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Title 29: Labor

PART 1910—OCCUPATIONAL SAFETY AND HEALTH STANDARDS (CONTINUED)

Subpart Z—Toxic and Hazardous Substances

§ 1910.1028 Benzene.

(a) *Scope and application.* (1) This section applies to all occupational exposures to benzene. Chemical Abstracts Service Registry No. 71-43-2, except as provided in paragraphs (a)(2) and (a)(3) of this section.

(2) This section does not apply to:

(i) The storage, transportation, distribution, dispensing, sale or use of gasoline, motor fuels, or other fuels containing benzene subsequent to its final discharge from bulk wholesale storage facilities, except that operations where gasoline or motor fuels are dispensed for more than 4 hours per day in an indoor location are covered by this section.

(ii) Loading and unloading operations at bulk wholesale storage facilities which use vapor control systems for all loading and unloading operations, except for the provisions of 29 CFR 1910.1200 as incorporated into this section and the emergency provisions of paragraphs (g) and (i)(4) of this section.

(iii) The storage, transportation, distribution or sale of benzene or liquid mixtures containing more than 0.1 percent benzene in intact containers or in transportation pipelines while sealed in such a manner as to contain benzene vapors or liquid, except for the provisions of 29 CFR 1910.1200 as incorporated into this section and the emergency provisions of paragraphs (g) and (i)(4) of this section.

(iv) Containers and pipelines carrying mixtures with less than 0.1 percent benzene and natural gas processing plants processing gas with less than 0.1 percent benzene.

(v) Work operations where the only exposure to benzene is from liquid mixtures containing 0.5 percent or less of benzene by volume, or the vapors released from such liquids until September 12, 1988; work operations where the only exposure to benzene is from liquid mixtures containing 0.3 percent or less of benzene by volume or the vapors released from such liquids from September 12, 1988, to September 12, 1989; and work operations where the only exposure to benzene is from liquid mixtures containing 0.1 percent or less of benzene by volume or the vapors released from such liquids after September 12, 1989; except that tire building machine operators using solvents with more than 0.1 percent benzene are covered by paragraph (i) of this section.

(vi) Oil and gas drilling, production and servicing operations.

(vii) Coke oven batteries.

(3) The cleaning and repair of barges and tankers which have contained benzene are excluded from paragraph (f) methods of compliance, paragraph (e)(1) exposure monitoring-general, and paragraph (e)

(6) accuracy of monitoring. Engineering and work practice controls shall be used to keep exposures below 10 ppm unless it is proven to be not feasible.

(b) *Definitions. Action level* means an airborne concentration of benzene of 0.5 ppm calculated as an 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 (l) of this section, or any other person authorized by the Act or regulations issued under the Act.

Benzene (C₆H₆) (CAS Registry No. 71-43-2) means liquefied or gaseous benzene. It includes benzene contained in liquid mixtures and the benzene vapors released by these liquids. It does not include trace amounts of unreacted benzene contained in solid materials.

Bulk wholesale storage facility means a bulk terminal or bulk plant where fuel is stored prior to its delivery to wholesale customers.

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

Day means any part of a calendar day.

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 may or does result in an unexpected significant release of benzene.

Employee exposure means exposure to airborne benzene which would occur if the employee were not using respiratory protective equipment.

Regulated area means any area where airborne concentrations of benzene exceed or can reasonably be expected to exceed, the permissible exposure limits, either the 8-hour time weighted average exposure of 1 ppm or the short-term exposure limit of 5 ppm for 15 minutes.

Vapor control system means any equipment used for containing the total vapors displaced during the loading of gasoline, motor fuel or other fuel tank trucks and the displacing of these vapors through a vapor processing system or balancing the vapor with the storage tank. This equipment also includes systems containing the vapors displaced from the storage tank during the unloading of the tank truck which balance the vapors back to the tank truck.

(c) *Permissible exposure limits (PELs)* —(1) *Time-weighted average limit (TWA)*. The employer shall assure that no employee is exposed to an airborne concentration of benzene in excess of one part of benzene per million parts of air (1 ppm) as an 8-hour time-weighted average.

(2) *Short-term exposure limit (STEL)*. The employer shall assure that no employee is exposed to an airborne concentration of benzene in excess of five (5) ppm as averaged over any 15 minute period.

(d) *Regulated areas*. (1) The employer shall establish a regulated area wherever the airborne concentration of benzene exceeds or can reasonably be expected to exceed the permissible exposure limits, either the 8-hour time weighted average exposure of 1 ppm or the short-term exposure limit of 5 ppm for 15 minutes.

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

(3) Regulated areas shall be determined from the rest of the workplace in any manner that minimizes the number of employees exposed to benzene within the regulated area.

(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 average exposure to airborne benzene.

(ii) Representative 8-hour TWA employee exposures shall be determined on the basis of one sample or samples representing the full shift exposure for each job classification in each work area.

(iii) Determinations of compliance with the STEL shall be made from 15 minute employee breathing zone samples measured at operations where there is reason to believe exposures are high, such as where tanks are opened, filled, unloaded or gauged; where containers or process equipment are opened and where benzene is used for cleaning or as a solvent in an uncontrolled situation. The employer may use objective data, such as measurements from brief period measuring devices, to determine where STEL monitoring is needed.

(iv) Except for initial monitoring as required under paragraph (e)(2) of this section, where the employer can document that one shift will consistently have higher employee exposures for an operation, the employer shall only be required to determine representative employee exposure for that operation during the shift on which the highest exposure is expected.

(2) *Initial monitoring*. (i) Each employer who has a place of employment covered under paragraph (a)(1) of this section shall monitor each of these workplaces and work operations to determine accurately the airborne concentrations of benzene to which employees may be exposed.

(ii) The initial monitoring required under paragraph (e)(2)(i) of this section shall be completed by 60 days after the effective date of this standard or within 30 days of the introduction of benzene into the workplace. Where the employer has monitored within one year prior to the effective date of this standard and the monitoring satisfies all other requirements of this section, the employer may rely on such earlier monitoring results to satisfy the requirements of paragraph (e)(2)(i) of this section.

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

(ii) If the monitoring required by paragraph (e)(2)(i) of this section reveals employee exposure above the TWA, the employer shall repeat such monitoring for each such employee at least every six (6) months.

(iii) The employer may alter the monitoring schedule from every six months to annually for any employee for whom two consecutive measurements taken at least 7 days apart indicate that the

employee exposure has decreased to the TWA or below, but is at or above the action level.

(iv) Monitoring for the STEL shall be repeated as necessary to evaluate exposures of employees subject to short term exposures.

(4) *Termination of monitoring.* (i) If the initial monitoring required by paragraph (e)(2)(i) 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).

(5) *Additional monitoring.* (i) 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 the production, process, control equipment, personnel or work practices which may result in new or additional exposures to benzene, or when the employer has any reason to suspect a change which may result in new or additional exposures.

(ii) Whenever spills, leaks, ruptures or other breakdowns occur that may lead to employee exposure, the employer shall monitor (using area or personal sampling) after the cleanup of the spill or repair of the leak, rupture or other breakdown to ensure that exposures have returned to the level that existed prior to the incident.

(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 benzene.

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

(ii) Whenever the PELs are exceeded, 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 PEL, or shall refer to a document available to the employee which states the corrective actions to be taken.

(f) *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 benzene at or below the permissible exposure limits, except to the extent that the employer can establish that these controls are not feasible or where the provisions of paragraph (f)(1)(iii) or (g)(1) 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 protection which complies with the requirements of paragraph (g) of this section.

(iii) Where the employer can document that benzene is used in a workplace less than a total of 30 days per year, the employer shall use engineering controls, work practice controls or respiratory protection or any combination of these controls to reduce employee exposure to benzene to or below the

PELs, except that employers shall use engineering and work practice controls, if feasible, to reduce exposure to or below 10 ppm as an 8-hour TWA.

(2) *Compliance program.* (i) When any exposures are over the PEL, the employer shall establish and implement a written program to reduce employee exposure to or below the PEL primarily by means of engineering and work practice controls, as required by paragraph (f)(1) of this section.

(ii) The written program shall include a schedule for development and implementation of the engineering and work practice controls. These plans shall be reviewed and revised as appropriate based on the most recent exposure monitoring data, to reflect the current status of the program.

(iii) Written compliance programs shall be furnished upon request for examination and copying to the Assistant Secretary, the Director, affected employees and designated employee representatives.

(g) *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 compliance with either the TWA or STEL through the use of engineering and work-practice controls is not feasible; for example, some maintenance and repair activities, vessel cleaning, or other operations for which engineering and work-practice controls are infeasible because exposures are intermittent and limited in duration.

(iii) Work operations for which feasible engineering and work-practice controls are not yet sufficient, or are not required under paragraph (f)(1)(iii) of this section, to reduce employee exposure to or below the PELs.

(iv) Emergencies.

(2) *Respirator program.* (i) The employer must implement a respiratory protection program in accordance with § 1910.134(b) through (d) (except (d)(1)(iii), (d)(3)(iii)(b)(1) and (2)), and (f) through (m), which covers each employee required by this section to use a respirator.

(ii) For air-purifying respirators, the employer must replace the air-purifying element at the expiration of its service life or at the beginning of each shift in which such elements are used, whichever comes first.

(iii) If NIOSH approves an air-purifying element with an end-of-service-life indicator for benzene, such an element may be used until the indicator shows no further useful life.

(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 employees with any organic vapor gas mask or any self-contained breathing apparatus with a full facepiece to use for escape.

(C) Use an organic vapor cartridge or canister with powered and non-powered air-purifying

respirators, and a chin-style canister with full facepiece gas masks.

(D) Ensure that canisters used with non-powered air-purifying respirators have a minimum service life of four hours when tested at 150 ppm benzene at a flow rate of 64 liters per minute (LPM), a temperature of 25 °C, and a relative humidity of 85%; for canisters used with tight-fitting or loose-fitting powered air-purifying respirators, the flow rates for testing must be 115 LPM and 170 LPM, respectively.

(ii) Any employee who cannot use a negative-pressure respirator must be allowed to use a respirator with less breathing resistance, such as a powered air-purifying respirator or supplied-air respirator.

(h) *Protective clothing and equipment.* Personal protective clothing and equipment shall be worn where appropriate to prevent eye contact and limit dermal exposure to liquid benzene. Protective clothing and equipment shall be provided by the employer at no cost to the employee and the employer shall assure its use where appropriate. Eye and face protection shall meet the requirements of 29 CFR 1910.133.

(i) *Medical surveillance* —(1) *General.* (i) The employer shall make available a medical surveillance program for employees who are or may be exposed to benzene at or above the action level 30 or more days per year; for employees who are or may be exposed to benzene at or above the PELs 10 or more days per year; for employees who have been exposed to more than 10 ppm of benzene for 30 or more days in a year prior to the effective date of the standard when employed by their current employer; and for employees involved in the tire building operations called tire building machine operators, who use solvents containing greater than 0.1 percent benzene.

(ii) The employer shall assure that all medical examinations and procedures are performed by or under the supervision of a licensed physician and that all laboratory tests are conducted by an accredited laboratory.

(iii) The employer shall assure that persons other than licensed physicians who administer the pulmonary function testing required by this section shall complete a training course in spirometry sponsored by an appropriate governmental, academic or professional institution.

(iv) The employer shall assure that all examinations and procedures are provided without cost to the employee and at a reasonable time and place.

(2) *Initial examination.* (i) Within 60 days of the effective date of this standard, or before the time of initial assignment, the employer shall provide each employee covered by paragraph (i)(1)(i) of this section with a medical examination including the following elements:

(A) A detailed occupational history which includes:

(1) Past work exposure to benzene or any other hematological toxins,

(2) A family history of blood dyscrasias including hematological neoplasms;

(3) A history of blood dyscrasias including genetic hemoglobin abnormalities, bleeding abnormalities, abnormal function of formed blood elements;

(4) A history of renal or liver dysfunction;

(5) A history of medicinal drugs routinely taken;

(6) A history of previous exposure to ionizing radiation and

(7) Exposure to marrow toxins outside of the current work situation.

(B) A complete physical examination.

(C) *Laboratory tests.* A complete blood count including a leukocyte count with differential, a quantitative thrombocyte count, hematocrit, hemoglobin, erythrocyte count and erythrocyte indices (MCV, MCH, MCHC). The results of these tests shall be reviewed by the examining physician.

(D) Additional tests as necessary in the opinion of the examining physician, based on alterations to the components of the blood or other signs which may be related to benzene exposure; and

(E) For all workers required to wear respirators for at least 30 days a year, the physical examination shall pay special attention to the cardiopulmonary system and shall include a pulmonary function test.

(ii) No initial medical examination is required to satisfy the requirements of paragraph (i)(2)(i) of this section if adequate records show that the employee has been examined in accordance with the procedures of paragraph (i)(2)(i) of this section within the twelve months prior to the effective date of this standard.

(3) *Periodic examinations.* (i) The employer shall provide each employee covered under paragraph (i)(1)(i) of this section with a medical examination annually following the previous examination. These periodic examinations shall include at least the following elements:

(A) A brief history regarding any new exposure to potential marrow toxins, changes in medicinal drug use, and the appearance of physical signs relating to blood disorders:

(B) A complete blood count including a leukocyte count with differential, quantitative thrombocyte count, hemoglobin, hematocrit, erythrocyte count and erythrocyte indices (MCV, MCH, MCHC); and

(C) Appropriate additional tests as necessary, in the opinion of the examining physician, in consequence of alterations in the components of the blood or other signs which may be related to benzene exposure.

(ii) Where the employee develops signs and symptoms commonly associated with toxic exposure to benzene, the employer shall provide the employee with an additional medical examination which shall include those elements considered appropriate by the examining physician.

(iii) For persons required to use respirators for at least 30 days a year, a pulmonary function test shall be performed every three (3) years. A specific evaluation of the cardiopulmonary system shall be made at the time of the pulmonary function test.

(4) *Emergency examinations.* (i) In addition to the surveillance required by (i)(1)(i), if an employee is exposed to benzene in an emergency situation, the employer shall have the employee provide a urine sample at the end of the employee's shift and have a urinary phenol test performed on the sample within 72 hours. The urine specific gravity shall be corrected to 1.024.

(ii) If the result of the urinary phenol test is below 75 mg phenol/L of urine, no further testing is

required.

(iii) If the result of the urinary phenol test is equal to or greater than 75 mg phenol/L of urine, the employer shall provide the employee with a complete blood count including an erythrocyte count, leukocyte count with differential and thrombocyte count at monthly intervals for a duration of three (3) months following the emergency exposure.

(iv) If any of the conditions specified in paragraph (i)(5)(i) of this section exists, then the further requirements of paragraph (i)(5) of this section shall be met and the employer shall, in addition, provide the employees with periodic examinations if directed by the physician.

(5) *Additional examinations and referrals.* (i) Where the results of the complete blood count required for the initial and periodic examinations indicate any of the following abnormal conditions exist, then the blood count shall be repeated within 2 weeks.

(A) The hemoglobin level or the hematocrit falls below the normal limit [outside the 95% confidence interval (C.I.)] as determined by the laboratory for the particular geographic area and/or these indices show a persistent downward trend from the individual's pre-exposure norms; provided these findings cannot be explained by other medical reasons.

(B) The thrombocyte (platelet) count varies more than 20 percent below the employee's most recent values or falls outside the normal limit (95% C.I.) as determined by the laboratory.

(C) The leukocyte count is below 4,000 per mm³ or there is an abnormal differential count.

(ii) If the abnormality persists, the examining physician shall refer the employee to a hematologist or an internist for further evaluation unless the physician has good reason to believe such referral is unnecessary. (See appendix C for examples of conditions where a referral may be unnecessary.)

(iii) The employer shall provide the hematologist or internist with the information required to be provided to the physician under paragraph (i)(6) of this section and the medical record required to be maintained by paragraph (k)(2)(ii) of this section.

(iv) The hematologist's or internist's evaluation shall include a determination as to the need for additional tests, and the employer shall assure that these tests are provided.

(6) *Information provided to the physician.* The employer shall provide the following information to the examining physician:

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

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

(iii) The employee's actual or representative exposure level:

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

(v) Information from previous employment-related medical examinations of the affected employee which is not otherwise available to the examining physician.

(7) *Physician's written opinions.* (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 the examination. The written opinion shall be limited to the following information:

(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's health at greater than normal risk of material impairment from exposure to benzene;

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

(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 benzene exposure which require further explanation or treatment.

(ii) The written opinion obtained by the employer shall not reveal specific records, findings and diagnoses that have no bearing on the employee's ability to work in a benzene-exposed workplace.

(8) *Medical removal plan.* (i) When a physician makes a referral to a hematologist/internist as required under paragraph (i)(5)(ii) of this section, the employee shall be removed from areas where exposures may exceed the action level until such time as the physician makes a determination under paragraph (i)(8)(ii) of this section.

(ii) Following the examination and evaluation by the hematologist/internist, a decision to remove an employee from areas where benzene exposure is above the action level or to allow the employee to return to areas where benzene exposure is above the action level shall be made by the physician in consultation with the hematologist/internist. This decision shall be communicated in writing to the employer and employee. In the case of removal, the physician shall state the required probable duration of removal from occupational exposure to benzene above the action level and the requirements for future medical examinations to review the decision.

(iii) For any employee who is removed pursuant to paragraph (i)(8)(ii) of this section, the employer shall provide a follow-up examination. The physician, in consultation with the hematologist/internist, shall make a decision within 6 months of the date the employee was removed as to whether the employee shall be returned to the usual job or whether the employee should be removed permanently.

(iv) Whenever an employee is temporarily removed from benzene exposure pursuant to paragraph (i)(8)(i) or (i)(8)(ii) of this section, the employer shall transfer the employee to a comparable job for which the employee is qualified (or can be trained for in a short period) and where benzene exposures are as low as possible, but in no event higher than the action level. The employer shall maintain the employee's current wage rate, seniority and other benefits. If there is no such job available, the employer shall provide medical removal protection benefits until such a job becomes available or for 6 months, whichever comes first.

(v) Whenever an employee is removed permanently from benzene exposure based on a physician's recommendation pursuant to paragraph (i)(8)(iii) of this section, the employee shall be given the opportunity to transfer to another position which is available or later becomes available for which the employee is qualified (or can be trained for in a short period) and where benzene exposures are as low as possible but in no event higher than the action level. The employer shall assure that such employee suffers no reduction in current wage rate, seniority or other benefits as a result of the transfer.

(9) *Medical removal protection benefits.* (i) The employer shall provide to an employee 6 months of medical removal protection benefits immediately following each occasion an employee is removed from exposure to benzene because of hematological findings pursuant to paragraphs (i)(8) (i) and (ii) of this section, unless the employee has been transferred to a comparable job where benzene exposures are below the action level.

(ii) For the purposes of this section, the requirement that an employer provide medical removal protection benefits means that the employer shall maintain the current wage rate, seniority and other benefits of an employee as though the employee had not been removed.

(iii) 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 from employment with another employer made possible by virtue of the employee's removal.

(j) *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 benzene.

(ii) In classifying the hazards of benzene at least the following hazards are to be addressed: Cancer; central nervous system effects; blood effects; aspiration; skin, eye, and respiratory tract irritation; and flammability.

(iii) Employers shall include benzene 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 benzene and to safety data sheets, and is trained in accordance with the requirements of HCS and paragraph (j)(3) of this section.

(2) *Warning signs and labels.* (i) The employer shall post signs at entrances to regulated areas. The signs shall bear the following legend:

DANGER
BENZENE
MAY CAUSE CANCER
HIGHLY FLAMMABLE LIQUID AND VAPOR
DO NOT SMOKE
WEAR RESPIRATORY PROTECTION IN THIS AREA
AUTHORIZED PERSONNEL ONLY

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

DANGER
BENZENE
CANCER HAZARD

FLAMMABLE—NO SMOKING
AUTHORIZED PERSONNEL ONLY
RESPIRATOR REQUIRED

(iii) The employer shall ensure that labels or other appropriate forms of warning are provided for containers of benzene within the workplace. There is no requirement to label pipes. The labels shall comply with the requirements of paragraph (j)(1) of this section and § 1910.1200(f).

(iv) Prior to June 1, 2015, employers shall include the following legend or similar language on the labels or other appropriate forms of warning:

DANGER
CONTAINS BENZENE
CANCER HAZARD

(3) *Information and training.* (i) The employer shall provide employees with information and training at the time of their initial assignment to a work area where benzene is present. If exposures are above the action level, employees shall be provided with information and training at least annually thereafter.

(ii) The training program shall be in accordance with the requirements of 29 CFR 1910.1200(h) (1) and (2), and shall include specific information on benzene for each category of information included in that section.

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

(A) Provide employees with an explanation of the contents of this section, including Appendices A and B, and indicate to them where the standard is available; and

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

(k) *Recordkeeping —(1) 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 1910.20.

(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) A description 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

1910.20.

(2) *Medical surveillance.* (i) The employer shall establish and maintain an accurate record for each employee subject to medical surveillance required by paragraph (i) of this section, in accordance with 29 CFR 1910.20.

(ii) This record shall include:

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

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

(C) Any employee medical complaints related to exposure to benzene;

(D) A copy of the information provided to the physician as required by paragraphs (i)(6) (ii) through (v) of this section; and

(E) A copy of the employee's medical and work history related to exposure to benzene or any other hematologic toxins.

(iii) The employer shall maintain this record for at least the duration of employment plus 30 years, in accordance with 29 CFR 1910.20.

(3) *Availability.* (i) The employer shall assure that all 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 paragraph shall be provided upon request for examination and copying to employees, employee representatives, and the Assistant Secretary in accordance with 29 CFR 1910.20 (a) through (e) and (g) through (i).

(iii) Employee medical records required by this paragraph 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 1910.20.

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

(l) *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 benzene conducted pursuant to paragraph (e) of this section.

(2) *Observation procedures.* When observation of the measuring or monitoring of employee exposure to benzene 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.

(m) [Reserved]

(n) *Appendices*. The information contained in Appendices A, B, C, and D is not intended, by itself, to create any additional obligations not otherwise imposed or to detract from any existing obligations.

APPENDIX A TO § 1910.1028—SUBSTANCE SAFETY DATA SHEET, BENZENE

I. SUBSTANCE IDENTIFICATION

A. Substance: Benzene.

B. Permissible Exposure: Except as to the use of gasoline, motor fuels and other fuels subsequent to discharge from bulk terminals and other exemptions specified in § 1910.1028(a)(2):

1. Airborne: The maximum time-weighted average (TWA) exposure limit is 1 part of benzene vapor per million parts of air (1 ppm) for an 8-hour workday and the maximum short-term exposure limit (STEL) is 5 ppm for any 15-minute period.

2. Dermal: Eye contact shall be prevented and skin contact with liquid benzene shall be limited.

C. Appearance and odor: Benzene is a clear, colorless liquid with a pleasant, sweet odor. The odor of benzene does not provide adequate warning of its hazard.

II. HEALTH HAZARD DATA

A. *Ways in which benzene affects your health*. Benzene can affect your health if you inhale it, or if it comes in contact with your skin or eyes. Benzene is also harmful if you happen to swallow it.

B. *Effects of overexposure*. 1. Short-term (acute) overexposure: If you are overexposed to high concentrations of benzene, well above the levels where its odor is first recognizable, you may feel breathless, irritable, euphoric, or giddy; you may experience irritation in eyes, nose, and respiratory tract. You may develop a headache, feel dizzy, nauseated, or intoxicated. Severe exposures may lead to convulsions and loss of consciousness.

2. Long-term (chronic) exposure. Repeated or prolonged exposure to benzene, even at relatively low concentrations, may result in various blood disorders, ranging from anemia to leukemia, an irreversible, fatal disease. Many blood disorders associated with benzene exposure may occur without symptoms.

III. PROTECTIVE CLOTHING AND EQUIPMENT

A. *Respirators*. Respirators are required for those operations in which engineering controls or work practice controls are not feasible to reduce exposure to the permissible level. However, where employers can document that benzene is present in the workplace less than 30 days a year, respirators may be used in lieu of engineering controls. If respirators are worn, they must have joint Mine Safety and Health Administration and the National Institute for Occupational Safety and Health (NIOSH) seal of approval, and cartridge or canisters must be replaced before the end of their service life, or the end of the shift, whichever occurs first. If you experience difficulty breathing while wearing a respirator, you may request a positive pressure respirator from your employer. You must be thoroughly trained to use the assigned respirator, and the training will be provided by your employer.

B. *Protective Clothing*. You must wear appropriate protective clothing (such as boots, gloves, sleeves, aprons, etc.) over any parts of your body that could be exposed to liquid benzene.

C. *Eye and Face Protection*. You must wear splash-proof safety goggles if it is possible that benzene may get into your eyes. In addition, you must wear a face shield if your face could be splashed with benzene liquid.

IV. EMERGENCY AND FIRST AID PROCEDURES

A. *Eye and face exposure.* If benzene is splashed in your eyes, wash it out immediately with large amounts of water. If irritation persists or vision appears to be affected see a doctor as soon as possible.

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

C. *Breathing.* If you or any other person breathes in large amounts of benzene, 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 benzene 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 benzene 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 benzene at a concentration at or above 0.5 ppm as an 8-hour time-weighted average, or have been exposed at or above 10 ppm in the past while employed by your current employer, your employer is required to provide a medical examination and 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 benzene (either by ingestion, inhalation, or skin/eye contact) under emergency conditions known or suspected to constitute toxic exposure to benzene, your employer is required to make special laboratory tests available to you.

VI. OBSERVATION OF MONITORING

Your employer is required to perform measurements that are representative of your exposure to benzene 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 or 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 benzene upon written request to your employer. Your medical examination records can be furnished to yourself, your physician or designated representative upon request by you to your employer.

VIII. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

Benzene liquid is highly flammable. It should be stored in tightly closed containers in a cool, well ventilated area. Benzene vapor may form explosive mixtures in air. All sources of ignition must be controlled. Use nonsparking tools when opening or closing benzene containers. Fire extinguishers, where provided, must be readily available. Know where they are located and how to operate them. Smoking is prohibited in areas where benzene is used or stored. Ask your supervisor where benzene is used in your area and for additional plant safety rules.

APPENDIX B TO § 1910.1028—SUBSTANCE TECHNICAL GUIDELINES, BENZENE

I. PHYSICAL AND CHEMICAL DATA

A. Substance identification.

1. *Synonyms:* Benzol, benzole, coal naphtha, cyclohexatriene, phene, phenyl hydride, pyrobenzol. (Benzin, petroleum benzin and Benzine do not contain benzene).

2. *Formula:* C₆ H₆ (CAS Registry Number: 71-43-2)

B. Physical data.

1. Boiling Point (760 mm Hg): 80.1 °C (176 °F)

2. Specific Gravity (water=1): 0.879

3. Vapor Density (air=1): 2.7

4. Melting Point: 5.5 °C (42 °F)

5. Vapor Pressure at 20 °C (68 °F): 75 mm Hg

6. Solubility in Water: .06%

7. Evaporation Rate (ether=1): 2.8

8. Appearance and Odor: Clear, colorless liquid with a distinctive sweet odor.

II. FIRE, EXPLOSION, AND REACTIVITY HAZARD DATA

A. Fire.

1. Flash Point (closed cup): -11 °C (12 °F)

2. Autoignition Temperature: 580 °C (1076 °F)

3. Flammable limits in Air. % by Volume: Lower: 1.3%, Upper: 7.5%

4. Extinguishing Media: Carbon dioxide, dry chemical, or foam.

5. Special Fire-Fighting procedures: Do not use solid stream of water, since stream will scatter and spread fire. Fine water spray can be used to keep fire-exposed containers cool.

6. Unusual fire and explosion hazards: Benzene is a flammable liquid. Its vapors can form explosive mixtures. All ignition sources must be controlled when benzene is used, handled, or stored. Where liquid or vapor may be released, such areas shall be considered as hazardous locations. Benzene vapors are heavier than air; thus the vapors may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which benzene is handled.

7. Benzene is classified as a 1 B flammable liquid for the purpose of conforming to the requirements of 29 CFR 1910.106. A concentration exceeding 3,250 ppm is considered a potential fire explosion hazard. Locations where benzene may be present in quantities sufficient to produce explosive or ignitable mixtures are considered Class I Group D for the purposes of conforming to the requirements of 29 CFR 1910.309.

B. Reactivity.

1. Conditions contributing to instability: Heat.
2. Incompatibility: Heat and oxidizing materials.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide).

III. SPILL AND LEAK PROCEDURES

A. Steps to be taken if the material is released or spilled. As much benzene as possible should be absorbed with suitable materials, such as dry sand or earth. That remaining must be flushed with large amounts of water. Do not flush benzene into a confined space, such as a sewer, because of explosion danger. Remove all ignition sources. Ventilate enclosed places.

B. Waste disposal method. Disposal methods must conform to other jurisdictional regulations. If allowed, benzene may be disposed of: (a) By absorbing it in dry sand or earth and disposing in a sanitary landfill; (b) if small quantities, by removing it to a safe location from buildings or other combustible sources, pouring it in dry sand or earth and cautiously igniting it; and (c) if large quantities, by atomizing it in a suitable combustion chamber.

IV. MISCELLANEOUS PRECAUTIONS

- A. High exposure to benzene can occur when transferring the liquid from one container to another. Such operations should be well ventilated and good work practices must be established to avoid spills.
- B. Use non-sparking tools to open benzene containers which are effectively grounded and bonded prior to opening and pouring.
- C. Employers must advise employees of all plant areas and operations where exposure to benzene could occur. Common operations in which high exposures to benzene may be encountered are: the primary production and utilization of benzene, and transfer of benzene.

APPENDIX C TO § 1910.1028—MEDICAL SURVEILLANCE GUIDELINES FOR BENZENE

I. ROUTE OF ENTRY

Inhalation; skin absorption.

II. TOXICOLOGY

Benzene is primarily an inhalation hazard. Systemic absorption may cause depression of the hematopoietic system, pancytopenia, aplastic anemia, and leukemia. Inhalation of high concentrations can affect central nervous system function. Aspiration of small amounts of liquid benzene immediately causes pulmonary edema and hemorrhage of pulmonary tissue. There is some absorption through the skin. Absorption may be more rapid in the case of abraded skin, and benzene may be more readily absorbed if it is present in a mixture or as a contaminant in solvents which are readily absorbed. The defatting action of benzene may produce primary irritation due to repeated or prolonged contact with the skin. High concentration are irritating to the eyes and the mucuous membranes of the nose, and respiratory tract.

III. SIGNS AND SYMPTOMS

Direct skin contact with benzene may cause erythema. Repeated or prolonged contact may result in drying, scaling dermatitis, or development of secondary skin infections. In addition, there is benzene absorption through the skin. Local effects of benzene vapor or liquid on the eye are slight. Only at very high concentrations is there any smarting sensation in the eye. Inhalation of high concentrations of benzene may have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation, and/or giddiness, followed by a period

of depression, drowsiness, or fatigue. A sensation of tightness in the chest accompanied by breathlessness may occur and ultimately the victim may lose consciousness. Tremors, convulsions and death may follow from respiratory paralysis or circulatory collapse in a few minutes to several hours following severe exposures.

The detrimental effect on the blood-forming system of prolonged exposure to small quantities of benzene vapor is of extreme importance. The hematopoietic system is the chief target for benzene's toxic effects which are manifested by alterations in the levels of formed elements in the peripheral blood. These effects have occurred at concentrations of benzene which may not cause irritation of mucous membranes, or any unpleasant sensory effects. Early signs and symptoms of benzene morbidity are varied, often not readily noticed and non-specific. Subjective complaints of headache, dizziness, and loss of appetite may precede or follow clinical signs. Rapid pulse and low blood pressure, in addition to a physical appearance of anemia, may accompany a subjective complaint of shortness of breath and excessive tiredness. Bleeding from the nose, gums, or mucous membranes, and the development of purpuric spots (small bruises) may occur as the condition progresses. Clinical evidence of leukopenia, anemia, and thrombocytopenia, singly or in combination, has been frequently reported among the first signs.

Bone marrow may appear normal, aplastic, or hyperplastic, and may not, in all situations, correlate with peripheral blood forming tissues. Because of variations in the susceptibility to benzene morbidity, there is no "typical" blood picture. The onset of effects of prolonged benzene exposure may be delayed for many months or years after the actual exposure has ceased and identification or correlation with benzene exposure must be sought out in the occupational history.

IV. TREATMENT OF ACUTE TOXIC EFFECTS

Remove from exposure immediately. Make sure you are adequately protected and do not risk being overcome by fumes. Give oxygen or artificial resuscitation if indicated. Flush eyes, wash skin if contaminated and remove all contaminated clothing. Symptoms of intoxication may persist following severe exposures. Recovery from mild exposures is usually rapid and complete.

V. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. General

The principal effects of benzene exposure which form the basis for this regulation are pathological changes in the hematopoietic system, reflected by changes in the peripheral blood and manifesting clinically as pancytopenia, aplastic anemia, and leukemia. Consequently, the medical surveillance program is designed to observe, on a regular basis, blood indices for early signs of these effects, and although early signs of leukemia are not usually available, emerging diagnostic technology and innovative regimes make consistent surveillance for leukemia, as well as other hematopoietic effects, essential.

Initial examinations are to be provided within 60 days of the effective date of this standard, or at the time of initial assignment, and periodic examinations annually thereafter. There are special provisions for medical tests in the event of hematologic abnormalities or for emergency situations.

The blood values which require referral to a hematologist or internist are noted in the standard in paragraph (i) (5). The standard specifies that blood abnormalities that persist must be referred "unless the physician has good reason to believe such referral is unnecessary" (paragraph (i)(5)). Examples of conditions that could make a referral unnecessary despite abnormal blood limits are iron or folate deficiency, menorrhagia, or blood loss due to some unrelated medical abnormality.

Symptoms and signs of benzene toxicity can be non-specific. Only a detailed history and appropriate investigative procedures will enable a physician to rule out or confirm conditions that place the employee at increased risk. To assist the examining physician with regard to which laboratory tests are necessary and when to refer an employee to the specialist, OSHA has established the following guidelines.

B. Hematology Guidelines

A minimum battery of tests is to be performed by strictly standardized methods.

1. Red cell, white cell, platelet counts, white blood cell differential, hematacrit and red cell indices must be performed by an accredited laboratory. The normal ranges for the red cell and white cell counts are influenced by altitude, race, and sex, and therefore should be determined by the accredited laboratory in the specific area where the tests are performed.

Either a decline from an absolute normal or an individual's base line to a subnormal value or a rise to a supra-normal value, are indicative of potential toxicity, particularly if all blood parameters decline. The normal total white blood count is approximately 7,200/mm³ plus or minus 3,000. For cigarette smokers the white count may be higher and the upper range may be 2,000 cells higher than normal for the laboratory. In addition, infection, allergies and some drugs may raise the white cell count. The normal platelet count is approximately 250,000 with a range of 140,000 to 400,000. Counts outside this range should be regarded as possible evidence of benzene toxicity.

Certain abnormalities found through routine screening are of greater significance in the benzene-exposed worker and require prompt consultation with a specialist, namely:

a. Thrombocytopenia.

b. A trend of decreasing white cell, red cell, or platelet indices in an individual over time is more worrisome than an isolated abnormal finding at one test time. The importance of trend highlights the need to compare an individual's test results to baseline and/or previous periodic tests.

c. A constellation or pattern of abnormalities in the different blood indices is of more significance than a single abnormality. A low white count not associated with any abnormalities in other cell indices may be a normal statistical variation, whereas if the low white count is accompanied by decreases in the platelet and/or red cell indices, such a pattern is more likely to be associated with benzene toxicity and merits thorough investigation.

Anemia, leukopenia, macrocytosis or an abnormal differential white blood cell count should alert the physician to further investigate and/or refer the patient if repeat tests confirm the abnormalities. If routine screening detects an abnormality, follow-up tests which may be helpful in establishing the etiology of the abnormality are the peripheral blood smear and the reticulocyte count.

The extreme range of normal for reticulocytes is 0.4 to 2.5 percent of the red cells, the usual range being 0.5 to 1.2 percent of the red cells, but the typical value is in the range of 0.8 to 1.0 percent. A decline in reticulocytes to levels of less than 0.4 percent is to be regarded as possible evidence (unless another specific cause is found) of benzene toxicity requiring accelerated surveillance. An increase in reticulocyte levels to about 2.5 percent may also be consistent with (but is not as characteristic of) benzene toxicity.

2. An important diagnostic test is a careful examination of the peripheral blood smear. As with reticulocyte count the smear should be with fresh uncoagulated blood obtained from a needle tip following venipuncture or from a drop of earlobe blood (capillary blood). If necessary, the smear may, under certain limited conditions, be made from a blood sample anticoagulated with EDTA (but never with oxalate or heparin). When the smear is to be prepared from a specimen of venous blood which has been collected by a commercial Vacutainer® type tube containing neutral EDTA, the smear should be made as soon as possible after the venesection. A delay of up to 12 hours is permissible between the drawing of the blood specimen into EDTA and the preparation of the smear if the blood is stored at refrigerator (not freezing) temperature.

3. The minimum mandatory observations to be made from the smear are:

a. The differential white blood cell count.

b. Description of abnormalities in the appearance of red cells.

c. Description of any abnormalities in the platelets.

d. A careful search must be made throughout of every blood smear for immature white cells such as band forms (in more than normal proportion, i.e., over 10 percent of the total differential count), any number of metamyelocytes, myelocytes or myeloblasts. Any nucleate or multinucleated red blood cells should be reported.

Large "giant" platelets or fragments of megakaryocytes must be recognized.

An increase in the proportion of band forms among the neutrophilic granulocytes is an abnormality deserving special mention, for it may represent a change which should be considered as an early warning of benzene toxicity in the absence of other causative factors (most commonly infection). Likewise, the appearance of metamyelocytes, in the absence of another probable cause, is to be considered a possible indication of benzene-induced toxicity.

An upward trend in the number of basophils, which normally do not exceed about 2.0 percent of the total white cells, is to be regarded as possible evidence of benzene toxicity. A rise in the eosinophil count is less specific but also may be suspicious of toxicity if the rises above 6.0 percent of the total white count.

The normal range of monocytes is from 2.0 to 8.0 percent of the total white count with an average of about 5.0 percent. About 20 percent of individuals reported to have mild but persisting abnormalities caused by exposure to benzene show a persistent monocytosis. The findings of a monocyte count which persists at more than 10 to 12 percent of the normal white cell count (when the total count is normal) or persistence of an absolute monocyte count in excess of 800/mm³ should be regarded as a possible sign of benzene-induced toxicity.

A less frequent but more serious indication of benzene toxicity is the finding in the peripheral blood of the so-called "pseudo" (or acquired) Pelger-Huet anomaly. In this anomaly many, or sometimes the majority, of the neutrophilic granulocytes possess two round nuclear segments—less often one or three round segments—rather than three normally elongated segments. When this anomaly is not hereditary, it is often but not invariably predictive of subsequent leukemia. However, only about two percent of patients who ultimately develop acute myelogenous leukemia show the acquired Pelger-Huet anomaly. Other tests that can be administered to investigate blood abnormalities are discussed below; however, such procedures should be undertaken by the hematologist.

An uncommon sign, which cannot be detected from the smear, but can be elicited by a "sucrose water test" of peripheral blood, is transient paroxysmal nocturnal hemoglobinuria (PNH), which may first occur insidiously during a period of established aplastic anemia, and may be followed within one to a few years by the appearance of rapidly fatal acute myelogenous leukemia. Clinical detection of PNH, which occurs in only one or two percent of those destined to have acute myelogenous leukemia, may be difficult; if the "sucrose water test" is positive, the somewhat more definitive Ham test, also known as the acid-serum hemolysis test, may provide confirmation.

e. Individuals documented to have developed acute myelogenous leukemia years after initial exposure to benzene may have progressed through a preliminary phase of hematologic abnormality. In some instances pancytopenia (i.e., a lowering in the counts of all circulating blood cells of bone marrow origin, but not to the extent implied by the term "aplastic anemia") preceded leukemia for many years. Depression of a single blood cell type or platelets may represent a harbinger of aplasia or leukemia. The finding of two or more cytopenias, or pancytopenia in a benzene-exposed individual, must be regarded as highly suspicious of more advanced although still reversible, toxicity. "Pancytopenia" coupled with the appearance of immature cells (myelocytes, myeloblasts, erythroblasts, etc.), with abnormal cells (pseudo Pelger-Huet anomaly, atypical nuclear heterochromatin, etc.), or unexplained elevations of white blood cells must be regarded as evidence of benzene overexposure unless proved otherwise. Many severely aplastic patients manifested the ominous finding of 5-10 percent myeloblasts in the marrow, occasional myeloblasts and myelocytes in the blood and 20-30% monocytes. It is evident that isolated cytopenias, pancytopenias, and even aplastic anemias induced by benzene may be reversible and complete recovery has been reported on cessation of exposure. However, since any of these abnormalities is serious, the employee must immediately be removed from any possible exposure to benzene vapor. Certain tests may substantiate the employee's prospects for progression or regression. One such test would be an examination of the bone marrow, but the decision to perform a bone marrow aspiration or needle biopsy is made by the hematologist.

The findings of basophilic stippling in circulating red blood cells (usually found in 1 to 5% of red cells following marrow injury), and detection in the bone marrow of what are termed "ringed sideroblasts" must be taken seriously,

as they have been noted in recent years to be premonitory signs of subsequent leukemia.

Recently peroxidase-staining of circulating or marrow neutrophil granulocytes, employing benzidine dihydrochloride, have revealed the disappearance of, or diminution in, peroxidase in a sizable proportion of the granulocytes, and this has been reported as an early sign of leukemia. However, relatively few patients have been studied to date. Granulocyte granules are normally strongly peroxidase positive. A steady decline in leukocyte alkaline phosphatase has also been reported as suggestive of early acute leukemia. Exposure to benzene may cause an early rise in serum iron, often but not always associated with a fall in the reticulocyte count. Thus, serial measurements of serum iron levels may provide a means of determining whether or not there is a trend representing sustained suppression of erythropoiesis.

Measurement of serum iron, determination of peroxidase and of alkaline phosphatase activity in peripheral granulocytes can be performed in most pathology laboratories. Peroxidase and alkaline phosphatase staining are usually undertaken when the index of suspicion for leukemia is high.

APPENDIX D TO § 1910.1028—SAMPLING AND ANALYTICAL METHODS FOR BENZENE MONITORING AND MEASUREMENT PROCEDURES

Measurements taken for the purpose of determining employee exposure to benzene 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). Sampling and analysis must be performed with procedures meeting the requirements of the standard.

There are a number of methods available for monitoring employee exposures to benzene. The sampling and analysis may be performed by collection of the benzene vapor or charcoal absorption tubes, with subsequent chemical analysis by gas chromatography. Sampling and analysis may also be performed by portable direct reading instruments, real-time continuous monitoring systems, passive dosimeters or other suitable methods. The employer has the obligation of selecting a 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 concentrations of benzene greater than or equal to 0.5 ppm.

The OSHA Laboratory modified NIOSH Method S311 and evaluated it at a benzene air concentration of 1 ppm. A procedure for determining the benzene concentration in bulk material samples was also evaluated. This work, reported in OSHA Laboratory Method No. 12, includes the following two analytical procedures:

I. OSHA METHOD 12 FOR AIR SAMPLES

Analyte: Benzene

Matrix: Air

Procedure: Adsorption on charcoal, desorption with carbon disulfide, analysis by GC.

Detection limit: 0.04 ppm

Recommended air volume and sampling rate: 10L to 0.2 L/min.

1. Principle of the Method.

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2. The charcoal in the tube is transferred to a small, stoppered vial, and the analyte is desorbed with carbon disulfide.
- 1.3. An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from standards.

2. Advantages and disadvantages of the method.

- 2.1 The sampling device is small, portable, and involved no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The samples are analyzed by means of a quick, instrumental method.
- 2.2 The amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25 percent of that found on the front section, the possibility of sample loss exists.

3. Apparatus.

- 3.1 A calibrated personal sampling pump whose flow can be determined within ± 5 percent at the recommended flow rate.
- 3.2. Charcoal tubes: Glass with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 °C prior to packing. The adsorbing section contains 100 mg of charcoal, the back-up section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the back-up section. A plug of silanized glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 3.3. Gas chromatograph equipped with a flame ionization detector.
- 3.4. Column (10-ft \times $\frac{1}{8}$ -in stainless steel) packed with 80/100 Supelcoport coated with 20 percent SP 2100, 0.1 percent CW 1500.
- 3.5. An electronic integrator or some other suitable method for measuring peak area.
- 3.6. Two-milliliter sample vials with Teflon-lined caps.
- 3.7. Microliter syringes: 10-microliter (10- μ L syringe, and other convenient sizes for making standards, 1- μ L syringe for sample injections.
- 3.8. Pipets: 1.0 mL delivery pipets
- 3.9. Volumetric flasks: convenient sizes for making standard solutions.

4. Reagents.

- 4.1. Chromatographic quality carbon disulfide (CS_2). Most commercially available carbon disulfide contains a trace of benzene which must be removed. It can be removed with the following procedure:
Heat under reflux for 2 to 3 hours, 500 mL of carbon disulfide, 10 mL concentrated sulfuric acid, and 5 drops of

concentrated nitric acid. The benzene is converted to nitrobenzene. The carbon disulfide layer is removed, dried with anhydrous sodium sulfate, and distilled. The recovered carbon disulfide should be benzene free. (It has recently been determined that benzene can also be removed by passing the carbon disulfide through 13x molecular sieve).

4.2. Benzene, reagent grade.

4.3. p-Cymene, reagent grade, (internal standard).

4.4. Desorbing reagent. The desorbing reagent is prepared by adding 0.05 mL of p-cymene per milliliter of carbon disulfide. (The internal standard offers a convenient means correcting analytical response for slight inconsistencies in the size of sample injections. If the external standard technique is preferred, the internal standard can be eliminated).

4.5. Purified GC grade helium, hydrogen and air.

5. Procedure.

5.1. Cleaning of equipment. All glassware used for the laboratory analysis should be properly cleaned and free of organics which could interfere in the analysis.

5.2. Calibration of personal pumps. Each pump must be calibrated with a representative charcoal tube in the line.

5.3. Collection and shipping of samples.

5.3.1. Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

5.3.2. The smaller section of the charcoal is used as the backup and should be placed nearest the sampling pump.

5.3.3. The charcoal tube should be placed in a vertical position during sampling to minimize channeling through the charcoal.

5.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

5.3.5. A sample size of 10 liters is recommended. Sample at a flow rate of approximately 0.2 liters per minute. The flow rate should be known with an accuracy of at least ± 5 percent.

5.3.6. The charcoal tubes should be capped with the supplied plastic caps immediately after sampling.

5.3.7. Submit at least one blank tube (a charcoal tube subjected to the same handling procedures, without having any air drawn through it) with each set of samples.

5.3.8. Take necessary shipping and packing precautions to minimize breakage of samples.

5.4. Analysis of samples.

5.4.1. Preparation of samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml vial. The separating section of foam is removed and discarded; the second section is transferred to another capped vial. These two sections are analyzed separately.

5.4.2. Desorption of samples. Prior to analysis, 1.0 mL of desorbing solution is pipetted into each sample container. The desorbing solution consists of 0.05 µL internal standard per mL of carbon disulfide. The sample vials are capped as soon as the solvent is added. Desorption should be done for 30 minutes with occasional shaking.

5.4.3. GC conditions. Typical operating conditions for the gas chromatograph are:

1.30 mL/min (60 psig) helium carrier gas flow.

2.30 mL/min (40 psig) hydrogen gas flow to detector.

3.240 mL/min (40 psig) air flow to detector.

4.150 °C injector temperature.

5.250 °C detector temperature.

6.100 °C column temperature.

5.4.4. Injection size. 1 µL.

5.4.5. Measurement of area. The peak areas are measured by an electronic integrator or some other suitable form of area measurement.

5.4.6. An internal standard procedure is used. The integrator is calibrated to report results in ppm for a 10 liter air sample after correction for desorption efficiency.

5.5. Determination of desorption efficiency.

5.5.1. Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and from one lot of chemical to another. Thus, it is necessary to determine, at least once, the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

5.5.2. Procedure for determining desorption efficiency. The reference portion of the charcoal tube is removed. To the remaining portion, amounts representing 0.5X, 1X, and 2X and (X represents target concentration) based on a 10 L air sample are injected into several tubes at each level. Dilutions of benzene with carbon disulfide are made to allow injection of measurable quantities. These tubes are then allowed to equilibrate at least overnight. Following equilibration they are analyzed following the same procedure as the samples. Desorption efficiency is determined by dividing the amount of benzene found by amount spiked on the tube.

6. Calibration and standards. A series of standards varying in concentration over the range of interest is prepared and analyzed under the same GC conditions that will be used on the samples. A calibration curve is prepared by plotting concentration (µg/mL) versus peak area.

7. Calculations. Benzene air concentration can be calculated from the following equation:

$$\text{mg/m}^3 = (A)(B)/(C)(D)$$

Where:

A=µg/mL benzene, obtained from the calibration curve

B=desorption volume (1 mL)

C=Liters of air sampled

D=desorption efficiency

The concentration in mg/m³ can be converted to ppm (at 25° and 760 mm) with following equation:

$$\text{ppm} = (\text{mg/m}^3) (24.46) / (78.11)$$

Where:

24.46=molar volume of an ideal gas

25 °C and 760 mm

78.11=molecular weight of benzene

8. Backup Data.

8.1 Detection limit—Air Samples.

The detection limit for the analytical procedure is 1.28 ng with a coefficient of variation of 0.023 at this level. This would be equivalent to an air concentration of 0.04 ppm for a 10 L air sample. This amount provided a chromatographic peak that could be identifiable in the presence of possible interferences. The detection limit data were obtained by making 1 µL injections of a 1.283 µg/mL standard.

Injection	Area Count	
1	655.4	
2	617.5	
3	662.0	X =640.2
4	641.1	SD=14.9
5	636.4	CV=0.023
6	629.2	

8.2. Pooled coefficient of variation—Air Samples. The pooled coefficient of variation for the analytical procedure was determined by 1 µL replicate injections of analytical standards. The standards were 16.04, 32.08, and 64.16 µg/mL, which are equivalent to 0.5, 1.0, and 2.0 ppm for a 10 L air sample respectively.

Injection	Area Counts		
	0.5 ppm	1.0 ppm	2.0 ppm
1	3996.5	8130.2	16481
2	4059.4	8235.6	16493
3	4052.0	8307.9	16535
4	4027.2	8263.2	16609
5	4046.8	8291.1	16552
6	4137.9	8288.8	16618

X =	4053.3	8254.0	16548.3
SD=	47.2	62.5	57.1
CV=	0.0116	0.0076	0.0034
C V =0.008			

8.3. Storage data—Air Samples

Samples were generated at 1.03 ppm benzene at 80% relative humidity, 22 °C, and 643 mm. All samples were taken for 50 minutes at 0.2 L/min. Six samples were analyzed immediately and the rest of the samples were divided into two groups by fifteen samples each. One group was stored at refrigerated temperature of -25 °C, and the other group was stored at ambient temperature (approximately 23 °C). These samples were analyzed over a period of fifteen days. The results are tabulated below.

PERCENT RECOVERY

Day analyzed	Refrigerated	Ambient
0	97.4 98.7 98.9	97.4 98.7 98.9
0	97.1 100.6 100.9	97.1 100.6 100.9
2	95.8 96.4 95.4	95.4 96.6 96.9
5	93.9 93.7 92.4	92.4 94.3 94.1
9	93.6 95.5 94.6	95.2 95.6 96.6
13	94.3 95.3 93.7	91.0 95.0 94.6
15	96.8 95.8 94.2	92.9 96.3 95.9

8.4. Desorption data.

Samples were prepared by injecting liquid benzene onto the A section of charcoal tubes. Samples were prepared that would be equivalent to 0.5, 1.0, and 2.0 ppm for a 10 L air sample.

PERCENT RECOVERY

Sample	0.5 ppm	1.0 ppm	2.0 ppm
1	99.4	98.8	99.5
2	99.5	98.7	99.7
3	99.2	98.6	99.8
4	99.4	99.1	100.0
5	99.2	99.0	99.7
6	99.8	99.1	99.9
X =	99.4	98.9	99.8
SD=	0.22	0.21	0.18
CV=	0.0022	0.0021	0.0018
X =99.4			

8.5. Carbon disulfide.

Carbon disulfide from a number of sources was analyzed for benzene contamination. The results are given in the following table. The benzene contaminant can be removed with the procedures given in section 4.1.

Sample	$\mu\text{g Benzene/mL}$	ppm equivalent (for 10 L air sample)
Aldrich Lot 83017	4.20	0.13
Baker Lot 720364	1.01	0.03
Baker Lot 822351	1.01	0.03
Malinkrodt Lot WEMP	1.74	0.05
Malinkrodt Lot WDSJ	5.65	0.18
Malinkrodt Lot WHGA	2.90	0.09
Treated CS ₂		

II. OSHA LABORATORY METHOD NO. 12 FOR BULK SAMPLES

Analyte: Benzene.

Matrix: Bulk Samples.

Procedure: Bulk Samples are analyzed directly by high performance liquid chromatography (HPLC).

Detection limits: 0.01% by volume.

1. Principle of the method.

- 1.1. An aliquot of the bulk sample to be analyzed is injected into a liquid chromatograph.
- 1.2. The peak area for benzene is determined and compared to areas obtained from standards.

2. Advantages and disadvantages of the method.

- 2.1. The analytical procedure is quick, sensitive, and reproducible.
- 2.2. Reanalysis of samples is possible.
- 2.3. Interferences can be circumvented by proper selection of HPLC parameters.
- 2.4. Samples must be free of any particulates that may clog the capillary tubing in the liquid chromatograph. This may require distilling the sample or clarifying with a clarification kit.

3. Apparatus.

- 3.1. Liquid chromatograph equipped with a UV detector.
- 3.2. HPLC Column that will separate benzene from other components in the bulk sample being analyzed. The column used for validation studies was a Waters uBondapack C18, 30 cm \times 3.9 mm.

3.3. A clarification kit to remove any particulates in the bulk if necessary.

3.4. A micro-distillation apparatus to distill any samples if necessary.

3.5. An electronic integrator or some other suitable method of measuring peak areas.

3.6. Microliter syringes—10 μL syringe and other convenient sizes for making standards. 10 μL syringe for sample injections.

3.7. Volumetric flasks, 5 mL and other convenient sizes for preparing standards and making dilutions.

4. Reagents.

4.1. Benzene, reagent grade.

4.2. HPLC grade water, methyl alcohol, and isopropyl alcohol.

5. Collection and shipment of samples.

5.1. Samples should be transported in glass containers with Teflon-lined caps.

5.2. Samples should not be put in the same container used for air samples.

6. Analysis of samples.

6.1. Sample preparation.

If necessary, the samples are distilled or clarified. Samples are analyzed undiluted. If the benzene concentration is out of the working range, suitable dilutions are made with isopropyl alcohol.

6.2. HPLC conditions.

The typical operating conditions for the high performance liquid chromatograph are:

1. Mobile phase—Methyl alcohol/water, 50/50

1. Analytical wavelength—254 nm

3. Injection size—10 μL

6.3. Measurement of peak area and calibration.

Peak areas are measured by an integrator or other suitable means. The integrator is calibrated to report results % in benzene by volume.

7. Calculations.

Since the integrator is programmed to report results in % benzene by volume in an undiluted sample, the following equation is used:

$$\% \text{ Benzene by Volume} = A \times B$$

Where:

A=% by volume on report

B=Dilution Factor

(B=1 for undiluted sample)

8. Backup Data.

8.1. Detection limit—Bulk Samples.

The detection limit for the analytical procedure for bulk samples is 0.88 µg, with a coefficient of variation of 0.019 at this level. This amount provided a chromatographic peak that could be identifiable in the presence of possible interferences. The detection limit data were obtained by making 10 µL injections of a 0.10% by volume standard.

Injection	Area Count	
1	45386	
2	44214	
3	43822	X =44040.1
4	44062	SD=852.5
6	42724	CV=0.019

8.2. Pooled coefficient of variation—Bulk Samples.

The pooled coefficient of variation for analytical procedure was determined by 50 µL replicate injections of analytical standards. The standards were 0.01, 0.02, 0.04, 0.10, 1.0, and 2.0% benzene by volume.

AREA COUNT (PERCENT)

Injection No.	0.01	0.02	0.04	0.10	1.0	2.0
1	45386	84737	166097	448497	4395380	9339150
2	44241	84300	170832	441299	4590800	9484900
3	43822	83835	164160	443719	4593200	9557580
4	44062	84381	164445	444842	4642350	9677060
5	44006	83012	168398	442564	4646430	9766240
6	42724	81957	173002	443975	4646260	
X =	44040.1	83703.6	167872	444149	4585767	9564986
SD =	852.5	1042.2	3589.8	2459.1	96839.3	166233
CV =	0.0194	0.0125	0.0213	0.0055	0.0211	0.0174
C V =	0.017					

Jan. 8, 1998; 63 FR 20099, Apr. 23, 1998; 70 FR 1142, Jan. 5, 2005; 71 FR 16673, Apr. 3, 2006; 71 FR 50189, Aug. 24, 2006; 73 FR 75585, Dec. 12, 2008; 76 FR 33608, June 8, 2011; 77 FR 17781, Mar. 26, 2012]

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