

The chromatograph columns and the corresponding operating parameters herein described have been represented as being useful for producing an adequate resolution of benzene. However, resolution interferences may be encountered on some sources. Also, the chromatograph operator may know of a column that will produce a superior resolution of benzene without reducing the response to benzene as specified in section 4.3.1.

¹ Mention of trade names or specific products does not constitute endorsement by the U. S. Environmental Protection Agency.

In any event, the chromatograph operator shall select a column which is best suited to his particular analysis problem, subject to the approval of the Administrator.

Such approval shall be considered automatic provided that confirming data produced through a demonstrably adequate supplemental analytical technique, such as analysis with a different column or G.C./mass spectroscopy, is available for review by the Administrator.

2. APPARATUS

4.1 Sampling. See Figure 110-1.

4.1.1 Probe. Stainless steel, Pyrex¹ glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample Line. Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3. Male (2) and female (2) stainless steel quick connects, with ball checks (one pair without) located as shown in Figure 110-1.

4.1.4. Tedlar or aluminized Mylar bags, 100 liter capacity. To contain sample.

4.1.5. Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

4.1.6 Needle Valve. To adjust sample flow rate.

4.1.7 Pump--Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal Tube. To prevent admission of benzene and other organics to the atmosphere in the vicinity of samplers.

4.1.9 Flow Meter. For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liters per minute.

4.1.10 Connecting Tubing. Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 110-1).

4.2 Sample Recovery.

4.2.1 Tubing. Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0 to 2.0 ml sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1 ppm benzene that is at least as great as the average noise level. (Response is measured from the average value of the baseline to the maximum of the waveform, while standard operating conditions are in use.)

4.3.2 Chromatographic Columns. Columns other than those listed below can be used, provided that the precision and accuracy of the analysis of benzene standards are not

impaired. Information confirming that adequate resolution of the benzene peak is accomplished should be available. Adequate resolution is defined as an area overlap of not more than 10 percent of the benzene peak. Calculation of area overlap is explained in Appendix E, Supplement A: *"Determination of Adequate Chromatographic Peak Resolution"*.

4.3.2.1 Column A: Benzene in the Presence of Aliphatics. Stainless Steel, 2.44m x 3.2mm, containing 10 percent 1, 2, 3, tris (2-cyanoethoxy) propane (TCEP) on 80/100 Chromosorb PAWEIGH. C

4.3.2.2 Column B: Benzene With Separation of the Isomers of Xylene. Stainless steel, 1.83 m x .3.2 mm, containing 5 percent SP 1200/1.75 percent Bentone 34 on 100/120 Supelcoport.

4.3.3 Flow Meters (2). Rotameter type, 0 to 100 ml/min capacity.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump--Leak-free. Minimum capacity 100 ml/min.

4.3.8 Recorder. Strip chart type, optionally equipped with disc integrator or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator, for 4.3.8 to measure chromatograph peak areas.

4.4 Calibration. 4.4.2 through 4.4.6 are for section 7.1 which is optional.

4.4.1 Tubing. Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar or Aluminized Mylar Bags. 50-liter capacity, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringe. 1.0 μ l, gas tight, individually calibrated, to dispense liquid benzene.

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4.4.5 Dry Gas Meter, with Temperature and Pressure Gauges. Accurate to ± 2 percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flowrate used to prepare standards.

4.4.6 Midget Impinger/Hot Plate Assembly. To vaporize benzene.

5. REAGENTS

It is necessary that all reagents be of chromatographic grade.

5.1 Analysis

5.1.1 Helium Gas or Nitrogen Gas. Zero grade, for chromatograph carrier gas.

5.1.2 Hydrogen Gas. Zero grade.

5.1.3 Oxygen Gas or Air as Required by the Detector. Zero grade.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Benzene. 99 Mol percent pure benzene certified by the manufacturer to contain a minimum of 99 Mol percent benzene; for use in the preparation of standard gas mixtures as described in Section 7.1.

5.2.2 Nitrogen Gas. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (50, 10, and 5 ppm benzene in nitrogen cylinders) for which the gas composition has been certified with an accuracy of ± 3 percent or better by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change by greater than ± 5 percent from the certified value. The date of gas cylinder preparation, certified benzene concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curved as described in Section 7.2.2.

5.2.3.1 Cylinder Standards Certification. The concentration of benzene in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) a high concentration standard (between 50 and 100 ppm) for preparation of a calibration curved by an appropriate dilution technique; (2) a low concentration standard (between 5 and 10 ppm) for verification of the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low concentration standard exceeds 5 percent of the true concentration, determine the source of error and correct it, then repeat the three-point calibration.

5.2.3.2 Establishment and Verification of Calibration Standards. The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent: (1) verification value determined by comparison with a gas

mixture prepared in accordance with the procedure described in Section 7.1.1 and using 99 Mol percent benzene, or (2) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards. All calibration standards must be reverified on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards identical in preparation to those in Section 5.2.3 (benzene in nitrogen cylinders), except the concentrations are only known to the person supervising the analysis of samples. The concentrations of the audit cylinders should be: one low concentration cylinder in the range of to 20 ppm benzene. When available audit cylinders may be obtained by contacting: EPA, Environmental Monitoring and Support Laboratory, Quality Assurance Branch (MD-77), Research Triangle Park, North Carolina 27711. If audit cylinders are not available at EPA, an alternate source must be secured.

6. PROCEDURE

6.1 Sampling. Assemble the sample train as in Figure 110-1. Perform a ban leak check according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. At all times, direct the gas exiting the rotameter away from sampling personnel. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate constant. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample Storage. Sample bags must be kept out of direct sunlight. Analysis must be performed within 4 days of sample

collection.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to a 0-100 ml/min rotameter with flow control valve followed by a charcoal tube and a 0-1 inch w.g. pressure gauge. Sample flow may be maintained either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

6.4 Analysis. Set the column temperature to 80°C for column A or 75°C for column B, and the detector temperature to 225°C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, note the peak having the retention time corresponding to benzene, as determined in Section 7.2.1. Measure the benzene peak area, A_m , by use of a disc integrator, electronic integrator, or a planimeter. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the benzene peak do not vary more than 5 percent. The average value for these two total areas will be used to compute the bag concentration.

6.5 Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a

decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

7. STANDARDS, CALIBRATION AND QUALITY ASSURANCE

7.1 Standards

7.1.1 Preparation of Benzene Standard Gas Mixtures. (Optional--delete if cylinder standards are used.) Assemble the apparatus shown in Figure 110-2. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 liters of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. While the bag is filling use the 10 μ l syringe to inject 10 μ l of 99 + percent benzene through the septum on top of the impinger. This gives a concentration of approximately 50 ppm of benzene. In a like manner, use the other syringe to prepare dilutions having approximately 10 and 5 ppm benzene concentrations. To calculate the specific concentrations, refer to section 8.1. These gas mixture standards may be used for seven days from the date of preparation, after which time preparation of new gas mixtures is required. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2 Calibration.

7.2.1 Determination of Benzene Retention Time. This section can be performed simultaneously with Section 7.2.2. Establish chromatograph conditions identical with those in section 6.3, above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of benzene. Maintain conditions, with the equipment plumbing arranged identically to section 6.3, and flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the benzene calibration mixtures. Then activate the

sample valve. Record the injection time. Select the peak that corresponds to benzene. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart speed, is defined as the benzene peak retention time. Since it is quite likely that there will be other organics present in the sample, it is very important that positive identification of the benzene peak be made.

7.2.2 Preparation of Chromatograph Calibration Curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 5.2.3 or 7.1.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard gas mixtures and activate the sample valve. Record C_c , the concentration of benzene injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values vs C_c . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.3 Quality Assurance.

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix E, Supplement B: *"Procedure for Field Auditing GC Analysis."*

7.3.2 Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows: to leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note:

an alternative leak check method is to pressurize the bag to 5-10 cm H₂O or 2-4 in. H₂O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. CALCULATIONS

8.1 Optional Benzene Standards Concentrations. Calculate each benzene standard concentration prepared in accordance with Section 7.1.1 as follows:

$$\begin{aligned}
 10^6 C_c &= \frac{B \mu l \cdot 8787 \text{ mg} \cdot 10^3 \mu\text{g} \cdot \mu\text{g mole} \cdot 24.055 \mu\text{l}}{V_m Y \frac{10^6 \mu\text{l}}{1} \frac{78.11 \mu\text{g}}{293} \frac{\text{P}_m}{\text{T}_m} \frac{\mu\text{g mole}}{760}} \\
 &= \frac{B (270.6)}{V_m Y \frac{293}{\text{T}_m} \frac{\text{P}_m}{760}}
 \end{aligned}$$

Equation 110-1

Where:

C_c = Benzene standard concentration in ppm.

B = Number of ml of benzene injected.

V_m = Gas volume measured by dry gas meter in liters.

Y = Dry gas meter calibration factor.

P_m = Absolute pressure of the dry gas meter, mm Hg.

T_m = Absolute temperature of the dry gas meter, °A.

.8787 = Density of benzene at 293°A.

78.11 = Molecular weight of benzene.

24.055 = Ideal gas at 293°A, 760 mm Hg.

10^6 = Conversion factor, ppm.

8.2 Benzene Sample Concentrations. From the calibration curve described in Section 7.2.2 above, select the value of

C_c that corresponds to A_c . Calculate C_s as follows:

$$C_s = C_c P_r T_i$$

Equation 110-

$$\frac{102}{P_i T_r T (1 - S_{wb})}$$

Where:

S_{wb} = The water vapor content of the bag sample, as analyzed.

C_s = The concentration of benzene in the sample in ppm.

C_c = The concentration of benzene indicated by the gas chromatograph, in ppm.

P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_i = The sample loop temperature on the absolute scale at the time of analysis, °A.

P_i = The laboratory pressure at time of analysis, mm Hg.

T_r = The reference temperature, the sample loop temperature recorded during calibration, °A.

9. REFERENCES

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