

APPENDIX D TO SUBPART C TO PART
197—SAMPLING AND ANALYTICAL
METHODS FOR BENZENE MONI-
TORING—MEASUREMENT PROCE-
DURES

Measurements taken for the purpose of determining employee exposure to benzene are best taken so that the representative average eight-hour exposure may be determined from a single eight-hour sample or two four-hour samples. Short-time interval samples (or grab samples) may also be used to determine average exposure level if a minimum of five measurements are taken in a random manner over the eight-hour work shift. In random sampling, any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all random samples taken on one work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (*i.e.*, air that would most nearly represent that inhaled by the employee). Sampling and analysis must be performed with procedures meeting the requirements of 46 CFR part 197, subpart C.

There are a number of methods available for monitoring employee exposures to benzene. The sampling and analysis may be performed by collection of the benzene vapor on charcoal adsorption tubes, with subsequent chemical analysis by gas chromatography. Sampling and analysis also may be performed by portable direct reading instruments, real-time continuous monitoring systems, passive dosimeters, or other suitable methods. The employer is required to select a monitoring method which meets the accuracy and precision requirements of 46 CFR 197.540(a)(6) for the weather conditions expected. Section 197.540(a)(6) requires that monitoring must have an accuracy, to a 95 percent confidence level, of not less than plus or minus 25 percent for concentrations of benzene greater than or equal to 0.5 ppm.

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

1. OSHA Method 12 for Air Samples

Analyte: Benzene.

Matrix: Air.

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

Detection limit: 0.04 ppm.

Recommended air volume and sampling rate: 10 liter at 0.2 liter/min.

1. Principle of the method

1.1. A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2. The charcoal in the tube is transferred to a small, stoppered vial and the analyte is desorbed with carbon disulfide.

1.3. An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4. The area of the resulting peak is determined and compared with areas obtained from standards.

2. Advantages and disadvantages of the method

2.1. The sampling device is small, portable, and involves no liquids. Interferences are minimal and most of those which do occur can be eliminated by altering chromatographic conditions. The samples are analyzed by means of a quick, instrumental method.

2.2. The amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25 percent of that found on the front section, the possibility of sample loss exists.

3. Apparatus

3.1. A calibrated personal sampling pump having a flow that can be determined within \pm five percent at the recommended flow rate.

3.2. Charcoal tubes: Glass with both ends flame sealed, seven cm long with a six mm O.D. and a four mm I.D., containing two sections of 20/40 mesh activated charcoal separated by a two mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 °C before packing. The adsorbing section contains 100 mg of charcoal and the back-up section 50 mg. A three mm portion of urethane foam is placed between the outlet end of the tube and the back-up section. A plug of silanized glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of one 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 and 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: ten microliter (ten μ l) syringe, and other convenient sizes for making standards. One μ l syringe for sample injections.

3.8. Pipets: 1.0 ml delivery pipets.

3.9. Volumetric flasks: convenient sizes for making standard solutions.

4. Reagents

4.1. Chromatographic quality carbon disulfide (CS₂). Most commercially available carbon disulfide contains a trace of benzene which must be removed. It can be removed with the following procedure. Heat, under reflux for two to three hours, 500 ml of carbon disulfide, ten ml concentrated sulfuric acid, and five drops of concentrated nitric acid. The benzene is converted to nitrobenzene. The carbon disulfide layer is removed, dried with anhydrous sodium sulfate, and distilled. The recovered carbon disulfide should be benzene free. (It has recently been determined that benzene can also be removed by passing the carbon disulfide through a 13x molecular sieve).

4.2. Benzene, reagent grade.

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

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

4.5. Purified GC grade helium, hydrogen, and air.

5. Procedure

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

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

5.3. Collection and shipping of samples.

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

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

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

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

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

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

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

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

5.4. Analysis of samples.

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

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

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

1. 30 ml/min (60 psig) helium carrier gas flow.

2. 30 ml/min (40 psig) hydrogen gas flow to detector.

3. 240 ml/min (40 psig) air flow to detector.

4. 150 °C injector temperature.

5. 250 °C detector temperature.

6. 100 °C column temperature.

5.4.4. Injection size. One µl.

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

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

5.5. Determination of desorption efficiency.

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

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

6. Calibration and standards

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

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	

7. Calculations

Benzene air concentration can be calculated from the following equation:

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

Where:

A=µg/ml benzene, obtained from the calibration curve; B=desorption volume (one ml); C=liters of air sampled; and D=desorption efficiency.

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

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

Where:

24.46=molar volume of an ideal gas 25 °C and 760 mm; and 78.11=molecular weight of benzene.

8. Backup data

8.1 Detection limit—Air Samples. The detection limit for the analytical procedure is 1.28 ng with a coefficient of variation of 0.023 at this level. This would be equivalent to an air concentration of 0.04 ppm for a 10 liter 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 one µl injections of a 1.283 µg/ml standard.

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

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

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.			

PERCENT RECOVERY

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

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

PERCENT RECOVERY

Sample	0.5 ppm	1.0 ppm	2.0 ppm
1	99.4	98.8	99.5
2	99.5	98.7	99.7
3	99.2	98.6	99.8
4	99.4	99.1	100.0
5	99.2	99.0	99.7
6	99.8	99.1	99.9

PERCENT RECOVERY—Continued

Sample	0.5 ppm	1.0 ppm	2.0 ppm
X=	99.4	98.9	99.8
SD=	0.22	0.21	0.18
C V=	0.0022	0.0021	0.0018
X=99.4.			

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

Sample	µg Benzene/ml	ppm equivalent (for 10 liter air sample)
ALDRICH Lot 83017	4.20	0.13
BAKER Lot 720364 ...	1.01	0.03
BAKER Lot 822351 ...	1.01	0.03
Malinkrodt Lot WEMP	1.74	0.05
Malinkrodt Lot WDSJ	5.65	0.18
Malinkrodt Lot WHGA	2.90	0.09
Treated CS ₂		

II. OSHA Laboratory Method No. 12 for Bulk Samples

Analyte: Benzene.

Matrix: Bulk Samples.

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

Detection limits: 0.01% by volume.

1. Principle of the method

1.1. An aliquot of the bulk sample to be analyzed is injected into a liquid chromatograph.

1.2. The peak area for benzene is determined and compared to areas obtained from standards.

2. Advantages and disadvantages of the method

2.1. The analytical procedure is quick, sensitive, and reproducible.

2.2. Reanalysis of samples is possible.

2.3. Interferences can be circumvented by proper selection of HPLC parameters.

2.4. Samples must be free of any particulates that may clog the capillary tubing in the liquid chromatograph. This may require distilling the sample or clarifying with a clarification kit.

3. Apparatus

3.1. Liquid chromatograph equipped with a UV detector.

3.2. HPLC Column that will separate benzene from other components in the bulk sample being analyzed. The column used for validation studies was a Waters uBondapak C18, 30 cm×3.9 mm.

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

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

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

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

3.7. Volumetric flasks, five ml and other convenient sizes for preparing standards and making dilutions.

4. Reagents

4.1. Benzene, reagent grade.

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

5. Collection and shipment of samples

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

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

6. Analysis of samples

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

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

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

6.2.2. Analytical wavelength—254 nm.

6.2.3. Injection size—10 µl.

6.3. Measurement of peak area and calibration. Peak areas are measured by an integrator or other suitable means. The integrator is calibrated to report results in % benzene by volume.

7. Calculations

Because the integrator is programmed to report results in % benzene by volume in an undiluted sample, the following equation is used: % Benzene by Volume=A×B.

Where: A=% by volume on report.
B=Dilution Factor. (B=one for undiluted sample).

8. Backup data

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

Injection	Area Count
1	45386
2	44214

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

8.2. Pooled coefficient of variation—Bulk Samples. The pooled coefficient of variation for the analytical procedure was determined by 50 µl replicate injections of analytical standards. The standards were 0.01, 0.02, 0.04, 0.10, 1.0, and 2.0% benzene by volume.

AREA COUNT (PERCENT)

Injection #	0.01	0.02	0.04	0.10	1.0	2.0
1	45386	84737	166097	448497	4395380	9339150
2	44241	84300	170832	441299	4590800	9484900
3	43822	83835	164160	443719	4593200	9557580
4	44062	84381	164445	444842	4642350	9677060
5	44006	83012	168398	442564	4646430	9766240
6	42724	81957	173002	443975	4646260	
X=	44040.1	83703.6	167872	444149	4585767	9564986
SD=	852.5	1042.2	3589.8	2459.1	96839.3	166233
CV=	0.0194	0.0125	0.0213	0.0055	0.0211	0.0174
CV=0.017.						

APPENDIX E TO SUBPART C TO PART 197—RESPIRATOR FIT TESTS

PROCEDURES

This appendix contains the procedures for properly fitting a respirator to employees who may be exposed to benzene and includes the Initial Fit Tests (IFT), the Qualitative Fit Tests (QLFT), and the Quantitative Fit Test (QNFT).

Note that respirators (negative pressure or positive pressure) must not be worn when conditions prevent a tight seal between the faceplate and the skin or the proper functioning of the inhalation or exhalation valves. In order for a respirator to protect the wearer, the facepiece must make a proper seal against the wearer's face. Several factors can negatively affect the respirator to face seal and reduce the level of protection afforded by the respirator. Among these are facial shape, temple pieces of eyeglasses, facial abnormalities (e.g., scars and indentations) absence of dentures, hair style or length of hair, specific skin conditions, and facial hair. Therefore, nothing can come between or otherwise interfere with the sealing surface of the respirator and the face or interfere with the function of the inhalation or exhalation valves.

I. Initial Fit Tests (IFT)

(a) The test subject must be allowed to select the most comfortable respirator from a selection of respirators of various sizes. The selection must include at least three sizes of elastomeric facepieces for the type of respirator that is to be tested (i.e., three sizes of half mask or three sizes of full facepiece).

(b) Before the selection process, the test subject must be shown how to put on a respirator, how it should be positioned on the face, how to set strap tension, and how to determine a comfortable fit. A mirror must be

available to assist the subject in evaluating the fit and positioning the respirator. This instruction is only a preliminary review and must not constitute the subject's formal training on respirator use.

(c) The test subject must be informed that he or she is being asked to select the respirator which provides the most comfortable fit. Each respirator represents a different size and shape and, if fitted and used properly, should provide adequate protection.

(d) The test subject must be instructed to hold each facepiece up to the face and eliminate those facepieces which obviously do not give a comfortable fit.

(e) The more comfortable facepieces must be noted and the most comfortable mask donned and worn at least five minutes to assess comfort. Assistance in assessing comfort may be given by discussing the points in section I(f) of this appendix. If the test subject is not familiar with using a particular respirator, the test subject must be directed to don the mask several times and to adjust the straps each time to become adept at setting proper tension on the straps.

(f) Assessment of comfort must include reviewing the following points with the test subject and allowing the test subject adequate time to determine the comfort of the respirator:

- (1) Position of the mask on the nose.
- (2) Room for eye protection.
- (3) Room to talk.
- (4) Position of mask on face and cheeks.

(g) The following criteria must be used to help determine the adequacy of the respirator fit:

- (1) Chin properly placed.
- (2) Adequate strap tension, not overly tightened.
- (3) Fit across nose bridge.
- (4) Respirator of proper size to span distance from nose to chin.
- (5) Tendency of respirator to slip.