



Designation: D5986 – 23

Standard Test Method for Determination of Oxygenates, Benzene, Toluene, C₈–C₁₂ Aromatics and Total Aromatics in Finished Gasoline by Gas Chromatography/Fourier Transform Infrared Spectroscopy¹

This standard is issued under the fixed designation D5986; 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 quantitative determination of oxygenates: methyl-t-butylether (MTBE), di-isopropyl ether (DIPE), ethyl-t-butylether (ETBE), t-amylmethyl ether (TAME), methanol (MeOH), ethanol (EtOH), 2-propanol (2-PrOH), t-butanol (t-BuOH), 1-propanol (1-PrOH), 2-butanol (2-BuOH), i-butanol (i-BuOH), 1-butanol (1-BuOH); benzene, toluene and C₈–C₁₂ aromatics, and total aromatics in finished motor gasoline by gas chromatography/Fourier Transform infrared spectroscopy (GC/FTIR).

1.2 This test method covers the following concentration ranges: 0.1 % to 20 % by volume per component for ethers and alcohols; 0.1 % to 2 % by volume benzene; 1 % to 15 % by volume for toluene, 10 % to 40 % by volume total (C₆–C₁₂) aromatics.

1.3 The method has not been tested by ASTM for refinery individual hydrocarbon process streams, such as reformates, fluid catalytic cracking naphthas, etc., used in blending of gasolines.

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

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 *Definitions:*

3.1.1 This test method makes reference to common gas chromatographic procedures, terms, and relationships. Detailed definitions of these can be found in Practice **E355** and Terminology **D4175**.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *aromatics, n*—refers to any organic compound containing a benzene or naphthalene ring.

3.2.2 *calibrated aromatic component, n*—in this test method, refers to the individual aromatic components which have a specific calibration.

3.2.3 *cool on-column injector, n*—in gas chromatography, a direct sample introduction system which is set at a temperature at or below the boiling point of solutes or solvent on injection and then heated at a rate equal to or greater than the column. Normally used to eliminate boiling point discrimination on injection or to reduce adsorption, or both, on glass liners within injectors. The sample is injected directly into the head of the capillary column tubing or retention gap.

¹ This test method is under the jurisdiction of ASTM Committee **D02** on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee **D02.04.0L** on Gas Chromatography 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.

*A Summary of Changes section appears at the end of this standard

3.2.4 *Gram-Schmidt chromatogram, n*—a nonselective summation of total intensity from a spectral scan per unit time which resembles in profile a flame ionization detector chromatogram.

3.2.5 *retention gap, n*—in gas chromatography, refers to a deactivated precolumn which acts as a zone of low retention power for reconcentrating bands in space. The polarity of the precolumn must be similar to that of the analytical column.

3.2.6 *selective wavelength chromatogram (SWC), n*—in this test method, refers to a selective chromatogram obtained by summing the spectral intensity in a narrow spectral wavelength or frequency range as a function of elution time which is unique to the compound being quantitated.

3.2.7 *uncalibrated aromatic component, n*—in this test method, refers to individual aromatics for which a calibration is not available and whose concentrations are estimated from the response factor of a calibrated aromatic component.

3.2.8 *wall coated open tubular (WCOT), n*—a type of capillary column prepared by coating or bonding the inside wall of the capillary with a thin film of stationary phase.

4. Summary of Test Method

4.1 A gas chromatograph equipped with a methylsilicone WCOT column is interfaced to a Fourier transform infrared spectrometer. The sample is injected through a cool on-column injector capable of injecting a small sample size without overloading the column.

4.2 Calibration is performed using mixtures of specified pure oxygenates and aromatic hydrocarbons on a mass basis. Volume percent data is calculated from the densities of the individual components and the density of the sample. Multi-point calibrations consisting of at least five levels and bracketing the concentration of the specified individual aromatics is required. Unidentified aromatic hydrocarbons present which have not been specifically calibrated for are quantitated using the response factor of 1,2,3,5-tetramethylbenzene and summed with the other calibrated aromatic components to obtain a total aromatic concentration of the sample.

4.3 Specified quality control mixture(s) are analyzed to monitor the performance of the calibrated GC/FTIR system.

5. Significance and Use

5.1 Test methods to determine oxygenates, benzene, and the aromatic content of gasoline are necessary to assess product quality and to meet new fuel regulations.

5.2 This test method can be used for gasolines that contain oxygenates (alcohols and ethers) as additives. It has been determined that the common oxygenates found in finished gasoline do not interfere with the analysis of benzene and other aromatics by this test method.

6. Apparatus

6.1 Gas Chromatograph:

6.1.1 System equipped with temperature programmable gas chromatograph suitable for cool-on-column injections. The injector must allow the introduction of small (for example,

0.1 μL) sample sizes at the head of the WCOT column or a retention gap. An autosampler is mandatory.

6.1.2 WCOT column containing a methylsilicone stationary phase which elutes the aromatic hydrocarbons according to their boiling points. A column containing a relatively thick film of stationary phase, such as 4 μm to 5 μm , is recommended to prevent column sample overload.

6.2 FTIR Spectrometer:

6.2.1 This test method requires a light-pipe GC/FTIR system (Fig. 1). No data have been acquired with matrix-isolation or other deposition type systems.

6.2.2 The spectrometer must be equipped with a mercury-cadmium-telluride (MCT) detector capable of detecting from at least 4000 cm^{-1} to 550 cm^{-1} .

6.2.3 The lower limit of 550 cm^{-1} is necessary for the accurate determination of benzene. Fig. 2 gives an acceptable infrared spectra of benzene.

7. Reagents and Materials

7.1 *Carrier Gas*—Helium and hydrogen have been used successfully. The minimum purity of the carrier gas used must be 99.85 mole %. Additional purification using commercially available scrubbing reagents is recommended to remove trace oxygen which may deteriorate the performance of the GC WCOT column.

7.2 *Dilution Solvents*—*n*-heptane and methylbenzene (toluene) used as a solvent in the preparation of the calibration mixture. Reagent grade. All at 99 % or greater purity. Free from detectable oxygenates and aromatics which may interfere with the analysis.

7.2.1 Toluene should be used as a solvent only for the preparation of C_9 + components and must be free from interfering aromatics. (**Warning**—The gasoline samples and solvents used as reagents such as heptane and toluene are flammable and may be harmful or fatal if ingested or inhaled. Benzene is a known carcinogen. Use with proper ventilation. Safety glasses and gloves are required while preparing samples and standards.)

7.3 *Internal Standard*—1,2-dimethoxyethane (DME) or deuterated compounds, or both, have been used successfully. A

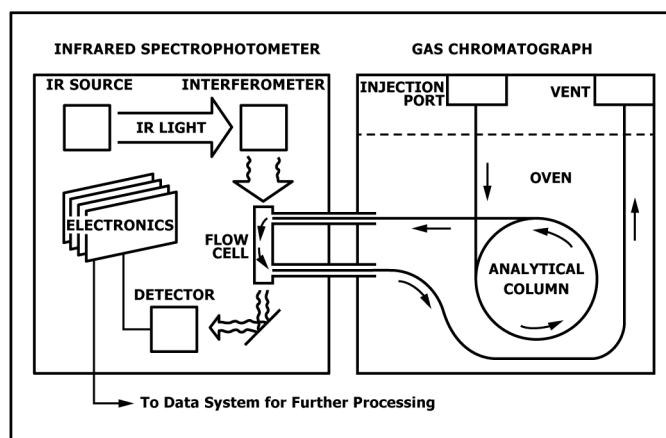


FIG. 1 Light-Pipe GC/FTIR System