

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** DIAZOMETHANE ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for DIAZOMETHANE

The basic text of this document contains the draft technical standard approved by the Joint Review Committee of the NIOSH/OSHA Standards Completion Program and the supporting documentation for the substance DIAZOMETHANE.

The SCP draft technical standards are recommendations to the Department of Labor 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.

The References and Sources, Respirator Table Documentation and Use/Exposure and 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 each substance and the regulatory statements were derived following a decision logic established for the various sections of the standard.

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(a) Definitions. (1) "Permissible exposure" means exposure of employees to airborne concentrations of diazomethane not in excess of 0.2 parts per million (ppm) (0.4 milligrams per cubic meter, mg/m³) averaged over an eight-hour work shift (time weighted average), as stated in § 1910.1000, Table Z-1.

(2) "Action level" means one half of the permissible exposure for diazomethane.

(b) Exposure determination and measurement. (1) Each employer who has a place of employment in which diazomethane is released into the workplace shall determine if any employee may be exposed to airborne concentrations of diazomethane 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 diazomethane.

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

(i) Any information, observations, or calculation which may indicate employee exposure to diazomethane;

(ii) Any measurements of diazomethane taken;

(iii) Any employee complaints of symptoms which may be attributable to exposure to diazomethane; and

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

(3) If the employer determines that any employee may be exposed to diazomethane 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.

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

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

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

(5) If an employee exposure measurement reveals that an employee is exposed to diazomethane 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.

(6) If an employee exposure measurement reveals that an employee is exposed to diazomethane above the permissible exposure, the employer shall:

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

(ii) Institute control measures as required by paragraph (d) of this section; and

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

(7) If two consecutive employee exposure measurements taken at least one week apart reveal that the employee is exposed to diazomethane below the action level, the employer may terminate measurement for the employee.

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(8) For purposes of this paragraph, employee exposure is that which would occur if the employee were not using a respirator.

(c) Methods of measurement. (1) An employee's exposure shall be obtained by any combination of long term or short term samples which represents the employee's actual exposure averaged over an eight-hour work shift (See Appendix B (iv) of this section).

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

Table 1

Concentration	Required Accuracy
Above permissible exposure	$\pm 25\%$
At or below permissible exposure and above the action level	$\pm 35\%$
At or below the action level	$\pm 50\%$

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

(2) Employee exposures to airborne concentrations of diazomethane shall be controlled to at or below the permissible exposure by engineering and work practice controls:

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

(ii) Wherever engineering and work practice controls are not sufficient to reduce exposures to at or below the permissible exposure, they shall nonetheless 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.

(3) Engineering controls. 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 diazomethane.

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

(i) During the time period necessary to install or implement engineering or work practice controls; or

(ii) In work situations in which engineering and work practice controls are technically not feasible; or

(iii) To supplement engineering and work practice controls when such controls fail to reduce airborne concentrations of diazomethane to at or below the permissible exposure; or

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- (iv) For operations which require entry into tanks or closed vessels; or
- (v) In emergencies.

(5) 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 DIAZOMETHANE

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION
Gas Concentration	
2 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
10 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 10 ppm or entry and escape from unknown 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.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

(6) 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.

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

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

(2) Sources of ignition such as smoking, open flames and hot surfaces are prohibited where diazomethane is used, handled, or stored.

(3) Diazomethane shall be stored so as not to come in contact with alkali metals, drying agents, sunlight, and bright illumination.

(4) Contact of diazomethane with sharp edges, such as ground glass, shall be avoided.

(5) For the purposes of compliance with § 1910.309, locations classified as hazardous locations due to the presence of diazomethane shall be Class I Group C.

(6) For the purposes of compliance with § 1910.178, locations classified as hazardous locations due to the presence of diazomethane shall be Class I Group C.

(f) Personal protective equipment. (1) Employers shall provide and ensure that employees use impervious clothing, gloves, face shields (eight-inch minimum) and other appropriate protective clothing necessary to prevent the skin from becoming contaminated with liquid diazomethane or solutions containing diazomethane or from becoming frozen from contact with vessels containing liquid diazomethane. Face shields shall comply with § 1910.133 (a)(2), (a)(4), (a)(5), and (a)(6).

(2) Employers shall ensure that clothing wet with flammable solutions containing diazomethane is placed in closed containers for storage until it can be discarded or until the employer provides for the removal of diazomethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the diazomethane, the employer shall inform the person performing the operation of the hazardous properties of diazomethane.

(3) Employers shall ensure that clothing which becomes wet with liquid diazomethane or flammable solutions containing diazomethane be removed immediately and not reworn until the flammable liquids have been removed from the clothing.

(4) Employers shall ensure that non-impervious clothing which becomes contaminated with solutions containing diazomethane be removed promptly and not reworn until the diazomethane is removed from the clothing.

(5) 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 there is any possibility of liquid diazomethane or solutions containing diazomethane contacting the eyes.

(6) Where there is any possibility that an employee's eyes may be exposed to liquid diazomethane or solutions containing diazomethane, employers shall provide an eye-wash fountain within the immediate work area for emergency use.

(g) Spills and disposal. In the event that diazomethane is inadvertently released or solutions containing diazomethane are spilled, the employer shall immediately eliminate potential sources of ignition, provide available ventilation and then clean up the spill.

(h) Sanitation. Employers shall ensure that employees whose skin becomes contaminated with solutions containing diazomethane promptly wash

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or shower with soap or mild detergent and water to remove the solutions from the skin.

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

(2) Each employer who has employees exposed to diazomethane above the action level or employees who may have skin or eye contact with liquid diazomethane or solutions containing diazomethane, or employees who work where diazomethane presents a fire or explosion hazard, shall annually:

(i) Inform affected employees of the information contained in the Substance Safety Data Sheet for diazomethane (Appendix A of this section);

(ii) Advise affected employees as to the signs and symptoms of exposure to diazomethane.

(iii) Instruct affected employees to advise the employer of the development of signs and symptoms of exposure to diazomethane which are listed in Appendix A of the section; and

(iv) Provide training to ensure that employees understand the precautions of safe use, emergency procedures, and the correct use of protective equipment relative to diazomethane.

(j) 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.

(2) The employer shall make available to each employee who is to be exposed to airborne concentrations of diazomethane at or above the action level, without regard to the use of respirators, a medical examination which shall include the following:

(i) A medical history and physical examination with emphasis on the lungs.

(ii) 14" x 17" chest roentgenogram.

(iii) Pulmonary function testing, FVC and FEV (1 sec).

(3) The employer shall obtain from the physician, as a record of the examination, the following information:

(i) A written opinion which conforms with paragraph (j)(7) of this section.

(ii) 14" x 17" chest roentgenogram or a medically acceptable copy.

(iii) A record of the results of the pulmonary function testing.

(4) The employer shall make available to each employee, exposed to diazomethane in excess of the action level at 12 months from the date of the employee's first exposure, and at every 12 months of exposure in excess of the action level thereafter, a medical examination which must include the following:

(i) A medical history and physical examination (see paragraph (j)(2)(i) of this section).

— (ii) Pulmonary function testing, FVC and FEV (1 sec).

(iii) 14" x 17" chest roentgenogram (only when indicated by results of pulmonary function testing, FVC and FEV (1 sec)).

(5) The employer shall obtain from the physician, as a record of the periodic examination, the following information:

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(i) A written opinion which conforms with paragraph (j)(7) of this section.

(ii) 14" x 17" chest roentgenogram or a medically acceptable copy.

(iii) A record of the results of the pulmonary function testing.

(6) The employer shall provide to the examining physician the following information:

(i) A copy of this regulation with its Appendixes A, B, and C for diazomethane;

(ii) A description of the employee's duties as they relate to his exposure to diazomethane;

(iii) A description of any personal protective equipment and respirators required to be used;

(iv) The results of any measurement which may indicate the affected employee's exposure;

(v) The affected employee's anticipated exposure; and

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

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

(B) Any recommended limitations upon the employee's exposure to diazomethane, including limitations upon the use of personal protective equipment and respirators;

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

(ii) The physician's written opinion shall not reveal specific medical findings or diagnoses unrelated to exposure to diazomethane.

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

(8) No employee shall be exposed to liquid diazomethane or airborne concentrations of diazomethane 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.

(9) The employer shall provide emergency and follow-up medical examinations and treatment for any employee injured through exposure to diazomethane.

(10) If the examining physician chooses to use alternative medical examinations to those specified in paragraphs (j)(2) and (4) of this section, the employer may accept such alternative medical surveillance examinations as meeting the requirements of this part provided that the employer:

(i) Obtains a statement from the examining physician setting forth the alternative medical examinations and the rationale for substitution and evidence that they will be equally effective.

(ii) Informs each exposed employee of the fact that alternative medical examinations to those required in paragraphs (j)(2) or (4) of this section are to be made available.

(11) If an employee refuses any required medical examination, the employer shall inform the employee of the possible health consequences of

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such refusal and obtain a signed statement from the employee indicating that the employee understands the risks involved by refusing to be examined.

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

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

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

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

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

(ii) This record shall include:

(A) The date of measurement;

(B) Operations involving exposure to diazomethane which are being monitored;

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

(D) Number, duration, and results of samples taken; and

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

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

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

(ii) This record shall include:

(A) Date of measurement;

(B) Type of measurement taken;

(C) Result of measurement.

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

(4) 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.

(ii) This record shall include:

(A) Date of training;

(B) Name and social security number of employee trained;

(C) Content or scope of training provided.

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

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

(ii) The record shall include:

(A) Results of tests required by paragraph (j)(2) and (j)(5) of this section;

(B) Any employee medical complaints relative to exposure to diazomethane;

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(C) A copy of information provided to the physician pursuant to paragraph (j)(6)(ii), (iii), (iv), (v), and (vi) of this section.

(D) Physician's written opinion; and

(E) A signed statement of any refusal to be examined.

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

(6) 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.

(ii) 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.

(iii) 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.

(1) Employee observation of measurement. (1) The employer shall give affected employees or their representatives an opportunity to observe any measurement of employee exposure to diazomethane which is conducted pursuant to this section.

(2) When observation of measurement of employee exposure to diazomethane requires entry into an area where the use of personal protective devices, including respirators, is required, the observer shall be provided with and required to use such equipment and comply with all other applicable safety procedures.

(3) Without interfering with the measurement, observers shall be entitled to:

(i) Receive an explanation of the measurement procedure.

(ii) Visually observe all steps related to the measurement of the airborne concentration of diazomethane that are being performed at the place of exposure; and

(iii) Record the results obtained.

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

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APPENDIX A

SUBSTANCE SAFETY DATA SHEET
FOR DIAZOMETHANE

I. SUBSTANCE IDENTIFICATION

- A. Substance: Diazomethane
- B. Permissible Exposure: 0.2 parts of diazomethane per million parts of air (ppm) (0.4 milligram of diazomethane per cubic meter of air, mg/cu m) averaged over an eight-hour work shift.
- C. Appearance: Yellow gas. When stored under pressure, diazomethane can be in the liquid form.

II. HEALTH HAZARD DATA

- A. Comments: Diazomethane is an extrahazardous chemical. It is a very severe irritant. With sensitization, very low exposures which previously did not cause problems may cause serious effects.
- B. Ways in Which the Chemical Affects Your Body: Diazomethane 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.
- C. Effects of Overexposure:
 - 1. Short-Term Exposure: Exposure to diazomethane vapor may cause severe irritation of the eyes, nose, throat, skin, and lungs. Symptoms include headache, weakness, cough, fever, chest pains, shortness of breath and wheezing. The onset of symptoms after exposure may be delayed. Skin and mucous membrane exposure to liquids containing diazomethane may cause burns with the loss of the skin or mucous membrane. If any of these symptoms appear, get medical attention immediately.
 - 2. Long-Term Exposure: Prolonged or repeated exposure to diazomethane may lead to sensitization. Should sensitization occur, you may experience asthma-like symptoms or fever from exposure to concentrations of diazomethane which had previously caused no symptoms. Diazomethane has been reported to cause cancer of the lung in animals.
 - 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 diazomethane.

-III. EMERGENCY FIRST AID PROCEDURES

- A. Eye Exposure: If liquid diazomethane or solutions containing diazomethane get into your eyes, wash the eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

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- B. Skin Exposure: If liquid diazomethane or solutions containing diazomethane gets on your skin, immediately flush the contaminated skin with water. If a containing diazomethane or solutions containing diazomethane soaks through your clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.
- C. Breathing: If you or any other person breathes in large amounts of diazomethane 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 diazomethane has been swallowed, get medical attention immediately. Do not make a person who has swallowed this chemical 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.

IV. RESPIRATORS AND PROTECTIVE CLOTHING

- A. Respirators: Respirators are not the best way to control exposure to diazomethane. 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 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 your skin becoming contaminated with liquid diazomethane or solutions containing diazomethane or becoming frozen from contact with vessels containing liquid diazomethane, where such contact may occur. Replace or repair impervious clothing that has developed leaks.
- C. Eye Protection: You must wear splash-proof safety goggles (cup-cover type dust and splash safety goggles) if there is any possibility of liquid diazomethane or solutions of diazomethane contacting your eyes.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

- A. Diazomethane is an explosive gas.
- B. Diazomethane must be stored in tightly closed containers in a cool, well ventilated area away from heat, light, sparks,

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flames, alkali metals and drying agents such as calcium sulfate.

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

VI. ACCESS TO INFORMATION

- A. Each year your employer is required to inform you of the information contained in this Substance Safety Data Sheet for diazomethane. In addition, your employer must instruct you in the safe use of diazomethane, emergency procedures, and the correct use of protective equipment.
- B. Your employer is required to determine whether you are being exposed to diazomethane. 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
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I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: azimethylene; diazirine
2. Formula: CH_2N_2
3. Molecular weight: 42

B. Physical Data

1. Boiling point (760 mm Hg): -23 C (-9 F)
2. Specific gravity (Water = 1): Data not available
3. Vapor density (air = 1 at boiling point of diazomethane): 1.
4. Melting point: -145 C (-229 F)
5. Vapor pressure at 20 C (68 F): not pertinent
6. Solubility in water, % by weight at 20 C (68 F): Reacts
7. Evaporation rate (butyl acetate = 1): not pertinent
8. Appearance: Yellow gas. When stored under pressure, diazomethane can be in the liquid form.

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: not pertinent
2. Autoignition temperature: Pure material explodes above 150 C (302 F). Impure material explodes at lower temperature.
3. Flammable limits in air, % by volume: data not available
4. Extinguishing media: Stop flow of gas.
5. Special fire-fighting procedures: Do not use a solid stream of water since the stream will scatter and spread the fire. Use water spray to cool containers exposed to a fire.
6. Unusual fire and explosion hazards: Diazomethane is an explosive gas. All ignition sources must be controlled where diazomethane is handled, used or stored in a manner that could create a potential fire or explosion hazard. Diazomethane is heavier than air and may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which diazomethane is handled. Diazomethane is often dissolved in flammable liquids such as ether.
7. For the purpose of complying with 29 CFR 1910.309, the classification of hazardous locations as described in Article 500 of the National Electric Code for diazomethane shall be Class I, Group C.

B. Reactivity

1. Conditions contributing to instability: Diazomethane may explode when not diluted with other inert gases such as nitrogen. Exposure of diazomethane gas or solutions

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in solvents to sunlight or other bright illumination may cause explosions. Contact with rough edges such as ground glass may cause explosion.

2. Incompatibilities: Contact of diazomethane gas with alkali metals or drying agents such as calcium sulfate will cause explosions.
3. Hazardous decomposition products: Data not available
4. Special precautions: Barriers or shields should be utilized to protect employees from accidental explosions.

III. LEAK AND DISPOSAL PROCEDURES

- A. If diazomethane is leaked, the following steps should be taken:
 1. Remove all ignition sources.
 2. Ventilate area of leak.
 3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair leak or allow cylinder to empty.
 4. If in the liquid form, allow to vaporize.
- B. Persons not wearing protective equipment should be restricted from areas of leaks until cleanup has been completed.
- C. Waste disposal methods: Diazomethane may be disposed of by burning at a safe location or in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

IV. MONITORING AND MEASUREMENT PROCEDURES

- A. Exposure Above the Action Level: Measurements taken for the purpose of determining employee exposure under this section are best taken such that the average 8-hour exposure may be determined from a single eight-hour sample or two (2) 4-hour samples. Several short time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling and analyses 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 diazomethane to plus or minus 35%.
- B. Exposure Above the Permissible Exposure: The monitoring and measurements under this section should be essentially the same as described under paragraph (IV)(A). 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 diazomethane to plus or minus 25%.
- C. Methods: Methods meeting the above accuracy requirements are available from NIOSH.

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- 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.

V. **MISCELLANEOUS PRECAUTIONS**

- A. Store diazomethane in tightly closed containers in a cool, well ventilated area.
- B. Apparatus in which diazomethane is handled should contain no ground glass joints or sharp glass edges.
- C. Ether solutions of diazomethane should not be distilled.
- D. Employers should advise employees of all areas and operations where exposure to diazomethane could occur.

VI. **COMMON OPERATIONS**

Common operations in which exposure to diazomethane is likely to occur are: during its production and its use as an intermediate in the synthesis of pharmaceuticals and a wide variety of organic chemicals, primarily on laboratory scale. It may be formed as an oxidative degradation product of methyl hydrazines.

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APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation.

II. TOXICOLOGY

Diazomethane gas is a severe respiratory irritant and sensitizer. It is one of the most dangerous products of the chemical laboratory, causing irritation of the eyes, chest pain, cough, fever, and severe asthmatic attacks. Exposure of cats to 175 ppm for 10 minutes resulted in pulmonary edema and hemorrhage, with death occurring in 3 days. A chemist briefly exposed to an unknown concentration in a laboratory developed a violent cough and shortness of breath leading to severe pulmonary edema; symptoms completely subsided within two weeks. In a fatal incident, another chemist exposed to an unknown concentration of diazomethane, as well as other irritant gases, experienced immediate respiratory distress leading to pneumonitis and death on the fourth day after exposure. A physician exposed to diazomethane from a laboratory spill noted only a faint odor, but immediately experienced severe headache, cough, mild anterior chest pain, generalized aching of muscles, and a sensation of overwhelming tiredness. Within five minutes he was stuporous, and on early admission to hospital was markedly flushed and feverish; he recovered in approximately 48 hours. Subsequent exposure to trace amounts of the gas produced wheezing, cough, and malaise, leading to the suspicion that this substance may have a sensitizing, as well as an irritating, effect upon the respiratory system. Skin irritation and sensitization occurs. Also mutagenic and carcinogenic effects have been reported in animals.

III. SIGNS AND SYMPTOMS

Cough and shortness of breath; headache; flushing of the skin and fever; fatigue; pain in the chest, pulmonary edema and pneumonitis; eye irritation; may produce asthmatic attacks.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

Remove from exposure. Give artificial resuscitation or oxygen if indicated. Consideration should be given to hospitalization and observation for possible delayed onset of pulmonary edema.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

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The warning properties of diazomethane are not adequate to prevent serious intoxication or fatalities. In view of the potentially lethal effect of unnoticed overexposure, and the potential development of hypersensitivity, it is justly recognized as an extrahazardous substance. It is important that the physician become familiar with plant operating conditions in which exposure to diazomethane occurs. Those with chronic respiratory disease may not tolerate the wearing of negative pressure respirators.

B. PREPLACEMENT

The following medical procedures must be made available to each employee who is exposed to diazomethane:

1. A complete history and physical examination -- The purpose is to detect preexisting conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of respiratory system should be stressed.
2. 14" x 17" chest roentgenogram -- Diazomethane may cause acute lung damage. Surveillance of the lungs is indicated.
3. FVC and FEV (1 sec) -- Diazomethane is reported to cause temporary pulmonary function impairment. Periodic surveillance is indicated.

C. PERIODIC EXAMINATIONS

The above medical examinations are to be repeated on an annual basis except that an x-ray is required only when indicated by pulmonary function testing.

References

1. American Conference of Governmental Industrial Hygienists: "Diazomethane," Documentation of the Threshold Limit Values for Substances in Workroom Air (3d ed., 2d printing), Cincinnati, 1974, pp. 71-72.
2. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 2213-2215.
3. Lewis, C. E.: "Diazomethane Poisoning, Report of a Case Suggesting Sensitization Reaction," Journal of Occupational Medicine, 6:91-93, 1964.
4. Schoental, R.: "Carcinogenic Action of Diazomethane and of Nitroso-N-methyl Urethane," Nature, 188:420-421, 1960.

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5. Schoental, R. and Magee, P.N.: "Induction of Squamous Carcinoma of the Lung and of the Stomach and Oesophagus by Diazomethane and N-Methyl-N-Nitroso-Urethane, Respectively," British Journal of Cancer, 16:92, 1962.

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REFERENCES AND SOURCES
DIAZOMETHANE
1910.93

- (e) Fire and Safety
(1) Electrical - Classification based on "Fire Hazard Classification 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. 31.
(f) Personal Protective Equipment, and, (h) Sanitation
Eye: Grant, "Toxicity of the Eye"
Skin: "Diazomethane," Encyclopedia of Occupational Safety and Health, International Labour Office; Grant, "Toxicology of the Eye;" Patty, "Industrial Hygiene and Toxicology"

COMMENTS

Eye - Classification: 1

Output statement numbers: 9, 13

Exceptions: None

Grant states that "a splash of concentrated solution in the eye would probably produce serious damage, increasing in severity for several hours or days after exposure."

Immediate pain and a burning sensation are reported.

A classification of 1 is concluded to be warranted.

Skin - Classification: 2

Output statement numbers: 7b, 21, 17g, 17i and certain low boiling liquid statements

Exceptions: See below

Because of the extreme chemical activity of diazomethane gas, it is not usually employed in this form but dissolved in ether or benzene solutions. This section deals with solutions containing the liquid. The ILO states "skin exposure was reported to produce denudation of the skin and mucous membranes" and it was claimed to resemble the toxicity of dimethyl sulphate. On this latter compound, Grant reports "on the skin liquid may cause no immediate discomfort but results several hours later in a burning and itching sensation with redness followed by severe blistering and necrosis." Contaminated clothing, especially in contact with wet, perspiring skin, should be removed as diazomethane slowly reacts with water to liberate nitrogen and form methyl alcohol. Patty also states that because of its high chemical reactivity and alkylating action, diazomethane is considered a mutagen. The ILO notes "skin application and subcutaneous injection have been shown to cause tumour development in experimental animals." The boiling point of the pure substance is -23 C. ILO notes that "either in the gaseous or liquid state, diazomethane explodes with flashes and even at -80 C, the liquid . . . may detonate."

The substance is given a classification of 2 for contact since the statement for preventing skin contact to low boiling liquids is used with the modification that clothing is to be worn to prevent skin becoming contaminated, not wet,

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with the substance. The specific wording used appropriately covers the case of skin contact with the pure liquid and its solutions. Statement 7b is used for flammable solutions containing the substance. Statement 21 is modified not only to cover the flammability problem of the liquid and its solutions but also the low boiling aspects of the pure liquid. Statement 17g and 17i cover the skin contact problems associated with liquid solutions.

Ingestion - Classification: 0

Output statement numbers: None

Exceptions: None

The physical properties make the chance of it being ingested in harmful quantities highly improbable.

SUBSTANCE TECHNICAL GUIDELINES

The references cited for this document include:

"Beilstein's Handbuch der Organischen Chemie, 23, 25; 1, 318
(supplements 1 - 4) (Beil)

H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, 1961, p. 21 (Zoll)

C. D. Gutsche, "Organic Reactions," Wiley, New York, 1954, Vol. 8, p. 364 (OR)

de Boer, T. J. and Backer, H. J., "Organic Synthesis," Coll. Vol. 4, 250 (1963) (OS)

Sources of data items used:

- I. A. 1. Synonyms: None listed
- 2. Formula: Beil
- 3. Molecular weight: Beil
- B. 1. Boiling point: Beil
- 2. Specific gravity: not applicable
- 3. Vapor density: ADL
- 4. Melting point: Beil
- 5. Vapor pressure: not applicable
- 6. Solubility in water: Beil
- 7. Evaporation rate: not applicable
- 8. Appearance and odor: Beil
- II. A. 1. Flash point: not applicable
- 2. Autoignition temperature: Beil
- 3. Flammable limits: data not available
- 4. Extinguishing media: not applicable
- 5. Special fire fighting procedures: ADL
- 6. Unusual fire and explosion hazards: OS
- B. 1. Conditions contributing to instability: OS
- 2. Incompatibilities: OR; Merk's Index
- 3. Hazardous decomposition products: Not applicable
- 4. Special precautions: ILO
- III. A. Steps if released or spilled: ADL
- C. Waste disposal method: OS
- V. Miscellaneous precautions: OS; OR; Zoll

USE/EXPOSURE AND CONTROL DOCUMENT

References used for the preparation of this document include:

Bucket, J. P. and Lauwerys, R. R., "Measurement of Urinary Hippuric and N-Methylhippuric Acids by Gas Chromatography," Brit. J. Ind. Med.,

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- 30(2), 125 - 8 (1972) (NIOSH Technical Information Service NIOSH 21528)
"Chemical Abstracts," 66 - 75 (1967 - 71); 78, 79 (1973); 80 (1974),
Chemical Abstracts Service (CA)
Cheng, H. H., "Picloram in Soil," Bull. Environ. Contamination and Toxicology,
6(1), 28 - 33 (1971) (NIOSH Technical Information Service NIOSH 15970)
Gros, E. G. and Flematti, S. M., "Methylation of Carbohydrates," Chem.
and Ind., Sept. 10, 1966, p. 1556 - 7 (Gros)
Hampel, C. A. and Hawley, G. G., "Encyclopedia of Chemistry," Van Nostrand
Reinhold, 1973 (Hampel)
International Labor Organization, "Encyclopedia of Occupational Health and
Safety," Geneva, 1972 (ILO)
Izzo, P. T. and Kende, A. S., "Reactions of Diazomethane with
Cyclopropanones," Chem. and Ind., May 1964, p. 839 - 40 (Izzo)
Kirk, R. and Othmer, D., "Encyclopedia of Chemical Technology," Interscience,
1st edition, 1954 (Chem Tech); 2nd edition, 1972 (K-O)
Mark, H. F., Gaylord, N. G. and Bikales, N. M., "Encyclopedia of Polymer
Science and Technology," Interscience, 1964 (Polymer Sci)
"Merck Index of Chemicals and Drugs," Merck and Co., Inc., 8th edition,
1968 (Merck)
Ord, W. O. and Bamford, P. C., "Preparation of Fatty Acid Methyl Esters,"
Chem. and Ind., Dec. 16, 1967, p. 2115 - 6 (Ord)
Patty, F. A., "Industrial Hygiene and Toxicology," Vol. II, Interscience,
1962 (Patty)
Plunkett, E. R., "Handbook of Industrial Toxicology," Chem. Pub. Co., 1966
(Plunkett)
Werner, H. and Richards, J. H., "Reaction of Nickelocene with Diazoalkanes,"
J. Am. Chem. Soc. 90(18), 4976 - 82 (1968 (Werner))
References for Specific Use/Exposure
1. CA, Merck, Izzo, Chem Tech, ILO, K-O, Hampel, Gros, Ord, Werner,
Polymer Sci
2. ILO, Patty
3. CA, NIOSH 21528, NIOSH 15970
References for Specific Control Methods
ILO, Merck, Patty, Plunkett were the references used for all numbers in
the Specific Control Methods.

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RESPIRATOR TABLE DOCUMENTATION

Substance: Diazomethane

D. O. L. Standard: 0.2 ppm

WARNING PROPERTIES:

Odor Threshold: Patty reports that diazomethane has a musty odor. No quantitative data are available, however, relating the odor to air concentrations of diazomethane.

Eye Irritation Level: Grant reports that "irritation of the eye from exposure to the gas has developed occasionally among those working with this substance." The concentrations causing eye irritation are not given.

Other Information: Patty reports that diazomethane is a severe respiratory tract irritant, but the concentrations producing this irritation are not given.

Evaluation of Warning Properties: Patty reports that "the warning properties of diazomethane are not adequate to prevent serious intoxication or fatalities." Based upon this report and upon the lack of quantitative data relating warning properties to air concentrations of diazomethane, this substance is treated as a material with poor warning properties. Gas sorbent respiratory equipment is not permitted.

IDLH: 10 ppm

Basis for IDLH Value: The only available acute inhalation toxicity information concerning diazomethane is the report in Patty that a 10-minute exposure to 175 ppm diazomethane was a lethal concentration for cats. Since this concentration is obviously too high for an IDLH concentration, the IDLH of 10 ppm diazomethane is based upon the statement in the Documentation of TLV's that "the toxicity of diazomethane seems comparable to that of phosgene." Patty points out that an exposure to 12.5 ppm phosgene might be dangerous within 30 - 60 minutes.

Other Toxicological Information: Patty reports that exposures to concentrations of diazomethane can produce "skin irritation, chest discomfort, asthmatic symptoms, and the development of hypersensitivity." Grant notes that "on the skin and respiratory mucous membranes diazomethane causes a severe, delayed inflammatory reaction." Death might occur from the poisonous action of diazomethane on the respiratory system.

Patty reports that cats which had been exposed to 175 ppm diazomethane for 10 minutes died from pulmonary edema and hemorrhage 3 days following the exposure.

The ILO notes that there have been several cases of acute diazomethane poisoning among laboratory workers and chemists. The literature on diazomethane poisoning, however, is scanty.

The Documentation of TLV's states that "the toxicity of diazomethane seems comparable to that of phosgene." Fairhall, according to the Documentation, "stated that diazomethane was undoubtedly one of the most dangerous products of the chemical laboratory, having caused irritation of eyes, dizziness, denudation of mucous membranes, and sensitization in laboratory workers."

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LFL: Data concerning the flammable limits of diazomethane are not available.

NOTE: Additional toxicological information is needed upon which to base an IDLH before this substance is promulgated as a standard.

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	Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1.	Inhalation of gas and skin contact with liquid* during use for laboratory organic synthesis (excellent methylating agent for preparation of ethers, ester, epoxides, pyrazoles, pyrazolines, polymers, used for aliphatic chain lengthening, addition and cycloaddition reactions)	A,B	Local exhaust ventilation; personal protective equipment (goggles, gloves, respiratory protective devices)
2.	Inhalation of gas and skin contact with liquid* during manufacture, distribution, and maintenance of storage containers	A,B	Local exhaust ventilation; personal protective equipment (goggles, gloves, respiratory protective devices)
3.	Inhalation of gas and skin contact with liquid* during use in chemical analysis as a methylating agent	A,B	Local exhaust ventilation; personal protective equipment (goggles, gloves, respiratory protective devices)

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

* Diazomethane is dissolved in solvents such as benzene or ethyl ether to prevent explosion.