

## VI. REFERENCES

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VII. APPENDIX I  
METHOD FOR  
SAMPLING AND ANALYTICAL PROCEDURES  
FOR DETERMINATION OF BENZENE

The following sampling and analytical method for analysis of benzene in air employs adsorption on charcoal, followed by desorption, and gas chromatographic measurement. This is a modified method derived from White et al [136] and Kupel and White. [137] Additional data are contained in Part IV under Sorbability of Benzene on Charcoal and Accuracy and Precision Data.

Atmospheric Sampling

(a) Equipment Used

The sampling train is composed of a charcoal tube, a vacuum pump, and a flowmeter. A personal sampler pump or a dependable hand pump, eg, a detector tube pump may be calibrated to produce the desired volume of air.

(b) Calibration of Sampling Instruments

Air sampling instruments may be calibrated with a wet test meter or other suitable reference over a normal range of flowrates and pressure drops. The calibration is conducted at least annually and at any time following repairs or modifications to the sampling system. Similarly, wet test meters should be calibrated upon procurement, at least annually, and after each repair. Calibration curves shall be established for each sampling pump and shall be used in adjusting the pumps prior to field use. The volumetric flowrate through the sampling system shall be spot checked

and the proper adjustments made before and during each study to assure obtaining accurate airflow data.

(1) Flowmeter Calibration Test Method

(A) With the wet test meter in a level position, check to ascertain that the water level just touches the calibration point on the meter. If the water level is low, add water 1 to 2 F warmer than room temperature to the fill point and run the meter for 30 minutes before calibration.

(B) Check the voltage of the pump battery with a voltmeter to assure adequate voltage for calibration. Charge the pump battery if needed.

(C) Break the tips of a charcoal tube to produce openings of a least 2 mm in diameter.

(D) Assemble the calibration train in series, with the test meter, then the charcoal tube, and finally the pump.

(E) Turn the pump on, adjusting the rotameter float to a selected reading on the rotameter scale. Wait until the float indicates a steady reading.

(F) The pointer on the meter should turn clockwise and indicate a pressure drop of not more than 1.0 inch of water. Operate the system for 10 minutes before starting the calibration. If the pressure is greater, recheck the system.

(G) Data for the calibration include the serial number; meter reading, start and finish; starting time, finish time, and elapsed time; air temperature; barometric pressure; serial number of the

pump and rotameter; the name of the person performing the calibration; and the date.

(H) Adjust the rotameter float to at least 3 other readings and record the pertinent data in step G at each reading.

(I) Correct the readings to standard conditions of pressure and temperature by means of the gas law equation.

(J) Use graph paper to plot the actual airflow and the rotameter readings. Determine the rotameter reading which will result in a 1 liter/minute flowrate for the pump being calibrated.

(c) Sampling Procedure

The equipment should be set up in a proper locale. The tips of the charcoal tube are broken off producing openings of at least 2 mm in diameter; the filled end of the tube is inserted toward the pump. The tube should always be in a vertical position during sampling. The pump is started and a 10-liter sample is taken at a flowrate of 1 liter/minute. Slower flowrates may be used to lengthen the sampling period but the 1 liter/minute rate should not be exceeded. After the sample is taken, each end of the tube should be capped (plastic caps are provided with commercial tubes). The samples will remain stable for at least 2 weeks which permits shipment for analysis; however, samples should be analyzed as soon as possible in keeping with good laboratory practices.

Analytical

(a) Principle of the Method

A known volume of air is drawn through a charcoal tube to trap the organic vapors present. The charcoal in the tube is transferred to a small

test tube and desorbed with carbon disulfide and an aliquot of the desorbed sample is injected into a gas chromatograph. The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

(b) Range and Sensitivity

The lower limit for benzene with instrument attenuation and splitter techniques is 0.01 mg for each sample. This value can be lowered by reducing the attenuation or by eliminating the splitter. The upper limit value for benzene is 6.0 mg/sample. This value is the number of milligrams of benzene which the front section will collect before a significant amount passes to the backup section. The charcoal tube consists of 2 sections of activated charcoal separated by a section of urethane foam [see description in (f)(2)]. If a particular atmosphere is suspected of containing a large amount of contaminant, it is recommended that a smaller than normal sampling volume be taken.

(c) Interferences

(1) When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Only water present as a mist is a problem, not water vapor.

(2) Any compound with the same retention time in the gas chromatograph as benzene at the operating conditions described in this method could be considered an interference. This type of interference can be overcome by changing the operating conditions of the instrument.

(d) Accuracy and Precision

The accuracy and precision determined by a representative laboratory test with benzene (see also Accuracy and Precision Data in Part IV) was found to be:

	<u>Accuracy</u>	<u>Precision</u>
Motor driven laboratory pump	7.6%	4.2%
Approved coal mine personal sampling pump (calibrated with no in-line resistance)	13.6%	10.1%
Approved coal mine personal sampling pump (calibrated with charcoal tube in line)	8.8%	11.6%

The accuracy includes single-day systematic error by 1 operator. Precision represents the single-day accuracy on several different tubes and includes tube-to-tube deviation under controlled laboratory conditions. [138]

(e) Advantages and Disadvantages of the Method

The sampling device is small, portable, and involves no liquids: one basic method is provided for determining many different organic solvents. Interferences are minimal and most can be eliminated by altering chromatographic conditions. In addition, the analysis is accomplished using a rapid instrumental method.

One disadvantage of the method is that the amount of sample which can be obtained is limited by the amount of benzene which the tube will hold before overloading as indicated by benzene recovery at the outlet end of the tube. Also, the precision is limited by the reproducibility of the pressure drop across the tubes, which affects the flowrate, thus causing the volume to be imprecisely measured.

(f) Apparatus consists of:

(1) An approved coal mine dust personal sampling pump or any vacuum pump whose flow can accurately be determined at 1 liter/minute or less for an area sample.

(2) Charcoal tubes: Glass tubes with both ends flame-sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The absorbing section contains 100 mg of charcoal, the backup section, 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flowrate of 1 liter/minute. Tubes with the above specifications are commercially available.

(3) Gas chromatograph equipped with a flame ionization detector.

(4) Column (20 ft x 1/8 in) with 10% FFAP stationary phase on 80/100 mesh acid washed DMCS Chromosorb W solid support.

(5) A mechanical or electronic integrator or a recorder and some method for determining peak area.

(6) Small glass-stoppered test tubes or equivalent tubes.



(7) Syringes: 10  $\mu$ liter syringe, and other convenient sizes for preparation of standards.

(g) Reagents

- (1) Spectroquality carbon disulfide
- (2) Benzene, preferably chromatquality grade.
- (3) Bureau of Mines Grade A helium.
- (4) Prepurified hydrogen.
- (5) Filtered compressed air.

(h) Procedure

(1) Cleaning of Equipment

All equipment used for the laboratory analysis should be washed in detergent followed by tap and distilled water rinses.

(2) Collection and Shipping of Samples

Both ends of the charcoal tube are broken to provide openings of at least 2 mm (one-half the I.D. of the tube). The smaller section of charcoal in the tube is used as a backup section and is, therefore, placed nearest the sampling pump. Tubing may be used to connect the back of the tube to the pump, but no tubing must ever be placed on the front of the charcoal tube. Because of the high resistance of the charcoal tube, the sampling method places a heavy load on the personal sampling pump; therefore, it should not be assumed that the pump will run a full 8 hours without a recharging of the battery.

One or more charcoal tubes serving as blanks are treated in the same manner as the sample tubes (break, seal, ship) except that no air is drawn through them.

If bulk samples are submitted in addition to charcoal tubes, they are to be shipped in a separate container.

(3) Analysis of Samples

(A) Preparation

Each charcoal tube is scored with a file and broken open in front of the first section of charcoal. The glass wool is removed and discarded, the charcoal in the first (larger) section is transferred to a small stoppered test tube, the foam separating section is removed and discarded, and the second section is transferred to another test tube. The two charcoal sections are then analyzed separately.

(B) Desorption

Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each test tube to desorb the benzene from the charcoal. Desorption is complete in 30 minutes if the sample is stirred occasionally.

EXTREME CAUTION MUST BE EXERCISED AT ALL TIMES WHEN USING CARBON DISULFIDE BECAUSE OF ITS HIGH TOXICITY AND FIRE AND EXPLOSION HAZARDS. IT CAN BE IGNITED BY HOT STEAM PIPES. ALL WORK WITH CARBON DISULFIDE MUST BE PERFORMED UNDER AN EXHAUST HOOD.

(C) Gas chromatographic conditions

Typical operating conditions for a gas chromatograph are:

- (i) 85 cc/min (70 psig) helium carrier gas flow.
- (ii) 65 cc/min (24 psig) hydrogen gas flow to detector.
- (iii) 500 cc/min (50 psig) airflow to detector.
- (iv) 200 C injector temperature.
- (v) 200 C manifold temperature (detector).

- (vi) 90 C oven temperature isothermal.
- (vii) Use either dual column differential operation or uncompensated mode.

(D) Injection

To eliminate difficulties arising from blowback or distillation within the syringe needle, the solvent flush injection technique is employed to inject the sample into the gas chromatograph. The 10- $\mu$ l syringe is first flushed with solvent several times to wet the barrel and plunger, then 3  $\mu$ l of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. Next, the needle is removed from the solvent and the plunger is pulled back about 0.2  $\mu$ l to separate the solvent flush from the sample with an air pocket to be used as a marker. The needle is then immersed in the sample and a 5- $\mu$ l aliquot is withdrawn. Prior to injection in the gas chromatograph, the plunger is pulled back a short distance to minimize sample evaporation from the needle tip. Duplicate injections should be made of each sample and the standard. No more than a 3% difference should result in the peak areas that are recorded.

(E) Measurement of area

The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement and preliminary sample results are read from a standard curve prepared as outlined below.

(i) Standards Preparation and Desorption Efficiency

(1) Preparation of Standards

It is convenient to prepare standards in terms of mg/ 0.5 ml of carbon disulfide because this is the quantity used for benzene desorption from the charcoal. To prepare a 0.3 mg/ 0.5 ml standard, 6.0 mg of benzene (converted to microliters for easy measurement) is injected into exactly 10 ml of carbon disulfide in a glass-stoppered flask. The excess quantity of benzene is used to minimize error due to carbon disulfide volatility. A series of standards is then prepared, varying in concentration over the desired range, and analyzed under the same gas chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration vs average peak area.

(2) Determination of Desorption Efficiency

The desorption efficiency, ie, the percentage of benzene desorbed from the charcoal, is determined only once, provided the same batch of charcoal is always used.

Activated charcoal, equivalent to the amount in the first section of the sampling tube (100 mg), is measured into a 2-in, 4-mm I.D. glass tube, flame-sealed at one end, and capped with a paraffin film or equivalent at the open end. A known volume of benzene, usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard, is injected directly into the activated charcoal with a microliter syringe and the tube again capped with more paraffin film. A minimum of 5 tubes are prepared in this manner and allowed to stand for at least 1 day to assure complete adsorption of the benzene onto the charcoal.

These tubes are desorbed and analyzed in exactly the same manner as the sampling tubes.

The results of each analysis are compared to the standards to determine the average percentage (desorption efficiency) that is desorbed. The desorption efficiency is then used as a factor in all sample analyses. The desorption efficiency, determined in this manner, has been shown to be essentially the same as that obtained by analysis of a known amount of benzene vapor trapped on the charcoal and the determined value, therefore, is used because of its simplicity. Each laboratory should determine its own desorption efficiency. For comparison purposes, NIOSH determined a value of 96% for benzene on one batch of charcoal.

(j) Calculations

(1) Read the weight in milligrams corresponding to each peak area from the standard curve. No correction is necessary for the volume injected, since it is the same for both the sample determination and the standard curve.

(2) The weight of benzene on the front section of the blank is subtracted from the weight determined for the front section of each sample; a similar procedure is followed for the backup sections. Amounts present on the front and backup sections of the same tube are then added together to determine the total amount detected in the sample. This total weight is then divided by the desorption efficiency to determine the corrected total number of milligrams in the sample. Milligrams are converted into ppm by volume in the air sampled by the following equation at 25 C and 760 mm Hg:

$$\text{ppm} = \frac{24,450 \text{ ml/mole} \times \text{mg/liter}}{\text{molecular wt}}$$

For a 10-liter air sample of benzene:

$$\text{ppm} = \frac{24,450 \text{ ml/mole} \times \text{mg in sample}/10 \text{ liters}}{78.11 \text{ g/mole}}$$

$$\text{ppm} = 31.30 \times \text{mg in sample}$$

VIII. APPENDIX II  
METHODS FOR DETERMINATION OF  
EXPOSURE AREAS TO BENZENE

Estimation of Concentration with Detector Tubes

(a) Atmospheric Sampling

(1) Equipment Used

A typical sampling train consists of a detector tube with a corresponding sampling pump. A specific manufacturer's pump may only be used with his detector tubes.

(2) Sampling Procedures

A specific procedure depends on the manufacturer's instructions but normally consists of breaking both tips off a detector tube, inserting the tube into the pump, and taking a specific number of strokes with the pump.

(3) Handling and Shipping of Samples

Detector tubes are not stable with time; the stain in some tubes fades in a few minutes. The tubes should be read immediately in accordance with the manufacturer's instructions and charts; no attempt should be made to save the used tubes.

(b) General Principles

Gas detector tubes contain a chemically impregnated packing which indicates the concentration of a contaminant in the air by means of a chemically produced color change. The color changes are not permanent or stable, so the stained tubes must be read immediately after the samples are taken. The length of stain or the color intensity is read according to the

manufacturer's instructions. This may involve comparing the stain with a chart, a color comparator, or a direct concentration reading from calibration marks on the tube. Detailed descriptions are provided by individual manufacturer's instructions.

Tubes obtained from commercial sources which bear the certified seal of NIOSH are considered to adhere to the requirements as specified for Approval of Gas Detector Tube Units in 42 CFR Part 84 (37 F.R. 19643). A user may perform his own calibration on commercially acquired tubes by generating accurately known concentrations of benzene in air and correlating concentration with stain length or color intensity.

(c) Range and Sensitivity

Certification standards require that certified tubes have a range from 1/2-5 times the time-weighted average concentration. The sensitivity varies with tube brands.

(d) Interferences

Interferences vary with tube brands. The manufacturer's instructions must be consulted.

(e) Accuracy

Certification standards by NIOSH under the provisions of 42 CFR Part 84 (37 F.R. 19643) specify reliability to within  $\pm 25\%$  of the actual concentration in the range 0.75-5 times the standard and  $\pm 35\%$  in the range from 0.5 up to, but not including, 0.75 times the standard.

(f) Advantages and Disadvantages

Unlike the charcoal tube method, the use of detector tubes (and portable instruments) is relatively inexpensive and rapid; there is far less time lag than that experienced with laboratory analytical results.



Rapid detecting units are valuable for determining whether a hazardous condition exists at a given location so that workers may be evacuated or suitable protective devices provided. In addition, industrial operators and process engineers need inexpensive and rapid tools for day-to-day evaluation of the atmospheric levels in a work area.

The accuracy of detector tubes is limited; at best they give only an indication of the contaminant concentration. In evaluating measurements performed with detector tubes, interferences, difficulty of end-point readings, and possible calibration inaccuracies must all be considered.

#### Measurement with Portable Instruments

##### (a) Atmospheric Sampling

##### (1) Equipment Used

Two classifications of portable meters that are applicable to atmospheric sampling are direct reading instruments and analytical instruments. Combustible gas meters and flame ionization meters are portable, direct reading instruments; portable variable-path infrared analyzers and gas chromatographs are both field analytical instruments. Any of the 4 meters mentioned are acceptable for benzene determinations if they are properly calibrated before use.

##### (2) Sampling Procedures

The most important sampling step is the meter calibration. Careful calibration must be performed either in the laboratory prior to on-site use or in the field using a container of specific benzene concentration. If calibration charts are inaccurate, erroneous readings will be made.

The actual field sampling is conducted according to the manufacturer's instructions. Readings should be corrected if necessary for variables such as temperature, humidity, atmospheric pressure, etc, and recorded along with time, place, temperature, etc.

(b) General Principles

Analysis is dependent on the type of meter used. The portable direct reading meters require no analysis because they usually provide usable concentration readings directly. Results obtained from the variable-path infrared analyzer and the gas chromatograph must be recorded, further analyzed, and compared with standards to obtain concentration values.

(c) Range and Sensitivity

The range and sensitivity vary with the instrument used; in general, the portable analysis meters are more sensitive than direct reading units.

(d) Interferences

Again, these vary with the instrument used. Water vapor or combustible gases interfere with benzene identification using combustible gas meters. Mixtures of any carbon containing compounds, other than benzene, will interfere in flame ionization determinations.

(e) Advantages and Disadvantages

The benefits and drawbacks of portable instruments are essentially the same as for detector tubes discussed previously. Where recording capability is possible, direct reading instruments have the advantage of continuous record availability.