



Standard Test Method for Paraffin, Naphthene, and Aromatic Hydrocarbon Type Analysis in Petroleum Distillates Through 200°C by Multi-Dimensional Gas Chromatography¹

This standard is issued under the fixed designation D 5443; 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.

^{ε1} NOTE—Warning notes were editorially moved into the standard text in August 2003.

1. Scope

1.1 This test method provides for the determination of paraffins, naphthenes, and aromatics by carbon number in low olefinic hydrocarbon streams having final boiling points of 200°C or less. Hydrocarbons with boiling points greater than 200°C and less than 270°C are reported as a single group. Olefins, if present, are hydrogenated and the resultant saturates are included in the paraffin and naphthene distribution. Aromatics boiling at C₉ and above are reported as a single aromatic group.

1.2 This test method is not intended to determine individual components except for benzene and toluene that are the only C₆ and C₇ aromatics, respectively, and cyclopentane, that is the only C₅ naphthene. The lower limit of detection for a single hydrocarbon component or group is 0.05 mass %.

1.3 This test method is applicable to hydrocarbon mixtures including virgin, catalytically converted, thermally converted, alkylated and blended naphthas.

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 7 and Table 1.

2. Referenced Documents

2.1 ASTM Standards:

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products²

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 on Hydrocarbon Analysis.

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² *Annual Book of ASTM Standards*, Vol 05.02.

TABLE 1 Hydrocarbon Test Mixture

Hydrocarbons	Warning
Cyclopentane	(Warning—Extremely Flammable. Harmful if inhaled.)
Pentane	(Warning—Extremely Flammable. Harmful if inhaled.)
Cyclohexane	(Warning—Extremely Flammable. Harmful if inhaled.)
2,3-Dimethylbutane	(Warning—Extremely Flammable. Harmful if inhaled.)
Hexane	(Warning—Extremely Flammable. Harmful if inhaled.)
1-Hexene	(Warning—Extremely Flammable. Harmful if inhaled.)
Methylcyclohexane	(Warning—Extremely Flammable. Harmful if inhaled.)
4-Methyl-1-hexene	(Warning—Extremely Flammable. Harmful if inhaled.)
Heptane	(Warning—Flammable. Harmful if inhaled.)
1,cis-2-Dimethylcyclohexane	(Warning—Extremely Flammable. Harmful if inhaled.)
2,2,4-Trimethylpentane (iso-octane)	(Warning—Flammable. Harmful if inhaled.)
Octane	(Warning—Flammable. Harmful if inhaled.)
1,cis-2,cis-4-Trimethylcyclohexane	(Warning—Flammable. Harmful if inhaled.)
Nonane	(Warning—Flammable. Harmful if inhaled.)
Decane	(Warning—Flammable. Harmful if inhaled.)
Undecane	(Warning—Flammable. Harmful if inhaled.)
Dodecane	(Warning—Flammable. Harmful if inhaled.)
Benzene	(Warning—Extremely Flammable. Harmful if inhaled.)
Methylbenzene (Toluene)	(Warning—Flammable. Harmful if inhaled.)
trans-Decahydronaphthalene (Decalin)	(Warning—Flammable. Harmful if inhaled.)
Tetradecane	(Warning—Harmful if inhaled.)
Ethylbenzene	(Warning—Extremely Flammable. Harmful if inhaled.)
1,2-Dimethylbenzene (o-Xylene)	(Warning—Extremely Flammable. Harmful if inhaled.)
Propylbenzene	(Warning—Extremely Flammable. Harmful if inhaled.)
1,2,4-Trimethylbenzene	(Warning—Extremely Flammable. Harmful if inhaled.)
1,2,3-Trimethylbenzene	(Warning—Extremely Flammable. Harmful if inhaled.)
1,2,4,5-Tetramethylbenzene	(Warning—Flammable. Harmful if inhaled.)
Pentamethylbenzene	(Warning—Harmful if inhaled.)

D 4307 Practice for Preparation of Liquid Blends for Use As Analytical Standards²

3. Summary of Test Method

3.1 A representative sample is introduced into a gas chromatographic system containing a series of columns and switching valves. As the sample passes through a polar column, the polar aromatic compounds, bi-naphthenes, and high boiling (>200°C) paraffins and naphthenes are retained. The fraction not retained elutes to a platinum column, that hydrogenates olefins, if present, in this fraction, and then to a molecular sieve column which performs a carbon number separation based on

TABLE 2 Typical Column Specifications

Specification	Column Type				
	Polar	Non-Polar	Tenax ³	Molsieve ^A	Platinum ^A
Column length, m	3	4	0.16 to 0.18	1.8	0.002 to 0.06
Column inside diameter, mm	2.0 to 2.1	1.8 to 2.0	2.5	1.6 to 2.0	1.6
Liquid phase	OV-275 ^B	OV-101 ^B
Percent liquid phase	30	4–5
Support material	Chromasorb ^C	Chromasorb ^C
	PAW	WAW
Packing material	Tenax ³	Molecular sieve 13X ^{D,E}	...
Mesh size	60/80	80/100	80/100

^A Available from AC Analytical Controls, 3448 Progress Dr., Bensalem, PA 19020.

^B OV-101 and OV-275 are registered trademarks of Ohio Valley Specialty Chemical Co., 115 Industry Rd., Marietta, OH 45750.

^C Chromasorb is a registered trademark of Marville Corp., Box 519, Lompoc, CA 93438.

^D Sodium form of molecular sieve 13X.

^E May also contain a mix of molecular sieves 13X and 5A to separate normal and iso-paraffins.

molecular structure, that is, naphthenes and paraffins. The fraction remaining on the polar column is further divided into three separate fractions that are then separated on a non-polar column by boiling point. Eluting compounds are detected by a flame ionization detector.

3.2 The mass concentration of each group is determined by the multiplication of detected peak areas by flame ionization detector response factors and normalization to 100 %.

4. Significance and Use

4.1 A knowledge of the composition of hydrocarbon refinery streams is useful for process control and quality assurance.

4.2 Aromatics in gasoline are soon to be limited by federal mandate. This test method can be used to provide such information.

5. Interferences

5.1 Chemicals of a non-hydrocarbon composition may elute within the hydrocarbon groups, depending on their polarity, boiling point, and molecular size. Included in this group are ethers (for example, methyl-tertiary butyl ether) and alcohols (for example, ethanol).

6. Apparatus

6.1 *Chromatograph*—A gas chromatograph capable of isothermal operation at $130 \pm 0.1^\circ\text{C}$. The gas chromatograph must contain the following:

6.1.1 A heated flash vaporization sample inlet system capable of operation in a splitless mode.

6.1.2 Associated gas controls with adequate precision to provide reproducible flows and pressures.

6.1.3 A flame ionization detection system optimized for use with packed columns and capable of the following:

Isothermal temperature operation	150 to 170°C
Sensitivity	>0.015 coulombs/g
Minimum detectability	5×10^{-12} g carbon/second
Linearity	>10 ⁷

Some instruments will produce a non-linear response for benzene, above approximately 5.5 mass %, and for toluene above approximately 15 mass %. The linearity of these components above these concentrations must be verified with appropriate blends. Where non-linearity has been shown to exist, samples, that contain no higher than C₁₃, can be analyzed if the sample is diluted with n-C₁₅ and the instrument is

equipped with a prefractionating column. The sample may also be diluted with a component that is not present in the sample and this component will then not be included in the normalized report.

6.2 *Sample Introduction System*—Manual or automatic liquid sample system operated in a splitless mode. Although this test method is intended primarily for use with syringe sample injection, automatic sampling valves have also been found satisfactory. Devices capable of a reproducible injection volume of 0.1 to 0.5 μL are suitable. The sample introduction system must be capable of heating the sample to a temperature that ensures total sample vaporization. A temperature range of 120 to 180°C has been found suitable.

6.3 *Electronic Data Acquisition System*—The data acquisition and integration device used for detection and integration must meet or exceed the following specifications:

6.3.1 Capacity for at least 75 peaks for each analysis,

6.3.2 Normalized area percent calculation,

6.3.3 Noise and spike rejection capability,

6.3.4 Sampling rates for fast (<2 s) peaks,

6.3.5 Peak width detection for narrow and broad peaks, and

6.3.6 Perpendicular drop and tangent skimming as required.

6.4 *Independent Temperature Control*—This test method requires the temperature control of five columns, column switching valves and sample lines. The columns consist of polar, non-polar, Tenax³, platinum, and molecular sieve columns. The specifications for these columns are listed in Table 2. The polar column, non-polar column, column switching valves, and sample lines require isothermal operation at a temperature equivalent to the temperature of the gas chromatograph oven. These components may be located in the gas chromatograph oven. The Tenax³ column, platinum column, and molecular sieve column require operation at temperatures other than the gas chromatograph oven temperature. These columns may be temperature controlled by any means that will meet the following specifications:

6.4.1 Ability to control the temperature of the Tenax³ column within a range from 60 to 280°C, with a tolerance of $\pm 5^\circ\text{C}$ at any point. The time required to heat this column

³ Tenax is a registered trademark of AKZO, Velperiveg 76, P.O. Box 9300, 6800 SB Arnhem, The Netherlands.

between any two points must be no more than 1 min. The time required to cool this column between any two points must be no more than 5 min.

6.4.2 Ability to control the temperature of the molecular sieve column within a range from 100 and 490°C, with a tolerance of $\pm 10^\circ\text{C}$ at any point. The time required to heat this column between any two points must be no more than 10 min. The time required to cool this column from 450 to 100°C must be no more than 15 min, and

6.4.3 Ability to control the platinum column within a temperature range of 170 and 350°C. During routine analysis, this column is operated within a temperature range of 170 to 220°C.

7. Materials

7.1 Carrier Gases:

7.1.1 *Hydrogen*, 99.999 % pure, <0.1 ppm H₂O. (**Warning**—Extremely flammable gas under high pressure.)

7.1.2 *Helium*, 99.999 % pure, <0.1 ppm H₂O. (**Warning**—Compressed gas under high pressure.)

7.2 Detector Gases:

7.2.1 *Hydrogen*, 99.99 % minimum purity. (**Warning**—Extremely flammable gas under high pressure.)

7.2.2 *Air*, less than 10 ppm each of total hydrocarbons and water. (**Warning**—Compressed gas under high pressure.)

7.3 *Valve Actuation Gas*—This test method permits the use of any type of valve switching or valve actuation. When pneumatic valves are used, air of any grade that will result in no water condensation or will not introduce oil or other contaminants in the switching valves may be used. Air from a piston operated compressor equipped with a water and oil separator has been found suitable. Column switching valves that do not require air to operate do not have this air requirement.

7.4 *Columns*—Five columns, as described in Table 2. These column specifications are to be considered as guidelines and have been found to be acceptable. Other materials or combinations of materials may also provide acceptable performance. The suitability of each column is determined by test criteria as defined in Section 8.

NOTE 1—It is not the intention of this test method to include detailed column preparation steps. Columns may be prepared in any way that follows accepted safety practices and results in columns that will meet the performance requirements of Section 9.

7.5 *Valves*—This test method uses valves for column switching and flow switching. Any commercially available valves may be used that are intended for, or adapted for use in gas chromatography that meet the following specifications:

7.5.1 The column switching valves are generally installed in the gas chromatograph oven. These valves must be capable of continuous operation at the operating temperature of the GC oven.

7.5.2 Materials used in the construction of the valves must be unreactive to hydrocarbons present in the sample under analysis conditions. Stainless steel, PFA, and vespel materials have been found suitable.

7.5.3 Valves must be sized such that they offer little restriction to carrier gas flow under the analysis conditions defined in this test method.

7.5.4 Care must be taken to prevent the introduction of any form of foreign material or contaminant into the valve that may adversely affect its performance.

7.6 *Hydrocarbon Test Mixture*—A quantitative synthetic mixture of pure hydrocarbons, an example of which is identified in Table 1, is used to tune the instrument analysis conditions and establish that the instrument is performing within specifications. Individual hydrocarbon components, in addition to those listed in Table 1, may be used to aid in the analysis. The concentration level of each component in the hydrocarbon test mixture is not critical as long as the concentration is accurately known. Percentage ranges from 1.0 to 6.0 mass % have been found suitable. Impurities in the individual components may have an adverse effect on the quantitative aspect of the analysis. If an impurity is of the same carbon number and basic molecular structure as the main component itself, it will be correctly grouped and quantitated within the group. As an example, isobutylicyclopentane and isopropylcyclohexane will both be determined as C₉ naphthenes. Each of the individual hydrocarbon components used for this test mixture must have a minimum purity level of 99 mol %. Refer to Practice D 4307 for instructions on the preparation of liquid blends for use as analytical standards.

7.7 Gas Flows and Pressures:

7.7.1 Carrier Gases:

7.7.1.1 The helium carrier gas through the injection port, polar column, platinum column and molecular sieve column is flow controlled. Flow rates of 16 to 23 mL/min have been found suitable. A helium supply pressure of 620 kDa (90 psi) has been found suitable to meet the helium flow requirement. The helium carrier gas flow will be referred to as the “A” flow within this test method.

7.7.1.2 The helium carrier gas used as the make up gas when the polar column is in stop flow is set to the same flow rate as the helium carrier gas through the injection port.

7.7.1.3 The hydrogen carrier gas flow through the Tenax³ column and non-polar column is flow controlled. Flow rates of 12 to 17 mL/min have been found suitable. A hydrogen supply pressure of 517 kDa (75 psi) has been found suitable to meet the hydrogen flow requirements. The hydrogen carrier gas flow will be referred to as the “B” flow within this test method.

7.7.1.4 The hydrogen flow to the platinum column is flow controlled. Flow rates of 10 to 15 mL/min have been found suitable.

7.7.2 *Detector Gases*—The flow rates of the air and hydrogen, as oxidant and fuel gases for the flame ionization detector, must be set according to the instrument manufacturer’s instructions.

7.7.3 *Valve Actuation Gases*—Pneumatic valves require air delivery at pressures and flows adequate to ensure correct actuation. When pneumatic valves are used for this test method, air pressure and flow must be provided in accordance with the valve manufacturer’s instructions.

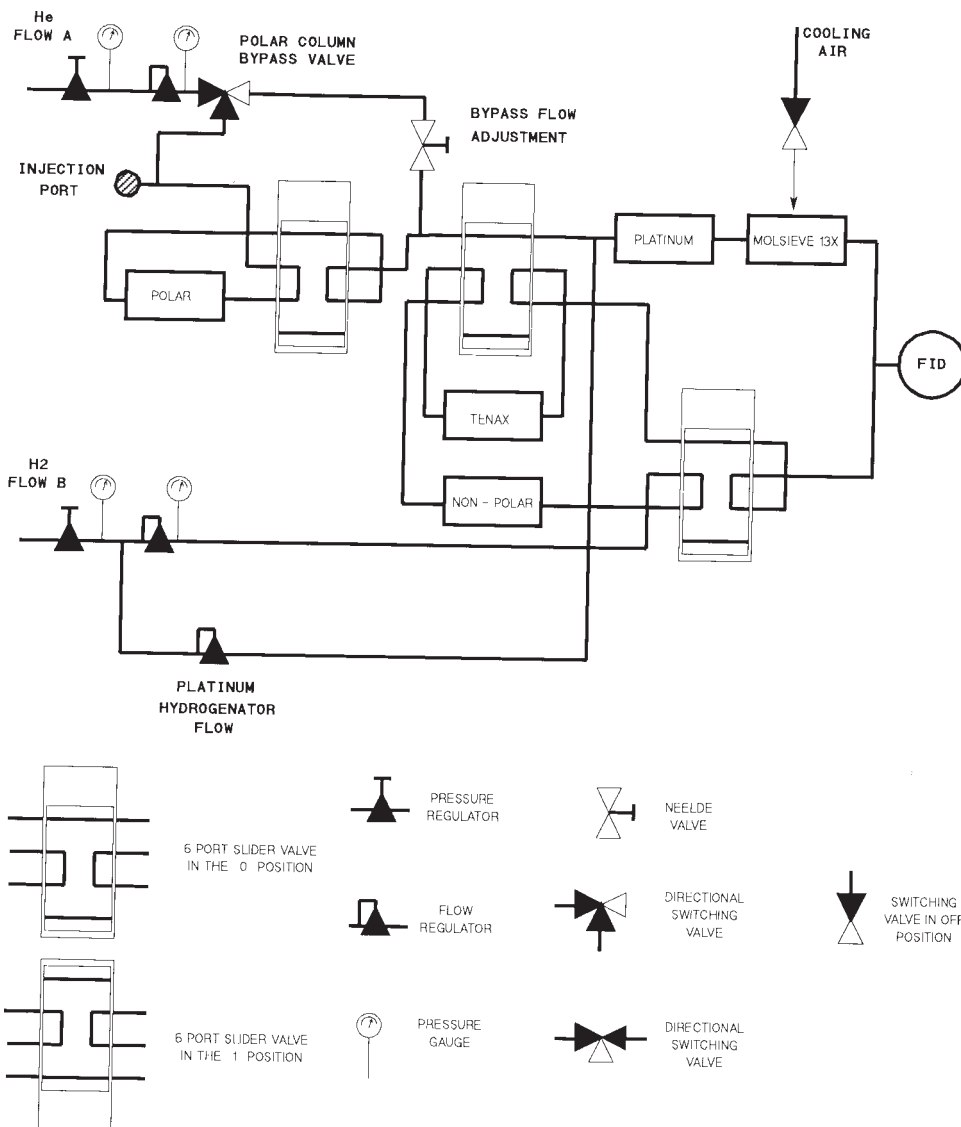


FIG. 1 Typical Instrument With Six Port Slider Valves

8. System Description

8.1 Commercial instruments are available that meet the specifications of this test method. One such system⁴ is based on pneumatic valves. Another system⁵ is based on rotary valves. Additional operating instructions are included in the operating and maintenance manuals for these instruments. The figures in this test method are applicable to these systems.

8.1.1 Fig. 1 and Fig. 2 illustrate typical instrument configurations that use different column valve switching techniques. This test method allows use of either configuration.

8.1.2 Figs. 3-13 illustrate the system flow configurations during the column test and sample analysis phases of this test method.

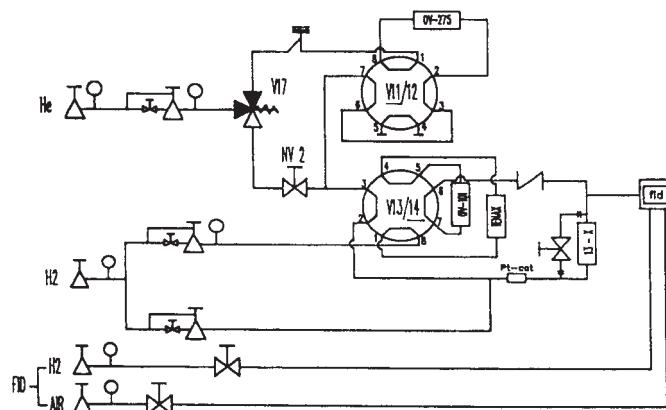


FIG. 2 Typical Instrument Configuration with Rotary Valves

8.1.3 Table 3 and Table 4 list the conditions that apply during the column test and sample analysis phases for the instrument configuration in Fig. 1.

⁴ Instrument commercially available from AC Analytical Controls, 3448 Progress Drive, Bensalem, PA 19020.

⁵ Instrument commercially available from Chrompack, International BV 4330 EA Middleburg, The Netherlands.

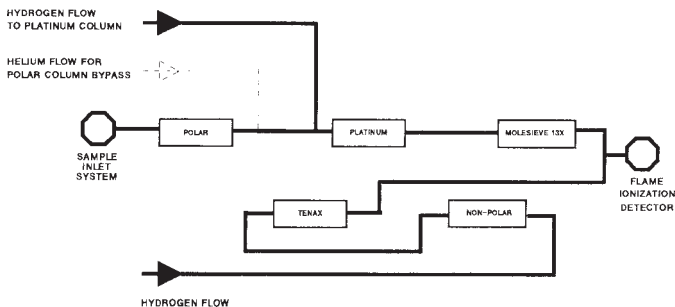
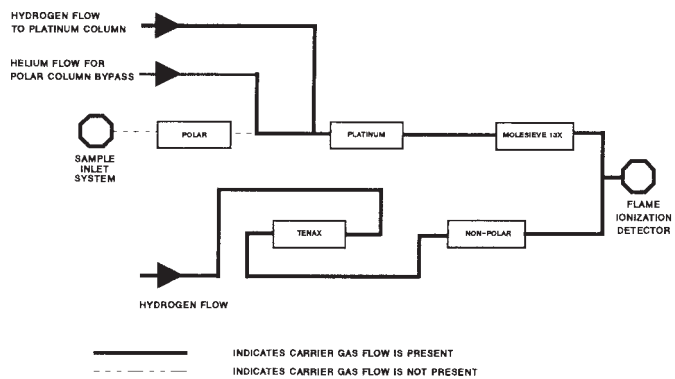
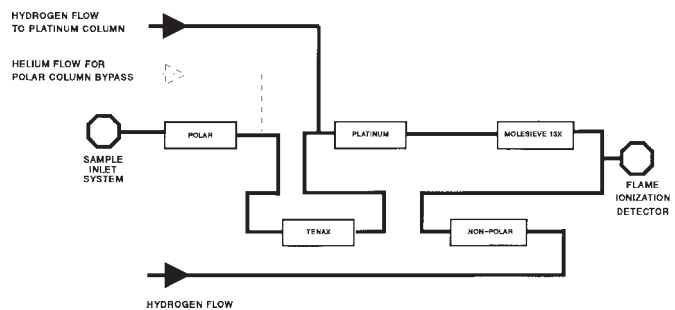


FIG. 3 Start of the "A" Time



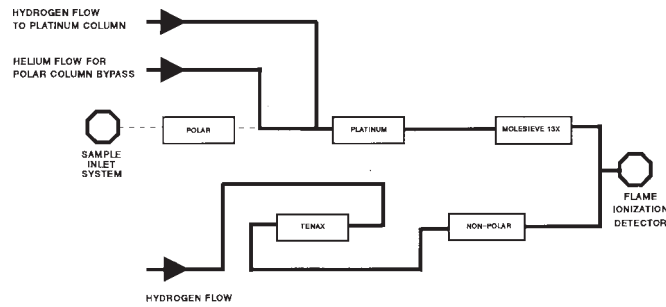
NOTE—Polar column is placed in stop flow.

FIG. 4 End of the "A" Time



NOTE—First aromatic elution from the polar column.

FIG. 5 Start of the "B" Time



INDICATES CARRIER GAS FLOW IS PRESENT
INDICATES CARRIER GAS FLOW IS NOT PRESENT

NOTE—Begin first aromatic elution to the detector.

FIG. 6 End of the "B" Time

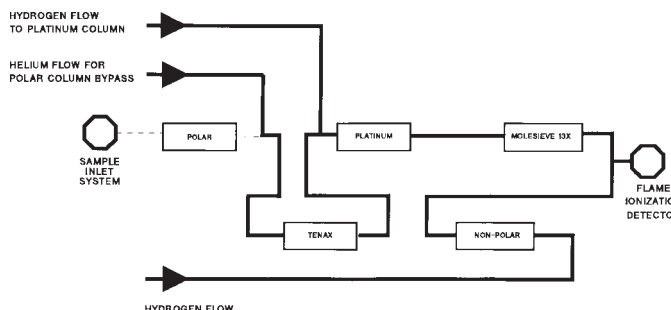
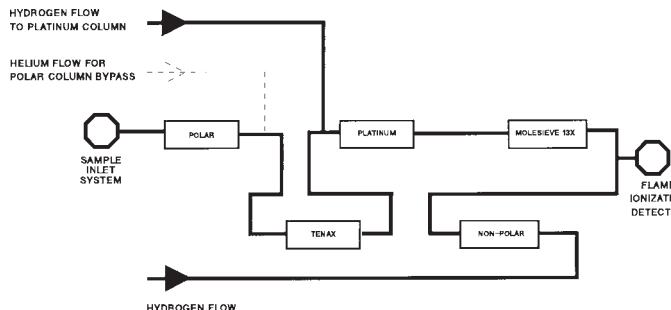


FIG. 7 Non-Polar Column Back Flush to the Detector



INDICATES CARRIER GAS FLOW IS PRESENT
INDICATES CARRIER GAS FLOW IS NOT PRESENT

NOTE—Second aromatic cut elution from the polar column.

FIG. 8 Start of the "C" Time

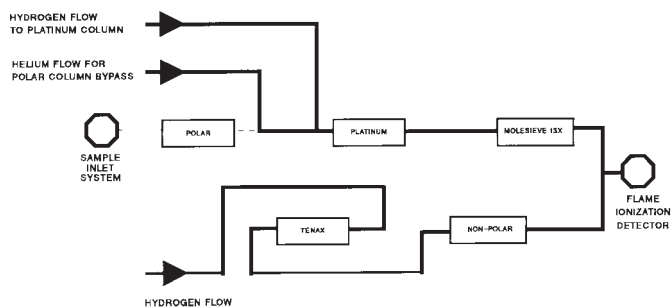
8.1.4 Table 5 and Table 6 list the conditions that apply during the column test and sample analysis phases for the instrument configuration in Fig. 2.

8.2 The polar column separates the sample into four fractions. The first three fractions are fore-flushed through the polar column and the last is back-flushed. Upon completion of each elution cycle, the flow through the column is stopped to maintain the relative position of non-eluted components within the column. For the purpose of simplicity, the three fore-flushes of the polar column will be called the "A," "B," and "C" cuts, respectively. The length of time associated with each cut will be called the "A," "B," and "C" times, respectively. These times are independent of each other and are a function of instrument configuration, column performance and carrier gas flow conditions.

9. Preparation of Apparatus

9.1 Place the gas chromatograph in service in accordance with the manufacturer's instructions. The initial settings listed in Table 3 and Table 4 have been found suitable for slider valve type instruments. The initial settings listed in Table 5 and Table 6 have been found suitable for rotary valve type instruments. Variances in column to column performance require that each flow setting and cut time be determined experimentally.

9.2 The carrier gas flow rates, A, B, and C times must be adjusted to produce acceptable analytical performance with the hydrocarbon test mixture in 7.6. These conditions are then recorded and must be used for sample analysis. The system is considered to meet the test method specifications if the



NOTE 1—Begin second aromatic elution to the detector.
FIG. 9 End of the "C" Time

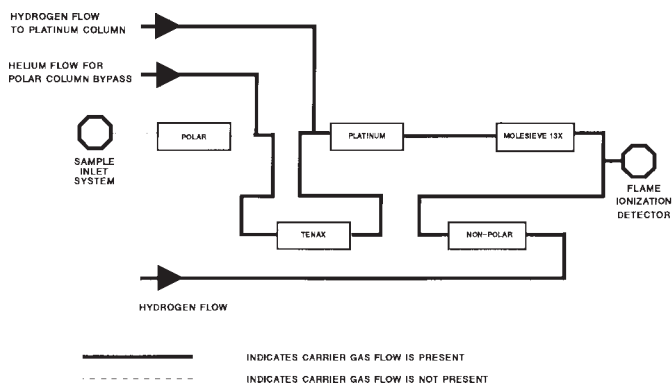


FIG. 10 Non-Polar Column Back Flush to the Detector

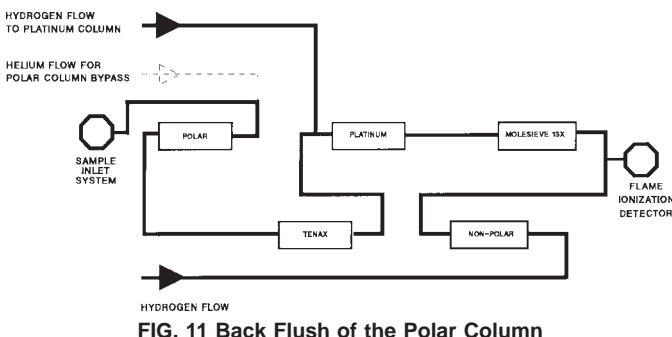


FIG. 11 Back Flush of the Polar Column

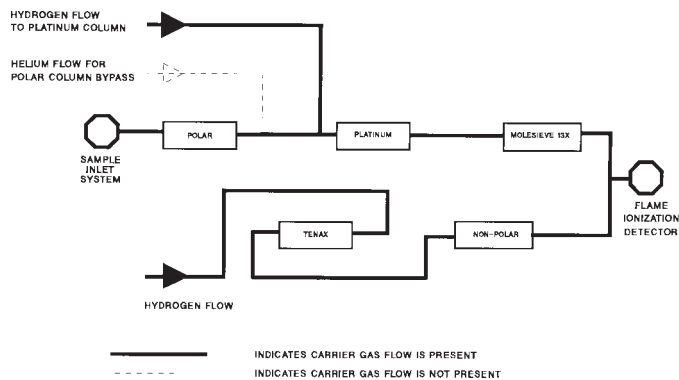


FIG. 12 Final Elution to the Non-Polar Column

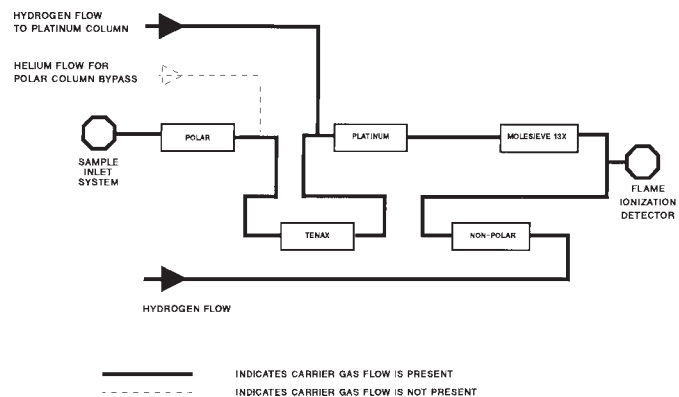


FIG. 13 Back Flush of the Non-Polar Column to the Detector

TABLE 3 Temperature Settings for Slider Valve Instruments (see Fig. 1)

Device	Initial Temperature, (°C)	Final Temperature, (°C)	Rate, (minutes)
Polar column	130	130	isothermal
Non-polar column	130	130	isothermal
Platinum column	220	220	isothermal
Detector	150	150	isothermal
Molecular sieve 13X	100	430, minimum	30±5, logarithmic
Tenax ³ column	60	280	1, maximum

TABLE 4 Flow Settings and Cut Times for Slider Valve Instruments (see Fig. 1)

Description	Initial Setting, minutes	Acceptable Range, minutes
Helium flow through injection port	20 mL/min	16 to 23 mL/min
Helium polar column bypass flow	same flow rate as injection port	flow rate
Hydrogen flow to platinum column	12 mL/min	10 to 15 mL/min
Hydrogen flow through non-polar column	14 mL/min	12 to 17 mL/min
A time	3.6	2.7 to 4.6
B time	3.4	2.7 to 4.6
C time	3.6	2.7 to 4.6

hydrocarbon test mixture analysis absolute errors, as calculated in Sections 11 and 12, are equal to or less than the following: ±0.3 % per carbon number per hydrocarbon type (for example, C₅ paraffins), and ±0.3 % per hydrocarbon class (for example, all paraffins).

9.3 Tuning Instrument Conditions with Hydrocarbon Test Mixture:

9.3.1 Configure the system initially as illustrated in Fig. 3. Use the conditions in Table 3 and Table 4 for slider valve type instruments or Table 5 and Table 6 for rotary valve type instruments.

9.3.2 Inject approximately 0.2 µL of the hydrocarbon test mixture and begin recording the signal from the detector. The sample injection marks the beginning of the A time. Allow paraffins and naphthenes with boiling points below 200°C to elute from the polar column. Retain aromatics, polynaphthenes, if present, and components boiling above 200°C on the polar column during the A time. If olefins are present in

the first elution, they are hydrogenated by the platinum column. All eluting components are trapped on the molecular sieve column.

9.3.3 During the A time, a minimum of 80 % of the dodecane must elute from the polar column. The A time is too

TABLE 5 Temperature Settings, For Rotary Valve Instruments (see Fig. 2)

Device	Initial Temperature, (°C)	Final Temperature, (°C)	Rate, minutes
Polar column	130	130	isothermal
Non-polar column	130	130	isothermal
Platinum column	170	170	isothermal
Detector	170	170	isothermal
Molecular sieve	100	430	10°C
Tenax ³ column	60	280	1, maximum

TABLE 6 Flow Settings and Cut Times, For Rotary Valve Instruments (see Fig. 2)

Description	Initial Setting, minutes	Acceptable Range, minutes
Helium flow through injection port	25 mL/min	20 to 35 mL/min
Helium polar column bypass flow	same flow rate as injection port	flow rate
Hydrogen flow to platinum column	7 mL/min	5 to 10 mL/min
Hydrogen flow through non-polar column	20 mL/min	15 to 30 mL/min
A time	2	1.7 to 2.5
B time	2	1.7 to 3.0
C time	2	1.7 to 3.0

short or the A flow is too low if the dodecane elution is less than 80 %. The A time is too long or the A flow is too high if benzene or trans-decalin, or both, elute during the A time. Adjust the A time or A flow to meet these requirements.

9.3.4 At the end of the A time, change the configuration to that of Fig. 4. Place the polar column in stop flow and program the temperature of the molecular sieve column from 100 to 430°C, minimum, at the rate specified in either Table 3 or Table 5. Components will elute from the molecular sieve column as groups, by carbon number and group type. Within each carbon number group, naphthenes will elute first followed by paraffins. If the molecular sieve column contains a mixture of 13 X and five A types of molecular sieves, the group elution order will be first naphthenes as a group, followed by iso-paraffins as a group and then the normal paraffin, by carbon number.

9.3.5 Upon completion of the naphthene and paraffin elution, change the configuration to that of Fig. 5. Begin cooling the molecular sieve column to 100°C and switch the Tenax³ column into the A flow to receive the next cut from the polar column. Take the polar column out of stop flow. This marks the beginning of the B time.

9.3.6 During the B time, most, if not all, of the benzene and toluene, some of the C₈ aromatics, decalin, naphthenes, and paraffins boiling above 200°C elute to the Tenax³ column. The B time is too short if all of the trans-decalin does not elute during the B time. The B time is too long if any of the o-Xylene or C₉ aromatics elute during the B time. Adjust the B time to meet these requirements.

9.3.7 At the end of the B time, change the configuration to that of Fig. 6. Heat the Tenax³ column to 280°C and allow all trapped components to elute to the non-polar column. The aromatics and decalin elute from the non-polar column in boiling point order. Naphthenes and paraffins boiling above 200°C do not elute from the non-polar column at this time.

9.3.8 Four minutes and 30 s after the Tenax³ column begins to heat, change the configuration to that of Fig. 7 and back-flush the non-polar column. Cool the Tenax³ column to 60°C at this time. Continue the back-flush cycle for 5.5 min. Back-flush the naphthenes and paraffins boiling above 200°C from the non-polar column to the detector at this time.

9.3.9 At the end of this back-flush cycle, change the configuration to that of Fig. 8. This marks the beginning of the C time. The second cut of aromatics elute from the polar column to the Tenax³ trap. This elution contains some of the C₈ aromatics, approximately one half of the C₉ aromatics and a minor amount of C₁₀ aromatics. Any remaining benzene and most, if not all, of the toluene that did not elute during the B time may elute at this time. Paraffins and naphthenes boiling above 200°C that did not totally elute during the B time may elute now.

9.3.10 The C time is too short if none of the o-Xylene elutes during the C time. The C time is too long if greater than 90 % of the o-Xylene elutes during the C time.

9.3.11 At the end of the C time, change the configuration to that of Fig. 9, place the polar column in stop flow. Heat the Tenax³ column to 280°C and allow all trapped components to elute to the non-polar column. The aromatics elute from the non-polar column in boiling point order.

9.3.12 Four minutes and 30 s after the Tenax³ trap begins to heat, change the configuration to that of Fig. 10 and back-flush the non-polar column. Cool the Tenax³ column to 60°C at this time. Continue this back-flush cycle for 5.5 min. Back-flush the naphthenes and paraffins boiling above 200°C from the non-polar column to the detector at this time.

9.3.13 At the end of this back-flush cycle, change the configuration to that of Fig. 11 and back-flush the polar column to the Tenax³ trap. This back-flush cycle lasts for approximately 10 min until all remaining components are back-flushed from the polar column to the Tenax³ column.

9.3.14 At the end of this back-flush cycle, change the configuration to that of Fig. 12. Heat the Tenax³ column to 280°C and allow all trapped components to elute to the non-polar column. The remaining aromatics with boiling points less than 200°C elute in boiling point order to the detector.

9.3.15 Approximately 6.5 min after the Tenax³ column begins to heat, change the configuration to that of Fig. 13 and back-flush the components boiling above 200°C from the non-polar column to the detector. Cool the Tenax³ column to 60°C and then stop the detector signal data collection.

9.4 Perform the steps outlined in Sections 11 and 12, below, to verify that the system is properly tuned. The system is considered to meet the test method specifications if the hydrocarbon test mixture analysis absolute errors are equal to or less than the following: ±0.3 % per carbon number per hydrocarbon type (for example, C₅ paraffins), and ±0.3 % per hydrocarbon class (for example, all paraffins).

9.5 Record the actual times and temperatures and flows found necessary to meet the separation requirements as described in the various steps of 9.3. Use these parameters for all subsequent sample analyses.

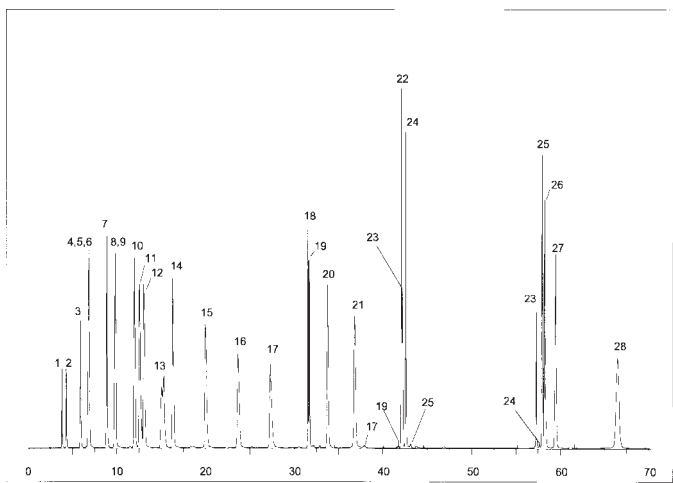


FIG. 14 Hydrocarbon Test Mixture

10. Procedure

10.1 Refer to Practice D 4057 for instructions on manual sampling from bulk storage into open containers. Stopper the container immediately after drawing sample.

10.2 Place the instrument in the initial configuration as illustrated in Fig. 3.

10.3 Adjust the operating conditions to those values that were experimentally determined in 9.3 to give the desired separations. This may be done programmatically for automated instruments.

10.4 Inject approximately 0.2 μL of sample and begin data acquisition of the detector signal. A chromatogram is required for hydrocarbon type group identification. Integrated peak areas are required for calculations of mass percent.

10.5 Stop the data acquisition after the final cut has been eluted.

11. Calculation

11.1 Identify each hydrocarbon type group by visually matching it with its counterpart in the hydrocarbon test mixture, Fig. 14 and Table 7. The performance characteristics of the molecular sieve column and the sample composition may result in separation of the normal and iso-paraffins by carbon number. These groups can be combined in the calculations and reported as paraffins, by carbon number. Each of the aromatic components may elute in several of the aromatic fractions. Identify and total each of these components within the appropriate hydrocarbon type group. Peak characteristics will vary and depend on component concentrations in the sample. A qualitative reformer feed may also be used to aid in identification, as in Fig. 15.

11.2 If a computing integrator is used for automatic peak identification, examine the report carefully to ensure that all peaks are properly identified and integrated.

11.3 *Response Factors*—All groups are reported in mass percent, normalized to 100 %. The following formula is used to calculate the flame ionization detector response factors, as listed in Table 8:

TABLE 7 Hydrocarbon Test Mixture Component Identification

Number Identification	Component Name
1	Cyclopentane
2	<i>n</i> -Pentane
3	Cyclohexane
4	2,3-Dimethylbutane
5	<i>n</i> -Hexane
6	1-Hexene
7	Methylcyclohexane
8	4-Methyl-1-Hexene
9	<i>n</i> -Heptane
10	1, <i>cis</i> -2-Dimethylcyclohexane
11	2,2,4-Trimethylpentane
12	<i>n</i> -Octane
13	1, <i>cis</i> -2, <i>cis</i> -4-Trimethylcyclohexane
14	<i>n</i> -Nonane
15	<i>n</i> -Decane
16	<i>n</i> -Undecane
17	<i>n</i> -Dodecane
18	Benzene
19	Toluene (Methylbenzene)
20	<i>trans</i> -Decahydronaphthalene (Decalin)
21	N-Tetradecane
22	Ethylbenzene
23	1,2-Dimethylbenzene (<i>o</i> -Xylene)
24	<i>n</i> -Propylbenzene
25	1,2,4-Trimethylbenzene
26	1,2,3-Trimethylbenzene
27	1,2,4,5-Tetramethylbenzene
28	Pentamethylbenzene

$$F_i = \frac{(C_{aw} \times C_n) + (H_{aw} \times H_n)}{C_n} \times 0.7487 \quad (1)$$

where:

- F_i = relative response factor for a hydrocarbon type group of a particular carbon number,
- C_{aw} = atomic weight of carbon, 12.011,⁶
- C_n = number of carbon molecules in the group,
- H_{aw} = atomic weight of hydrogen, 1.008,⁶
- H_n = number of hydrogen molecules in the group, and
- 0.7487 = corrects the response of methane to unity.

Methane will be considered to have a unity (1) response factor.

11.3.1 Use an average response factor of 0.88 for the first three fractions boiling above 200°C. Use a response factor of 0.85 for the last fraction boiling above 200°C. Use an average response factor of 0.835 for C_9 and above aromatics.

11.4 Multiply the area associated with each of the identified groups by the appropriate response factor to produce a corrected area for each of the groups:

$$A_{ic} = A_i \times F_i \quad (2)$$

where:

- A_{ic} = corrected area of an identified group, and
- A_i = raw area of identified group.

11.5 Add all of the individual, corrected areas from 11.4.

$$T = \sum A_{ic} \quad (3)$$

⁶ ASTM Publication DS 4B, *Physical Constants of Hydrocarbons C1 to C10*, ASTM International, W. Conshohocken.

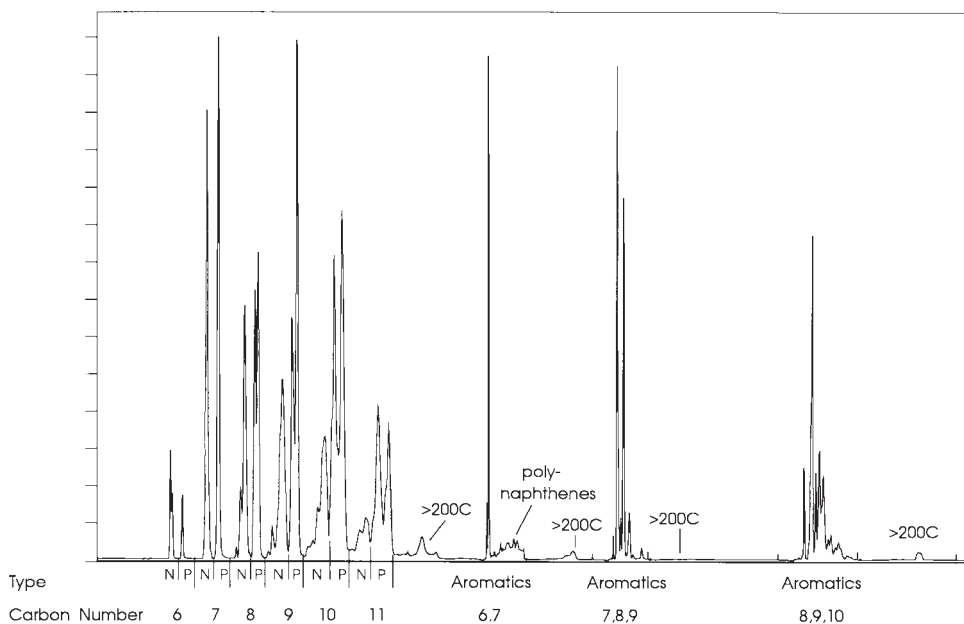


FIG. 15 Qualitative Naphtha Sample

TABLE 8 Flame Ionization Detector Response Factors Based on Percentage by Mass of Carbon, Methane Used as Unity

Number of Carbon Atoms	Paraffins	Naphthenes	Aromatics
3	0.916
4	0.906
5	0.899	0.874	...
6	0.895	0.874	0.811
7	0.892	0.874	0.820
8	0.890	0.874	0.827
9	0.888	0.874	0.835
10	0.887	0.874	...
11	0.886	0.874	...

where:

T = total of corrected areas.

11.6 Divide each of the identified groups by the total corrected area determined in 11.5 to produce the normalized mass percent for each group:

$$M_i = \frac{A_{ic}}{T} \quad (4)$$

where:

M_i = normalized mass % of an identified group.

12. Report

12.1 Report the following information:

12.1.1 The mass % and hydrocarbon group type of each group through C_{11} to the nearest 0.01 %,

12.1.2 The mass % of the fraction boiling above 200°C to the nearest 0.01 %,

12.1.3 The mass % of poly-naphthenes boiling below 200°C (for example, trans-Decahydronaphthalene) to the nearest 0.01 %, and

12.1.4 The C_9 and above aromatics as C_9+ aromatics to the nearest 0.01 %.

13. Precision and Bias⁷

13.1 *Precision*—The precision of any individual measurement resulting from the application of this test method depends on several factors related to the individual or group of components including the volatility, concentration and the degree to which the component or group of components are resolved from closely eluting components or groups of components. As it is not practical to determine the precision of measurement for every component or group of components at different levels of concentration separated by this test method, Table 9 presents the repeatability and reproducibility values for selected, representative components and groups of components.

13.1.1 *Repeatability*—The difference between successive test results obtained by the same operator and same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the repeatability values shown in Table 9 only one case in twenty.

13.1.2 *Reproducibility*—The difference between two single and independent test results obtained by different operators working in different laboratories on identical test materials would, in the long run, in the correct operation of this test method, exceed the values shown in Table 9 only one case in twenty.

13.1.3 *Bias*—Bias is the measurement resulting from the application of this test method cannot be determined since there is no accepted reference material suitable for determining bias.

14. Keywords

14.1 aromatics; gas chromatography; hydrocarbon type; multidimensional; naphthenes; paraffins; petroleum distillates

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1315.

TABLE 9 Repeatability and Reproducibility for Selected Naphtha Components and Groups of Components

Component or Group	Repeatability ^A	Reproducibility ^A
Benzene	0.066(x) ^{0.20}	0.20(x) ^{0.20}
Toluene	0.051(x) ^{0.67}	0.22(x) ^{0.67}
C ₈ Aromatics	0.041(x)	0.17(x)
C ₉ + Aromatics	0.092(x) ^{0.50}	0.50(x) ^{0.50}
C ₇ Paraffins	0.16 %	0.61 %
C ₈ Paraffins	0.066(x) ^{0.50}	0.18(x) ^{0.50}
C ₉ Paraffins	0.098(x) ^{0.50}	0.17(x) ^{0.50}
C ₆ Naphthenes	0.046(x) ^{0.50}	0.11(x) ^{0.50}
C ₇ Naphthenes	0.14(x)	0.33(x)
C ₈ Naphthenes	0.067(x) ^{0.33}	0.13(x) ^{0.33}
Total paraffins	0.064(x) ^{0.50}	0.17(x) ^{0.50}
Total naphthenes	0.059(x) ^{0.50}	0.11(x) ^{0.50}
Total aromatics	0.077(x) ^{0.50}	0.28(x) ^{0.50}

^A (x) Refers to the mass percent of the component or group of components found.

ANNEX

(Mandatory Information)

A1. CALCULATION AND REPORTING OF LIQUID VOLUME PERCENT

TABLE A1.1 Average Relative 15/15°C Density of Hydrocarbon Type Groups⁶

Number of Carbon Atoms	Paraffins	Naphthenes	Aromatics
3	0.5070
4	0.5735
5	0.6177	0.7603	...
6	0.6622	0.7688	0.8829
7	0.6911	0.7695	0.8743
8	0.7143	0.7768	0.8738
9	0.7318	0.8058	0.8762
10	0.7425	0.8179	...
11	0.7445	0.8200	...

A1.1 Calculate and report the liquid volume percent of each hydrocarbon type group normalized to 100 %, using the normalized mass % data as calculated in Section 11 and the average relative density of each hydrocarbon type group from Table A1.1.

A1.2 Use an average relative density factor of 0.8000 for the first three fractions boiling above 200°C. Use an average relative density factor of 0.8800 for the last fraction boiling above 200°C. Use an average relative density factor of 0.8762 for C₉ and above aromatics.

A1.3 Divide each of the hydrocarbon group type mass % data, as reported in by the appropriate average relative density factor to produce the corrected liquid volume % for each of the identified groups:

$$V_{ic} = \frac{M_n}{D_a} \quad (\text{A1.1})$$

where:

V_{ic} = corrected liquid volume % of an identified group,
 M_n = normalized mass % of an identified group, and
 D_a = average relative density of an identified group.

A1.4 Add all of the individual, corrected liquid volume percent data from A1.2 to produce the total corrected liquid volume %:

$$T_v = \sum V_{ic} \quad (\text{A1.2})$$

where:

T_v = total corrected liquid volume %.

A1.5 Divide each of the corrected liquid volume % data for each identified group from A1.3 by the total of the corrected liquid volume % data from A1.4 to produce the normalized liquid volume percent for each identified group:

$$V_i = \frac{V_{ic}}{T_v} \quad (\text{A1.3})$$

where:


V_i = normalized liquid volume percent of an identified group.

A1.6 Report the liquid volume % and hydrocarbon group type of each group through C₁₁ to the nearest 0.01 %.

A1.7 Report the liquid volume % of the fraction boiling above 200°C to the nearest 0.01 %.

A1.8 Report the liquid volume % of the poly-naphthenes boiling below 200°C (for example, trans-Decahydronaphthalene) to the nearest 0.01 %.

A1.9 Report the liquid volume % of the C₉ and above aromatics as C₉+ aromatics to the nearest 0.01 %.

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