

State of California
Air Resources Board

Method 410A

Determination of Benzene from
Stationary Sources
(Low Concentration Gas Chromatographic Technique)

Adopted: March 28, 1986

METHOD 410A
DETERMINATION OF BENZENE FROM STATIONARY SOURCES (LOW
CONCENTRATION GAS CHROMATOGRAPHIC TECHNIQUE)

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability:

This method applies to the measurement of low concentration emissions of benzene from stationary sources. The method does not account for benzene contained in particulate matter.

1.2 Principle:

An integrated bag sample of stack gas containing benzene and other organics is subjected to gas chromatographic (GC) analysis, using a photo ionization detector (PID).

2. RANGE AND SENSITIVITY

The range of this method is 1.0 to 1000 ppb. The upper limit may be raised by extending the calibration range or by diluting the sample. The lower limit may be improved depending on the skill of the operator and the quality of the equipment.

3. INTERFERENCES

The chromatographic columns and the corresponding operating parameters herein described normally provide an adequate resolution of benzene; but interferences may be encountered from some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis problem, subject to the approval of the Executive Officer. Approval is automatic provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Executive Officer.

Note: L = liter
ml = milliliter
ul = microliter

3.1 Information regarding the stationary source being tested, such as the industrial process, fuel, waste material being treated, and other pertinent information should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as benzene at the operating conditions described in this method is a potential interference. Retention time data on a single column cannot be

considered proof of chemical identity. If there are significant potential interferences, separate conditions (column packing, temperature, detector, etc.) must be changed to circumvent the problem.

- 3.3 If other gas chromatographic conditions or other techniques are used, the tester is required to substantiate the data through an adequate quality assurance program approved by the Executive Officer.

4. APPARATUS

The following sampling apparatus has been successfully field tested and is recommended. Any other sampling apparatus which, after review of the Executive Officer, is deemed equivalent for the purposes of this test method, may be used.

- 4.1 Sampling (see Figure 1 in part 6. PROCEDURE):
The sampling train consists of the following components.
- 4.1.1 Probe: Stainless steel, Pyrex glass or Teflon tubing (as stack temperature permits), equipped with an optional glass wool plug to remove particulate matter.
 - 4.1.2 Sample Lines: Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. Thick walled tubing (4.8 mm inside diameter) is best where strength and kink resistance are needed. Use an unused piece for each series of bag samples that constitutes an emission test and discard upon completion of the test.
 - 4.1.3 Quick Connects: Stainless steel male (2) and female (2), with ball checks (one pair without) located as shown in Figure 1.
 - 4.1.4 Tedlar Bags: At least 10L capacity, to contain sample.
 - 4.1.5 Bag Containers: Rigid leakproof containers with viewing ports for filling sample bags and covering to protect contents from sunlight.
 - 4.1.6 Needle Valve: To adjust sample flow rate.
 - 4.1.7 Pump: Leak-free with minimum of 2 L/min capacity.
 - 4.1.8 Charcoal Tube (optional): To prevent venting 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 2 L/min.
- 4.1.10 Connecting Tubing: Teflon (or other suitably inert material), 6.4 mm outside diameter, to assemble sampling train (Figure 1).

4.2 Sample Recovery:
Teflon tubing (or other suitably inert material), 6.4 mm outside diameter, is required to connect the sample bag to the chromatograph sample loop for sample recovery. Use a new unused piece for each series of bag samples that constitutes an emission test and discard upon conclusion of analysis of those bags.

4.3 Analysis:
The following equipment is needed:

- 4.3.1 Gas Chromatograph: With PID, potentiometric strip chart recorder and 1.0 to 2.0 ml cryogenic sampling loop with automatic sample valve. The chromatographic system shall be capable of producing a response to 1.0 ppb benzene that is at least as great as the average noise level.

The signal to noise ratio shall be reported with all lab results and the following significance shall be inferred:

- 1:1 information
- 2:1 detection
- 3:1 quantification

(Response is measured from the average value of the base line to the maximum of the waveform, while standard operating conditions are in use.)

- 4.3.2 Chromatographic Columns: Columns are as listed below. The analyst may use other columns provided that the precision and accuracy of the analysis of benzene standards are not impaired and he has available for review information confirming that there is adequate resolution of the benzene peak. (For the listed or alternative columns, the resolution goal shall be an area overlap of not more than 10 percent of the benzene peak by an interferent peak. Any such area overlap shall be reported with all lab results.) Calculation of

area overlap is explained in Appendix A: "Determination of Adequate Chromatographic Peak Resolution.")

- 4.3.2.1 Column A: Stainless steel, 6 ft. by 1/8 in., packed with 10% N, N-bis (2-cyanoethyl) formamide on 100/120 mesh Chromasorb PAW. The packing is a suspect carcinogen. There are other columns at least as sensitive to benzene.
- 4.3.2.2 Column B: Stainless steel, 6 ft. by 1/8 in., 6C column, packed with 10% 1,2,3 – tris (2-cyanoethoxy) propane.
- 4.3.3 Flow Meters (2): Rotameter type, 100 ml/min capacity.
- 4.3.4 Gas Regulators: For required gas cylinders.
- 4.3.5 Thermometer: Accurate to 1°C, to measure temperature of heated sample loop at time of sample injection.
- 4.3.6 Barometer: Accurate to 5 mmHg, to measure atmospheric pressure around gas chromatograph during sample analysis.
- 4.3.7 Pump (optional): Leak-free, with minimum of 100 ml/min capacity.
- 4.3.8 Recorder: Strip chart type, optionally equipped with either disc or electronic integrator.
- 4.3.9 Planimeter: Optional, in place of disc or electronic integrator, or recorder, to measure chromatograph peak areas.
- 4.3.10 Syringe: Ground glass, 100 ml, or other suitable device to transfer gas samples from Tedlar bags to the GC sample inlet. Establish background level of benzene concentration in syringe as less than one percent of level measured for test.
- 4.4 Calibration:
Sections 4.4.2 through 4.4.5 are for the optional procedure in Section 7.1.
 - 4.4.1 Syringe: As in 4.3.10. Background level measured for each test.

- 4.4.2 Tedlar or Aluminized Mylar Bags: 50 L capacity, with valve; separate bag marked for each calibration concentration.
- 4.4.3 Syringes: 1.0 uL, 10 uL, and 100 uL, individually calibrated to dispense liquid benzene.
- 4.4.4 Dry Gas Meter with Temperature and Pressure Gauges: Accurate to ± 2 percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.
- 4.4.5 Midget Impinger/Hot Plate Assembly: To vaporize benzene.

5. REAGENTS

Use only reagents that are of chromatographic grade.

5.1 Analysis:

The following are needed for analysis.

- 5.1.1 Helium or Nitrogen: Zero grade, for chromatograph carrier gas; also, helium is for flushing sample gases.

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: 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, Zero grade: For preparation of standard gas mixtures as described in Section 7.1.
- 5.2.3 Cylinder Standards (3): Gas mixture standards (500, 50, and 5 ppb benzene in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 7.2.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of ± 3 percent or better (see Section 5.2.3.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than ± 5 percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified benzene concentration, and

recommended maximum shelf life to the cylinder before shipment to the buyer.

5.2.3.1 Cylinder Standards Certification: The manufacturer shall certify the concentration of benzene in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating the analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 5 and 10 ppm) to prepare his calibration curve by an appropriate dilution technique; and (2) a low-concentration calibration standard (between 5 and 10 ppb) to verify 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, the manufacturer shall determine the source of error and correct it, then repeat the three-point calibration.

5.2.3.2 Verification of Manufacturer's Calibration Standards: Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 Mol percent benzene) in accordance with the procedure described in Section 7.1 or by (b) having it analyzed by the National Bureau of Standards. The agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2): Gas mixture standards with concentrations known only to the person supervising the analysis of samples. The audit cylinder standards shall be identically prepared as those in Section 5.2.3 (benzene in nitrogen cylinders). The concentrations of the audit cylinder should be: one low-concentration cylinder in the range of 5 to 20 ppm benzene and one high-concentration cylinder in the range of 100 to 300 ppm benzene. When available, the tester may obtain audit cylinders by contacting: U.S. Environmental Protection Agency, Environmental Monitoring

and Support Laboratory, Quality Assurance Branch (MD-77), Research Triangle Park, North Carolina 27711. If audit cylinders are not available at the Environmental Protection Agency, the tester must secure an alternative source.

6. PROCEDURE

The following sampling procedure has been successfully field tested and is recommended. Any other sampling procedure which, after review of the Executive Officer, is deemed equivalent for the purposes of this test method, may be used.

6.1 Sampling:

Assemble the sample train as shown in Figure 1. Perform a bag 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 that will more than half fill the bag in the specified sample period. After allowing sufficient time to purge the line several times, 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. Again connect the sample train as shown in Figure 1 and begin sampling. 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. Keep the bag container in shade.

6.2 Sample Storage:

Keep the sample bags out of direct sunlight. Perform the analysis within 4 days of sample collection.

6.3 Sample Recovery/Freezeout/Injection:

CAUTION: serial dilutions may be necessary for highly concentrated samples to protect the GC system from overloading.

6.3.1 Sample Recovery: Immerse the sample loops in liquid nitrogen (LN₂) and allow the temperature to stabilize (approximately 5 minutes).

After flushing the 100 ml syringe with about 40 ml of the sample, withdraw 40 ml from the sample bag.

6.3.2 Freeze-out: Transfer the sample into the cryogenic sampling loop (trap).

Back fill the syringe with 40 ml of helium and flush the 40 ml through the trap. Then flush helium through the trap for 2 minutes at 20 ml/min.

Stop the helium flushing. Remove the ¼ inch U-trap from the LN₂.

Isolate the cryogenic trap by using an "isolation valve" which allows the carrier gas to by-pass the trap. Replace the LN₂ Dewar with a Dewar containing 80°C water and immerse the trap. Allow all ice to melt from the trap.

6.3.3 Injection: Using the valve, introduce the sample into the carrier gas stream.

6.4 Analysis:

CAUTION, serial dilution, may be necessary for highly concentrated samples to prevent overloading. Set the column temperature to ambient for column A or column B, and the detector temperature to 150°C. 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. If necessary, adjust flow rate for best detector response. Observe the base line periodically and determine that the noise level has stabilized and that base-line drift has ceased. 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. 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. Use the average value of these two total areas to compute the bag concentration.

6.5 Determination of Bag Water Vapor Content:

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. PREPARATION OF STANDARD GAS MIXTURES, CALIBRATION, AND QUALITY ASSURANCE

7.1 Preparation of Benzene Standard Gas Mixtures:

This procedure may only be used if no cylinder standard is available. Assemble the apparatus shown in Figure 2. Evacuate a 50 L Tedlar bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 L 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 1.0 uL syringe to inject 1.0 uL of 99+ percent liquid benzene through the septum on top of the impinger. This gives a concentration of approximately 5 ppm of benzene. In a like manner, use the 10 uL and 100 uL syringes to prepare dilutions having approximately 50 ppm and 500 ppm benzene concentrations. Using the same apparatus, the 100 uL syringe, and appropriate dilution techniques, inject 50 mL of each dilution into 3 different empty Tedlar bags and fill each with 50 L of nitrogen to obtain 3 standard gas mixtures of 5, 50, and 500 ppb. To calculate the specific concentrations, refer to Section 8.1. These gas mixture standards may be used for 7 days from the date of preparation, after which time preparation of new gas mixtures is required. (Caution: If the new gas mixture standard is a lower concentration than the previous gas mixture standard, contamination may be a problem when a bag is reused.)

7.2 Calibration:

7.2.1 Determination of Benzene Retention Time: (This section can be performed simultaneously with Section 7.2.2.) CAUTION, serial dilutions may be necessary for highly concentrated samples to protect GC plumbing. Establish chromatograph conditions identical with those in Section 6.4, 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, and flush the sample loop for 30 sec 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) using conditions identical with those listed in Sections 6.3 and 6.4. Record C_c , the concentration of benzene injected, the attenuator setting, chart speed, peak areas, 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 versus C_c . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. 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 before the sample analyses, perform a check for drift against a cylinder of known concentration traceable to the last analysis audit. At least twice a year, perform the analysis audit described in Appendix B: "Procedure for Field Auditing GC Analysis."

7.3.2 Leak Checks: While performance of this section is required after bag use, it is also advised that it be performed before bag use. After each use, make sure a bag did not develop leaks by connecting a water manometer and pressurizing the bag to 5 to 10 cm H_2O (2 to 4 in H_2O). Allow to stand for 10 min. 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 to 10 cm H_2O (2 to 4 in H_2O) 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.

7.3.3 Bag Check. To insure no contamination or interferences from the Tedlar bag, a sufficient number of bags should be checked before use. This can be accomplished by filling the bag with N_2 or zero air & making an injection on the GC under normal analysis conditions. It is recommended that

new bags be used each time, but, if this is not possible, it is necessary to check every bag prior to use.

7.3.4 Syringe Check. Prior to use, the GC injection syringe should be checked for contamination by inserting the needle through the injector septum, drawing a volume of carrier gas into the barrel of the syringe and re-injecting it back onto the column. This procedure should also be done periodically during the analysis to insure no contamination of the syringe.

8. CALCULATIONS:

8.1 Optional Benzene Standards Concentrations:
Calculate each benzene standard concentration (C_c in ppm) prepared in accordance with Section 7.1 as follows:

$$C_c = \frac{B(0.2706)(10^3)}{V_m Y \frac{293}{T_m} \frac{P_m}{760}}$$
$$C_c = 701.9 \frac{B T_m}{V_m Y P_m}$$

where:

B	=	Volume of benzene injected, microliters.
V_m	=	Gas volume measured by dry gas meter, liters.
Y	=	Dry gas meter calibration factor, dimensionless.
P_m	=	Absolute pressure of the dry gas meter, mmHg.
T_m	=	Absolute temperature of the dry gas meter, °K.
0.2706	=	Ideal gas volume of benzene at 293°K and 760 mmHg L/ml.
10^3	=	Conversion factor [(ppm) (ml)/ul].

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 the concentration of benzene in the sample (C_s in ppm) as follows:

$$C_s = \frac{C_c P_r T_i}{P_i T_r (1 - S_{wb})}$$

where:

C_s = Concentration of benzene in the sample, ppm.

C_c = Concentration of benzene indicated by the gas chromatograph, ppm.

P_r = Reference pressure, the barometric pressure recorded during calibration, mmHg.

T_i = Sample loop temperature at the time of analysis, °K.

P_i = Barometric pressure at time of analysis, mmHg.

T_r = Reference temperature, the sample loop temperature recorded during calibration, °K.

S_{wb} = Water vapor content of the bag sample, volume fraction.

APPENDIX A

Determination of Adequate Chromatographic Peak Resolution

In this method of dealing with resolution, the extent to which one chromatographic peak overlaps another is determined.

For convenience, consider the range of the elution curve of each compound as running from -2 to $+2$. This range is used in other resolution criteria, and it contains 95.45 percent of the area of a normal curve. If two peaks are separated by a known distance, b , one can determine the fraction of the area of one curve that lies within the range of the other. The extent to which the elution curve of a contaminant compound overlaps the curve of a compound that is under analysis is found by integrating the contaminant curve over limits $b-2\sigma_s$ to $b+2\sigma_s$ where σ_s is the standard deviation of the sample curve.

There are several ways this calculation can be simplified. Overlap can be determined for curves of unit area; then actual areas can be introduced. The desired integration can be resolved into two integrals of the normal distribution function for which there are convenient calculation programs and tables. An example would be Program 15 Texas Instruments Program Manual ST1. 1975, Texas Instruments, Inc., Dallas, Texas 75222.

$$\frac{1}{\sqrt{2\pi}\sigma_c} \int_{b-2\sigma_s}^{b+2\sigma_s} e^{-\frac{tc^2}{2\sigma_c}} dt = \frac{1}{\sqrt{2\pi}} \int_{\frac{b-2\sigma_s}{c}}^{\infty} e^{-\frac{x^2}{2}} dx - \frac{1}{\sqrt{2\pi}} \int_{\frac{b+2\sigma_s}{\sigma_c}}^{\infty} e^{-\frac{x^2}{2}} dx$$

The following calculation steps are required:

1. $2\sigma_s = t_s / 2 \ln 2$
2. $c = t_c / 2 \ln 2$
3. $x_1 = (b-2\sigma_s) / \sigma_c$
4. $x_2 = (b+2\sigma_s) / \sigma_c$
5. $Q(x_1) = \frac{1}{\sqrt{2\pi}} \int_{x_1}^{\infty} e^{-\frac{x^2}{2}} dx$
6. $Q(x_2) = \frac{1}{\sqrt{2\pi}} \int_{x_2}^{\infty} e^{-\frac{x^2}{2}} dx$
7. $I_o = Q(x_1) - Q(x_2)$
8. $A_o = I_o A_c / A_s$

9. Percentage overlap = $A_o \times 100$

where:

- A_s = The area of the sample peak of interest determined by electronic integration, or by the formula $A_s = h_s t_s$.
- A_c = The area of the contaminant peak, determined in the same manner as A_s .
- b = The distance on the chromatographic chart that separates the maxima of the two peaks.
- H_s = The peak height of the sample compound of interest, measured from the average value of the baseline to the maximum of the curve.
- t_s = The width of the sample peak of interest at $\frac{1}{2}$ of peak height.
- t_c = The width of the contaminant peak at $\frac{1}{2}$ of peak height.
- σ_s = The standard deviation of the sample compound of interest elution curve.
- σ_c = The standard deviation of the contaminant elution curve.
- $Q(x_1)$ = The integral of the normal distribution function from x_1 to infinity.
- $Q(x_2)^*$ = The integral of the normal distribution function from x_2 to infinity.
- I_o = The overlap integral.
- A_o = The area overlap fraction.

In judging the suitability of alternate gas chromatographic columns, or the effects of altering chromatographic conditions, one can employ the area overlap as the resolution parameter with a specific maximum permissible value.

The use of Gaussian functions to describe chromatographic elution curves is widespread. However, some elution curves are highly asymmetric. In those cases where the sample peak is followed by a contaminant that has a leading edge that rises sharply but the curve then tails off, it may be possible to define an effective width for t_c as "twice the distance from the leading edge to a perpendicular line through the maximum of the contaminant curve, measured along a perpendicular bisection of that line."

* In most instances, $Q(x_2)$ is very small and may be neglected.

APPENDIX B

Procedure for Field Auditing GC Analysis.

Responsibilities of audit supervisor and analyst at the source sampling site include the following:

- A. Check that audit cylinders are stored in a safe location both before and after the audit to prevent vandalism of same.
- B. At the beginning and conclusion of the audit, record each cylinder number and cylinder pressure. Never analyze an audit cylinder when the pressure drops below 200 psi.