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Title 29: Labor

PART 1910—OCCUPATIONAL SAFETY AND HEALTH STANDARDS
(CONTINUED)

Subpart Z—Toxic and Hazardous Substances

§ 1910.1050 Methyleneedianiline.

(a) *Scope and application.* (1) This section applies to all occupational exposures to MDA, Chemical Abstracts Service Registry No. 101-77-9, except as provided in paragraphs (a)(2) through (a)(7) of this section.

(2) Except as provided in paragraphs (a)(8) and (e)(5) of this section, this section does not apply to the processing, use, and handling of products containing MDA where initial monitoring indicates that the product is not capable of releasing MDA in excess of the action level under the expected conditions of processing, use, and handling which will cause the greatest possible release; and where no “dermal exposure to MDA” can occur.

(3) Except as provided in paragraph (a)(8) of this section, this section does not apply to the processing, use, and handling of products containing MDA where objective data are reasonably relied upon which demonstrate the product is not capable of releasing MDA under the expected conditions of processing, use, and handling which will cause the greatest possible release; and where no “dermal exposure to MDA” can occur.

(4) This section does not apply to the storage, transportation, distribution or sale of MDA in intact containers sealed in such a manner as to contain the MDA dusts, vapors, or liquids, except for the provisions of 29 CFR 1910.1200 and paragraph (d) of this section.

(5) This section does not apply to the construction industry as defined in 29 CFR 1910.12(b). (Exposure to MDA in the construction industry is covered by 29 CFR 1926.60).

(6) Except as provided in paragraph (a)(8) of this section, this section does not apply to materials in any form which contain less

than 0.1% MDA by weight or volume.

(7) Except as provided in paragraph (a)(8) of this section, this section does not apply to “finished articles containing MDA.”

(8) Where products containing MDA are exempted under paragraphs (a)(2) through (a)(7) of this section, the employer shall maintain records of the initial monitoring results or objective data supporting that exemption and the basis for the employer's reliance on the data, as provided in the recordkeeping provision of paragraph (n) of this section.

(b) *Definitions.* For the purpose of this section, the following definitions shall apply:

Action level means a concentration of airborne MDA of 5 ppb as an eight (8)-hour time-weighted average.

Assistant Secretary means the Assistant Secretary of Labor for Occupational Safety and Health, U.S. Department of Labor, or designee.

Authorized person means any person specifically authorized by the employer whose duties require the person to enter a regulated area, or any person entering such an area as a designated representative of employees, for the purpose of exercising the right to observe monitoring and measuring procedures under paragraph (o) of this section, or any other person authorized by the Act or regulations issued under the Act.

Container means any barrel, bottle, can, cylinder, drum, reaction vessel, storage tank, commercial packaging or the like, but does not include piping systems.

Dermal exposure to MDA occurs where employees are engaged in the handling, application or use of mixtures or materials containing MDA, with any of the following non-airborne forms of MDA:

(i) Liquid, powdered, granular, or flaked mixtures containing MDA in concentrations greater than 0.1% by weight or volume; and

(ii) Materials other than “finished articles” containing MDA in concentrations greater than 0.1% by weight or volume.

Director means the Director of the National Institute for Occupational Safety and Health, U.S. Department of Health and Human Services, or designee.

Emergency means any occurrence such as, but not limited to, equipment failure, rupture of containers, or failure of control equipment which results in an unexpected and potentially hazardous

release of MDA.

Employee exposure means exposure to MDA which would occur if the employee were not using respirators or protective work clothing and equipment.

Finished article containing MDA is defined as a manufactured item:

(i) Which is formed to a specific shape or design during manufacture;

(ii) Which has end use function(s) dependent in whole or part upon its shape or design during end use; and

(iii) Where applicable, is an item which is fully cured by virtue of having been subjected to the conditions (temperature, time) necessary to complete the desired chemical reaction.

4,4' Methylene dianiline or MDA means the chemical, 4,4'-diaminodiphenylmethane, Chemical Abstract Service Registry number 101-77-9, in the form of a vapor, liquid, or solid. The definition also includes the salts of MDA.

Regulated areas means areas where airborne concentrations of MDA exceed or can reasonably be expected to exceed, the permissible exposure limits, or where dermal exposure to MDA can occur.

STEL means short term exposure limit as determined by any 15 minute sample period.

(c) *Permissible exposure limits (PEL)*. The employer shall assure that no employee is exposed to an airborne concentration of MDA in excess of ten parts per billion (10 ppb) as an 8-hour time-weighted average or a STEL of 100 ppb.

(d) *Emergency situations* —(1) *Written plan*. (i) A written plan for emergency situations shall be developed for each workplace where there is a possibility of an emergency. Appropriate portions of the plan shall be implemented in the event of an emergency.

(ii) The plan shall specifically provide that employees engaged in correcting emergency conditions shall be equipped with the appropriate personal protective equipment and clothing as required in paragraphs (h) and (i) of this section until the emergency is abated.

(iii) The plan shall specifically include provisions for alerting and evacuating affected employees as well as the elements prescribed in 29 CFR 1910.38 and 29 CFR 1910.39, "Emergency action plans" and "Fire prevention plans," respectively.

(2) *Alerting employees.* Where there is the possibility of employee exposure to MDA due to an emergency, means shall be developed to alert promptly those employees who have the potential to be directly exposed. Affected employees not engaged in correcting emergency conditions shall be evacuated immediately in the event that an emergency occurs. Means shall also be developed and implemented for alerting other employees who may be exposed as a result of the emergency.

(e) *Exposure monitoring* —(1) *General.* (i) Determinations of employee exposure shall be made from breathing zone air samples that are representative of each employee's exposure to airborne MDA over an eight (8) hour period. Determination of employee exposure to the STEL shall be made from breathing zone air samples collected over a 15 minute sampling period.

(ii) Representative employee exposure shall be determined on the basis of one or more samples representing full shift exposure for each shift for each job classification in each work area where exposure to MDA may occur.

(iii) Where the employer can document that exposure levels are equivalent for similar operations in different work shifts, the employer shall only be required to determine representative employee exposure for that operation during one shift.

(2) *Initial monitoring.* Each employer who has a workplace or work operation covered by this standard shall perform initial monitoring to determine accurately the airborne concentrations of MDA to which employees may be exposed.

(3) *Periodic monitoring and monitoring frequency.* (i) If the monitoring required by paragraph (e)(2) of this section reveals employee exposure at or above the action level, but at or below the PELs, the employer shall repeat such representative monitoring for each such employee at least every six (6) months.

(ii) If the monitoring required by paragraph (e)(2) of this section reveals employee exposure above the PELs, the employer shall repeat such monitoring for each such employee at least every three (3) months.

(iii) The employer may alter the monitoring schedule from every three months to every six months for any employee for whom two consecutive measurements taken at least 7 days apart indicate that the employee exposure has decreased to below the TWA but above the action level.

(4) *Termination of monitoring.* (i) If the initial monitoring required by paragraph (e)(2) of this section reveals employee exposure to be below the action level, the employer may discontinue the monitoring for that employee, except as otherwise required by paragraph (e)(5)

of this section.

(ii) If the periodic monitoring required by paragraph (e)(3) of this section reveals that employee exposures, as indicated by at least two consecutive measurements taken at least 7 days apart, are below the action level the employer may discontinue the monitoring for that employee, except as otherwise required by paragraph (e)(5) of this section.

(5) *Additional monitoring.* The employer shall institute the exposure monitoring required under paragraphs (e)(2) and (e)(3) of this section when there has been a change in production process, chemicals present, control equipment, personnel, or work practices which may result in new or additional exposures to MDA, or when the employer has any reason to suspect a change which may result in new or additional exposures.

(6) *Accuracy of monitoring.* Monitoring shall be accurate, to a confidence level of 95 percent, to within plus or minus 25 percent for airborne concentrations of MDA.

(7) *Employee notification of monitoring results.* (i) The employer shall, within 15 working days after the receipt of the results of any monitoring performed under this standard, notify each employee of these results, in writing, either individually or by posting of results in an appropriate location that is accessible to affected employees.

(ii) The written notification required by paragraph (e)(7)(i) of this section shall contain the corrective action being taken by the employer to reduce the employee exposure to or below the PELs, wherever the PELs are exceeded.

(8) *Visual monitoring.* The employer shall make routine inspections of employee hands, face and forearms potentially exposed to MDA. Other potential dermal exposures reported by the employee must be referred to the appropriate medical personnel for observation. If the employer determines that the employee has been exposed to MDA the employer shall:

(i) Determine the source of exposure;

(ii) Implement protective measures to correct the hazard; and

(iii) Maintain records of the corrective actions in accordance with paragraph (n) of this section.

(f) *Regulated areas* —(1) *Establishment* —(i) *Airborne exposures.* The employer shall establish regulated areas where airborne concentrations of MDA exceed or can reasonably be expected to exceed, the permissible exposure limits.

(ii) *Dermal exposures.* Where employees are subject to dermal

exposure to MDA the employer shall establish those work areas as regulated areas.

(2) *Demarcation.* Regulated areas shall be demarcated from the rest of the workplace in a manner that minimizes the number of persons potentially exposed.

(3) *Access.* Access to regulated areas shall be limited to authorized persons.

(4) *Personal protective equipment and clothing.* Each person entering a regulated area shall be supplied with, and required to use, the appropriate personal protective clothing and equipment in accordance with paragraphs (h) and (i) of this section.

(5) *Prohibited activities.* The employer shall ensure that employees do not eat, drink, smoke, chew tobacco or gum, or apply cosmetics in regulated areas.

(g) *Methods of compliance* —(1) *Engineering controls and work practices.* (i) The employer shall institute engineering controls and work practices to reduce and maintain employee exposure to MDA at or below the PELs except to the extent that the employer can establish that these controls are not feasible or where the provisions of paragraph (g)(1)(ii) or (h)(1) (i) through (iv) of this section apply.

(ii) Wherever the feasible engineering controls and work practices which can be instituted are not sufficient to reduce employee exposure to or below the PELs, the employer shall use them to reduce employee exposure to the lowest levels achievable by these controls and shall supplement them by the use of respiratory protective devices which comply with the requirements of paragraph (h) of this section.

(2) *Compliance program.* (i) The employer shall establish and implement a written program to reduce employee exposure to or below the PELs by means of engineering and work practice controls, as required by paragraph (g)(1) of this section, and by use of respiratory protection where permitted under this section. The program shall include a schedule for periodic maintenance (e.g., leak detection) and shall include the written plan for emergency situations as specified in paragraph (d) of this section.

(ii) Upon request this written program shall be furnished for examination and copying to the Assistant Secretary, the Director, affected employees, and designated employee representatives. The employer shall review and, as necessary, update such plans at least once every 12 months to make certain they reflect the current status of the program.

(3) *Employee rotation.* Employee rotation shall not be permitted

as a means of reducing exposure.

(h) *Respiratory protection* —(1) *General*. For employees who use respirators required by this section, the employer must provide each employee an appropriate respirator that complies with the requirements of this paragraph. Respirators must be used during:

(i) Periods necessary to install or implement feasible engineering and work-practice controls.

(ii) Work operations for which the employer establishes that engineering and work-practice controls are not feasible.

(iii) Work operations for which feasible engineering and work-practice controls are not yet sufficient to reduce employee exposure to or below the PEL.

(iv) Emergencies.

(2) *Respirator program*. The employer must implement a respiratory protection program in accordance with § 1910.134 (b) through (d) (except (d)(1)(iii)), and (f) through (m), which covers each employee required by this section to use a respirator.

(3) *Respirator selection*. (i) Employers must:

(A) Select, and provide to employees, the appropriate respirators specified in paragraph (d)(3)(i)(A) of 29 CFR 1910.134.

(B) Provide HEPA filters for powered and non-powered air-purifying respirators.

(C) For escape, provide employees with one of the following respirator options: Any self-contained breathing apparatus with a full facepiece or hood operated in the positive-pressure or continuous-flow mode; or a full facepiece air-purifying respirator.

(D) Provide a combination HEPA filter and organic vapor canister or cartridge with powered or non-powered air-purifying respirators when MDA is in liquid form or used as part of a process requiring heat.

(ii) Any employee who cannot use a negative-pressure respirator must be given the option of using a positive-pressure respirator, or a supplied-air respirator operated in the continuous-flow or pressure-demand mode.

(i) *Protective work clothing and equipment* —(1) *Provision and use*. Where employees are subject to dermal exposure to MDA, where liquids containing MDA can be splashed into the eyes, or where airborne concentrations of MDA are in excess of the PEL, the

employer shall provide, at no cost to the employee, and ensure that the employee uses, appropriate protective work clothing and equipment which prevent contact with MDA such as, but not limited to:

(i) Aprons, coveralls or other full-body work clothing;

(ii) Gloves, head coverings, and foot coverings; and

(iii) Face shields, chemical goggles; or

(iv) Other appropriate protective equipment which comply with § 1910.133.

(2) *Removal and storage.* (i) The employer shall ensure that, at the end of their work shift, employees remove MDA-contaminated protective work clothing and equipment that is not routinely removed throughout the day in change rooms provided in accordance with the provisions established for change rooms.

(ii) The employer shall ensure that, during their work shift, employees remove all other MDA-contaminated protective work clothing or equipment before leaving a regulated area.

(iii) The employer shall ensure that no employee takes MDA-contaminated work clothing or equipment out of the change room, except those employees authorized to do so for the purpose of laundering, maintenance, or disposal.

(iv) MDA-contaminated work clothing or equipment shall be placed and stored in closed containers which prevent dispersion of the MDA outside the container.

(v) Containers of MDA-contaminated protective work clothing or equipment which are to be taken out of change rooms or the workplace for cleaning, maintenance, or disposal, shall bear labels warning of the hazards of MDA.

(3) *Cleaning and replacement.* (i) The employer shall provide the employee with clean protective clothing and equipment. The employer shall ensure that protective work clothing or equipment required by this paragraph is cleaned, laundered, repaired, or replaced at intervals appropriate to maintain its effectiveness.

(ii) The employer shall prohibit the removal of MDA from protective work clothing or equipment by blowing, shaking, or any methods which allow MDA to re-enter the workplace.

(iii) The employer shall ensure that laundering of MDA-contaminated clothing shall be done so as to prevent the release of

MDA in the workplace.

(iv) Any employer who gives MDA-contaminated clothing to another person for laundering shall inform such person of the requirement to prevent the release of MDA.

(v) The employer shall inform any person who launders or cleans protective clothing or equipment contaminated with MDA of the potentially harmful effects of exposure.

(vi) MDA-contaminated clothing shall be transported in properly labeled, sealed, impermeable bags or containers.

(j) *Hygiene facilities and practices* —(1) *Change rooms.* (i) The employer shall provide clean change rooms for employees, who must wear protective clothing, or who must use protective equipment because of their exposure to MDA.

(ii) Change rooms must be equipped with separate storage for protective clothing and equipment and for street clothes which prevents MDA contamination of street clothes.

(2) *Showers.* (i) The employer shall ensure that employees, who work in areas where there is the potential for exposure resulting from airborne MDA (e.g., particulates or vapors) above the action level, shower at the end of the work shift.

(A) Shower facilities required by this paragraph shall comply with § 1910.141(d)(3).

(B) The employer shall ensure that employees who are required to shower pursuant to the provisions contained herein do not leave the workplace wearing any protective clothing or equipment worn during the work shift.

(ii) Where dermal exposure to MDA occurs, the employer shall ensure that materials spilled or deposited on the skin are removed as soon as possible by methods which do not facilitate the dermal absorption of MDA.

(3) *Lunch facilities* —(i) *Availability and construction.* (A) Whenever food or beverages are consumed at the worksite and employees are exposed to MDA at or above the PEL or are subject to dermal exposure to MDA the employer shall provide readily accessible lunch areas.

(B) Lunch areas located within the workplace and in areas where there is the potential for airborne exposure to MDA at or above the PEL shall have a positive pressure, temperature controlled, filtered air supply.

(C) Lunch areas may not be located in areas within the

workplace where the potential for dermal exposure to MDA exists.

(ii) The employer shall ensure that employees who have been subjected to dermal exposure to MDA or who have been exposed to MDA above the PEL wash their hands and faces with soap and water prior to eating, drinking, smoking, or applying cosmetics.

(iii) The employer shall ensure that employees exposed to MDA do not enter lunch facilities with MDA-contaminated protective work clothing or equipment.

(k) *Communication of hazards* —(1) *Hazard communication—general.*

(i) Chemical manufacturers, importers, distributors and employers shall comply with all requirements of the Hazard Communication Standard (HCS) (§ 1910.1200) for MDA.

(ii) In classifying the hazards of MDA at least the following hazards are to be addressed: Cancer; liver effects; and skin sensitization.

(iii) Employers shall include MDA in the hazard communication program established to comply with the HCS (§ 1910.1200). Employers shall ensure that each employee has access to labels on containers of MDA and to safety data sheets, and is trained in accordance with the requirements of HCS and paragraph (k)(4) of this section.

(2) *Signs and labels* —(i) *Signs.* (A) The employer shall post and maintain legible signs demarcating regulated areas and entrances or access ways to regulated areas that bear the following legend:

DANGER

MDA

MAY CAUSE CANCER

CAUSES DAMAGE TO THE LIVER

RESPIRATORY PROTECTION AND PROTECTIVE CLOTHING MAY BE
REQUIRED IN THIS AREA

AUTHORIZED PERSONNEL ONLY

(B) Prior to June 1, 2016, employers may use the following legend in lieu of that specified in paragraph (k)(2)(i)(A) of this section:

DANGER

MDA

MAY CAUSE CANCER

LIVER TOXIN

AUTHORIZED PERSONNEL ONLY

RESPIRATORS AND PROTECTIVE CLOTHING MAY BE REQUIRED TO
BE WORN IN THIS AREA

(ii) *Labels.* Prior to June 1, 2015, employers may include the following information workplace labels in lieu of the labeling requirements in paragraph (k)(1) of this section:

(A) For pure MDA:

DANGER

CONTAINS MDA

MAY CAUSE CANCER

LIVER TOXIN

(B) For mixtures containing MDA:

DANGER

CONTAINS MDA

CONTAINS MATERIALS WHICH MAY CAUSE CANCER

LIVER TOXIN

(3) *Safety data sheets (SDS).* In meeting the obligation to provide safety data sheets, employers shall make appropriate use of the information found in Appendices A and B to § 1910.1050.

(4) *Information and training.* (i) The employer shall provide employees with information and training on MDA, in accordance with 29 CFR 1910.1200(h), at the time of initial assignment and at least annually thereafter.

(ii) In addition to the information required under 29 CFR 1910.1200, the employer shall:

(A) Provide an explanation of the contents of this section, including appendices A and B, and indicate to employees where a copy of the standard is available;

(B) Describe the medical surveillance program required under paragraph (m) of this section, and explain the information contained in appendix C; and

(C) Describe the medical removal provision required under

paragraph (m) of this section.

(5) *Access to training materials.* (i) The employer shall make readily available to all affected employees, without cost, all written materials relating to the employee training program, including a copy of this regulation.

(ii) The employer shall provide to the Assistant Secretary and the Director, upon request, all information and training materials relating to the employee information and training program.

(l) *Housekeeping.* (1) All surfaces shall be maintained as free as practicable of visible accumulations of MDA.

(2) The employer shall institute a program for detecting MDA leaks, spills, and discharges, including regular visual inspections of operations involving liquid or solid MDA.

(3) All leaks shall be repaired and liquid or dust spills cleaned up promptly.

(4) Surfaces contaminated with MDA may not be cleaned by the use of compressed air.

(5) Shoveling, dry sweeping, and other methods of dry clean-up of MDA may be used where HEPA-filtered vacuuming and/or wet cleaning are not feasible or practical.

(6) Waste, scrap, debris, bags, containers, equipment, and clothing contaminated with MDA shall be collected and disposed of in a manner to prevent the re-entry of MDA into the workplace.

(m) *Medical surveillance* —(1) *General.* (i) The employer shall make available a medical surveillance program for employees exposed to MDA:

(A) Employees exposed at or above the action level for 30 or more days per year;

(B) Employees who are subject to dermal exposure to MDA for 15 or more days per year;

(C) Employees who have been exposed in an emergency situation;

(D) Employees whom the employer, based on results from compliance with paragraph (e)(8) of this section, has reason to believe are being dermally exposed; and

(E) Employees who show signs or symptoms of MDA exposure.

(ii) The employer shall ensure that all medical examinations and procedures are performed by, or under the supervision of, a licensed physician, at a reasonable time and place, and provided without cost to the employee.

(2) *Initial examinations.* (i) Within 150 days of the effective date of this standard, or before the time of initial assignment, the employer shall provide each employee covered by paragraph (m)(1)(i) of this section with a medical examination including the following elements:

(A) A detailed history which includes:

(1) Past work exposure to MDA or any other toxic substances;

(2) A history of drugs, alcohol, tobacco, and medication routinely taken (duration and quantity); and

(3) A history of dermatitis, chemical skin sensitization, or previous hepatic disease.

(B) A physical examination which includes all routine physical examination parameters, skin examination, and signs of liver disease.

(C) Laboratory tests including:

(1) Liver function tests and

(2) Urinalysis.

(D) Additional tests as necessary in the opinion of the physician.

(ii) No initial medical examination is required if adequate records show that the employee has been examined in accordance with the requirements of this section within the previous six months prior to the effective date of this standard or prior to the date of initial assignment.

(3) *Periodic examinations.* (i) The employer shall provide each employee covered by this section with a medical examination at least annually following the initial examination. These periodic examinations shall include at least the following elements:

(A) A brief history regarding any new exposure to potential liver toxins, changes in drug, tobacco, and alcohol intake, and the appearance of physical signs relating to the liver, and the skin;

(B) The appropriate tests and examinations including liver function tests and skin examinations; and

(C) Appropriate additional tests or examinations as deemed necessary by the physician.

(ii) If in the physicians' opinion the results of liver function tests indicate an abnormality, the employee shall be removed from further MDA exposure in accordance with paragraph (m)(9) of this section. Repeat liver function tests shall be conducted on advice of the physician.

(4) *Emergency examinations.* If the employer determines that the employee has been exposed to a potentially hazardous amount of MDA in an emergency situation as addressed in paragraph (d) of this section, the employer shall provide medical examinations in accordance with paragraphs (m)(3)(i) and (ii) of this section. If the results of liver function testing indicate an abnormality, the employee shall be removed in accordance with paragraph (m)(9) of this section. Repeat liver function tests shall be conducted on the advice of the physician. If the results of the tests are normal, tests must be repeated two to three weeks from the initial testing. If the results of the second set of tests are normal and, on the advice of the physician, no additional testing is required.

(5) *Additional examinations.* Where the employee develops signs and symptoms associated with exposure to MDA, the employer shall provide the employee with an additional medical examination including a liver function test. Repeat liver function tests shall be conducted on the advice of the physician. If the results of the tests are normal, tests must be repeated two to three weeks from the initial testing. If the results of the second set of tests are normal and, on the advice of the physician, no additional testing is required.

(6) *Multiple physician review mechanism.* (i) If the employer selects the initial physician who conducts any medical examination or consultation provided to an employee under this section, and the employee has signs or symptoms of occupational exposure to MDA (which could include an abnormal liver function test), and the employee disagrees with the opinion of the examining physician, and this opinion could affect the employee's job status, the employee may designate an appropriate, mutually acceptable second physician:

(A) To review any findings, determinations, or recommendations of the initial physician; and

(B) To conduct such examinations, consultations, and laboratory tests as the second physician deems necessary to facilitate this review.

(ii) The employer shall promptly notify an employee of the right to seek a second medical opinion after each occasion that an initial physician conducts a medical examination or consultation pursuant to this section. The employer may condition its participation in, and payment for, the multiple physician review mechanism upon the

employee doing the following within fifteen (15) days after receipt of the foregoing notification, or receipt of the initial physician's written opinion, whichever is later:

(A) The employee informing the employer that he or she intends to seek a second medical opinion, and

(B) The employee initiating steps to make an appointment with a second physician.

(iii) If the findings, determinations, or recommendations of the second physician differ from those of the initial physician, then the employer and the employee shall assure that efforts are made for the two physicians to resolve any disagreement.

(iv) If the two physicians have been unable to resolve quickly their disagreement, then the employer and the employee through their respective physicians shall designate a third physician;

(A) To review any findings, determinations, or recommendations of the prior physicians; and

(B) To conduct such examinations, consultations, laboratory tests, and discussions with the prior physicians as the third physician deems necessary to resolve the disagreement of the prior physicians.

(v) The employer shall act consistent with the findings, determinations, and recommendations of the third physician, unless the employer and the employee reach an agreement which is otherwise consistent with the recommendations of at least one of the three physicians.

(7) *Information provided to the examining and consulting physicians.* (i) The employer shall provide the following information to the examining physician:

(A) A copy of this regulation and its appendices;

(B) A description of the affected employee's duties as they relate to the employee's potential exposure to MDA;

(C) The employee's current actual or representative MDA exposure level;

(D) A description of any personal protective equipment used or to be used; and

(E) Information from previous employment-related medical examinations of the affected employee.

(ii) The employer shall provide the foregoing information to a second physician under this section upon request either by the second physician, or by the employee.

(8) *Physician's written opinion.* (i) For each examination under this section, the employer shall obtain, and provide the employee with a copy of, the examining physician's written opinion within 15 days of its receipt. The written opinion shall include the following:

(A) The occupationally-pertinent results of the medical examination and tests;

(B) The physician's opinion concerning whether the employee has any detected medical conditions which would place the employee at increased risk of material impairment of health from exposure to MDA;

(C) The physician's recommended limitations upon the employee's exposure to MDA or upon the employee's use of protective clothing or equipment and respirators; and

(D) A statement that the employee has been informed by the physician of the results of the medical examination and any medical conditions resulting from MDA exposure which require further explanation or treatment.

(ii) The written opinion obtained by the employer shall not reveal specific findings or diagnoses unrelated to occupational exposures.

(9) *Medical removal* —(i) *Temporary medical removal of an employee* —(A) *Temporary removal resulting from occupational exposure.* The employee shall be removed from work environments in which exposure to MDA is at or above the action level or where dermal exposure to MDA may occur, following an initial examination (paragraph (m)(2) of this section), periodic examinations (paragraph (m)(3) of this section), an emergency situation paragraph (m)(4) of this section, or an additional examination (paragraph (m)(5) of this section) in the following circumstances:

(1) When the employee exhibits signs and/or symptoms indicative of acute exposure to MDA; or

(2) When the examining physician determines that an employee's abnormal liver function tests are not associated with MDA exposure but that the abnormalities may be exacerbated as a result of occupational exposure to MDA.

(B) *Temporary removal due to a final medical determination.*

(1) The employer shall remove an employee from work environments in which exposure to MDA is at or above the action level or where dermal exposure to MDA may occur, on each

occasion that there is a final medical determination or opinion that the employee has a detected medical condition which places the employee at increased risk of material impairment to health from exposure to MDA.

(2) For the purposes of this section, the phrase “final medical determination” shall mean the outcome of the physician review mechanism used pursuant to the medical surveillance provisions of this section.

(3) Where a final medical determination results in any recommended special protective measures for an employee, or limitations on an employee's exposure to MDA, the employer shall implement and act consistent with the recommendation.

(ii) *Return of the employee to former job status.* (A) The employer shall return an employee to his or her former job status:

(1) When the employee no longer shows signs or symptoms of exposure to MDA, or upon the advice of the physician.

(2) When a subsequent final medical determination results in a medical finding, determination, or opinion that the employee no longer has a detected medical condition which places the employee at increased risk of material impairment to health from exposure to MDA.

(B) For the purposes of this section, the requirement that an employer return an employee to his or her former job status is not intended to expand upon or restrict any rights an employee has or would have had, absent temporary medical removal, to a specific job classification or position under the terms of a collective bargaining agreement.

(iii) *Removal of other employee special protective measure or limitations.* The employer shall remove any limitations placed on an employee, or end any special protective measures provided to an employee, pursuant to a final medical determination, when a subsequent final medical determination indicates that the limitations or special protective measures are no longer necessary.

(iv) *Employer options pending a final medical determination.* Where the physician review mechanism used pursuant to the medical surveillance provisions of this section, has not yet resulted in a final medical determination with respect to an employee, the employer shall act as follows:

(A) *Removal.* The employer may remove the employee from exposure to MDA, provide special protective measures to the employee, or place limitations upon the employee, consistent with the medical findings, determinations, or recommendations of any of

the physicians who have reviewed the employee's health status.

(B) *Return.* The employer may return the employee to his or her former job status, and end any special protective measures provided to the employee, consistent with the medical findings, determinations, or recommendations of any of the physicians who have reviewed the employee's health status, with two exceptions.

(1) If the initial removal, special protection, or limitation of the employee resulted from a final medical determination which differed from the findings, determinations, or recommendations of the initial physician; or

(2) If the employee has been on removal status for the preceding six months as a result of exposure to MDA, then the employer shall await a final medical determination.

(v) *Medical removal protection benefits* —(A) *Provisions of medical removal protection benefits.* The employer shall provide to an employee up to six (6) months of medical removal protection benefits on each occasion that an employee is removed from exposure to MDA or otherwise limited pursuant to this section.

(B) *Definition of medical removal protection benefits.* For the purposes of this section, the requirement that an employer provide medical removal protection benefits means that the employer shall maintain the earnings, seniority, and other employment rights and benefits of an employee as though the employee had not been removed from normal exposure to MDA or otherwise limited.

(C) *Follow-up medical surveillance during the period of employee removal or limitations.* During the period of time that an employee is removed from normal exposure to MDA or otherwise limited, the employer may condition the provision of medical removal protection benefits upon the employee's participation in follow-up medical surveillance made available pursuant to this section.

(D) *Workers' compensation claims.* If a removed employee files a claim for workers' compensation payments for a MDA-related disability, then the employer shall continue to provide medical removal protection benefits pending disposition of the claim. To the extent that an award is made to the employee for earnings lost during the period of removal, the employer's medical removal protection obligation shall be reduced by such amount. The employer shall receive no credit for workers' compensation payments received by the employee for treatment-related expenses.

(E) *Other credits.* The employer's obligation to provide medical removal protection benefits to a removed employee shall be reduced to the extent that the employee receives compensation for earnings lost during the period of removal either from a publicly or employer-funded compensation program, or receives income from non-MDA-

related employment with any employer made possible by virtue of the employee's removal.

(F) *Employees who do not recover within the 6 months of removal.* The employer shall take the following measures with respect to any employee removed from exposure to MDA:

(1) The employer shall make available to the employee a medical examination pursuant to this section to obtain a final medical determination with respect to the employee;

(2) The employer shall assure that the final medical determination obtained indicates whether or not the employee may be returned to his or her former job status, and, if not, what steps should be taken to protect the employee's health;

(3) Where the final medical determination has not yet been obtained, or, once obtained indicates that the employee may not yet be returned to his or her former job status, the employer shall continue to provide medical removal protection benefits to the employee until either the employee is returned to former job status, or a final medical determination is made that the employee is incapable of ever safely returning to his or her former job status; and

(4) Where the employer acts pursuant to a final medical determination which permits the return of the employee to his or her former job status, despite what would otherwise be an abnormal liver function test, later questions concerning removing the employee again shall be decided by a final medical determination. The employer need not automatically remove such an employee pursuant to the MDA removal criteria provided by this section.

(vi) *Voluntary removal or restriction of an employee.* Where an employer, although not required by this section to do so, removes an employee from exposure to MDA or otherwise places limitations on an employee due to the effects of MDA exposure on the employee's medical condition, the employer shall provide medical removal protection benefits to the employee equal to that required by paragraph (m)(9)(v) of this section.

(n) *Recordkeeping* —(1) *Monitoring data for exempted employers.* (i) Where as a result of the initial monitoring the processing, use, or handling of products made from or containing MDA are exempted from other requirements of this section under paragraph (a)(2) of this section, the employer shall establish and maintain an accurate record of monitoring relied on in support of the exemption.

(ii) This record shall include at least the following information:

(A) The product qualifying for exemption;

(B) The source of the monitoring data (e.g., was monitoring performed by the employer or a private contractor);

(C) The testing protocol, results of testing, and/or analysis of the material for the release of MDA;

(D) A description of the operation exempted and how the data support the exemption (e.g., are the monitoring data representative of the conditions at the affected facility); and

(E) Other data relevant to the operations, materials, processing, or employee exposures covered by the exemption.

(iii) The employer shall maintain this record for the duration of the employer's reliance upon such objective data.

(2) *Objective data for exempted employers.* (i) Where the processing, use, or handling of products made from or containing MDA are exempted from other requirements of this section under paragraph (a) of this section, the employer shall establish and maintain an accurate record of objective data relied upon in support of the exemption.

(ii) This record shall include at least the following information:

(A) The product qualifying for exemption;

(B) The source of the objective data;

(C) The testing protocol, results of testing, and/or analysis of the material for the release of MDA;

(D) A description of the operation exempted and how the data support the exemption; and

(E) Other data relevant to the operations, materials, processing, or employee exposures covered by the exemption.

(iii) The employer shall maintain this record for the duration of the employer's reliance upon such objective data.

(3) *Exposure measurements.* (i) The employer shall establish and maintain an accurate record of all measurements required by paragraph (e) of this section, in accordance with 29 CFR 1910.1020.

(ii) This record shall include:

(A) The dates, number, duration, and results of each of the samples taken, including a description of the procedure used to determine representative employee exposures;

(B) Identification of the sampling and analytical methods used;

(C) A description of the type of respiratory protective devices worn, if any; and

(D) The name, social security number, job classification and exposure levels of the employee monitored and all other employees whose exposure the measurement is intended to represent.

(iii) The employer shall maintain this record for at least 30 years, in accordance with 29 CFR 1910.1020.

(4) *Medical surveillance.* (i) The employer shall establish and maintain an accurate record for each employee subject to medical surveillance required by paragraph (m) of this section, in accordance with 29 CFR 1910.1020.

(ii) This record shall include:

(A) The name, social security number and description of the duties of the employee;

(B) The employer's copy of the physician's written opinion on the initial, periodic, and any special examinations, including results of medical examination and all tests, opinions, and recommendations;

(C) Results of any airborne exposure monitoring done for that employee and the representative exposure levels supplied to the physician; and

(D) Any employee medical complaints related to exposure to MDA;

(iii) The employer shall keep, or assure that the examining physician keeps, the following medical records:

(A) A copy of this standard and its appendices, except that the employer may keep one copy of the standard and its appendices for all employees provided the employer references the standard and its appendices in the medical surveillance record of each employee;

(B) A copy of the information provided to the physician as required by any paragraphs in the regulatory text;

(C) A description of the laboratory procedures and a copy of any standards or guidelines used to interpret the test results or references to the information;

(D) A copy of the employee's medical and work history related to exposure to MDA; and

(iv) The employer shall maintain this record for at least the duration of employment plus 30 years, in accordance with 29 CFR 1910.1020.

(5) *Medical removals.* (i) The employer shall establish and maintain an accurate record for each employee removed from current exposure to MDA pursuant to paragraph (m) of this section.

(ii) Each record shall include:

(A) The name and social security number of the employee;

(B) The date of each occasion that the employee was removed from current exposure to MDA as well as the corresponding date on which the employee was returned to his or her former job status;

(C) A brief explanation of how each removal was or is being accomplished; and

(D) A statement with respect to each removal indicating the reason for the removal.

(iii) The employer shall maintain each medical removal record for at least the duration of an employee's employment plus 30 years.

(6) *Availability.* (i) The employer shall assure that records required to be maintained by this section shall be made available, upon request, to the Assistant Secretary and the Director for examination and copying.

(ii) Employee exposure monitoring records required by this section shall be provided upon request for examination and copying to employees, employee representatives, and the Assistant Secretary in accordance with 29 CFR 1910.1020 (a)-(e) and (g)-(i).

(iii) Employee medical records required by this section shall be provided upon request for examination and copying, to the subject employee, to anyone having the specific written consent of the subject employee, and to the Assistant Secretary in accordance with 29 CFR 1910.1020.

(7) *Transfer of records.* The employer shall comply with the requirements involving transfer of records set forth in 29 CFR 1910.1020(h).

(o) *Observation of monitoring* —(1) *Employee observation.* The employer shall provide affected employees, or their designated representatives, an opportunity to observe the measuring or monitoring of employee exposure to MDA conducted pursuant to paragraph (e) of this section.

(2) *Observation procedures.* When observation of the measuring or monitoring of employee exposure to MDA requires entry into areas where the use of protective clothing and equipment or respirators is required, the employer shall provide the observer with personal protective clothing and equipment or respirators required to be worn by employees working in the area, assure the use of such clothing and equipment or respirators, and require the observer to comply with all other applicable safety and health procedures.

(p) [Reserved]

(q) *Appendices.* The information contained in Appendices A, B, C, and D of this section is not intended, by itself, to create any additional obligations not otherwise imposed by this standard nor detract from any existing obligation.

APPENDIX A TO § 1910.1050—SUBSTANCE DATA SHEET, FOR 4,4'-METHYLENEDIANILINE

I. Substance Identification

A. Substance: Methylenedianiline (MDA)

B. Permissible Exposure:

1. Airborne: Ten parts per billion parts of air (10 ppb), time-weighted average (TWA) for an 8-hour workday and an action level of five parts per billion parts of air (5 ppb).

2. Dermal: Eye contact and skin contact with MDA are not permitted.

C. Appearance and odor: White to tan solid; amine odor

II. Health Hazard Data

A. *Ways in which MDA affects your health.* MDA can affect your health if you inhale it, or if it comes in contact with your skin or eyes. MDA is also harmful if you happen to swallow it. Do not get MDA in eyes, on skin, or on clothing.

B. *Effects of overexposure.* 1. Short-term (acute) overexposure: Overexposure to MDA may produce fever, chills, loss of appetite, vomiting, jaundice. Contact may irritate skin, eyes and mucous membranes. Sensitization may occur.

2. *Long-term (chronic) exposure.* Repeated or prolonged exposure to MDA, even at relatively low concentrations, may cause cancer. In addition, damage to the liver, kidneys, blood, and spleen may occur with long term exposure.

3. *Reporting signs and symptoms.* You should inform your employer if you develop any signs or symptoms which you suspect are caused by exposure to MDA including yellow staining of the skin.

III. Protective Clothing and Equipment

A. *Respirators.* Respirators are required for those operations in which engineering controls or work-practice controls are not adequate or feasible to reduce exposure to the permissible limit. If respirators are worn, they must have a label issued by the National Institute for Occupational Safety and Health under the provisions of 42 CFR part 84 stating that the respirators have been approved for this purpose, and cartridges and canisters must be replaced in accordance with the requirements of 29 CFR 1910.134. If you experience difficulty breathing while wearing a respirator, you can request a positive-pressure respirator from your employer. You must be thoroughly trained to use the assigned respirator, and the training must be provided by your employer.

MDA does not have a detectable odor except at levels well above the permissible exposure limits. Do not depend on odor to warn you when a respirator canister is exhausted. If you can smell MDA while wearing a respirator, proceed immediately to fresh air. If you experience difficulty breathing while wearing a respirator, tell your employer.

B. *Protective Clothing.* You may be required to wear coveralls, aprons, gloves, face shields, or other appropriate protective clothing to prevent skin contact with MDA. Where protective clothing is required, your employer is required to provide clean garments to you, as necessary, to assure that the clothing protects you adequately. Replace or repair impervious clothing that has developed leaks.

MDA should never be allowed to remain on the skin. Clothing and shoes which are not impervious to MDA should not be allowed to become contaminated with MDA, and if they do, the clothing and shoes should be promptly removed and decontaminated. The clothing should be laundered to remove MDA or discarded. Once MDA penetrates shoes or other leather articles, they should not be worn again.

C. *Eye protection.* You must wear splashproof safety goggles in areas where liquid MDA may contact your eyes. Contact lenses should not be worn in areas where eye contact with MDA can occur. In addition, you must wear a face shield if your face could be splashed with MDA liquid.

IV. Emergency and First Aid Procedures

A. *Eye and face exposure.* If MDA is splashed into the eyes, wash the eyes for at least 15 minutes. See a doctor as soon as possible.

B. *Skin exposure.* If MDA is spilled on your clothing or skin, remove the contaminated clothing and wash the exposed skin with large amounts of soap and water immediately. Wash contaminated clothing before you wear it again.

C. *Breathing.* If you or any other person breathes in large amounts of MDA, get the exposed person to fresh air at once. Apply artificial respiration if breathing has stopped. Call for medical assistance or a doctor as soon as possible. Never enter any vessel or confined space where the MDA concentration might be high without proper safety equipment and at least one other person present who will stay outside. A life line should be used.

D. *Swallowing.* If MDA has been swallowed and the patient is

conscious, do not induce vomiting. Call for medical assistance or a doctor immediately.

V. Medical Requirements

If you are exposed to MDA at a concentration at or above the action level for more than 30 days per year, or exposed to liquid mixtures more than 15 days per year, your employer is required to provide a medical examination, including a medical history and laboratory tests, within 60 days of the effective date of this standard and annually thereafter. These tests shall be provided without cost to you. In addition, if you are accidentally exposed to MDA (either by ingestion, inhalation, or skin/eye contact) under conditions known or suspected to constitute toxic exposure to MDA, your employer is required to make special examinations and tests available to you.

VI. Observation of Monitoring

Your employer is required to perform measurements that are representative of your exposure to MDA and you or your designated representative are entitled to observe the monitoring procedure. You are entitled to observe the steps taken in the measurement procedure and to record the results obtained. When the monitoring procedure is taking place in an area where respirators or personal protective clothing and equipment are required to be worn, you and your representative must also be provided with, and must wear, the protective clothing and equipment.

VII. Access to Records

You or your representative are entitled to see the records of measurements of your exposure to MDA upon written request to your employer. Your medical examination records can be furnished to your physician or designated representative upon request by you to your employer.

VIII. Precautions for Safe Use, Handling and Storage

A. Material is combustible. Avoid strong acids and their anhydrides. Avoid strong oxidants. Consult supervisor for disposal requirements.

B. Emergency clean-up. Wear self-contained breathing apparatus and fully clothe the body in the appropriate personal protective clothing and equipment.

APPENDIX B TO § 1910.1050—SUBSTANCE TECHNICAL GUIDELINES, MDA

I. Identification

A. Substance identification.

1. Synonyms: CAS No. 101-77-9, 4,4'-methylenedianiline; 4,4'-methylenebisaniiline; methylenedianiline; dianilinomethane.

2. Formula: C₁₃ H₁₄ N₂

II. Physical Data

1. Appearance and Odor: White to tan solid; amine odor
2. Molecular Weight: 198.26
3. Boiling Point: 398-399 degrees C at 760 mm Hg
4. Melting Point: 88-93 degrees C (190-100 degrees F)
5. Vapor Pressure: 9 mmHg at 232 degrees C
6. Evaporation Rate (n-butyl acetate = 1): Negligible
7. Vapor Density (Air=1): Not Applicable
8. Volatile Fraction by Weight: Negligible
9. Specific Gravity (Water=1): Slight
10. Heat of Combustion: -8.40 kcal/g
11. Solubility in Water: Slightly soluble in cold water, very soluble in alcohol, benzene, ether, and many organic solvents.

III. Fire, Explosion, and Reactivity Hazard Data

1. Flash Point: 190 degrees C (374 degrees F) Setflash closed cup
2. Flash Point: 226 degrees C (439 degrees F) Cleveland open cup
3. Extinguishing Media: Water spray; Dry Chemical; Carbon dioxide.
4. Special Fire Fighting Procedures: Wear self-contained breathing apparatus and protective clothing to prevent contact with skin and eyes.
5. Unusual Fire and Explosion Hazards: Fire or excessive heat may cause production of hazardous decomposition products.

IV. Reactivity Data

1. Stability: Stable
2. Incompatibility: Strong oxidizers
3. Hazardous Decomposition Products: As with any other organic material, combustion may produce carbon monoxide. Oxides of nitrogen may also be present.

4. Hazardous Polymerization: Will not occur.

V. Spill and Leak Procedures

1. Sweep material onto paper and place in fiber carton.
2. Package appropriately for safe feed to an incinerator or dissolve in compatible waste solvents prior to incineration.
3. Dispose of in an approved incinerator equipped with afterburner and scrubber or contract with licensed chemical waste disposal service.
4. Discharge treatment or disposal may be subject to federal, state, or local laws.
5. Wear appropriate personal protective equipment.

VI. Special Storage and Handling Precautions

- A. High exposure to MDA can occur when transferring the substance from one container to another. Such operations should be well ventilated and good work practices must be established to avoid spills.
- B. Pure MDA is a solid with a low vapor pressure. Grinding or heating operations increase the potential for exposure.
- C. Store away from oxidizing materials.
- D. Employers shall advise employees of all areas and operations where exposure to MDA could occur.

VII. Housekeeping and Hygiene Facilities

- A. The workplace should be kept clean, orderly, and in a sanitary condition.

The employer should institute a leak and spill detection program for operations involving MDA in order to detect sources of fugitive MDA emissions.

- B. Adequate washing facilities with hot and cold water are to be provided and maintained in a sanitary condition. Suitable cleansing agents should also be provided to assure the effective removal of MDA from the skin.

VIII. Common Operations

Common operations in which exposure to MDA is likely to occur include the following: Manufacture of MDA; Manufacture of Methylene diisocyanate; Curing agent for epoxy resin structures; Wire coating operations; and filament winding.

FOR MDA

I. Route of Entry

Inhalation; skin absorption; ingestion. MDA can be inhaled, absorbed through the skin, or ingested.

II. Toxicology

MDA is a suspect carcinogen in humans. There are several reports of liver disease in humans and animals resulting from acute exposure to MDA. A well documented case of an acute cardiomyopathy secondary to exposure to MDA is on record. Numerous human cases of hepatitis secondary to MDA are known. Upon direct contact MDA may also cause damage to the eyes. Dermatitis and skin sensitization have been observed. Almost all forms of acute environmental hepatic injury in humans involve the hepatic parenchyma and produce hepatocellular jaundice. This agent produces intrahepatic cholestasis. The clinical picture consists of cholestatic jaundice, preceded or accompanied by abdominal pain, fever, and chills. Onset in about 60% of all observed cases is abrupt with severe abdominal pain. In about 30% of observed cases, the illness presented and evolved more slowly and less dramatically, with only slight abdominal pain. In about 10% of the cases only jaundice was evident. The cholestatic nature of the jaundice is evident in the prominence of itching, the histologic predominance of bile stasis, and portal inflammatory infiltration, accompanied by only slight parenchymal injury in most cases, and by the moderately elevated transaminase values. Acute, high doses, however, have been known to cause hepatocellular damage resulting in elevated SGPT, SGOT, alkaline phosphatase and bilirubin.

Absorption through the skin is rapid. MDA is metabolized and excreted over a 48-hour period. Direct contact may be irritating to the skin, causing dermatitis. Also MDA which is deposited on the skin is not thoroughly removed through washing.

MDA may cause bladder cancer in humans. Animal data supporting this assumption is not available nor is conclusive human data. However, human data collected on workers at a helicopter manufacturing facility where MDA is used suggests a higher incidence of bladder cancer among exposed workers.

III. Signs and Symptoms

Skin may become yellow from contact with MDA.

Repeated or prolonged contact with MDA may result in recurring dermatitis (red-itchy, cracked skin) and eye irritation. Inhalation, ingestion or absorption through the skin at high concentrations may result in hepatitis, causing symptoms such as fever and chills, nausea and vomiting, dark urine, anorexia, rash, right upper quadrant pain and jaundice. Corneal burns may occur when MDA is splashed in the eyes.

IV. Treatment of Acute Toxic Effects/Emergency Situation

If MDA gets into the eyes, immediately wash eyes with large amounts of water. If MDA is splashed on the skin, immediately wash contaminated skin with mild soap or detergent. Employee should be removed from

exposure and given proper medical treatment. Medical tests required under the emergency section of the medical surveillance section (M)(4) must be conducted.

If the chemical is swallowed do not induce vomiting but remove by gastric lavage.

APPENDIX D TO § 1910.1050—SAMPLING AND ANALYTICAL METHODS FOR MDA MONITORING AND MEASUREMENT PROCEDURES

Measurements taken for the purpose of determining employee exposure to MDA are best taken so that the representative average 8-hour exposure may be determined from a single 8-hour sample or two (2) 4-hour samples. Short-time interval samples (or grab samples) may also be used to determine average exposure level if a minimum of five measurements are taken in a random manner over the 8-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random samples taken on one work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

There are a number of methods available for monitoring employee exposures to MDA. The method OSHA currently uses is included below.

The employer, however, has the obligation of selecting any monitoring method which meets the accuracy and precision requirements of the standard under his unique field conditions. The standard requires that the method of monitoring must have an accuracy, to a 95 percent confidence level, of not less than plus or minus 25 percent for the select PEL.

OSHA Methodology

Sampling Procedure

Apparatus

Samples are collected by use of a personal sampling pump that can be calibrated within $\pm 5\%$ of the recommended flow rate with the sampling filter in line.

Samples are collected on 37 mm Gelman type A/E glass fiber filters treated with sulfuric acid. The filters are prepared by soaking each filter with 0.5 mL of 0.26N H_2SO_4 . (0.26 N H_2SO_4 can be prepared by diluting 1.5 mL of 36N H_2SO_4 to 200 mL with deionized water.) The filters are dried in an oven at 100 degrees C for one hour and then assembled into two-piece 37 mm polystyrene cassettes with backup pads. The cassettes are sealed with shrink bands and the ends are plugged with plastic plugs.

After sampling, the filters are carefully removed from the cassettes and individually transferred to small vials containing approximately 2 mL deionized water. The vials must be tightly sealed. The water can be added before or after the filters are transferred. The vials must be sealable and capable of holding at least 7 mL of liquid. Small glass scintillation vials with

caps containing Teflon liners are recommended.

Reagents

Deionized water is needed for addition to the vials.

Sampling Technique

Immediately before sampling, remove the plastic plugs from the filter cassettes.

Attach the cassette to the sampling pump with flexible tubing and place the cassette in the employee's breathing zone.

After sampling, seal the cassettes with plastic plugs until the filters are transferred to the vials containing deionized water.

At some convenient time within 10 hours of sampling, transfer the sample filters to vials.

Seal the small vials lengthwise.

Submit at least one blank filter with each sample set. Blanks should be handled in the same manner as samples, but no air is drawn through them.

Record sample volumes (in L of air) for each sample, along with any potential interferences.

Retention Efficiency

A retention efficiency study was performed by drawing 100 L of air (80% relative humidity) at 1 L/min through sample filters that had been spiked with 0.814 μg MDA. Instead of using backup pads, blank acid-treated filters were used as backups in each cassette. Upon analysis, the top filters were found to have an average of 91.8% of the spiked amount. There was no MDA found on the bottom filters, so the amount lost was probably due to the slight instability of the MDA salt.

Extraction Efficiency

The average extraction efficiency for six filters spiked at the target concentration is 99.6%.

The stability of extracted and derivatized samples was verified by reanalyzing the above six samples the next day using fresh standards. The average extraction efficiency for the reanalyzed samples is 98.7%.

Recommended Air Volume and Sampling Rate

The recommended air volume is 100 L.

The recommended sampling rate is 1 L/min.

Interferences (Sampling)

MDI appears to be a positive interference. It was found that when MDI was spiked onto an acid-treated filter, the MDI converted to MDA after air was drawn through it.

Suspected interferences should be reported to the laboratory with submitted samples.

Safety Precautions (Sampling)

Attach the sampling equipment to the employees so that it will not interfere with work performance or safety.

Follow all safety procedures that apply to the work area being sampled.

Analytical Procedure

Apparatus: The following are required for analysis.

A GC equipped with an electron capture detector. For this evaluation a Tracor 222 Gas Chromatograph equipped with a Nickel 63 High Temperature Electron Capture Detector and a Linearizer was used.

A GC column capable of separating the MDA derivative from the solvent and interferences. A 6 ft × 2 mm ID glass column packed with 3% OV-101 coated on 100/120 Gas Chrom Q was used in this evaluation.

A electronic integrator or some other suitable means of measuring peak areas or heights.

Small resealable vials with Teflon-lined caps capable of holding 4 mL.

A dispenser or pipet for toluene capable of delivering 2.0 mL.

Pipets (or repipets with plastic or Teflon tips) capable of delivering 1 mL for the sodium hydroxide and buffer solutions.

A repipet capable of delivering 25 μ L HFAA.

Syringes for preparation of standards and injection of standards and samples into a GC.

Volumetric flasks and pipets to dilute the pure MDA in preparation of standards.

Disposable pipets to transfer the toluene layers after the samples are extracted.

Reagents

0.5 NaOH prepared from reagent grade NaOH.

Toluene, pesticide grade. Burdick and Jackson distilled in glass toluene was used.

Heptafluorobutyric acid anhydride (HFAA). HFAA from Pierce Chemical Company was used.

pH 7.0 phosphate buffer, prepared from 136 g potassium dihydrogen phosphate and 1 L deionized water. The pH is adjusted to 7.0 with saturated sodium hydroxide solution.

4,4' -Methylenedianiline (MDA), reagent grade.

Standard Preparation

Concentrated stock standards are prepared by diluting pure MDA with toluene. Analytical standards are prepared by injecting μL amounts of diluted stock standards into vials that contain 2.0 mL toluene.

25 μL HFAA are added to each vial and the vials are capped and shaken for 10 seconds.

After 10 min, 1 mL of buffer is added to each vial.

The vials are recapped and shaken for 10 seconds.

After allowing the layers to separate, aliquots of the toluene (upper) layers are removed with a syringe and analyzed by GC.

Analytical standard concentrations should bracket sample concentrations. Thus, if samples fall out of the range of prepared standards, additional standards must be prepared to ascertain detector response.

Sample Preparation

The sample filters are received in vials containing deionized water.

1 mL of 0.5N NaOH and 2.0 mL toluene are added to each vial.

The vials are recapped and shaken for 10 min.

After allowing the layers to separate, approximately 1 mL aliquots of the toluene (upper) layers are transferred to separate vials with clean disposable pipets.

The toluene layers are treated and analyzed.

Analysis

GC conditions

Zone temperatures:

Column—220 degrees C

Injector—235 degrees C

Detector—335 degrees C

Gas flows, Ar/CH₄, Column—28 mL/min

(95/5) Purge—40 mL/min

Injection volume: 5.0 uL

Column: 6 ft × ⅛ in ID glass, 3% OV-101 on 100/120 Gas Chrom Q

Retention time of MDA derivative: 3.5 min

Chromatogram

Peak areas or heights are measured by an integrator or other suitable means.

A calibration curve is constructed by plotting response (peak areas or heights) of standard injections versus ug of MDA per sample. Sample concentrations must be bracketed by standards.

Interferences (Analytical)

Any compound that gives an electron capture detector response and has the same general retention time as the HFAA derivative of MDA is a potential interference. Suspected interferences reported to the laboratory with submitted samples by the industrial hygienist must be considered before samples are derivatized.

GC parameters may be changed to possibly circumvent interferences.

Retention time on a single column is not considered proof of chemical identity. Analyte identity should be confirmed by GC/MS if possible.

Calculations

The analyte concentration for samples is obtained from the calibration curve in terms of ug MDA per sample. The extraction efficiency is 100%. If any MDA is found on the blank, that amount is subtracted from the sample amounts. The air concentrations are calculated using the following formulae.

$$\mu\text{g}/\text{m}^3 = (\mu\text{g MDA per sample}) (1000)/(\text{L of air sampled})$$

$$\text{ppb} = (\mu\text{g}/\text{m}^3) (24.46)/(198.3) = (\mu\text{g}/\text{m}^3) (0.1233) \text{ where } 24.46 \text{ is the molar volume at } 25 \text{ degrees C and } 760 \text{ mm Hg}$$

Safety Precautions (Analytical)

Avoid skin contact and inhalation of all chemicals.

Restrict the use of all chemicals to a fume hood if possible.

Wear safety glasses and a lab coat at all times while in the lab area.

[57 FR 35666, Aug. 10, 1992, as amended at 57 FR 49649, Nov. 3, 1992; 61 FR 5508, Feb. 13, 1996; 63 FR 1293, Jan. 8, 1998; 67 FR 67965, Nov. 7, 2002; 71 FR 16672, 16673, Apr. 3, 2006; 71 FR 50190, Aug. 24, 2006; 73 FR 75586, Dec. 12, 2008; 76 FR 33609, June 8, 2011; 77 FR 17785, Mar. 26, 2012]

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