# CWRU WRITTEN PROGRAM FOR BENZENE

29 CFR 1910.1028

Written 09/1999 Revised 08/2011

## **CWRU WRITTEN PROGRAM FOR BENZENE**

## I. Scope and Application

- A. A n umber o f ch emicals ar e r egulated b yt he O ccupational S afety and Health Administration (OSHA) under 29 CFR 1910. The standard for benzene (CAS# 71-43-2) is listed under 29 CFR 1910.1028. It applies to persons working with gaseous or liquefied benzene at concentrations greater than 0.1% by volume.
- B. According to Case Western Reserve University's (CWRU) Chemical Safety Manual, the Primary Investigator (PI) is ultimately responsible for safety in his/her laboratory. The PI must write and implement a lab specific Chemical Hygiene Plan unique to the work area. This pl an i s t hen reviewed a nd a pproved b y the E nvironmental H ealth a nd S afety Department (EHS). As part of the implementation of the chemical hygiene plan, the PI shares responsibility in maintaining his/her employees' training, medical evaluations, and enforcing necessary s afety p recautions. W hen n ew ch emicals or procedures ar e introduced into the lab's protocol, the Chemical Hygiene Plan needs updated to reflect this change and resubmitted for approval. If benzene is used in your lab, the Chemical Hygiene Plan must address those items required by 29 CFR 1910.1028.

## II. Hazards

- A. Health Hazards
  - 1. Acute exposure
    - a. Acute exposure to benzene may act as a central nervous system depressant with headaches, dizziness, or even convulsions depending on the exposure level.
    - b. It is also a skin and respiratory irritant. Benzene removes natural oils in the skin upon dermal absorption. The degree of irritation depends on the individual, the concentration, and exposure duration.
  - 2. Chronic exposure
    - a. Chronic exposure to benzene m ay lead to hematopoietic toxicity including, but not limite d to, a plastic a nemia o r acute m yelogenous l eukemia. Benzene i s metabolized in the body to a number of metabolites including phenol, catechol, hydroquinone, benzo-quinone, and muconaldehyde. These metabolites are toxic to the bone marrow. As a result of genetic damage to the DNA of developing stem cells i n b one m arrow, an i ncreased growth of m yeloblasts (white b lood c ell precursor) develop with low counts of red blood cells and platelets. This condition can lead to acute myelogenous leukemia.

- b. Aplastic an emia r efers t o a d ecrease i n r ed b lood cel ls, white bl ood c ells, a nd platelets i n t he bl ood (pancytopenia) and a d ecrease i n s tem cel ls i n t he b one marrow (hypoplastic bone marrow).
- c. Benzene is also a known reproductive ha zard. It reduces fertility in men and women and h as reportedly been associated with menstrual d isorders a nd impotence. It is also a teratogen affecting fetus development.
- B. Physical Hazards
  - 1. Benzene is a Class IB flammable liquid with a flash point of 12° F.
  - 2. Benzene is a moderate explosion hazard. Vapor/air mixtures are explosive.

## **III. Exposure Limits**

A. The permissible exposure limit (PEL) is 1ppm and the short-term exposure limit (STEL) is 5ppm. No employee may be exposed to time-weighted average concentrations above 1ppm for an eight hour time period and above 5ppm for a fifteen minute time period. The action le vel (AL) is 0.5ppm and is a lso a time-weighted a verage concentration for a n eight hour time period. Monitoring requirements become effective if the PEL, STEL, or AL are exceeded in a work area.

## **IV. Exposure Monitoring**

- A. Air monitoring is conducted by EHS. To assess airborne exposure to benzene, personal air samples must be collected representative of each potentially exposed work group in each work area. Future monitoring will not be necessary if the results are less than the exposure limits; however, additional monitoring may be required if there are complaints or a change in lab protocol concerning benzene usage.
- B. If 8-hr sample results are greater than the AL but less than the PEL, annual monitoring is conducted.
- C. If 8-hr sample results are greater than the PEL and 15-min sample results are greater than the STEL, monitoring is conducted every six months.
- D. Monitoring m ay be di scontinued i f t wo c onsecutive s ample r esults collected at l east seven days apart are less than the AL.
- E. Employees must be notified within 15 w orking days by EHS if the personal sampling results exceed the exposure limits. The notification must also include corrective actions to minimize employee exposure.

## V. Regulated Areas

- A. OSHA defines a regulated area as "any area where airborne concentrations of benzene exceed or can reasonably be expected to exceed, the permissible exposure limits..."
- B. Access t o l abs d etermined t o b e r egulated a reas m ust b e r estricted t o designated personnel so the number of people exposed to benzene is minimized.

## **VI.** Control Methods

- A. Exposure t o be nzene i n t he l ab m ust be a voided t o prevent ad verse health effects, especially exposure vi a i nhalation a nd d ermal a bsorption. Established e ngineering controls, pe rsonal pr otective e quipment, a nd w ork practices u sed t o r educe b enzene exposure must be included in the lab's Chemical Hygiene Plan.
- B. Engineering controls
  - 1. Engineering c ontrols m ust be e stablished first to r educe be nzene exposure t o t he lowest p ossible le vel; th en, if s till w arranted personal pr otective e quipment (PPE) must be used. The necessary types of engineering controls and PPE are lab-specific and must be included in the lab's Chemical Hygiene Plan.
  - 2. Fume hoods are provided in most l abs as the most c ommon engineering c ontrol. Additional ventilation and containment may be required depending on the procedures performed. Such risk assessments must be determined on an individual basis.
- C. Personal protective equipment (PPE)
  - 1. The minimum PPE requirement when working in a lab includes goggles, lab coat, and gloves. A dditional P PE with m ore protection may be required d epending on t he procedures performed.
  - 2. When or dering t he a ppropriate P PE f or a 1 ab, chemical p rotective clothing c harts must be reviewed since PPE material formulations vary by supplier.
  - 3. If r espirators ar e d eemed n ecessary, E HS will s upply them in accordance with 29 CFR 1910.134 and 29 CFR 1910.1028 (g).
  - 4. PPE must be provided by the employer to the employee free of charge.

## D. Laboratory Work Practices

- 1. Benzene solutions must be used in fume hoods as the designated work area.
- 2. Eyewash stations and safety showers must be within the immediate work area.

- 3. Gloves, goggles, and lab coats must be worn when working with benzene. Additional PPE may be required depending on the procedure.
- 4. Benzene m ust be s tored a t r oom t emperature away f rom he at and incompatible materials in a certified flammable cabinet.
- 5. Benzene containers must be correctly labeled.
- 6. A copy of CWRU's Benzene Program should be present in the lab.

#### VII. Labels and Signs

- A. The Hazard Communication Standard requires chemical containers to be labeled with the chemical i dentity, ha zard w arnings, a nd m anufacturer. The f ollowing are a dditional labeling requirements f or be nzene und er 29 CFR 1910.1028. T hese l abels c an be obtained from EHS free of charge.
- B. Container labels

DANGER CONTAINS BENZENE CANCER HAZARD

C. Signs to entrances of regulated areas

DANGER BENZENE CANCER HAZARD FLAMMABLE – NO SMOKING AUTHORIZED PERSONNEL ONLY RESPIRATOR REQUIRED

#### VIII. Training

- A. Frequency
  - 1. Employees working in areas where benzene is present must be trained when they are initially hired.

- 2. If exposures are above the AL in a particular work area, the employees in that area must be trained annually.
- 3. Training is conducted by EHS.
- B. Contents
  - 1. Presence of chemicals
  - 2. Health hazards
  - 3. Work practices
  - 4. Emergency procedures
  - 5. Engineering controls & personal protective equipment
  - 6. Labels
  - 7. Material Safety Data Sheets
  - 8. Summary of the 29 CFR 1910.1028
  - 9. Medical Surveillance Program

## IX. Medical Surveillance Program

- A. General
  - 1. Without c ost to the e mployee, me dical s urveillance is a vailable f or employees exposed to benzene concentrations above the AL or STEL. Employees covered under the standard should have annual exams.
  - 2. Examinations are performed by a licensed physician and specimen samples sent to an accredited lab for testing.
- B. Initial Examinations
  - 1. Occupational history
    - a. Work exposure to benzene and other hematological agents
    - b. Family history of blood dyscrasias
    - c. History of renal or liver dysfunction

- d. Medicines routinely taken
- e. Previous exposure to ionizing radiation
- f. Exposure to marrow toxins outside of work
- g. Complete physical exam
- 2. Complete Blood Count
- 3. Any additional tests deemed necessary by the physician
- 4. For workers required to wear respirators, the exam must pay special attention to the cardiopulmonary system and include a pulmonary function test.
- C. Periodic Examinations
  - 1. Exams provided annually to covered employees and include:
    - a. List of new exposures to marrow toxins
    - b. Changes in medicinal usage
    - c. Physical signs related to blood disorders
    - d. Complete blood count
    - e. Any other tests deemed necessary by physician
  - 2. Exams pr ovided w hen e mployee de velops s igns a nd s ymptoms associated w ith benzene exposure.
  - 3. Respirator us ers m ust ha ve pul monary function t ests e very 3 years and t heir cardiopulmonary system evaluated.
  - 4. Exams provided when there has been an emergency related to benzene exposure. A urinary phenol test is performed within 72 hours.
- D. Additional Examinations
  - 1. If the complete blood count indicates anything abnormal, it must be repeated within two weeks. If the abnormality persists, the employee is referred to a hematologist.
- E. Other

- 1. The e mployer m ust pr ovide t o t he ph ysician a c opy of 29 C FR 1910.1028, a description of t he e mployee's duties, t he de termined exposure l evel, a nd pe rsonal protective equipment used.
- 2. The employer must provide the employee a copy of the physician's written opinion and results within 15 days of the exam. The written opinion from the physician to the employer must pertain only to the employee's ability to work with benzene.

## X. Recordkeeping

- A. Exposure Results
  - 1. The records must include the results' number, date, duration, analytical method, the procedure p erformed w hile s amples w ere collected, a nd a ny pe rsonal pr otective equipment worn by person monitored. It must also include the person's name, social security number, and position.
  - 2. Air monitoring results are kept on file by EHS for duration of employment plus at least 30 years.
- B. Medical Surveillance
  - 1. A record of each employee subject to medical surveillance must be maintained by Health Services.
  - 2. The r ecord m ust i nclude t he em ployee's n ame and s ocial s ecurity number, t he physician's w ritten opi nion of e ach e xam, t est r esults, employee c omplaints concerning benzene exposure, and a history of hematotoxin exposure.

#### BENZENE STANDARD OSHA 29 CFR 1910.1028

Standard Number: 1910.1028 Standard Title: Benzene. SubPart Number: Z SubPart Title: Toxic and Hazardous Substances

- (a) Scope and application.
  - (a)(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.
  - (a)(2) This section does not apply to:
    - (a)(2)(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 ope rations where gasoline or motor fuels a re di spensed f or more than 4 hours per day in an indoor location are covered by this section.
    - (a)(2)(ii) Loading a nd unl oading ope rations a t bul k w holesale s torage facilities w hich u se v apor c ontrol s ystems for a ll lo ading a nd unloading op erations, except f or t he p rovisions of 29 C FR 1910.1200 a s i ncorporated i nto t his s ection a nd t he em ergency provisions of paragraphs (g) and (i)(4) of this section.
    - (a)(2)(iii) The s torage, t ransportation, di stribution or s ale of be nzene o r liquid mixtures containing more than 0.1 percent benzene in intact containers o r i n t ransportation pi pelines w hile sealed i n s uch a manner a s t o c ontain b enzene va pors or 1 iquid, e xcept f or t he provisions of 29 C FR 1910.1200 a s incorporated into this section and the emergency provisions of paragraphs (g) and (i)(4) of this section.
    - (a)(2)(iv) Containers a nd pipelines c arrying mix tures w ith le ss th an 0 .1 percent benzene and natural gas processing plants processing gas with less than 0.1 percent benzene.
    - (a)(2)(v) Work operations where the only exposure to benzene is from liquid mixtures containing 0.5 pe rcent or less of benzene by volume, or the va pors r eleased from s uch liquids until S eptember 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 op erators using solvents with more than 0.1 percent benzene are covered by paragraph (i) of this section.

- (a)(2)(vi) Oil and gas drilling, production and servicing operations.
- (a)(2)(vii) Coke oven batteries.
- (a)(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) a ccuracy 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 d esignated r epresentative of employees f or t he p urpose of exercising t he r ight t o observe monitoring and measuring procedures under paragraph (l) of this section, or any other person a uthorized by t he A ct or r egulations i ssued under the A ct.

"Benzene" (C(6)H(6)) (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 i nclude t race a mounts of unreacted be nzene c ontained i n s olid 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" me ans the D irector of the N ational Institute f or O ccupational S afety and Health, U.S. Department of Health and Human Services, or designee.

"Emergency" m eans a ny occurrence s uch a s, but not l imited t o, e quipment f ailure, rupture of c ontainers, or failure of c ontrol e quipment w hich m ay or doe s r esult i n a n unexpected significant release of benzene.

"Employee exposure" m eans e xposure t o airborne be nzene which w ould oc cur i f t he 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 a verage exposure of 1 ppm or the short-term exposure limit of 5 ppm for 15 minutes.

"Vapor c ontrol s ystem" m eans a ny equipment us ed f or c ontaining t he t otal va pors displaced dur ing t he loading of gasoline, motor fuel or ot her fuel tank trucks and t he displacing of these vapors through a vapor processing system or balancing the vapor with the storage tank. This equipment also includes s ystems 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) -
  - (c)(1) Time-weighted average limit (TWA).

The em ployer s hall as sure t hat n o employee i s e xposed t o a n a irborne concentration of benzene in excess of one part of benzene per million parts of air (1 ppm) as an 8-hour time-weighted average.

(c)(2) Short-term exposure limit (STEL).

The employers hall a ssure t hat no employee i s exposed t o a n a irborne concentration of be nzene i n excess of five (5) ppm a s a veraged over a ny 15 minute period.

- (d) Regulated areas.
  - (d)(1) The employer shall establish a regulated area wherever the airborne concentration of b enzene ex ceeds o r can r easonably b e ex pected t o ex ceed t he p ermissible 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.
  - (d)(2) Access to regulated areas shall be limited to authorized persons.

- (d)(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 -
  - (e)(1) General.
    - (e)(1)(i) Determinations of e mployee e xposure s hall be m ade from breathing z one ai r s amples t hat ar e r epresentative o f ea ch employee's average exposure to airborne benzene.
    - (e)(1)(ii) Representative 8 -hour T WA e mployee exposures s hall be determined on the basis of one sample or samples representing the full shift exposure for each job classification in each work area.
    - (e)(1)(iii) Determinations of compliance with the STEL shall be made from 15 m inute em ployee breathing z one s amples m easured at operations w here t here is r eason t o be lieve e xposures a re hi gh, 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.
    - (e)(1)(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 s hall onl y b e r equired t o de termine r epresentative employee exposure for that operation during the shift on which the highest exposure is expected.
  - (e)(2) Initial monitoring.
    - (e)(2)(i) Each employer w ho has a pl ace of employment c overed unde r paragraph (a)(1) o ft his s ection s hall m onitor e ach o ft hese workplaces and w ork operations t o de termine a ccurately t he airborne c oncentrations of be nzene t o w hich employees m ay be exposed.
    - (e)(2)(ii) The i nitial m onitoring r equired unde r pa ragraph (e)(2)(i) of t his section s hall be c ompleted by 60 d ays after the effective d ate o f this standard or within 30 days of the introduction of benzene into

the workplace. Where the employer has monitored within one year prior t o t he e ffective d ate of t his s tandard a nd t he m onitoring satisfies all o ther r equirements of this s ection, the employer may rely on such earlier monitoring results to satisfy the requirements of paragraph (e)(2)(i) of this section.

- (e)(3) Periodic monitoring and monitoring frequency.
  - (e)(3)(i) If t he monitoring r equired b y p aragraph (e)(2)(i) of th is s ection reveals employee exposure at or above the action level but at or below t he T WA, t he employer s hall r epeat s uch monitoring f or each such employee at least every year.
  - (e)(3)(ii) If t he monitoring r equired b y p aragraph (e)(2)(i) of t his section reveals em ployee ex posure ab ove t he T WA, t he em ployer s hall repeat such monitoring for each such employee at least every six (6) months.
  - (e)(3)(iii) The employer may alter the monitoring schedule from every six months to annually for any employee for whom two consecutive measurements t aken at 1 east 7 d ays apart i ndicate t hat t he employee exposure has decreased to the TWA or below, but is at or above the action level.
  - (e)(3)(iv) Monitoring for the STEL shall be repeated as necessary to evaluate exposures of employees subject to short term exposures.
- (e)(4) Termination of monitoring.
  - (e)(4)(i) If the in itial monitoring r equired by p aragraph (e)(2)(i) of this section reveals employee exposure to be below the action level the employer m ay di scontinue the monitoring f or t hat e mployee, except as otherwise required by paragraph (e)(5) of this section.
  - (e)(4)(ii) If t he pe riodic m onitoring r equired b y paragraph (e)(3) of t his section r eveals t hat em ployee ex posures, as indicated b y at least two c onsecutive m easurements t aken at l east 7 d ays apart, are below t he a ction l evel t he e mployer m ay discontinue t he monitoring f or t hat e mployee, e xcept a s ot herwise r equired b y paragraph (e)(5).
- (e)(5) Additional monitoring.
  - (e)(5)(i) The e mployer s hall in stitute the e xposure m onitoring r equired under paragraphs (e)(2) and (e)(3) of this section when there has

been a c hange i n t he pr oduction, pr ocess, c ontrol e quipment, personnel or work practices which may result in new or additional exposures t o be nzene, o r w hen the employer h as an y reason t o suspect a change which may result in new or additional exposures.

- (e)(5)(ii) Whenever s pills, l eaks, r uptures or ot her br eakdowns oc cur t hat 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.
- (e)(6) Accuracy of monitoring. Monitoring shall be accurate, to a confidence level of 95 percent, t o w ithin pl us or m inus 25 p ercent for a irborne c oncentrations of benzene.
- (e)(7) Employee notification of monitoring results.
  - (e)(7)(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.
  - (e)(7)(ii) Whenever the PELs are exceeded, the written notification required by p aragraph (e)(7)(i) of t his section s hall c ontain the c orrective action b eing t aken b y t he em ployer t o reduce t he em ployee exposure t o or b elow the P EL, or s hall r efer t o a do cument available to the employee which states the corrective actions to be taken.
- (f) Methods of compliance -
  - (f)(1) Engineering controls and work practices.
    - (f)(1)(i) The e mployer s hall in stitute e ngineering c ontrols a nd w ork practices to reduce and maintain employee exposure to benzene at or below the permissible exposure limits, except to the extent that the employer c an establish that these controls are not feasible or where t he p rovisions o f p aragraph (f)(1)(iii) or (g)(1) o f t his section apply.
    - (f)(1)(ii) Wherever t he f easible engineering controls an d w ork p ractices which c an be i nstituted a re not s ufficient t o reduce e mployee exposure t o or be low the P ELs, the e mployer s hall us e t hem t o reduce employee exposure to the lowest levels achievable by these

controls a nd s hall s upplement t hem b y t he us e of r espiratory protection which complies with the requirements of paragraph (g) of this section.

- (f)(1)(iii) Where t he e mployer c an doc ument t hat be nzene i s us ed i n a workplace less than a total of 30 days per year, the employer shall use e ngineering c ontrols, w ork pr actice c ontrols o r r espiratory protection or a ny combination of t hese c ontrols t o r educe employee exposure to benzene to or below the PELs, except that employers s hall us e e ngineering a nd w ork pr actice c ontrols, i f feasible, t o reduce exposure t o or be low 1 0 p pm as an 8 -hour TWA.
- (f)(2) Compliance program.
  - (f)(2)(i) When any exposures are over the PEL, the employer shall establish and implement a written program to reduce employee exposure to or be low t he P EL pr imarily b y m eans of e ngineering a nd w ork practice controls, as required by paragraph (f)(1) of this section.
  - (f)(2)(ii) The written program shall include a schedule for development and implementation of t he engineering a nd work practice c ontrols. These plans shall be reviewed and revised as appropriate based on the m ost r ecent e xposure m onitoring da ta, t o r eflect t he c urrent status of the program.
  - (f)(2)(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.
  - (g)(1) General.

For employees who us e respirators required by this section, the employer must provide e ach employee an appropriate respirator t hat complies with the requirements of this paragraph. Respirators must be used during:

CWRU has a<br/>separate Respirator(g)(1)(i)Periods necessary to install or implement feasible engineering and<br/>work-practice controls.Program. PleaseProgram. Please

*call the EHS Office* (g)(1)(ii) Work operations f or which t he employer establishes t hat compliance with either the T WA or S TEL t hrough t he use of engineering a nd work-practice c ontrols is n ot f easible; f or example, some maintenance and repair activities, vessel cleaning,

or ot her ope rations f or w hich e ngineering a nd w ork-practice controls ar e i nfeasible because exposures a re intermittent a nd limited in duration.

- (g)(1)(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.
- (g)(1)(iv) Emergencies.
- (g)(2) Respirator program.
  - (g)(2)(i) The employer must implement a respiratory protection program in accordance w ith § 191 0.134(b) t hrough (d) (except (d)(1)(iii), (d)(3)(iii)(b)(1) and (2)), and (f) t hrough (m), which covers each employee required by this section to use a respirator.
  - (g)(2)(ii) For a ir-purifying r espirators, th e e mployer must r eplace th e a irpurifying element at the e xpiration of its s ervice life or at the beginning of e ach s hift i n w hich s uch e lements ar e u sed, whichever comes first.
  - (g)(2)(iii) If NIOSH ap proves an ai r-purifying e lement with a n e nd-ofservice-life i ndicator f or b enzene, s uch an el ement m ay b e u sed until the indicator shows no further useful life.
- (g)(3) Respirator selection.
  - (g)(3)(i) Employers must:
    - (g)(3)(i)(A) Select, and provide to employees, the appropriate respirators specified in paragraph (d)(3)(i)(A) of 29 CFR 1910.134.
    - (g)(3)(i)(B) Provide e mployees w ith a ny organic v apor gas mask or any self-contained breathing apparatus with a full facepiece to use for escape.
    - (g)(3)(i)(C) Use an o rganic v apor cartridge o r can ister w ith powered and non-powered air-purifying respirators, and a ch in-style canister w ith f ull f acepiece gas masks.

- (g)(3)(i)(D) Ensure t hat c anisters u sed with non -powered a irpurifying respirators have a minimum service life of four hour s w hen t ested at 150 ppm b enzene at a flow r ate o f 6 4 lite rs p er min ute (LPM), a temperature of 25 [deg]C, and a relative humidity of 85%; for c anisters us ed with tight-fitting or loose-fitting p owered a ir-purifying r espirators, t he f low rates for t esting m ust be 115 LPM and 170 LPM, respectively.
- (g)(3)(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 c ontact a nd limit d ermal e xposure to liq uid benzene. P rotective c lothing a nd equipment s hall be pr ovided b y t he e mployer a t no c ost t o t he e mployee a nd t he employer shall as sure its use where appropriate. Eye and face protection shall meet the requirements of 29 CFR 1910.133.

- (i) Medical surveillance -
  - (i)(1) General.
    - (i)(1)(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 be nzene for 30 or more days in a year prior to the effective d ate of t he s tandard when employed b y their current employer; a nd f or e mployees i nvolved in t he t ire building operations called tire building machine operators, who use solvents containing greater than 0.1 percent benzene.
    - (i)(1)(ii) The e mployer s hall a ssure that a ll me dical e xaminations a nd procedures are performed by or under the supervision of a licensed physician an dt hat al 11 aboratory tests a re conducted by an accredited laboratory.
    - (i)(1)(iii) The e mployer s hall a ssure t hat pe rsons ot her t han l icensed physicians who administer the pulmonary function testing required by th is s ection s hall complete a training c ourse in s pirometry

sponsored b y a n a ppropriate governmental, a cademic or professional institution.

- (i)(1)(iv) The employer shall assure that all examinations and procedures are provided without cost to the employee and at a reasonable time and place.
- (i)(2) Initial examination.
  - (i)(2)(i) Within 60 days of the effective date of this standard, or before the time o f in itial a ssignment, th e e mployer s hall p rovide e ach employee c overed b y p aragraph (i)(1)(i) of t his s ection w ith a medical examination including the following elements:
    - (i)(2)(i)(A) A detailed occupational history which includes:
      - (i)(2)(i)(A)(1) Past w ork e xposure t o be nzene or any other hematological toxins,
      - (i)(2)(i)(A)(2) A family history of blood dyscrasias including hematological neoplasms;
      - (i)(2)(i)(A)(3) A hi story of bl ood d yscrasias including g enetic he moglobin abnormalities, b leeding abnormalities, a bnormal f unction of formed blood elements;
      - (i)(2)(i)(A)(4) A hi story of r enal or l iver dysfunction;
      - (i)(2)(i)(A)(5) A hi story of m edicinal dr ugs routinely taken;
      - (i)(2)(i)(A)(6) A hi story o f pr evious exposure t o ionizing radiation and
      - (i)(2)(i)(A)(7) Exposure t o m arrow t oxins out side of the current work situation.
    - (i)(2)(i)(B) A complete physical examination.
    - (i)(2)(i)(C) Laboratory tests.

A complete blood count including a leukocyte count with differential, a quantitative thrombocyte count, hematocrit, he moglobin, e rythrocyte c ount a nd erythrocyte i ndices ( MCV, M CH, M CHC). T he results o f th ese te sts s hall be r eviewed b y t he examining physician.

- (i)(2)(i)(D) Additional tests as necessary in the opinion of the examining ph ysician, b ased on alterations t o t he components of the blood or other signs which may be related to benzene exposure; and
- (i)(2)(i)(E) For all workers r equired 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.
- (i)(2)(ii) No in itial me dical e xamination is r equired t os atisfy th e requirements of pa ragraph (i)(2)(i) of t his s ection i f a dequate 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.
- (i)(3) Periodic examinations.
  - (i)(3)(i) The e mployers hall pr ovide e ach e mployee c overed unde r paragraph (i)(1)(i) o f th is s ection w ith a me dical e xamination annually following t he pr evious e xamination. T hese pe riodic examinations shall include at least the following elements:
    - (i)(3)(i)(A) A br ief hi story regarding any ne w e xposure to potential marrow toxins, changes in medicinal drug use, and the appearance of physical signs relating to blood disorders:
    - (i)(3)(i)(B) A complete blood count including a leukocyte count with di fferential, qu antitative t hrombocyte c ount, hemoglobin, he matocrit, e rythrocyte c ount a nd erythrocyte indices (MCV, MCH, MCHC); and
    - (i)(3)(i)(C) Appropriate additional t ests a s ne cessary, i n t he opinion of the examining physician, in consequence of a lterations i n t he c omponents of t he bl ood or other s igns w hich m ay be r elated t o be nzene exposure.

- (i)(3)(ii) Where t he e mployee d evelops s igns and s ymptoms c ommonly associated w ith t oxic e xposure t o be nzene, t he e mployer s hall provide th e employee with a n a dditional me dical e xamination which shall include those elements considered a ppropriate by the examining physician.
- (i)(3)(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.

#### (i)(4) Emergency examinations.

- (i)(4)(i) In addition to the surveillance required by (i)(1)(i), if an employee is exposed t o be nzene i n a n e mergency s ituation, t he e mployer shall have the employee provide a urine sample at the end of the employee's shift and have a urinary phenol test performed on t he sample w ithin 72 hour s. T he ur ine s pecific gravity s hall b e corrected to 1.024.
- (i)(4)(ii) If the result of the urinary phenol test is below 75 mg phenol/L of urine, no further testing is required.
- (i)(4)(iii) If the result of the urinary phenol test is equal to or greater than 75 mg phe nol/L of ur ine, the employer shall pr ovide the employee with a c omplete bl ood c ount i ncluding a n e rythrocyte c ount, leukocyte c ount w ith di fferential a nd t hrombocyte c ount a t monthly intervals for a duration of three (3) months following the emergency exposure.
- (i)(4)(iv) If any of t he c onditions s pecified i n pa ragraph (i)(5)(i) of t his section exists, then the further requirements of paragraph (i)(5) of this s ection s hall b e me t a nd th e e mployer s hall, in a ddition, provide the employees with periodic examinations i f di rected b y the physician.
- (i)(5) Additional examinations and referrals.
  - (i)(5)(i) Where t he r esults of t he c omplete bl ood c ount r equired f or t he initial a nd p eriodic e xaminations in dicate a ny of th e f ollowing abnormal conditions exist, then the blood c ount shall be repeated within 2 weeks.

- (i)(5)(i)(A) The hemoglobin level or the hematocrit falls below the nor mal l imit [ outside t he 95% confidence interval (C.I.)] as determined by the laboratory for the particular geographic area an d/or these i ndices show a pe rsistent dow nward t rend f rom t he individual's pr e-exposure nor ms; pr ovided t hese findings c annot be e xplained b y ot her m edical reasons.
- (i)(5)(i)(B) The thrombocyte (platelet) c ount varies more than 20 percent below the employee's most recent values or fa lls o utside th e n ormal limit (95% C .I.) as determined by the laboratory.
- (i)(5)(i)(C) The leukocyte c ount is below 4,000 pe r m m 3 or there is an abnormal differential count.
- (i)(5)(ii) If the abnormality persists, the examining physician shall refer the employee to a hematologist or an internist for further evaluation unless t he physician h as g ood r eason t o be lieve s uch r eferral i s unnecessary. (See Appendix C for examples of conditions where a referral may be unnecessary.)
- (i)(5)(iii) The employer shall provide the hematologist or internist with the information r equired t o be pr ovided t o t he physician unde r paragraph (i)(6) of this section and the medical record required to be maintained by paragraph (k)(2)(ii) of this section.
- (i)(5)(iv) The he matologist's o r in ternist's e valuation s hall in clude a determination as to the need for additional tests, and the employer shall assure that these tests are provided.
- (i)(6) Information provided to the physician.

The employer shall provide the following information to the examining physician:

- (i)(6)(i) A copy of this regulation and its appendices;
- (i)(6)(ii) A description of the affected employee's duties as they relate to the employee's exposure;
- (i)(6)(iii) The employee's actual or representative exposure level:
- (i)(6)(iv) A description of any personal protective equipment used or to be used; and

- (i)(6)(v) Information f rom p revious e mployment-related m edical examinations o f t he af fected em ployee w hich is n ot o therwise available to the examining physician.
- (i)(7) Physician's written opinions.
  - (i)(7)(i) For each examination under this section, the employer shall obtain and provide the employee with a copy of the examining physician's written opi nion w ithin 15 days of the examination. The written opinion shall be limited to the following information:
    - (i)(7)(i)(A) The oc cupationally pertinent results of the medical examination and tests;
    - (i)(7)(i)(B) The ph ysician's opi nion c oncerning whether the employee h as an y detected m edical conditions which would place the employee's health at greater than n ormal risk o f material imp airment from exposure to benzene;
    - (i)(7)(i)(C) The physician's recommended limitations upon the employee's exposure t o be nzene o r upon t he employee's use of protective clothing or equipment and respirators.
    - (i)(7)(i)(D) A s tatement t hat t he employee h as b een i nformed by th e p hysician o f th e r esults o f th e me dical examination a nd a ny m edical c onditions r esulting from be nzene e xposure w hich r equire f urther explanation or treatment.
  - (i)(7)(ii) The w ritten opi nion obt ained by the employer shall not r eveal specific r ecords, findings and diagnoses that have no be aring on the employee's ability to work in a benzene-exposed workplace.
- (i)(8) Medical removal plan.
  - (i)(8)(i) When a p hysician makes a referral to a hematologist/internist as required unde r pa ragraph (i)(5)(ii) of t his s ection, t he e mployee shall b e r emoved f rom ar eas w here ex posures m ay exceed t he action level until such time as the physician makes a determination under paragraph (i)(8)(ii) of this section.

- (i)(8)(ii) Following th e e xamination a nd e valuation b v th e hematologist/internist, a d ecision to r emove a n e mployee f rom 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 s hall s tate t he r equired probable dur ation of r emoval from occupational exposure to benzene above the action level and the r equirements f or f uture me dical e xaminations to r eview th e decision.
- (i)(8)(iii) For any employee who is removed pursuant to paragraph (i)(8)(ii) of t his s ection, t he e mployer s hall pr ovide a follow-up examination. T he ph ysician, i n consultation w ith t he hematologist/internist, s hall make a d ecision w ithin 6 months of the d ate t he employee was removed as to whether the employee shall be returned to the usual job or whether the employee should be removed permanently.
- (i)(8)(iv) Whenever an employee is t emporarily r emoved f rom be nzene 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, s eniority and other benefits. If there is no s uch job available, the employer shall provide medical removal protection benefits until such a job becomes available or for 6 months, whichever comes first.
- (i)(8)(v) Whenever a n e mployee i s r emoved pe rmanently from be nzene exposure ba sed on a ph ysician's r ecommendation pur suant t o paragraph (i)(8)(iii) of this section, the employee shall be given the opportunity t o t ransfer t o a nother pos ition w hich i s a vailable 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 a ssure that such employee suffers no r eduction in current wage r ate, s eniority or ot her be nefits as a r esult of t he transfer.
- (i)(9) Medical removal protection benefits.

- (i)(9)(i) The employer shall provide to an employee 6 m onths of medical removal protection benefits immediately following each o ccasion an employee i s r emoved f rom e xposure t o be nzene b ecause o f hematological findings pursuant to paragraphs (i)(8)(i) and (ii) o f this s ection, u nless t he em ployee h as b een t ransferred t o a comparable j ob w here benzene e xposures a re below t he a ction level.
- (i)(9)(ii) For the purposes of this section, the requirement that an employer provide m edical r emoval pr otection be nefits m eans t hat t he employer shall maintain the current wage rate, seniority and other benefits o f an em ployee as t hough t he employee h ad n ot b een removed.
- (i)(9)(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 c ompensation for earnings lost during the period of r emoval e ither f rom a publicly or employer-funded compensation pr ogram, or f rom e mployment w ith a nother employer made possible by virtue of the employee's removal.
- (j) Communication of benzene hazards to employees -
  - (j)(1) Signs and labels.
    - (j)(1)(i) The employer shall post signs at entrances to regulated areas. The signs shall bear the following legend:

## DANGER BENZENE CANCER HAZARD FLAMMABLE - NO SMOKING AUTHORIZED PERSONNEL ONLY RESPIRATOR REQUIRED

(j)(1)(ii) The employer shall ensure that labels or other appropriate forms of warning a re p rovided for c ontainers o f benzene w ithin t he workplace. There is no requirement to label pipes. The labels shall comply w ith t he r equirements of 29 C FR 191 0.1200(f) a nd i n addition shall include the following legend:

## DANGER CONTAINS BENZENE CANCER HAZARD

- (j)(2) Material safety data sheets.
  - (j)(2)(i) Employers s hall obt ain or de velop, a nd s hall p rovide a ccess t o their em ployees, t o a m aterial s afety d ata s heet (MSDS) w hich addresses benzene and complies with 29 CFR 1910.1200.
  - (j)(2)(ii) Employers who are manufacturers or importers shall:
    - (j)(2)(ii)(A) Comply with paragraph (a) of this section, and
      (j)(2)(ii)(B) Comply with t he r equirement i n O SHA's H azard Communication S tandard, 29 C FR 1910.1200, t hat they d eliver t o dow nstream e mployers an M SDS which addresses benzene.
- (j)(3) Information and training.
  - (j)(3)(i) The e mployer s hall pr ovide e mployees w ith information a nd training at the time of their initial assignment to a work area where benzene i s p resent. If ex posures ar e ab ove the act ion l evel, employees shall be provided with information and training at least annually thereafter.
  - (j)(3)(ii) The training program shall be in accordance with the requirements of 29 C FR 1910.1200( h)(1) and (2), and s hall i nclude s pecific information on be nzene for each category of information included in that section.
  - (j)(3)(iii) In addition to the information required under 29 CFR 1910.1200, the employer shall:
    - (j)(3)(iii)(A) Provide e mployees w ith a n e xplanation of t he contents of t his s ection, i neluding A ppendices A and B, and indicate to them where the standard is available; and
    - (j)(3)(iii)(B) Describe the medical surveillance program required under paragraph (i) of this section, and explain the information contained in Appendix C.
- (k) Recordkeeping -
  - (k)(1) Exposure measurements.

- (k)(1)(i) The employer shall establish and maintain an accurate record of all measurements required b y paragraph (e) of t his s ection, i n accordance with 29 CFR 1910.1020.
- (k)(1)(ii) This record shall include:
  - (k)(1)(ii)(A) The dates, number, duration, and results of each of the s amples t aken, i ncluding a de scription of t he procedure u sed t o d etermine r epresentative employee exposures;
  - (k)(1)(ii)(B) A de scription of t he s ampling a nd a nalytical methods used;
  - (k)(1)(ii)(C) A description of the type of respiratory protective devices worn, if any; and
  - (k)(1)(ii)(D) The name, social security number, job classification and exposure levels of the employee monitored and all ot her e mployees w hose e xposure t he measurement is intended to represent.
- (k)(1)(iii) The employer shall maintain this record for at least 30 years, in accordance with 29 CFR 1910.1020.
- (k)(2) Medical surveillance.
  - (k)(2)(i) The employer shall establish and maintain an accurate record for each em ployee s ubject t o m edical s urveillance r equired b y paragraph (i) o ft his s ection, i n a ccordance w ith 29 C FR 1910.1020.
  - (k)(2)(ii) This record shall include:
    - (k)(2)(ii)(A) The na me a nd s ocial s ecurity num ber of the employee;
    - (k)(2)(ii)(B) The em ployer's co py of t he p hysician's w ritten opinion on t he i nitial, pe riodic a nd s pecial examinations, in cluding r esults o f me dical examinations a nd a ll t ests, opi nions a nd recommendations;
    - (k)(2)(ii)(C) Any e mployee me dical c omplaints r elated to exposure to benzene;

- (k)(2)(ii)(D) A copy of the information provided to the physician as re quired b y p aragraphs (i)(6)(ii) t hrough (v) of this section; and
- (k)(2)(ii)(E) A copy of the employee's medical and work history related t o e xposure t o be nzene or a ny ot her hematologic toxins.
- (k)(2)(iii) The employer shall maintain this record for at least the duration of employment plus 30 years, in accordance with 29 CFR 1910.1020.

(k)(3) Availability.

- (k)(3)(i) The e mployers hall assure t hat all r ecords r equired t o b e maintained by this section shall be made available upon request to the A ssistant S ecretary and t he D irector f or examination and copying.
- (k)(3)(ii) Employee exposure monitoring records required by this paragraph shall be provided upon r equest for examination and copying t o employees, employee r epresentatives, and the A ssistant S ecretary in a ccordance w ith 29 C FR 1910.1020 (a) t hrough (e) and (g) through (i).
- (k)(3)(iii) Employee m edical r ecords r equired b y t his p aragraph s hall b e provided upon request for examination and copying, to the subject employee, t o an yone having t he s pecific w ritten c onsent of t he subject em ployee, and t o t he A ssistant S ecretary in ac cordance with 29 CFR 1910.1020.
- (k)(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 -
  - (l)(1) Employee observation.

The e mployers hall provide a ffected employees, or t heir de signated representatives, a n opp ortunity t o obs erve t he m easuring or m onitoring of employee ex posure t o benzene co nducted pu rsuant t o pa ragraph (e) of t his section.

(l)(2) Observation procedures.

When obs ervation of t he m easuring or m onitoring of employee exposure t o benzene r equires e ntry i nto a reas w here t he use of pr otective c lothing 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.

[61 FR 5507, Feb. 13, 1996; 63 FR 1152, Jan. 8, 1998; 63 FR 20098, April 23,1998; 70 FR 1142, Jan. 5, 2005; 71 FR 16673, April 3, 2006; 71 FR 50189, August 24, 2006; 73 FR 75585, Dec. 12, 2008; 76 FR 33608, June 8, 2011]

OSHA Regulations (Standards - 29 CFR) Substance safety data sheet, Benzene - 1910.1028 App A Standard Number: 1910.1028 App A Standard Title: Substance safety data sheet, Benzene SubPart Number: Z SubPart Title: Toxic and Hazardous Substances

- 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 c ontact s hall be pr evented and s kin contact with l iquid be nzene s hall 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 a re ove rexposed t o hi gh c oncentrations of be nzene, w ell a bove t he l evels where its odor is first r ecognizable, you may feel br eathless, irritable, euphoric, or giddy; you may experience i rritation in e yes, n ose, and r espiratory 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 be nzene, e ven at relatively low concentrations, may r esult in v arious bl ood di sorders, r anging f rom a nemia t o l eukemia, a n irreversible, f atal di sease. M any blood di sorders a ssociated with b enzene e xposure may occur without symptoms.

- III. Protective Clothing and Equipment
  - A. Respirators.

*CWRU has a separate Respirator Program. Please call the EHS Office for information.* Respirators ar e r equired f or those ope rations i n w hich e ngineering c ontrols or w ork 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, r espirators may be used in lieu of engineering controls. If r espirators are w orn, they must have joint Mine S afety and Health A dministration and the N ational Institute for Occupational Safety and Health (NIOSH) seal of approval, and cartridge or canisters must be r eplaced 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 pos itive pr essure r espirator f rom your e mployer. Y ou m ust be t horoughly trained to use the assigned respirator, and the training will be provided by your employer.

B. Protective Clothing.

You m ust w ear appropriate pr otective clothing (such a s boot s, gloves, s leeves, 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 as sistance or a d octor as s oon 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 timeweighted 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 e mployer is r equired t o perform m easurements t hat a rer epresentative of your exposure to benzene and you or your designated representative are entitled to observe the monitoring procedure. Y ou are entitled to observe the steps taken in the measurement procedure, and to record the results obtained. When the monitoring procedure is taking place i n a n a rea w here respirators or p ersonal protective clothing and equipment a re required to be w orn, you or your representative m ust also be provided with, and m ust wear the protective clothing and equipment.

VII. Access to Records

You or your representative a re 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 us ed or s tored. Ask your s upervisor where benzene i s us ed i n your a rea and for additional plant safety rules.

OSHA Regulations (Standards - 29 CFR) Substance technical guidelines, Benzene - 1910.1028 App B Standard Number: 1910.1028 App B Standard Title: Substance technical guidelines, Benzene SubPart Number: Z SubPart Title: Toxic and Hazardous Substances

- I. Physical and Chemical Data
  - A. Substance identification.
    - 1. Synonyms:

Benzol, be nzole, c oal na phtha, c yclohexatriene, phe ne, phe nyl h ydride, pyrobenzol. (Benzin, petroleum benzin and Benzine do not contain benzene).

- 2. Formula: C(6)H(6) (CAS Registry Number: 71-43-2)
- B. Physical data.
  - 1. Boiling Point (760 mm Hg); 80.1 deg. C (176 deg. F)
  - 2. Specific Gravity (water = 1): 0.879
  - 3. Vapor Density (air = 1): 2.7
  - 4. Melting Point: 5.5 deg. C (42 deg. F)
  - 5. Vapor Pressure at 20 deg. C (68 deg. 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 deg. C (12 deg. F)
    - 2. Autoignition Temperature: 580 deg. C (1076 deg. 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 s catter and spread fire. Fine water s pray can be used to keep fire-exposed containers cool.
- 6. Unusual fire and explosion hazards: Benzene is a flammable liquid. Its vapors can f orm explosive mix tures. A ll ig nition s ources must be c ontrolled w hen 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 C FR 1910.106. A concentration exceeding 3,250 ppm is considered a pot ential fire explosion ha zard. Locations where be nzene may be present i n qua ntities s ufficient t o pr oduce explosive o r ig nitable mix tures a re 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 de composition pr oducts: Toxic g ases a nd va pors (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 s ewer, because of explosion d anger. R emove all ignition s ources. Ventilate enclosed places.
  - B. Waste disposal method.

Disposal m ethods m ust c onform t o ot her j urisdictional r egulations. If allowed, benzene may be disposed of: (a) By absorbing it in dry sand or earth and disposing in a sanitary l andfill; (b) if s mall q uantities, b y r emoving it to a s afe lo cation f rom buildings or other combustible sources, pouring it in dry sand or earth and cautiously

igniting it; a nd ( c) if large quantities, b y a tomizing it in a suitable c ombustion 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.

OSHA Regulations (Standards - 29 CFR) Medical surveillance guidelines for Benzene - 1910.1028 App C Standard Number: 1910.1028 App C Standard Title: Medical surveillance guidelines for Benzene SubPart Number: Z SubPart Title: Toxic and Hazardous Substances

#### I. Route of Entry

Inhalation; skin absorption.

#### II. Toxicology

Benzene is primarily an inhalation hazard. Systemic absorption may cause depression of the hematopoietic s ystem, pa ncytopenia, aplastic a nemia, a nd l eukemia. Inhalation of high concentrations c an a ffect c entral ne rvous s ystem f unction. A spiration of s mall amounts of l iquid benzene i mmediately c auses pulmonary e dema a nd he morrhage of pulmonary tissue. There is some absorption through the skin. A bsorption may be more rapid in the c ase of a braded skin, and be nzene may be more r eadily a bsorbed i f i t i s present i n a m ixture o r as a contaminant i n solvents which a re r eadily absorbed. The defatting action of benzene may produce primary irritation due to repeated or prolonged contact w ith the skin. H igh c oncentration a re irritating to the e yes a nd t he m ucous membranes of the nose, and respiratory tract.

#### III. Signs and Symptoms

Direct skin contact with b enzene may cause erythema. R epeated or p rolonged 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 t he e ve are slight. O nly at v ery high c oncentrations is t here a ny s marting sensation in the eye. Inhalation of high concentrations of benzene may have an initial stimulatory effect on t he central nervous system characterized by exhilaration, nervous excitation, and/or giddiness, followed by a period of depression, drowsiness, or fatigue. A sensation of t ightness i n t he c hest a ccompanied b y breathlessness m ay oc cur a nd ultimately the v ictim may lo se c onsciousness. T remors, c onvulsions and de ath m av follow from respiratory paralysis or circulatory collapse in a few minutes to several hours following s evere e xposures. The de trimental e ffect on t he bl ood-forming s ystem o f 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 a t concentrations of be nzene which m ay not cause i rritation of m ucous membranes, or any unpleasant sensory effects. Early signs and symptoms of be nzene morbidity are varied, often not readily noticed and non-specific. Subjective complaints of headache, di zziness, and loss of appetite may precede or follow clinical signs. Rapid pulse and low blood pressure, in addition to a physical appearance of a nemia, may

accompany a s ubjective c omplaint of s hortness of br eath a nd e xcessive t iredness. Bleeding from the nose, gums, or mucous membranes, and the development of purpuric spots (small b ruises) may oc cur a s t he c ondition pr ogresses. C linical e vidence of leukopenia, anemia, and thrombocytopenia, singly or in combination, has been frequently reported a mong t he f irst s igns. Bone m arrow m ay ap pear normal, a plastic, or hyperplastic, a nd m ay not, i n a ll s ituations, correlate w ith pe ripheral bl ood f orming tissues. B ecause of va riations i n t he s usceptibility t o benzene m orbidity, t here i s no "typical" bl ood pi cture. The ons et o f e ffects of pr olonged b enzene exposure m ay b e 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, w ash skin i f c ontaminated a nd r emove a ll c ontaminated c lothing. S ymptoms of intoxication may p ersist following s evere exposures. R ecovery 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, r eflected by changes in the peripheral blood and manifesting clinically as pancytopenia, aplastic a nemia, 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, es sential. Initial e xaminations a re t o be pr ovided w ithin 60 da ys o f t he effective d ate of t his s tandard, or at the time of in itial a ssignment, and p eriodic examinations annually thereafter. There are special provisions for medical tests in the event of he matologic a bnormalities or f or em ergency situations. The bl ood values which r equire r eferral t o a he matologist or internist a renot ed 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 c onditions that could make a r eferral 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 ar e n ecessary and when t o r efer an em ployee t o t he s pecialist, O SHA h as 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 cel l i ndices must be performed b y a n a ccredited l aboratory. T he 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 l aboratory in the specific a rea where the tests are performed. Either a de cline from an absolute normal or a n individual's base line to a subnormal value or a rise to a supranormal value, are in dicative of p otential to xicity, p articularly if a ll b lood parameters de cline. T he nor mal t otal white blood c ount i s a pproximately 7,200/mm(3) plus or minus 3,000. For cigarette smokers the white count may be higher a nd t he upp er range m ay b e 2,000 c ells higher t han nor mal for t he 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 t o 400,000. C ounts out side t his range should be regarded as possible evidence of benzene t oxicity. Certain abnormalities f ound t hrough r outine 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 a bnormal 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 a ny abnormalities in o ther c ell indices may b e a n ormal s tatistical 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 p hysician to f urther in vestigate and/or r efer the p atient if r epeat te sts confirm the abnormalities. If routine screening detects an abnormality, followup 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 t o 2.5 p ercent 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 di agnostic t est i s a c areful e xamination of the peripheral blood smear. A s 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 ne cessary, the s mear may, u nder c ertain limited conditions, be made from a blood sample anticoagulated with EDTA (but never with ox alate or heparin). When the smear is to be prepared from a specimen of venous blood which has be en collected by a commercial V acutainer type t ube 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 t he t otal d ifferential count), a ny n umber of m etamyelocytes, myelocytes or m yeloblasts. A ny nuc leate or multinucleated r ed b lood c ells 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, t he a ppearance of m etamyelocytes, in t he a bsence of another probable cause, is to be considered a possible indication of benzeneinduced 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 p ercent. 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/mm(3) should be regarded as a possible sign

of be nzene-induced toxicity. A less frequent but more serious indication of benzene t oxicity i s t he f inding i n t he pe ripheral blood of t he s o-called "pseudo" (or a cquired) P elger-Huet a nomaly. In t his a nomaly m any, o r 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 a bout two percent of patients who ultimately develop acute myelogenous leukemia show the acquired Pelger-Huet anomaly. Other tests that can be administered to in vestigate blood abnormalities a re di scussed be low; how ever, s uch 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 t est" of pe ripheral bl ood, i s t ransient pa roxysmal noc turnal 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 ap pearance of r apidly fatal acu te m yelogenous l eukemia. C linical 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 he matologic abnormality. In some instances p ancytopenia (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 a plasia or leukemia. The finding of two or more cytopenias, or pancytopenia in a be nzene-exposed individual, must be regarded as highly suspicious of m ore advanced a lthough s till r eversible, to xicity. "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 c ells m ust be r egarded as e vidence of be nzene ove rexposure unless pr oved ot herwise. Many s everely aplastic p atients m anifested t he ominous f inding of 5 -10 pe rcent m yeloblasts i n the m arrow, oc casional 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 b e r eversible an d complete r ecovery h as b een r eported o n cessation of exposure. However, since any of these abnormalities is serious, the employee must immediately be removed from any possible exposure to benzene va por. C ertain 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 a spiration or ne edle 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 c irculating or m arrow ne utrophil g ranulocytes, e mploying benzidine dihydrochloride, ha ver evealed t he di sappearance of , o r di minution i n, 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 s teady de cline i n l eukocyte a lkaline phos phatase ha s a lso be en reported as suggestive of early acute leukemia. Exposure to be nzene 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 s uppression of e rythropoiesis. Measurement of s erum i ron, determination of peroxidase and of alkaline phosphatase activity in peripheral granulocytes can be performed in most pathology laboratories. Peroxidase and alkaline p hosphatase s taining a re us ually und ertaken w hen t he i ndex of suspicion for leukemia is high.

OSHA Regulations (Standards - 29 CFR) Sampling and analytical methods for Benzene monitoring and measurement procedures - 1910.1028 App D Standard Number: 1910.1028 App D Standard Title: Sampling and analytical methods for Benzene monitoring and measurement procedures SubPart Number: Z SubPart Title: Toxic and Hazardous Substances

Measurements t aken f or t he pur pose of d etermining e mployee e xposure to b enzene ar e b est taken so that the representative average 8-hour exposure may be determined from a single 8-hour sample or t wo (2) 4-hour samples. S hort-time in terval samples (or grab samples) may also be used t o d etermine average ex posure l evel if a minimum of five measurements are taken in a random m anner over t he 8-hour w ork s hift. R andom s ampling m eans t hat a ny por tion of t he work shift has the same change of being sampled as any other. The arithmetic average of all such random s amples t aken on one w ork s hift is an e stimate of a n employee's a verage l evel 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 be nzene. The sampling a nd a nalysis may be p erformed b y collection of t he be nzene va por or c harcoal absorption t ubes, with subsequent c hemical a nalysis b y gas c hromatography. S ampling a nd analysis m ay al so b e p erformed b y portable d irect r eading i nstruments, r eal-time c ontinuous monitoring s ystems, pa ssive dos imeters or ot her s uitable m ethods. T he e mployer ha s t he obligation of s electing a m onitoring m ethod w hich m eets t he a ccuracy and pr ecision requirements of the standard under his unique field c onditions. 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 be nzene greater than or equal to 0.5 ppm . The OSHA Laboratory m odified N IOSH M ethod S 311 a nd e valuated it a t a be nzene a ir 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: B enzene M atrix: A ir P rocedure: A dsorption on c harcoal, de sorption w ith c arbon 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 know n vol ume of a ir is dr awn through a c harcoal t ube t o t rap t he or ganic 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 m ost of those w hich do oc cur can be e liminated b y altering chromatographic c onditions. T he samples ar e an alyzed b y m eans o f a q uick, 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 (+ or -) 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., c ontaining 2 s ections o f 20/40 m esh a ctivated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from c oconut shells and is fired at 600 deg. 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 be tween the out let 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 X 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-uL syringe, and other convenient sizes for making standards, 1-uL 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 t race of benzene which must be removed. It can be removed with the following procedure:

Heat und er reflux f or 2 t o 3 hour s, 500 m L of c arbon di sulfide, 1 0 m L concentrated sulfuric acid, and 5 drops of concentrated nitric acid. The benzene is converted t o ni trobenzene. T he c arbon disulfide l ayer i s removed, dr ied w ith 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 m L of pcymene p er milliliter o f c arbon d isulfide. (The in ternal s tandard offers a convenient means correcting an alytical response for slight inconsistencies in the size o f s ample in jections. If t he ex ternal s tandard technique i s pr eferred, t he 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 pe rsonal pum ps. E ach pum p m ust be c alibrated with a representative charcoal tube in the line.
  - 5.3. Collection and shipping of samples.
    - 5.3.1. Immediately before s ampling, break the ends of the tube to provide a n 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 r ecommended. Sample at a flow r ate of approximately 0.2 liters per minute. The flow rate should be known with an accuracy of at least (+ or -) 5 percent.
- 5.3.6. The c harcoal t ubes s hould be c apped with t he s upplied pl astic caps immediately after sampling.
- 5.3.7. Submit at l east one bl ank t ube (a charcoal t ube s ubjected t o t he s ame 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 t ransferred t o a 2 -ml v ial. The s eparating section of f oam 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 m L of desorbing solution is pipetted i nto each sample c ontainer. The de sorbing s olution c onsists of 0.05 uL 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 c onditions. T ypical ope rating c onditions f or t he g as c hromatograph 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 deg. C injector temperature.

5.250 deg. C detector temperature.

- 6.100 deg. C column temperature.
- 5.4.4. Injection size. 1 uL.
- 5.4.5. Measurement o f area. T he p eak ar eas a re m easured b y an el ectronic integrator or some other suitable form of area measurement.
- 5.4.6. An i nternal s tandard pr ocedure i s us ed. T he i ntegrator i s c alibrated t o report r esults i n ppm for a 1 0 l iter ai r s ample af ter co rrection f or desorption efficiency.
- 5.5. Determination of desorption efficiency.
  - 5.5.1. Importance o f d etermination. T he de sorption e fficiency o f a p articular compound c an vary from one l aboratory t o another and from one l ot of chemical to another. Thus, it is necessary to determine, at least once, the percentage of t he s pecific c ompound t hat i s r emoved in t he desorption process, provided the same batch of charcoal is used.
  - 5.5.2. Procedure for determining desorption efficiency. The reference portion of the ch arcoal t ube is r emoved. T ot he remaining portion, a mounts 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 (ug/mL) versus peak area.
- 7. Calculations. Benzene air concentration can be calculated from the following equation:

mg/m(3) = (A)(B)/(C)(D)

Where: A = ug/mL benzene, obtained from the calibration curve

B = desorption volume (1 mL)

C = Liters of air sampled

D = desorption efficiency

The concentration in mg/m(3) can be converted to ppm (at 25 de g. and 760 mm) with following equation:

ppm = (mg/m(3))(24.46)/(78.11)

Where: 24.46 = molar volume of an ideal gas 25 deg. 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 n g 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 uL injections of a 1.283 ug/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 t he analytical p rocedure w as d etermined b y 1 u L r eplicate i njections o f analytical standards. The standards were 16.04, 32.08, a nd 64.16 ug /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
CV = 0.008.

8.3. Storage data - Air Samples

Samples were generated at 1.03 ppm benzene at 80% relative humidity, 22 deg. C, and 643 mm. All samples were taken for 50 minutes at 0.2 L/min. Six samples were an alyzed i mmediately and the r est of the samples were divided i nto t wo groups by fifteen samples each. One group was stored at refrigerated temperature of 25 de g. C , and t he ot her group w as s tored a t a mbient temperature (approximately 23 deg. 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
2
5
9
13
15
· · ·

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, a nd 2.0 ppm for a 10 L air sample.

#### PERCENT RECOVERY

|||| Sample | 0.5 | 1.0 | 2.0| ppm | ppm | ppm||||1 .....| 99.4 | 98.8 | 99.52 .....| 99.5 | 98.7 | 99.73 .....| 99.2 | 98.6 | 99.84 .....| 99.4 | 99.1 | 100.05 .....| 99.2 | 99.0 | 99.76 .....| 99.8 | 99.1 | 99.9X = ....| 99.4 | 98.9 | 99.8SD = ....| 0.22 | 0.21 | 0.18CV = ....| 0.0022 | 0.0021 | 0.0018X = 99.4 |||

8.5. Carbon disulfide.

Carbon di sulfide f rom a num ber of s ources w as a nalyzed f or benzene contamination. T he r esults are given i n t he following t able. The b enzene contaminant can be removed with the procedures given in section 4.1.

|| |ug|ppm |Benzene/mL|equivalent Sample || (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 CS2 |......

## 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 a liquot of t he bul k s ample t o b e analyzed i s i njected i nto a l iquid chromatograph.
  - 1.2. The peak area for benzene is determined and compared to a reas 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 C olumn that will s eparate be nzene f rom ot her c omponents i n the bul k sample b eing analyzed. The co lumn u sed f or v alidation s tudies w as a Waters uBondapack C18, 30 cm x 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 s yringes 10 u L s yringe a nd ot her c onvenient s izes f or m aking standards. 10 uL syringe for sample injections.
  - 3.7. Volumetric flasks, 5 m L 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 n ecessary, the s amples a red istilled or clarified. S amples ar e a nalyzed undiluted. If t he benzene c oncentration i s out of t he w orking r ange, s uitable dilutions are made with isopropyl alcohol.

6.2. HPLC conditions.

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

6.2.1. Mobile phase - Methyl alcohol/water, 50/50

- 6.2.2. Analytical wavelength 254 nm
- 6.2.3. Injection size 10 uL
- 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 r eport r esults in % b enzene b y vol ume in an undiluted sample, the following equation is used:

% 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 ug, with a coefficient of variation of 0.019 a tt his l evel. T his a mount pr ovided a chromatographic peak that could be identifiable i n t he pr esence of pos sible interferences. The detection limit date were obtained by making 10 uL injections of a 0.10% by volume standard.

Injection   Area Count
· · · · · · · · · · · · · · · · · · ·
1   45386
2   44214
$3 \dots 43822 \mid X = 44040.1$
4
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 uL r eplicate injections of a nalytical s tandards. The s tandards w ere 0.0 1, 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   8473'	7   166097   4	148497	4395380	9339150		
2 44241 84300	0   170832   4	441299	4590800	9484900		
3 43822 83833	5   164160   4	443719	4593200	9557580		
4   44062   8438	164445   4	444842	4642350	9677060		
5 44006 83012	2   168398   4	442564	4646430	9766240		
6   42724   8195'	7   173002   4	443975	4646260			
X =   44040.1   83	703.6   1678	372   444	149   4585	767   956498	36	
SD =   852.5   104	2.2   3589.8	2459.1	96839.3	166233		
CV =  0.0194   0.0	0125   0.0213	3   0.005	5   0.0211	0.0174		
CV =  0.017	-					