

# BENZENE by portable GC

3700



MW: 78.11

CAS: 71-43-2

RTECS: CY1400000

**METHOD:** 3700, Issue 2

**EVALUATION:** PARTIAL

**Issue 1:** 15 August 1987

**Issue 2:** 15 August 1994

**OSHA :** 1 ppm; STEL 5 ppm  
**NIOSH:** 0.1 ppm; C 1ppm/15 min (suspect carcinogen)  
**ACGIH:** 10 ppm; (suspect carcinogen)  
 (1 ppm = 3.19 mg/m<sup>3</sup> @ NTP)

**PROPERTIES:** liquid; d 0.879 g/mL @ 20 °C;  
 BP 80.1 °C; MP 5.5 °C;  
 VP 12.7 kPa (95.2 mm Hg;  
 12.5% v/v) @ 25 °C; explosive range  
 1.3 to 7.1% v/v

**SYNONYMS:** benzol; cyclohexatriene

**APPLICABILITY:** The working range is 0.02 to 500 ppm (0.06 to 1600 mg/m<sup>3</sup>) (see EVALUATION OF METHOD).

**INTERFERENCES:** Any compounds having the same or nearly the same retention time as benzene on the column in use are potential interferences. Such compounds cause positive interferences, however, and the actual benzene concentration will be less than or equal to the total of the benzene plus these compounds. The presence of a large number of compounds with retention time similar to benzene will cause a high background resulting in decreased sensitivity, possibly to the point where the LOQ approaches 1 ppm. Butane, styrene, toluene and xylenes have been shown not to affect this method [1]. Acceptable estimates of benzene concentration in diesel and gasoline vapors have been made with this method [2].

**OTHER METHODS:** Methods 1500 (Hydrocarbons, BP 36 - 126 °C) and 1501 (Hydrocarbons, aromatic) use activated charcoal sampler tubes.

**REAGENTS:**

1. Benzene\* in air, working standards prepared in the field by filling Tedlar bags with commercially prepared and certified standards (preferred) or prepared in the field by injecting known amounts of pure benzene into Tedlar bags containing a metered volume of pure air or nitrogen.
2. Cylinder of air, nitrogen or helium for use as carrier gas and field blanks.\*

\* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Portable gas chromatograph (GC), with photoionization detector, preferably with gas sampling loop and (if appropriate) strip chart recorder.
2. Personal sampling pump, 0.02 to 5 L/min or other rate suitable for filling sample bag, with flexible connecting tubing.  
NOTE: Pumps lubricated with petroleum products should not be used.
3. Sample bags, Tedlar, 1- to 20-L or other appropriate sizes.
4. Syringes, gas-tight, of various sizes appropriate to the GC.  
NOTE: To reduce the possibility of contamination, use separate, previously unused syringes for working standards and samples. Test syringes for contamination occasionally by filling them with clean air and analyzing the contents.
5. Label tape and marking pen for labeling bags.

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**SPECIAL PRECAUTIONS:** Benzene is a suspect carcinogen [3,4]. Shipment of compressed gases must comply with 49 CFR 171-177 regulations regarding shipment of hazardous materials.

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**SAMPLING:**

1. Start GC instrument and recorder and allow to warm up according to manufacturer's instructions.  
NOTE: A straight baseline should be attained at the highest sensitivity likely to be used.
2. Select one of the following sampling modes:
  - a. Spot sample. Draw air sample into the gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.  
NOTE: A large contributor to random error in the method is imprecision of replicate injections. To improve precision:
    - (1) use a gas sampling loop for injections, if available;
    - (2) make at least three replicate determinations per sample;
    - (3) use an injection volume large enough to be precisely readable, and consistent with that used in calibration.
  - b. Integrated air sample for TWA determination.
    - (1) Evacuate a clean sample bag using the inlet port of a personal sampling pump.  
NOTE: To reduce memory effects and contamination, use only previously unused sample bags. Alternatively, purge used bags at least two times with clean air, then fill with clean air and analyze for benzene as in step (4) below.
    - (2) Attach the sample bag to the outlet port of a personal sampling pump with a minimum length of flexible tubing. To the inlet port of the pump attach a length of Teflon tubing sufficient to reach the desired site. Alternatively, a rubber squeeze bulb can be used in place of a personal sampling pump when sample size is small. In either case, tubing and pump/bulb should be flushed with sample air prior to, and clean air subsequent to, sample collection.

NOTE: Tygon tubing has been shown to adsorb some materials in complex hydrocarbon mixtures and to off-gas during later sample collection causing an increase in hydrocarbon concentration in those subsequent samples.

- (3) Pump the air sample into the bag at a rate calculated to fill  $\leq 80\%$  of the sample bag capacity over the sampling period.

NOTE: The flow rate must be constant throughout the sampling period.

- (4) Within 4 h after completion of sampling, introduce an aliquot of the sample into the GC (as in step 2.a).

3. Obtain the benzene peak height or area of the injected sample.

#### CALIBRATION AND QUALITY CONTROL:

4. Perform the following in the laboratory before field work begins:
- Establish a laboratory calibration graph with at least three replicate determinations of at least six working standards. Plot peak height or area vs. mass or concentration of benzene.
  - Determine detector drift, averaged over the time period(s) expected to be used in the field.
  - Determine the ability of the GC column to separate the benzene peak from other substances known or predicted to be present in the field samples.
5. Establish a daily field calibration graph (peak height vs. mass or concentration of benzene) with triplicate determinations of working standards under the same conditions as for samples (step 2.a). Alternate analyses of samples and working standards, if possible.

#### CALCULATIONS:

6. Calculate mass,  $W$  (ng), of benzene in sample by comparison of sample peak height with daily calibration graph (step 5). Determine concentration,  $C$ , of benzene in the injected sample,  $V$  (mL):

$$C = \frac{W}{V}, \text{ mg/m}^3.$$

NOTE: Some GCs will perform this calculation electronically.

#### EVALUATION OF METHOD:

This method was evaluated over the range 0.03 to 100 ppm benzene using a Photovac 10S portable GC. Certified standard gas mixtures of benzene in air were obtained from Scott Specialty Gases Inc., and these were used to establish the calibration graph. Once this graph was established, bias was assessed by analyzing a bag sample containing an unknown concentration and comparing the concentration obtained with that obtained from analysis of replicate charcoal tube sample taken from the same bag. Additionally, a field evaluation was subsequently conducted in which results obtained using this method were compared with results obtained using conventional laboratory GC analysis and with results obtained using laboratory GC/MS analysis. Instruments used in the field evaluation include the Photovac 10S, the Sentex Scentoscreen and the MSI-301B by Microsensor Systems, Inc.

Previous issues of this method discussed the use of portable GC with ambient temperature packed columns. That technique was considered to be limited in its ability to separate the analyte from any interferences present. Evaluation of this method, which uses a capillary column, indicates that benzene can be separated from butane, styrene, toluene and xylenes, and that a response corresponding to benzene can be identified in such complex mixtures as gasoline and diesel vapors [1].

**REFERENCES:**

- [1] Burroughs, G.E. and W.J. Woodfin. "On-Site Screening for Benzene in Complex Environments." A report to the U.S. Coast Guard, Research and Development Center, Groton, CT, in partial fulfillment of MIPR No. Z51100-2-E00528, August, 1993.
- [2] Burroughs, G.E. and W.J. Woodfin, "On-Site Screening for Benzene in Complex Environments - A Report to the U.S. Coast Guard Research and Development Center," NIOSH/DPSE (unpublished, August, 1993).
- [3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, US DHHS (NIOSH) Publ. 81-123 (1981).
- [4] Criteria for a Recommended Standard...Occupational Exposure to Benzene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 74-137 (1974); as revised in August, 1976, and by E. J. Baier, NIOSH Testimony to U.S. Department of Labor, July, 1977.

**METHOD WRITTEN BY:**

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