Designation: D7753 − 12 (Reapproved 2016)

Standard Test Method for Hydrocarbon Types and Benzene in Light Petroleum Distillates by Gas Chromatography[1]

This standard is issued under the fixed designation D7753; 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 and provides for the quantitative determination of total saturates, total olefins, total aromatics and benzene in light petroleum distillates having a final boiling point below 215 °C by multidimensional gas chromatography. Each hydrocarbon grouping as well as benzene can be reported in both volume and mass percent.

1.2 This test method is applicable to light petroleum distillates such as oxygenate-free motor gasoline or spark ignition fuels, naphthas and hydrocarbon solvents over the content ranges from 1 % (V/V) to 70 % (V/V) total olefins, 1 % (V/V) to 80 % (V/V) total aromatics and 0.2 % to 10 % (V/V) benzene. This test method may apply to concentrations outside these ranges, but the precision has not been determined. Interlaboratory testing for precision used full range blending streams, such as FCC, reformates and spark ignition fuel or blended motor gasolines.

1.3 This test method is not intended to determine oxygenated components. Light petroleum distillate products such as motor gasoline may contain oxygenates. Oxygenates such as methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), ethyl *tert*-butyl ether (ETBE), ethanol and methanol etc. will coelute with specific hydrocarbon groups. If there is any suspicion the sample contains oxygenates, the absence of oxygenates should be confirmed by other standard test methods such as Test Methods D4815, D5599, or D6839 before using this test method.

1.4 This test method is not applicable for the determination of individual hydrocarbon components with the exception of benzene. Test Method D6733 may be used to determine a large number of individual hydrocarbons to complement this test method.

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

1.6 *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:*[2]

D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography

D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

D6733 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 50-Metre Capillary High Resolution Gas Chromatography

D6839 Test Method for Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *aromatics, n*—mass or volume % of monocyclic aromatics and polycyclic aromatics (for example, naphthalenes), aromatic olefins and C_8^+ cyclodienes compounds.

3.1.2 *C_7^+ aromatics, n*—mass or volume % of all other aromatics compounds (see 3.1.1) in sample not including benzene.

3.1.3 *olefins, n*—mass or volume % of alkenes, plus cycloalkenes and some di-olefins.

3.1.4 *olefins trap, n*—specific column utilized to selectively retain olefins from mixture of olefins and saturates. The trap must have good reversibility to capture and release olefins by changing the temperature.

3.2 *Acronyms:*

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[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.

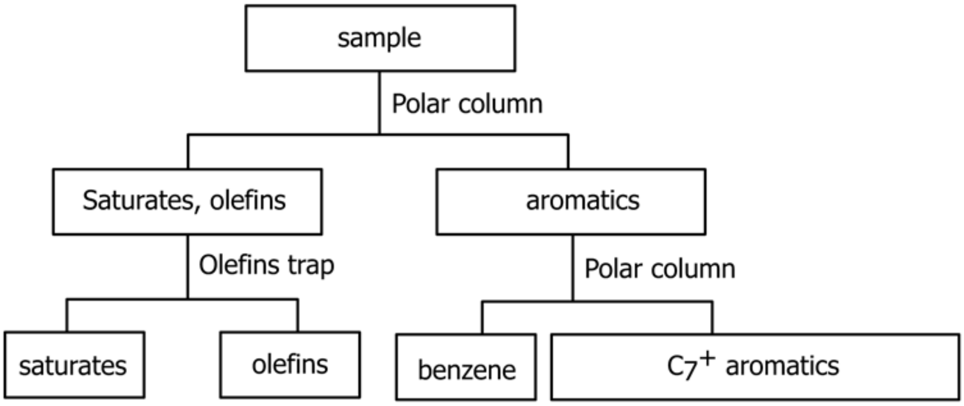


FIG. 1 Separation Scheme of Hydrocarbon Types and Benzene Analysis

3.2.1 *BCEF- N,N-bis(α-cyanoethyl) formamide*—gas chromatography stationary phase.

4. Summary of Test Method

4.1 Fig. 1 shows a separation scheme of the various hydrocarbon types and benzene analysis. The instrumental configuration is shown in Fig. 2. The valves are actuated at predetermined times to direct different components to different columns. As the analysis proceeds, different hydrocarbon types and benzene elute and are detected by a flame ionization detector (FID).

4.2 The mass concentration of different hydrocarbon types and benzene are determined by the application of average relative response factors to the areas of the detected peaks followed by normalization to 100 %.

4.3 The volume percent concentration of different hydrocarbon types and benzene can be determined by the application of average density factors to the calculated mass concentration of the detected peaks followed by normalization to 100 %.

4.4 This test method is not intended to determine compounds that contain oxygenates, such as ethanol, etc. Such oxygenates interfere with the analysis of the hydrocarbons.

4.5 Analysis time of a sample is approximately 15 min.

5. Significance and Use

5.1 Knowledge of the olefinic, aromatic, and benzene content is very important in quality specifications of petroleum products, such as spark ignition fuels (gasoline) and hydrocarbon solvents. Fast and accurate determination of hydrocarbon types and benzene of petroleum distillates and products is also important in optimization of process units.

5.2 This test method provides a fast standard procedure for determination of hydrocarbon types and benzene in light oxygenate-free petroleum distillates and products.

6. Interferences

6.1 C_{12}^+ aliphatic hydrocarbon compounds (not including C_{12}) may not be fully separated from benzene in the polar column, thus the determination of aromatics and benzene may be affected.

6.2 Different types of oxygenated compounds in some petroleum products will elute with specific hydrocarbon groups and interfere with the analysis of the hydrocarbons.

6.3 Commercial detergent, antioxidant, antiknock additives and dyes utilized in some petroleum products have been found not to interfere with this test method.

6.4 Dissolved water in samples has been found not to interfere with this test method.

7. Apparatus

7.1 The analysis system is comprised of a gas chromatograph with manual or automated sample injection, and specific hardware modifications. These modifications include columns, olefins trap, valves, and temperature controllers.

7.2 *Gas Chromatograph*—capable of temperature programmed operation at specified temperature, equipped with a vaporization inlet that can be a packed column inlet, a flame ionization detector (FID), and necessary flow controllers.

7.3 *Sample Introduction System*—manual or automatic injector, capable of injecting a 0.1 µL volume of sample. Automated injector is recommended.

7.4 *Gas Flow or Pressure Controllers*—with adequate precision to provide reproducible flow rate of carrier gas to the chromatographic system, hydrogen and air for the flame ionization detector. Control of air pressure for automated valves operation is required.

7.5 *Data Acquisition System*—chromatographic workstation shall meet the following specifications:

7.5.1 Sampling rate of at least 10 points per second.

7.5.2 Capacity for 100 peaks for each analysis.

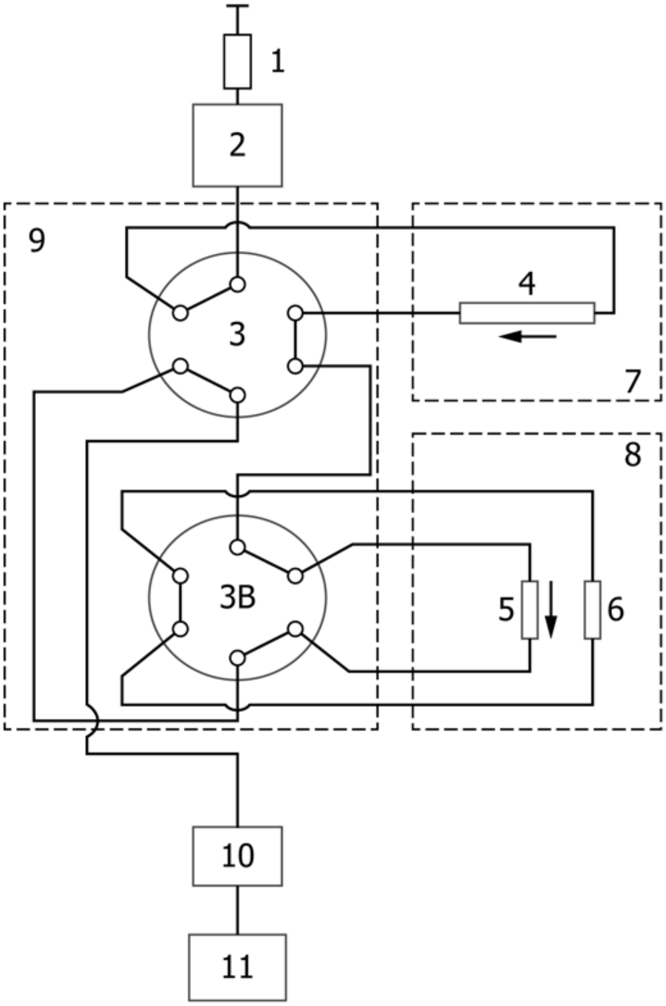
7.5.3 Normalized areas percent calculation with response factors.

7.5.4 Area summation of peaks that are split or of groups of components that elute at specific retention times.

7.5.5 Noise and spike rejection capability.

7.5.6 Manual baseline adjusting function, as required.

7.6 *Valves*—column and trap switching, automated rotary valves are recommended.



NOTE 1—Legend:
1—injector
2—vaporization room
3, 3B—valve 1
4—polar column
5—olefins trap
6—balance column
7—polar column oven 1
8—olefins trap oven
9—valves oven
10—FID
11—data processing unit

FIG. 2 Configuration of Analytical System

7.7 *Gas Purifiers*—to remove moisture and oxygen from carrier gas.

7.8 *Temperature Controllers*—the independent temperature control of the polar column, olefins trap, switching valves and sample connecting lines is required. All of the system components that contact the sample should be heated to a temperature that will prevent condensation of any sample component. Table 1 lists the system components and approximate operating temperatures. Some of the components operate isothermally, while others require temperature programming. Temperature control may be by any means that will meet the requirements listed in Table 1.

TABLE 1 Temperature Control Ranges of System Components

Component	Typical Operating Temperature, °C	Heating Mode
Polar Column	100~120	isothermal
Olefin Trap	125~210	temperature programmed ~40°C/min
Switching Valves	100~140	isothermal
Sample Lines	100~140	isothermal

8. Reagents and Materials

8.1 *Gases:*

8.1.1 *Carrier Gas*—Nitrogen or Helium. ILS precision of this test method was obtained using nitrogen as the carrier gas.

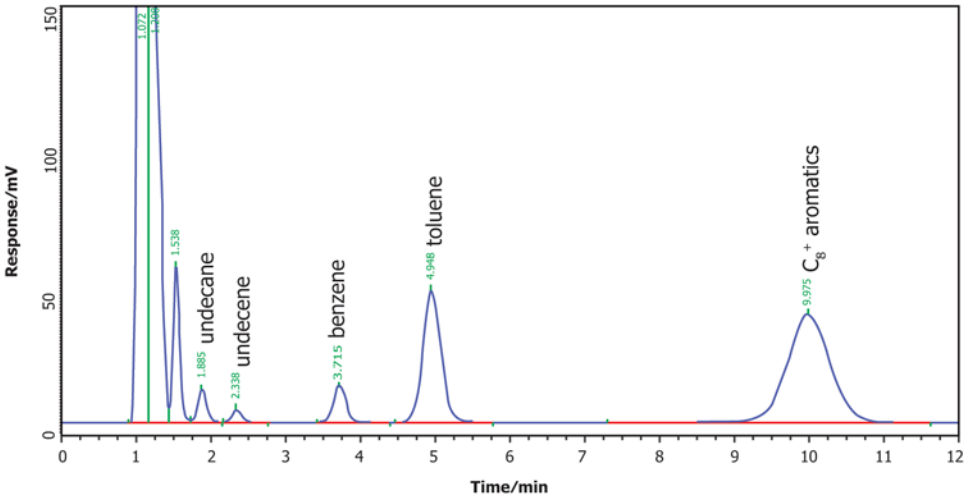


FIG. 3 Polar Column Separation Performance Check Chromatogram

Better than 99.999 % pure. (**Warning—**Compressed gases under high pressure.) Gas purifiers may be used to attain the required purity or to ensure a stable signal baseline.

8.1.2 *Hydrogen*—Better than 99.999 % pure. (**Warning—**Extremely flammable gas under high pressure.) Gas purifiers may be used to attain the required purity or to ensure a stable signal baseline.

8.1.3 *Air, Compressed*—<10 mg⁄kg each of total hydrocarbons and H_2O. (**Warning—**Compressed gas under high pressure that supports combustion.) Gas purifiers may be used to attain the required purity or to ensure a stable signal baseline.

8.2 *Columns and Traps*—This test method requires the use of a polar column and a reversible olefin trap. The following contains guidelines that are to be used to judge column and trap suitability. The guidelines describe temperatures as used in the current system. Alternatives can be used provided that the separation requirement as described is obtained.

8.2.1 *Polar Column*—At an optimal operating temperature, the column should meet the baseline separation between benzene and aliphatic components up to undecene; between toluene and benzene. The system validation test sample can be used to check the polar column separation performance. The retention time ratio of undecene and benzene ($t_{benzene}/t_{undecene}$) shall be larger than 1.5, the resolution shall be >2.0. The retention time ratio of benzene and toluene ($t_{toluene}/t_{benzene}$) shall be larger than 1.25, the resolution shall be >1.1 (see Note 1). A BCEF column which is 25 % BCEF coated on acid washing diatomite supporter is recommended as the polar column. The length of the polar column is approximately 5 m and the inside diameter is approximately 2 mm. Other columns which meet the separation requirements can be used. Fig. 3 is a polar column separation performance check chromatogram with system validation test sample.

$$t_{benzene}/t_{undecene} = 1.59$$
$$R_{benzene}/t_{undecene} = 2.4$$
$$t_{toluene}/t_{benzene} = 1.31$$
$$R_{toluene}/t_{benzene} = 1.25$$

NOTE 1—

$$R_S = \frac{2(t_{R2} - t_{R1})}{W_{b2} + W_{b1}} \doteq \frac{(t_{R2} - t_{R1})}{W_{b1}}$$

where: $t_{R2} > t_{R1}$

8.2.2 *Olefin Trap*—The olefin trap shall have excellent reversibility performance. At a lower temperature, for example, 130 °C, the trap shall retain the olefins in the sample and pass all saturates before benzene elutes from the polar column. At a higher temperature, for example, 210 °C, the trap shall quantitatively release the retained olefins. The adsorbent of olefins usually is a silver ion based material. Any olefin trap which satisfies the performance requirements can be used. The performance of the trap can be verified first with the system validation test sample (10.2) and, once established, can be monitored either with the validation test sample or actual production or consensus reference quality sample.

8.3 *System Gravimetric Validation Test Sample*—Quantitative mixtures of pure hydrocarbons are used to verify the operating temperature, valve switching times and validation of the system analysis accuracy. The validation sample composition and approximate component concentrations are shown in Table 2.

8.4 *Quality Control Samples*—Production or consensus samples, or both, used to routinely monitor validation of analysis system. Any production or interlaboratory or certified reference sample which approximates similar compositions to the samples to be analyzed may be designated as the quality control sample. Quality control samples shall be selected such that they fall within the range and composition of samples to be analyzed. The quality control samples shall be stable for a specified period of use and storage conditions. It is preferred that the quality control samples be ampoulized to safeguard their composition integrity.

9. Preparation of Apparatus

9.1 The configuration of the analyzer system is shown in Fig. 1. Some system modules may have independent temperature controlled components. If using a commercial analyzer,

TABLE 2 System Validation Test Sample

Type	Component	Approximate Concentration, Mass %
Saturates	Pentane	5.0
	Hexane	4.5
	Cyclohexane	4.0
	Heptane	4.5
	Methylcyclohexane	4.0
	Octane	4.0
	2,2,4-Trimethylpetane	6.0
	Dimethylcyclohexane	3.0
	Nonane	3.0
	Decane	2.5
	Undecane	1.5
Olefins	Pentene	5.0
	Hexene	6.0
	Heptene	5.0
	Octene	3.5
	Nonene	2.5
	Decene	2.0
	Undecene	1.0
Aromatics	Benzene	1.0
	Toluene	5.0
	Dimethylbenzene	8.0
	Ethylbenzene	5.0
	Propylbenzene	4.0
	Trimethylbenzene	6.0
	Tetramethylbenzene	4.0
Type Totals		100
Saturates		42.0
Olefins		25.0
Benzene		1
Aromatics	(including benzene)	33.0

consult the manufacturer's instructions or guidelines for preparation of the instrument.

9.2 All supply gas pressure shall be adequate to ensure proper mass flow control and air or nitrogen actuated valve operation. The approximate supplying gas pressure values are listed in Table 3.

9.3 Impurities in the carrier gas will have a detrimental effect on the performance of column and olefin trap. Therefore, appropriate gas purifiers shall be installed to ensure good quality gases.

9.4 The system validation test sample or quality control sample can be used to determine the valve switching times. The olefins trap temperature is determined in order to meet the retention requirement for olefins. The approximate instrument operating conditions are listed in Table 4.

TABLE 3 Supply Gas Pressure

Gas	Pressure, MPa
Carrier gas	0.35
Hydrogen	0.3
Air (FID)	0.35
Air (Valve)	0.35

TABLE 4 Chromatographic Operating Conditions

Condition	Parameter
Vaporization temperature, °C	200
Polar column temperature, °C	110
Olefins trapped temperature, °C	...
Olefins desorption temperature, °C	200~220
Column Switching valves	100-140
Sample lines	100-140
Carrier gas flow rate, mL/min (Nitrogen or helium)	25~30
Detector gas flow rate, mL/min	
Air	350~450
Hydrogen	30~35
Sample charged, µL	0.1
Valve actuated pressure, kPa	250~300

10. System Checks and Standardization

10.1 *Instrument System Reliability Checking*—The checking of the analytical system is very important to ensure test results reliability. The following gives a guideline:

10.1.1 Use the system gravimetric validation test sample in 8.3 to establish the quantitative performance of the system. The standard is used during setting up the instrument and periodically afterwards to verify its performance. The required absolute deviation between obtained results and blending concentration values as specified in Table 2 is 1.6 % for total saturates, 1.2 % for total olefins, 1.4 % for total aromatics, and 0.05 % for benzene.

10.1.2 *Quality Control (QC) Sample*—Preferably from similar production, or from an interlaboratory study or equivalent, or a combination thereof. Such quality control samples is used to routinely monitor the operation of the chromatographic system and verify that reported concentrations are within the precision of the test method. The quality sample shall be analyzed for each batch of samples. Depending on the range and composition of the samples to be analyzed, more than one quality control sample may be necessary. The QC sample shall be of sufficient volume to provide an ample supply for the intended period of use and it shall be homogeneous and stable under the anticipated storage conditions. The quality control sample should have similar composition and hydrocarbon distribution as the sample with highest olefin concentration routinely analyzed to safeguard against potential olefin breakthrough from the olefin trap. The sample is analyzed using procedure described in 11.3 and monitored by SQC.

10.2 *Olefin Trap Performance Checking*—The olefin trap is one of the most critical parts in the test system. If the olefin trap is ineffective or cannot meet the performance requirements, the test results will be significantly affected. The gravimetric validation test mixture and a quality control sample as described in 10.1.1. can be used to check the olefin trap performance.

10.2.1 *Saturates Delay Checking*—Saturates in the sample should pass through the olefin trap before benzene elutes from the polar column. Usually, the olefin adsorbent in the trap has slight delay effect on the saturates. If the delay effect of the olefin trap is obvious, some of the long chain saturates in sample may be remained in the olefin trap. Therefore, a system validation sample or quality control sample should be used to determine whether some saturates are remained in the trap. Fig. 4 is a chromatogram of the system gravimetric validation sample. To ensure all saturates pass through the olefin trap, the retention time ratio of benzene and undecane ($t_{benzene}/t_{undecene}$) should be larger than 1.5 with the undecane passing through the olefin trap.

10.2.2 *Olefins Breakthrough Checking*—A reliable olefin trap shall ensure the olefins in the sample are retained in the

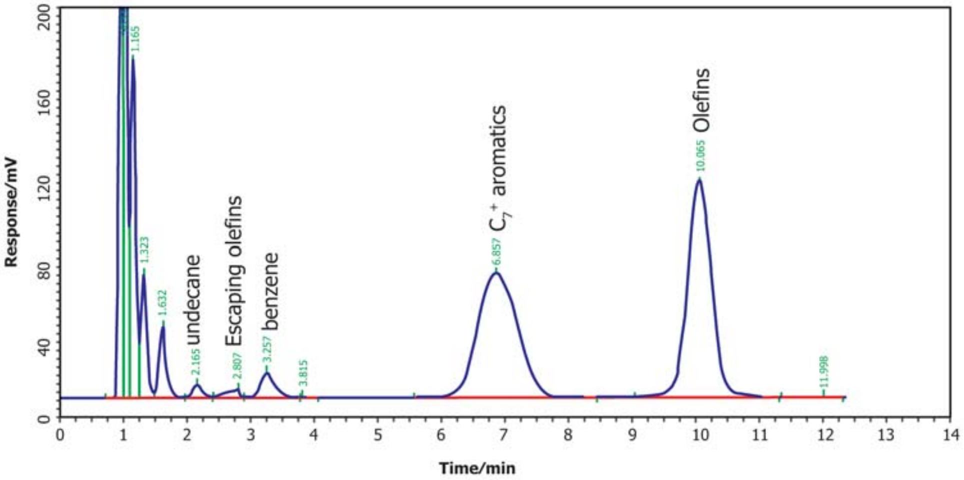


FIG. 4 Chromatogram of Quality Control Sample

trap before benzene elutes from the polar column. The quality control sample can be used to check the olefin trap performance. In routine chromatographic operation conditions, 0.1 µL quality control sample is injected into the chromatographic system. If the olefin trap is ineffective or does not meet the performance requirement, some olefins may elute or breakthrough from the trap. If the olefins are not fully retained in the trap, an olefins escaping peak might be observed. Escaping olefinic components can be located after the elution of undecane and before the olefin trap is closed. Fig. 5 is a typical chromatogram when escaping of the olefins occurs. Typically, when the performance of the olefin trap degrades or when the sample contains light (for example, C4, C5) olefin in high concentration, the breakthrough of the olefins may occur more readily, resulting in the co-elution with the saturates, thus making the olefin breakthrough impossible to recognize. Routine checking of the system with system gravimetric performance mixture *and* quality control sample(s) can identify poor olefin trap performance.

10.3 *Measuring Retention Time of Hydrocarbon Components*—When the analysis system is properly optimized, a quality control sample or actual test sample can be analyzed by the procedure given in Section 11. The typical retention times of hydrocarbon components are listed in Table 5. Fig. 4 is a chromatogram of production quality control sample.

11. Procedure

11.1 *Sample Preparation*—To avoid volatilization of light components in the sample, the samples should be refrigerated until ready to be transferred into vials and analyzed.

11.2 *Preparation of Analyzer*—Prior to analysis, verify the instrument parameters. The parameters include initial component temperatures, valve switching times and valves initial positions. Use quality control samples and mixtures to ensure proper operation prior to analysis of sample.

11.3 When all temperatures are stable at the prescribed analysis conditions, 0.1 µL representative sample is injected into analysis system. At the same time, temperature programming and the valve switching program are started, and the response signal of the FID is recorded by the data acquisition software. The detail analysis sequence is as follows:

11.3.1 After injecting the sample, the aliphatic (saturates plus olefins) components are separated from the aromatics in the polar column. As shown in Fig. 2, at the valve positions, all of the saturated aliphatic components are eluted from the polar column, pass through the olefin trap, and are then detected by the FID. The olefins portion of the aliphatic components is retained in the trap.

11.3.2 Before benzene elutes from the polar column, valve 3B is switched. The valves positions are shown in Fig. 6a. The olefins are trapped. Benzene elutes through the balance column and is detected by the FID.

11.3.3 After benzene has eluted and detected, valve 3 is switched. The valves positions are shown in Fig. 6b. The other aromatics (C_7^+ aromatics) are backflushed from polar column and detected by the FID.

11.3.4 After the C_7^+ aromatics are detected, valve 3B is switched again. The valves positions are shown in Fig. 6c. With the olefin trap temperature increased, the olefin components are desorbed from the trap and detected by the FID.

11.3.5 A typical chromatogram of gasoline sample is shown in Fig. 7.

11.3.6 The detected peaks are integrated, and from the resulting areas, the mass or volume concentrations are calculated and reported.

12. Calculation

12.1 The analysis results of benzene, total olefins, total aromatics and total saturates are reported in mass% and volume%.

12.2 Review the chromatogram to ensure that all peaks have been integrated correctly.

12.3 *Average Relative Response Factors for Hydrocarbon Types in Light Distillate Products*—The relative response factors for different carbon number hydrocarbon components are different. The relative FID response factor for a given carbon number and compound type can be quite similar for petroleum distillates. The average relative response factors to

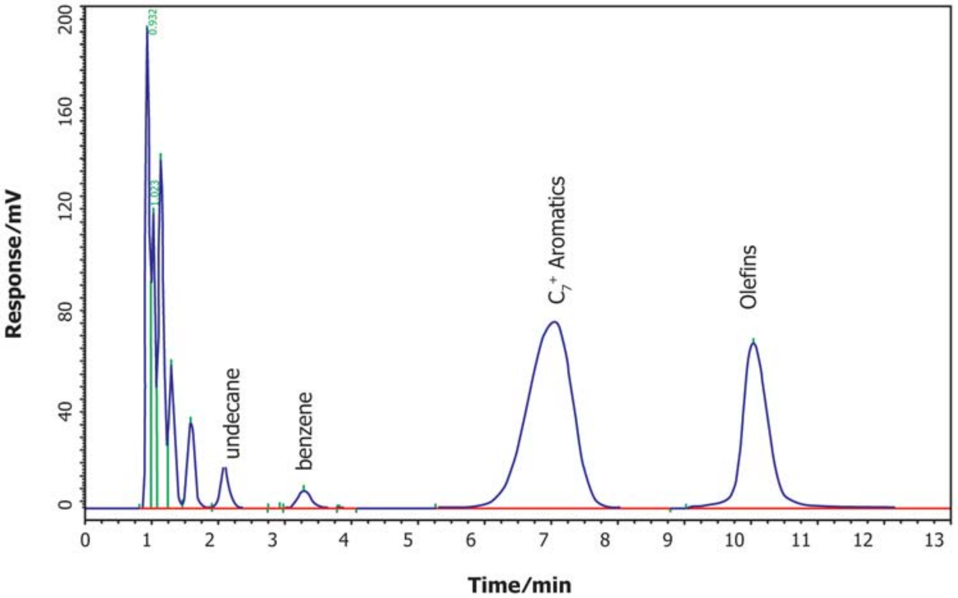


FIG. 5 Typical Chromatogram with Escaping Olefins

TABLE 5 Typical Different Hydrocarbon Components Retention Times

Hydrocarbon Component	Retention Time, min
Saturates	0.6~3.0
Benzene	3.0~4.0
C_7^+ Aromatics	5.0~8.0
Olefins	9.0~12.0

be used for full range gasoline distillate samples are given in Table 6. For other type of samples (for example, narrow cuts of naphthas, and solvents) deviating significantly from normal gasoline range carbon distributions (for example, C4 to C12), the average response factors for saturates, olefins and C_7^+ aromatics can be calculated by the method given in Annex A1 or determined experimentally through QC sample with similar known composition.

12.4 The mass% of saturates, olefins, aromatics and benzene in sample can be calculated using Eq 1.

$$m_i = \frac{P_i f_i}{\sum P_i f_i} \times 100 \quad (1)$$

where:

m_i = hydrocarbon component i mass%,
$P_i f_i$ = hydrocarbon component i peak area%,
f_i = hydrocarbon component i average relative response factor.

12.5 *Weighted Average Relative Density of Light Distillate Products*—The relative density of various hydrocarbon groups of same type in different carbon number ranges is not the same. Therefore, according to carbon number distribution of each hydrocarbon type, a weighted average relative density for each hydrocarbon type is calculated by the method given in Annex A2. The weighted average relative density values of different hydrocarbon types and benzene in full range gasoline distillates are given in Table 7. For samples having specific composition, the weighted relative density for saturates, olefins and C_7^+ aromatics can be calculated by the method given in Annex A2.

12.6 The volume% of saturates, olefins, aromatics and benzene in sample can be calculated using Eq 2.

$$V_i = \frac{P_i f_i / d_i}{\sum P_i f_i / d_i} \times 100 \quad (2)$$

where:

V_i = hydrocarbon component i volume%,
f_i = hydrocarbon component i average relative response factor,
P_i = hydrocarbon component i peak area%,
d_i = weighted average relative density of saturates, olefins and C_7^+ aromatics and relative density of benzene.

13. Report

13.1 Report the mass% and volume% for each hydrocarbon group type (saturates, olefins, aromatics, benzene).

13.2 Report the volume% or mass% for saturates, olefins and aromatics to the nearest 0.1 %.

13.3 Report the volume% or mass% for benzene to the nearest 0.01 %.

14. Precision and Bias[3]

14.1 *Precision*—The precision of any individual measurement of this test method depends on several factors including volatility, distillate range, blending compositions, concentration value, etc. Tables 8-10 present the repeatability and reproducibility of the test method.

14.1.1 *Repeatability*—The difference between two successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1738.

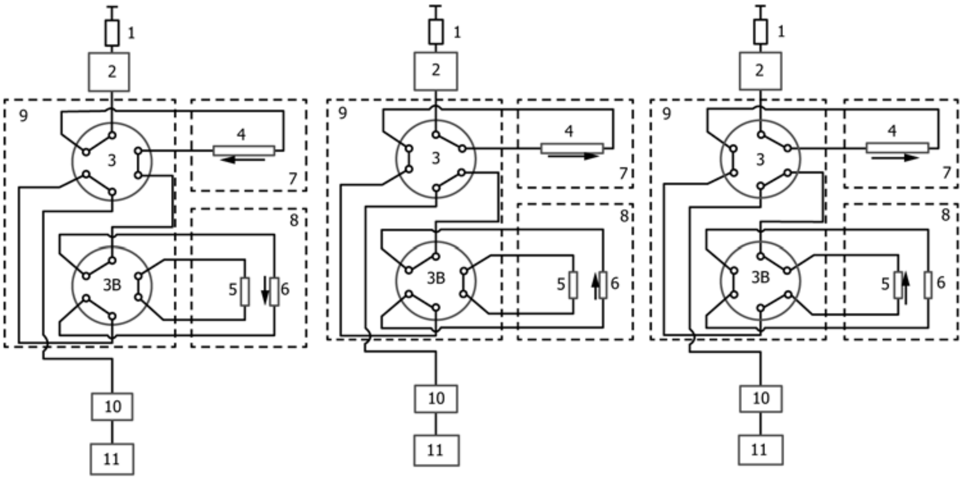

FIG. 6 Valves Positions During Analysis

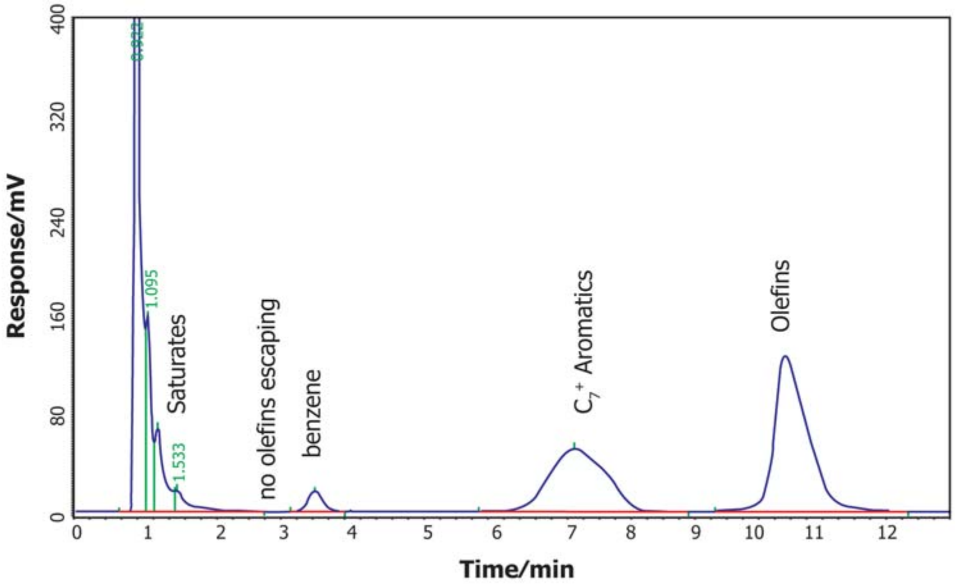

FIG. 7 Typical Gasoline Chromatogram

TABLE 6 Average Relative Response Factors in FID for Hydrocarbon Types

Hydrocarbon Types	Average Relative Response Factor
Saturates	0.889
Olefins	0.874
C_7^+ Aromatics	0.828
Benzene	0.811

TABLE 7 Weighted Average Relative Densities of Hydrocarbon Types

Hydrocarbon Components	Weight Average, Relative Density
Saturates	0.686
Olefins	0.688
C_7^+ Aromatics	0.870
Benzene	0.879

sample, in the long run, in the normal and correct operation of the test method, exceed the repeatability values given in Tables 8-10 only in one case in twenty.

14.1.2 *Reproducibility*—The difference between two single and independent test results, obtained by different operators working in different laboratories on identical sample, in the long run, in the normal and correct operation of the test method, exceed the reproducibility values given in Tables 8-10 only in one case in twenty.

14.2 *Bias*—No information can be presented on the bias of the procedure in this test method.

15. Keywords

15.1 aromatics; benzene; gas chromatography; gasoline; hydrocarbon type; light petroleum distillates; olefins; saturates; spark ignition fuel

TABLE 8 Repeatability and Reproducibility (Oxygenate-Free samples)[A]

Component	Repeatability, % (V/V)	Reproducibility, % (V/V)	Range, % (V/V)
Saturates	$0.37\ (98.3\ X)^{0.37}$	$0.43\ (98.3X)^{0.37}$	15~90
Olefins	$0.19\ X^{0.58}$	$0.23\ X^{0.58}$	1~70
Aromatics	$0.13\ X^{0.67}$	$0.16\ X^{0.67}$	1~80
Benzene	$0.0515\ X^{0.68}$	$0.0689\ X^{0.68}$	0.2~10
C_7^+ Aromatics	$0.17\ X^{0.62}$	$0.19\ X^{0.62}$	1~70

X is the mean of two results being compared, % (V/V).

[A] Precision data was obtained from interlaboratory study conducted in China using local full range process streams and blended gasolines containing no added oxygenates. Precision statement did not apply to solvents.

TABLE 9 Calculated Repeatability and Reproducibility at Various Levels (Oxygenate-Free samples)

Component	Concentration Level, % (V/V)	Repeatability, % (V/V)	Reproducibility, % (V/V)
Olefins	1	0.19	0.23
	5	0.48	0.58
	15	0.91	1.10
	25	1.23	1.49
	35	1.49	1.81
	40	1.61	1.95
	50	1.84	2.22

TABLE 10 Calculated Repeatability and Reproducibility at Various Levels (Oxygenate-Free samples)

Component	Concentration Level, % (V/V)	Repeatability, % (V/V)	Reproducibility, % (V/V)
Aromatics	5	0.38	0.47
	10	0.61	0.75
	20	0.97	1.19
	30	1.27	1.56
	40	1.54	1.89
Benzene	0.5	0.02	0.03
	1.0	0.05	0.07
	2.5	0.10	0.13
	5.0	0.15	0.21

ANNEXES

(Mandatory Information)

A1. CALCULATION OF AVERAGE RELATIVE RESPONSE FACTOR FOR HYDROCARBON TYPE

A1.1 Calculation of Response Factor Relative to Methane for Hydrocarbon Component

A1.1.1 According to Test Method D6839, the FID response factor relative to methane for each hydrocarbon component is calculated by Eq A1.1. The calculated results are listed in Table A1.1.

$$f^M = \frac{[(12.011 \times C_n) + (1.008 \times H_n)] \times 0.7487}{12.011 \times C_n} \qquad (A1.1)$$

where:

f^M = hydrocarbon component response factor relative to methane,
C_n = the number of carbon atoms in hydrocarbon compound,
H_n = the number of hydrogen atoms in hydrocarbon compound,
12.011 = carbon atomic mass,

TABLE A1.1 Calculated Relative Response Factors for Hydrocarbons

Carbon number	Paraffins, *P*	Naphthenes, *N*	Olefins, *O*	Aromatics, *A*
4	0.906	...	0.874	...
5	0.899	0.874	0.874	...
6	0.895	0.874	0.874	0.811
7	0.892	0.874	0.874	0.820
8	0.890	0.874	0.874	0.827
9	0.888	0.874	0.874	0.832
10	0.887	0.874	0.874	0.837
11^+	0.887	...	0.874	0.840

TABLE A1.2 Different Carbon Number Composition Distribution, % mass percent

Carbon number	Paraffins, *P*	Naphthenes, *N*	Olefins, *O*	Aromatics, *A*
4	P_4		O_4	
5	P_5	N_5	O_5	
6	P_6	N_6	O_6	A_6
7	P_7	N_7	O_7	A_7
8	P_8	N_8	O_8	A_8
9	P_9	N_9	O_9	A_9
10	P_{10}	N_{10}	O_{10}	A_{10}
11^+	P_{11^+}		O_{11^+}	A_{11^+}

1.008 = hydrogen atomic mass,
0.7484 = factor to normalize the result to a methane response of unity.

A1.2 Determination of Different Carbon Number Hydrocarbon components

A1.2.1 The content of each hydrocarbon type at different carbon numbers in the specific boiling range and composition of the sample can be determined by Test Method D6839. Test Method D6733 may be used for certain samples as described in the scope of Test Method D6733 and adhering to the limitations of such test method as described in its Scope. The results determined can be listed in form of Table A1.2.

A1.3 Calculation of Average Response Factor Relative to Methane for Each Hydrocarbon Type

A1.3.1 Calculate the paraffin average mass response factor relative to methane by Eq A1.2.

$$f_P^M = \frac{\sum_i P_i \cdot f_{Pi}^M}{P_T} \tag{A1.2}$$

where:

$f_P{}^M$ = the paraffins average mass response factor relative to methane,
P_i = paraffins mass percent, %, at the specific carbon number,
$f_{Pi}{}^M$ = paraffins mass response factor relative to methane, at the specific carbon number,
P_T = the sum of all paraffins in sample, mass percent, %.

A1.3.2 Calculate naphthenes average mass response factor relative to methane by Eq A1.3.

$$f_N^M = \frac{\sum_i N_i \cdot f_{Ni}^M}{N_T} \tag{A1.3}$$

where:

$f_N{}^M$ = the naphthenes average mass response factor relative to methane,
N_i = naphthenes mass percent, % , at the specific carbon number,
$f_{Ni}{}^M$ = naphtheness mass response factor relative to methane, at the specific carbon number
N_T = the sum of all naphthenes in sample, mass percent, %.

A1.3.3 Calculate the saturates average mass response factor relative to methane by Eq A1.4.

$$f_M^S = \frac{P_T \cdot f_P^M + N_T \cdot f_N^M}{S_T} \tag{A1.4}$$

where:

$f_M{}^S$ = the saturates average mass reponse factor relative to methane,
$f_P{}^M$ = the paraffins average mass response factor relative to methane,
$f_N{}^M$ = the naphthenes average mass response factor relative to methane,
P_T = the sum of all paraffins in sample mass percent, %,
N_T = the sum of all naphthenes in sample mass percent, %,
S_T = the saturates mass percent, it is sum of P_T and N_T%.

A1.3.4 Calculate the olefins average mass response factor relative to methane by Eq A1.5:

$$f_O^M = \frac{\sum_i O_i \cdot f_{Oi}^M}{O_T} \tag{A1.5}$$

where:

$f_O{}^M$ = olefins average mass response factor relative to methane,
O_i = olefins mass percent, %,, at the specific carbon number
$f_{Oi}{}^M$ = olefins mass reponse factor relative to methane, , at the specific carbon number
O_T = the sum of all olefins in sample, mass percent, %.

A1.3.5 Calculate $C_7{}^+$ aromatics average mass response factor relative to methane by Eq A1.6:

$$f_A^M = \frac{\sum_i A_i \cdot f_{Ai}^M}{A_T} \tag{A1.6}$$

where:

$f_A{}^M$ = $C_7{}^+$ aromatics average response factor relative to methane,
Ai = C7 + aromatics mass percent, % , at the specific carbon number
$f_A{}^M$ = $C_7{}^+$ aromatics reponse factor relative to methane, at the specific carbon number
A_T = the sum of all $C_7{}^+$ aromatics in sample, mass percent, %.

A2. CALCULATION OF WEIGHTED AVERAGE RELATIVE DENSITY OF HYDROCARBON TYPES

TABLE A2.1 Relative Density of Different Hydrocarbon Types, kg/L, at 20 °C

Carbon Number	Paraffins, *P*	Naphthenes, *N*	Cyclo Olefins	Olefins, *O*	Aromatics, *A*
4	0.5788	...	...	0.6037	...
5	0.6262	0.7454	0.7720	0.6474	...
6	0.6594	0.7636	0.7803	0.6794	0.8789
7	0.6837	0.7649	0.7854	0.7023	0.8670
8	0.7025	0.7747	0.8000	0.7229	0.8681
9	0.7176	0.7853	0.8073	0.7327	0.8707
10	0.7300	0.8103	...	0.7408	0.8724
11^+	0.7402	...	...	0.7503	0.8730

A2.1 The Weighted Average Relative Density of each hydrocarbon type at different carbon numbers is listed in Table A2.1 and is cited from Test Method D6839.

A2.2 Hydrocarbon Type Weighted Average Relative Density Calculation

A2.2.1 Calculate the Paraffin Weighted Average Relative Density Using Eq A2.1:

$$d_P = \frac{\sum_i P_i \cdot d_{Pi}}{P_T} \tag{A2.1}$$

where:

d_P = the paraffin weighted average relative density,
P_i = paraffins mass percent, %, at the specific carbon number,
d_{Pi} = paraffins relative density, at the specific carbon number, and
P_T = the sum of all the paraffins in sample, mass percent, %.

A2.2.2 Calculate Naphthenes Weighted Average Relative Density Using Eq A2.2.

$$d_N = \frac{\sum_i N_i \cdot d_{Ni}}{N_T} \tag{A2.2}$$

where:

d_N = the naphthenes weighted average relative density,
N_i = naphthenes mass percent, %, at the specific carbon number
d_{Ni} = naphthenes relative density, at the specific carbon number
N_T = the sum of all naphthenes in sample, mass percent, %.

A2.2.3 Calculate saturates weighted average relative density using Eq A2.3:

$$d_S = \frac{P_T \cdot d_P + N_T \cdot d_N}{S_T} \tag{A2.3}$$

where:

S_T = total saturates mass percent, which is the sum of P_T and N_T.

A2.2.4 Calculate olefins (including the Cyclo olefin) weighted average relative density using Eq A2.4:

$$d_O = \frac{\sum_i O_i \cdot d_{Oi}}{O_T} \tag{A2.4}$$

where:

d_O = the olefins weighted average relative density,
O_i = olefins mass percent, %, at the specific carbon number and specific group (cyclo- or mono- and diolefin)
d_{Oi} = olefins relative density, at the specific carbon number and group
O_T = the sum of all olefins in sample, mass percent, %

A2.2.5 Calculate C_7^+ Aromatics weighted average relative density using Eq A2.5:

$$d_A = \frac{\sum_i A_i \cdot d_{Ai}}{A_T} \tag{A2.5}$$

where:

d_A = C_7^+ aromatics weighted relative density,
A_i = different carbon number C_7^+ aromatics mass percent, %,
d_{Ai} = different carbon number C_7^+ aromatics relative density,
A_T = the sum of different carbon number C_7^+ aromatics mass percent, %.