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Standard Test Method for Determination of Benzene in Spark-Ignition Engine Fuels Using Mid Infrared Spectroscopy[1]

This standard is issued under the fixed designation D 6277; 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 percentage of benzene in spark-ignition engine fuels. It is applicable to concentrations from 0.1 to 5 volume %.

1.2 SI units of measurement are preferred and used throughout this standard.

1.3 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1298 Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method[2]

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[3]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[3]

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards[3]

D 5769 Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry[4]

D 5842 Practice for Sampling and Handling of Fuels for Volatility Measurements[4]

D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products[4]

E 168 Practices for General Techniques of Infrared Quantitative Analysis[5]

E 1655 Practices for Infrared Multivariate Quantitative Analysis[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *multivariate calibration*—a process for creating a calibration model in which multivariate mathematics is applied to correlate the absorbances measured for a set of calibration samples to reference component concentrations or property values for the set of samples.

3.1.1.1 *Discussion*—The resultant multivariate calibration model is applied to the analysis of spectra of unknown samples to provide an estimate of the component concentration or property values for the unknown sample.

3.1.1.2 *Discussion*—Included in the multivariate calibration algorithms are Partial Least Squares, Multilinear Regression, and Classical Least Squares Peak Fitting.

3.1.2 *oxygenate*—an oxygen-containing organic compound which may be used as a fuel or fuel supplement, for example, various alcohols and ethers.

4. Summary of Test Method

4.1 A sample of spark-ignition engine fuel is introduced into a liquid sample cell. A beam of infrared light is imaged through the sample onto a detector, and the detector response is determined. Wavelengths of the spectrum, that correlate highly with benzene or interferences, are selected for analysis using selective bandpass filters or by mathematically selecting areas of the whole spectrum. A multivariate mathematical analysis converts the detector response for the selected areas of the spectrum of an unknown to a concentration of benzene.

5. Significance and Use

5.1 Benzene is a compound that endangers health, and the concentration is limited by environmental protection agencies to produce a less toxic gasoline.

5.2 This test method is fast, simple to run, and inexpensive.

5.3 This test method is applicable for quality control in the production and distribution of spark-ignition engine fuels.

6. Interferences

6.1 The primary spectral interferences are toluene and other monosubstituted aromatics. In addition, oxygenates can interfere with measurements made with filter apparatus. Proper choice of the apparatus, proper design of a calibration matrix, and proper utilization of multivariate calibration techniques can minimize these interferences.

[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol. 05.02.

[4] *Annual Book of ASTM Standards*, Vol. 05.03.

[5] *Annual Book of ASTM Standards*, Vol. 03.06.

7. Apparatus

7.1 *Mid-IR Spectrometric Analyzer (of one of the following types)*:

7.1.1 *Filter-based Mid-IR Test Apparatus*—The type of apparatus suitable for use in this test method minimally employes an IR source, an infrared transmission cell or a liquid attenuated total internal reflection cell, wavelength discriminating filters, a chopper wheel, a detector, an A-D converter, a microprocessor, and a method to introduce the sample. The frequencies and bandwidths of the filters are specified in Table 1.

7.1.2 *Fourier Transform Mid-IR Spectrometer*—The type of apparatus suitable for use in this test method employs an IR source, an infrared transmission cell or a liquid attenuated total internal reflection cell, a scanning interferometer, a detector, an A-D converter, a microprocessor, and a method to introduce the sample. The following performance specifications (through the ATR cell) must be met:

scan range	4000 to 600 cm^{-1}
resolution	4 cm^{-1}
S/N at 674 cm^{-1}	>300:1 RMS

The signal to noise level will be established by taking a single beam spectrum using air or nitrogen as the reference and declaring that spectrum as the background. The background single beam spectrum obtained can be the average of multiple FTIR scans, but the total collection time shall not exceed 60 s. If interference from water vapor or carbon dioxide is a problem, the instrument shall be purged with dry air or nitrogen. A subsequent single beam spectrum shall be taken under the same conditions and ratioed to the background spectrum. The RMS noise of the ratioed spectra, the 100 % line, shall not exceed 0.3 % transmittance in the region from 700 to 664 cm $^{-1}$.

7.2 *Absorption Cell*— The absorption cell can be either transmission or attenuated total reflectance.

7.2.1 *Transmission Cells*, shall have windows of potassium bromide, zinc selenide, or other material having a significant transmission from 712 cm^{-1} to 660 cm $^{-1}$. The cell path length of the transmission cell shall be 0.025 (+/–0.005) mm. The use of a wedged transmission cell with the same nominal path length is acceptable.

7.2.2 *Attenuated Total Reflectance (ATR) Cells*, shall have the following specifications:

TABLE 1 Specification for Filters Used in Filter-based Mid-IR Test

Center Wavenumber (+/− 0.15 % of wavenumber)	Bandwidth (in wavelength units) (full width at half height)
673 cm^{-1}	1 % of λ_c
729 cm^{-1}	1 % of λ_c
769 cm^{-1}	1 % of λ_c
1205 cm^{-1}	1 % of λ_c
1054 cm^{-1}	1 % of λ_c
1188 cm^{-1}	1 % of λ_c
1117 cm^{-1}	1 % of λ_c

ATR element material	ZnSe
beam condensing optics	conical, non-focussing optics integral to cell body
element configuration	circular cross section with coaxial conical ends
cone half angle	60°
element length	1.55 in.
element diameter	0.125 in.
angle of incidence at sample interface	53.8°
maximum range of incidence angles	+/– 1.5°
standard absorbance (1428 cm−1 band of acetone)	0.38 +/– 0.02 AU
material of construction	316 stainless steel
seals	Chemraz or Kalraz o-rings

8. Reagents and Materials (see Note 1 and Note 2)

8.1 *Standards for Calibration, Qualification, and Quality Control Check Standards*—Use of chemicals of at least 99 % purity, where available, for quality control checks is required when preparing samples.

8.1.1 *tert*-Amyl methyl ether, TAME [994-05-8].

8.1.2 Benzene [1076-43-3].

8.1.3 *tert*-Butyl ethyl ether, ETBE [637-92-3].

8.1.4 *tert*-Butyl methyl ether, MTBE [1634-04-4].

8.1.5 1,3 Dimethylbenzene (*m*-xylene).

8.1.6 Ethanol [64-17-5].

8.1.7 Ethylbenzene [100-41-4].

8.1.8 3–Ethyltoluene [620-14-4].

8.1.9 Heavy aromatic/reformate petroleum stream (high boiling cut: IPB of 150 +/− 5° C and EP of 245 +/− 8° C) certified to contain less than 0.025 % benzene (an absorbance of less than 0.03 at 675 cm^{-1} using a 0.2 mm cell and a baseline between approximately 680 cm^{-1} and 670 cm^{-1}) [64741-68-0].

8.1.10 Hexane (an absorbance versus water of less than 0.1 at 250 nm using a 1cm cell) [110-54-3].

8.1.11 2,2,4-Trimethylpentane (*iso*octane) [540-84-1].

8.1.12 Pentane (an absorbance versus water of less than 0.1 at 250 nm using a 1 cm cell) [109-66-0].

8.1.13 Propylbenzene [103-65-1].

8.1.14 Toluene [108-88-3].

8.1.15 1,3,5-Trimethylbenzene (mesitylene) [108-67-8].

8.1.16 *m*-Xylene [108-38-3].

NOTE 1—**Warning:** These materials are flammable and may be harmful if ingested or inhaled.

NOTE 2—Only some of the reagents are required in each calibration or qualification procedure.

9. Sampling and Sample Handling

9.1 *General Requirements*:

9.1.1 The sensitivity of the measurement of benzene to the loss of benzene or other components through evaporation and the resulting changes in composition is such that the utmost precaution and the most meticulous care in the drawing and handling of samples is required.

9.1.2 Fuel samples to be analyzed by the test method shall be sampled using procedures outlined in Practices D 4057, D 4177, or D 5842, where appropriate. Do not use the "Sampling by Water Displacement." With some alcohol containing samples, the alcohol will dissolve in the water phase.

9.1.3 Protect samples from excessive temperatures prior to testing. This can be accomplished by storage in an appropriate

ice bath or refrigerator at 0 to 5°C.

9.1.4 Do not test samples stored in leaky containers. Discard and obtain a new sample if leaks are detected.

9.2 *Sample Handling During Analysis:*

9.2.1 When analyzing samples by the mid infrared apparatus, the sample must be between a temperature of 15 to 38° C. Equilibrate all samples to the temperature of the laboratory (15 to 38°C) prior to analysis by this test method.

9.2.2 After analysis, if the sample is to be saved, reseal the container and store the sample in an ice bath or a refrigerator at 0 to 5°C.

10. Calibration and Standardization of the Apparatus

10.1 *Calibration Matrix*—Calibration standards shall be prepared in accordance with Practice D 4307 or appropriately scaled for larger blends and Practices D 5842 and D 5854, where appropriate. Whenever possible, use chemicals of at least 99 % purity. To minimize the evaporation of light components, chill all chemicals and fuels used to prepare standards.

10.1.1 *Calibration Matrix for Filter Based Mid IR Instruments*—Prepare the set of calibration standards as defined in Table 2.

TABLE 2 Filter Based Mid IR Instrument Calibration Sample Set (mass %)

Sample	Benzene	Toluene	Xylenes	Hvy. Ref.[A]	MTBE	EtOH	TAME	ETBE	Isooctane	C_5 C_6[B]
1	0.00	2.50	12.5	5.00	0.00	00.0	20.0	0.00	30.0	30.0
2	0.00	2.50	25.0	2.50	0.00	0.00	0.00	0.00	35.0	35.0
3	0.00	5.00	7.50	10.0	1.00	0.00	2.50	15.0	25.0	34.0
4	0.00	12.5	12.5	3.00	20.0	0.00	2.50	0.00	25.0	24.5
5	0.00	20.0	10.0	1.00	0.00	10.00	0.00	0.00	25.0	34.0
6	0.00	25.0	7.50	2.50	0.00	0.00	0.00	0.00	40.0	25.0
7	0.00	25.0	2.50	7.50	0.00	4.00	0.00	0.00	20.0	41.0
8	0.25	0.00	10.0	5.00	0.00	0.00	0.00	20.00	25.0	39.75
9	0.25	2.50	6.00	2.50	0.00	0.00	0.00	0.00	35.0	53.75
10	0.25	4.75	15.0	1.00	0.00	7.50	0.00	0.00	25.0	46.50
11	0.25	10.0	0.00	10.0	15.00	0.00	0.00	0.00	30.0	34.75
12	0.25	14.0	7.50	3.00	0.00	5.00	0.00	0.00	30.0	40.25
13	0.50	2.50	12.5	5.00	5.00	0.00	5.00	5.00	20.0	44.5
14	0.50	5.00	10.0	2.00	0.00	0.00	0.00	0.00	30.0	42.5
15	0.50	6.00	7.50	7.50	0.00	0.00	20.0	0.00	25.0	33.5
16	0.50	10.0	15.0	2.50	0.00	12.5	0.00	0.00	25.0	34.5
17	0.50	12.5	4.00	7.50	0.00	0.00	0.00	20.0	20.0	35.5
18	0.50	25.0	10.0	1.00	0.00	0.00	0.00	0.00	25.0	38.5
19	0.75	5.00	25.0	1.00	0.00	0.00	0.00	0.00	30.0	38.25
20	0.75	10.0	10.0	5.00	0.00	0.00	0.00	0.00	30.0	44.25
21	0.75	12.5	0.00	10.0	0.00	5.00	0.00	0.00	35.0	36.75
22	0.75	12.5	12.5	1.00	0.00	0.00	0.00	0.00	30.0	43.25
23	0.75	25.0	20.0	10.0	0.00	0.00	0.00	0.00	14.25	30.0
24	1.00	15.00	25.0	1.00	7.50	0.00	15.0	2.50	10.0	23.0
25	1.00	5.00	7.50	10.0	0.00	2.00	0.00	0.00	35.0	39.5
26	1.00	7.50	10.0	7.50	20.00	0.00	0.00	0.00	20.0	34.0
27	1.00	10.0	10.0	5.00	0.00	10.0	0.00	0.00	30.0	34.0
28	1.00	15.0	2.00	2.5	15.0	0.00	2.50	7.50	20.0	37.0
29	1.00	25.0	20.0	0.00	0.00	0.00	0.00	0.00	25.0	29.0
30	1.50	5.00	15.0	5.00	5.00	0.00	10.00	5.00	20.0	33.5
31	1.50	15.0	15.0	1.00	0.00	0.00	5.00	20.0	20.0	22.5
32	1.50	15.0	15.0	1.00	0.00	0.00	0.00	0.00	30.0	37.5
33	1.50	10.0	5.00	7.50	0.00	7.50	0.00	2.50	25.0	41.0
34	1.50	25.0	10.0	0.00	0.00	0.00	0.00	0.00	25.0	38.5
35	2.00	5.00	7.50	2.50	7.50	0.00	2.50	2.00	30.0	41.0
36	2.00	5.00	20.0	0.00	0.00	0.00	0.00	0.00	30.0	43.0
37	2.00	12.5	12.5	5.00	0.00	8.00	0.00	0.00	25.00	35.0
38	2.00	25.0	5.00	3.00	20.00	0.00	0.00	0.00	20.0	25.0
39	2.00	25.0	20.0	0.00	0.00	0.00	0.00	0.00	20.0	33.0
40	2.50	0.00	15.0	2.50	0.00	0.00	15.0	0.00	25.0	40.0
41	2.50	5.00	5.00	10.0	15.0	0.00	0.00	0.00	25.0	37.5
42	2.50	15.0	0.00	7.50	0.00	10.0	0.00	0.00	30.0	35.0
43	2.50	10.0	15.0	2.5	0.00	0.00	0.00	15.0	25.0	30.0
44	2.50	20.0	20.0	3.00	0.00	0.00	0.00	0.00	25.0	29.5
45	3.00	5.00	25.0	5.00	0.00	0.00	7.50	7.50	20.0	27.0
46	3.00	10.0	15.0	5.00	0.00	7.50	0.00	7.50	20.0	32.0
47	3.00	15.0	5.00	2.00	2.50	0.00	10.0	2.50	25.0	35.0
48	3.00	20.0	20.0	5.00	0.00	0.00	0.00	0.00	25.0	27.0
49	3.00	25.0	10.0	2.00	0.00	0.00	0.00	0.00	30.0	30.0
50	4.00	0.00	20.0	2.50	0.00	5.00	0.00	0.00	25.0	43.5
51	4.00	2.50	5.00	10.0	5.00	0.00	5.00	5.00	25.0	38.5
52	4.00	15.0	2.50	5.00	2.00	10.0	2.00	0.00	20.0	39.5
53	4.00	20.0	15.0	2.00	0.00	0.00	0.00	0.00	25.0	34.0

TABLE 2 *Continued*

Sample	Benzene	Toluene	Xylenes	Hvy. Ref.[A]	MTBE	EtOH	TAME	ETBE	Isooctane	C_5 C_6[B]
54	4.00	25.0	20.0	1.00	0.00	0.00	0.00	0.00	25.0	25.0
55	5.00	5.00	25.00	4.00	0.00	0.00	0.00	0.00	25.0	36.0
56	5.00	7.50	5.00	7.50	0.00	0.00	0.00	15.0	25.0	35.0
57	5.00	12.5	12.5	2.50	15.0	0.00	0.00	0.00	20.0	32.5
58	5.00	20.0	5.00	5.00	0.00	5.00	0.00	0.00	25.0	35.0
59	5.00	20.0	2.50	2.50	0.00	0.00	7.50	0.00	25.0	37.5
60	5.00	25.0	20.0	0.00	0.00	0.00	0.00	0.00	20.0	30.0

[A]Heavy reformate petroleum stream
[B]50 volume % pentane in hexane

10.1.1.1 Measure the density for each of the calibration standards according to either Practice D 1298 or Test Method D 4052.

10.1.1.2 For each of the calibration standards, convert the mass % benzene to volume % benzene according to the equation presented in 13.1.

10.1.2 *Calibration Matrices for FTIR Instruments Using a PLS Calibration*— To obtain the best precision and accuracy of calibration, prepare two benzene calibration sets as set forth in Table 3 and Table 4. The first set (Set A) has 35 samples with benzene concentrations between 0 to 1.5 mass %. The second set (Set B) has at least 25 samples with benzene concentrations between 1 to 6 mass %. Each of the subsets in Set B shall have a minimum of five samples with the benzene concentration evenly spaced over the 1 to 6 mass % range.

10.1.2.1 Measure the density for each of the calibration standards according to either Practice D 1298 or Test Method D 4052.

TABLE 3 FTIR Instruments PLS Calibration Sample Set A (mass %)

Sample	Benzene (mass %)	Toluene (mass %)	Mixed Xylenes (mass %)	Isoctane (mass %)
1	0	0	0	100
2	0	7	0	93
3	0	14	0	86
4	0	21	0	79
5	0	15	15	70
6	0.25	0	0	99.75
7	0.5	0	0	99.5
8	0.75	0	0	99.25
9	1	0	0	99
10	1.25	0.	0	98.75
11	1.5	0	0	98.5
12	0.25	7	0	92.75
13	0.5	7	0	92.5
14	0.75	7	0	92.25
15	1	7	0	92
16	1.25	7	0	91.75
17	1.5	7	0	91.5
18	0.25	14	0	85.75
19	0.5	14	0	85.5
20	0.75	14	0	85.25
21	1	14	0	85
22	1.25	14	0	84.75
23	1.5	14	0	84.5
24	0.25	21	0	78.75
25	0.5	21	0	78.5
26	0.75	21	0.	78.25
27	1	21	0	78
28	1.25	21	0	77.75
29	1.5	21	0	77.5
30	0.25	15	15	69.75
31	0.5	15	15	69.5
32	0.75	15	15	69.25
33	1	15	15	69
34	1.25	15	15	68.75
35	1.5	15	15	68.5

TABLE 4 FTIR Instruments PLS Calibration Sample Set B (mass %)

Subset (minimum 5 samples) in each subset)	Benzene (mass %)	Toluene (mass %)	Mixed Xylenes (mass %)	Isooctane (mass %)
Subset 1	1–6	0	0	to 100 %
Subset 2	1–6	7–9	0	to 100 %
Subset 3	1–6	14–17	0	to 100 %
Subset 4	1–6	21–25	0	to 100 %
Subset 5	1–6	15–18	15–18	to 100 %

10.1.2.2 For each of the calibration standards, convert the mass % benzene to volume % benzene according to the equation presented in 13.1. If the densities of the calibration standards can not be measured, it is acceptable to convert to volume % using the densities of the individual components measured using Practice D 1298 or Test Method D 4052.

10.1.3 *Calibration Matrix for FTIR Instruments Using Classical Least Squares Peak Fitting Calibration*—Prepare a benzene calibration set as detailed in Table 5. The set has samples with benzene concentrations between 0 to 6 mass %.

10.1.4 *Background Correction Mixtures for FTIR Instruments Using Classical Least Squares Peak Fitting Calibration* —Prepare one mixture containing 80 mass % hexane and 20 mass % of the respective aromatic for each of the six substances (toluene, 1,3-dimethylbenzene, 3–ethyltoluene, 1,3,5-trimethylbenzene, ethylbenzene, and propylbenzene) as set forth in Table 6.

TABLE 5 FTIR Instruments Calibration (Classical Least Squares Peak Fitting) Sample Set (mass %)

Sample	Benzene	Toluene	Isooctane
1	0	5	95
2	0	15	85
3	0.5	5	94.5
4	0.5	15	84.5
5	1	5	94
6	1	15	84
7	1.5	5	93.5
8	1.5	15	83.5
9	2	5	93
10	2	15	83
11	3	5	92
12	3	15	82
13	4	5	91
14	4	15	81
15	5	5	90
16	5	15	80
17	6	5	89
18	6	15	79