers exposed as suggested in Table I-2, and as indicated by a professional industrial hygienist.

(d) When exposure levels are found to be greater than those prescribed in Section 1(a), environmental concentrations shall be reduced by suitable engineering controls. Exposures shall be monitored at least weekly until the effectiveness of the controls is established.

(e) All records of sampling and of pertinent medical examinations shall be maintained for at least 5 years after the individual's employment is terminated. Records shall indicate the type of personal protective devices, if any, in use at the time of sampling. Each employee shall have access to information on his own environmental exposure.

TABLE I-2  
SAMPLING SCHEDULE

Number of Employees Exposed	Number of TWA Determinations
1-20	50% of the number of workers
21-100	10 plus 25% of the excess over 20 workers
more than 100	30 plus 5% of the excess over 100 workers



## II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon which were prepared to meet the need for preventing occupational diseases arising from exposure to methylene chloride. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare, under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "...develop criteria dealing with toxic materials and harmful physical agents and substance which will describe ...exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

The National Institute for Occupational Safety and Health after a review of data and consultations with others, formalized a system for the development of criteria upon which standards can be established to protect the health of workers from exposure to hazardous chemical and physical agents. It should be pointed out that any criteria and recommended standard should enable management and labor to develop better engineering controls resulting in more healthful work environments and simply complying with the standard should not be the final goal.

These criteria for a standard for methylene chloride are part of a continuing series of criteria developed by NIOSH. The proposed standard applies to the processing, manufacture, and use of methylene chloride as applicable under the Occupational Safety and Health Act of 1970.

These criteria were developed to assure that the standard based thereon would (1) protect against development of acute and chronic

methylene chloride poisoning, (2) be measurable by techniques that are valid, reproducible, and available to industry and governmental agencies, and (3) be attainable with existing technology.