



Standard Test Method for Benzene in Motor and Aviation Gasoline by Infrared Spectroscopy¹

This standard is issued under the fixed designation D4053; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the percent benzene in full-range gasoline. It is applicable to concentrations from 0.1 % to 5 volume %.

1.2 This test method has not been validated for gasolines containing oxygenates. Certain oxygenates interfere with the measurement described in this test method. Test Method D6277 is recommended for gasolines containing oxygenates.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see Section 8 and 9.1.

2. Referenced Documents

2.1 ASTM Standards:²

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D6277 Test Method for Determination of Benzene in Spark-Ignition Engine Fuels Using Mid Infrared Spectroscopy

E131 Terminology Relating to Molecular Spectroscopy

E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers

E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests

3. Terminology

3.1 Definitions:

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0F on Absorption Spectroscopic Methods.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.1.1 Definitions of terms and symbols relating to absorption spectroscopy in this test method shall conform to Terminology E131. Terms of particular significance are the following:

3.1.2 *absorbance, A, n*—the molecular property of a substance that determines its ability to take up radiant power, expressed by:

$$A = \log_{10}(1/T) = -\log_{10}T \quad (1)$$

where

T = the transmittance as defined in 3.1.5.

3.1.3 *radiant energy, n*—energy transmitted as electromagnetic waves.

3.1.4 *radiant power, P, n*—the rate at which energy is transported in a beam of radiant energy.

3.1.5 *transmittance, T, n*—the molecular property of a substance that determines its transportability of radiant power, expressed by:

$$T = P/P_o \quad (2)$$

where:

P = the radiant power passing through the sample, and

P_o = the radiant power incident upon the sample.

4. Summary of Test Method

4.1 A sample of gasoline is examined by infrared spectroscopy and, following a correction for interference, compared with calibration blends of known benzene concentration. From this comparison the amount of benzene in the gasoline is determined.

5. Significance and Use

5.1 Benzene is classed as a toxic material. A knowledge of the concentration of this compound may be an aid in evaluating the possible health hazard to persons handling and using the gasoline. This test method is not intended to evaluate such hazards.

6. Interferences

6.1 Toluene and heavier aromatic compounds have some interference in this test method. In order to minimize the effect of such interference, this test method includes a procedure that corrects for the error caused by the presence of toluene. Error

due to other sources of interference may be partially compensated for by calibrating with gasoline stocks containing little or no benzene but which otherwise are similar in aromatic content to the samples to be analyzed.

7. Apparatus

7.1 *Absorption Cell*, sealed. Windows of potassium bromide or other material having sufficient transmittance out to 440 cm^{-1} ($22.73\text{ }\mu\text{m}$), in a cell having TFE-fluorocarbon plugs and nominal path length of 0.025 mm known to three significant numbers.

7.2 *Clear Reference Block*—A block made from the same material as cell windows for use in the reference beam path of a double-beam spectrometer.

7.3 *Infrared Spectrometer*, double-beam or single-beam, suitable for recording accurate measurements between 690 cm^{-1} ($14.49\text{ }\mu\text{m}$) and 440 cm^{-1} ($22.73\text{ }\mu\text{m}$). Refer to Practices [E932](#) and [E1421](#).

NOTE 1—Absorbances for the bands specified in this test method are expected to fall within the linear operating range of modern spectrometers for the concentration range as defined.

8. Reagents

8.1 *Benzene*, spectroscopic or research grade. (**Warning**—Poison, carcinogen, harmful, or fatal if swallowed. Extremely flammable.)

8.2 *Toluene*, spectroscopic or research grade. (**Warning**—Flammable, harmful if inhaled.)

8.3 *Isooctane (2,2,4-trimethylpentane) or n-Heptane*, spectroscopic or research grade. (**Warning**—*Isooctane* and *n-Heptane* are extremely flammable, harmful if inhaled.)

9. Sampling

9.1 Follow the procedures and precautions contained in Practice [D4057](#). (**Warning**—Gasolines are extremely flammable, harmful if inhaled.)

9.2 Cool the sample container and contents to 0 to 4°C before opening the container and transferring material to other containers.

10. Calibration and Standardization

10.1 *Reference Standards*—Prepare standard blends of benzene, using fresh, full-range gasoline of low benzene content (less than 1 volume %) as the solvent. Measure and dilute all components at ambient temperature. Accurately pipet the required volume of benzene into 100-mL volumetric flasks partially filled with the gasoline. Dilute to volume with additional gasoline. Prepare the blends in 1 volume % increments.

10.2 *Toluene Standard*—Prepare a blend of toluene in either *isooctane* or *n-heptane* as the solvent. Measure and dilute all components at ambient temperature. Accurately pipet 2 mL of toluene into a 10-mL volumetric flask partially filled with either *isooctane* or *n-heptane*. Dilute to volume with the chosen solvent.

10.3 Calibration:

10.3.1 Following the steps of Section 11, Procedure, for each of the standard blends and the gasoline base stock,

determine three absorbance values: (1) at the point of maximum absorbance near 673 cm^{-1} ($14.86\text{ }\mu\text{m}$), designated the benzene band; (2) at the point of maximum absorbance near 460 cm^{-1} ($21.74\text{ }\mu\text{m}$), designated the toluene band; and (3) at 500 cm^{-1} ($20.00\text{ }\mu\text{m}$), designated the baseline position.

10.3.2 Following the steps of Section 11, Procedure, for the toluene standard, determine the absorbances at the locations described in 10.3.1 for the benzene band, the toluene band, and the baseline position. Subtract the baseline position value at about 500 cm^{-1} from those found for benzene at about 673 cm^{-1} and toluene at about 460 cm^{-1} in order to obtain the net absorbance for each. Take the ratio of the benzene band net absorbance to the toluene band net absorbance to obtain the toluene correction factor.

10.3.3 For the gasoline base stock and each blend examined in 10.3.1, obtain the net absorbances at the benzene and the toluene bands by subtracting the baseline position value from the absorbances found for the band maxima. Continuing, for each liquid, multiply the toluene band net absorbance by the toluene correction factor found in 10.3.2 and subtract this value from the benzene band net absorbance in order to obtain the corrected net absorbance for the benzene band.

10.3.4 Construct a curve by plotting the benzene band corrected net absorbance for each calibration liquid, as found in 10.3.3, divided by the cell path length in millimetres, versus the volume % of added benzene for each.

10.3.5 Extrapolate the curve to zero absorbance. The absolute value of the intercept is the concentration of benzene in the gasoline used as the solvent.

10.3.6 Construct a standard reference curve by replotting the baseline absorbances per millimetre thickness, corrected in 10.3.5, against total concentration of benzene in percent by volume so that the curve passes through the origin.

NOTE 2—A linear equation can be used instead of the plot.

11. Procedure

11.1 Clean the cell with *isooctane* or similar solvent and dry by means of a source of vacuum.

11.2 Fill the absorption cell with the gasoline to be tested. Both cell and sample should be at ambient temperature during this operation. If moisture condensation is a problem, blanket the cell with a dry, inert atmosphere. Use care to avoid formation of air pockets in the cell and scan immediately to prevent bubbles from forming. Observe the cell during the scan period to check for bubble formation.

11.3 Scan the infrared spectrum from 690 cm^{-1} ($14.99\text{ }\mu\text{m}$) to 440 cm^{-1} ($22.73\text{ }\mu\text{m}$) versus a clear reference block in the reference beam (for double-beam operation); follow the directions of the manufacturer for quantitative analysis.

11.4 Determine the corrected net absorbance of the benzene band as described in 10.3.3.

11.5 Divide the benzene band corrected net absorbance, as found in 11.4, by the cell path length in millimetres.

12. Calculation

12.1 Calculate the benzene content of the gasoline in liquid volume % by entering the calibration curve of 10.3.6 or the equation in Note 2 with the value of the benzene band found in 11.5.

12.2 If the results are desired on a weight basis, convert to mass %, as follows:

$$B = V \times 0.8844/R \quad (3)$$

where:

B = benzene, mass %

V = benzene, volume % and

R = relative density of sample, 15/15°C.

13. Report

13.1 Report numerical results to the nearest 0.1 volume %.

14. Precision and Bias

14.1 The precision of the test method as obtained by statistical examination of interlaboratory results is as follows:

14.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same

apparatus under constant operating conditions on identical test materials, would in the long run, in normal and correct operation of the test method, exceed 0.08 volume % only in one case in twenty.

14.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method exceed 0.18 volume % only in one case in twenty.

14.2 *Bias*—There are no interlaboratory test data to establish a statistical statement on bias.

15. Keywords

15.1 aviation gasoline; benzene; infrared spectroscopy; motor gasoline

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