ASTM INTERNATIONAL

Designation: D8396 – 22

Standard Test Method for
Group Types Quantification of Hydrocarbons in Hydrocarbon Liquids with a Boiling Point between 36 °C and 343 °C by Flow Modulated GCxGC – FID[1]

1. Scope

1.1 This test method covers the quantitative determination of total n-paraffins, total i-paraffins, total naphthenes (cycloparaffins), total one ring (1R) and total two ring plus (2R+) aromatic hydrocarbons in hydrocarbon liquids having a boiling point between 36 °C and 343 °C by GCxGC (flow modulated comprehensive two-dimensional gas chromatography). The method has been applied to aviation turbine fuels and is applicable to other low olefinic fuels in the stated boiling point range.

1.2 This test method has an interim precision. An expanded full interlaboratory study is to be completed in <5 years. The test method working concentration ranges in mass percent for which the interim precision has been determined are as follows:

Hydrocarbon Type	Lower limit (mass percent)	Upper limit (mass percent)
Total i-paraffins	22.0	24.3
Total n-paraffins	19.0	21.9
Total naphthenes (cycloparaffins)	34.3	36.7
Total one ring aromatics	18.7	21.8
Total two ring plus aromatics	0.5	1.9

1.3 This test method is applicable to other group type concentration ranges, to other hydrocarbon types such as selected individual components, for example, benzene, toluene, or n-paraffins by carbon number, or to other hydrocarbon streams; however, precision has not been determined at this time. A future ILS will include a variety of sample types and extend the reporting.

1.4 This test method is not intended to determine unsaturated hydrocarbons, such as olefins, content which may interfere with the cycloparaffins; this test method is applicable to samples with < 1% by mass total olefins as determined by D1319.

1.5 This test method is not intended to determine FAME (fatty acid methyl esters). For such applications, Test Method D7797, IP 585, or equivalent test methods are available.

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

1.7 This standard test method does not mandate or describe a specific software package for data processing and display. Any commercially available GCxGC software used for data processing and display shall meet the requirements for the calculation of the results. Appendix X1 provides some guidelines.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

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

2. Referenced Documents

2.1 *ASTM Standards:*

D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

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

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

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants

D6730 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre

---

Capillary (with Precolumn) High-Resolution Gas Chromatography

D7797 Test Method for Determination of the Fatty Acid Methyl Esters Content of Aviation Turbine Fuel Using Flow Analysis by Fourier Transform Infrared Spectroscopy—Rapid Screening Method

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175 and Practice E355.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *comprehensive two-dimensional gas chromatography (GCxGC), n*—an analytical technique which utilizes two different columns with two distinct orthogonal polarity stationary phases that separate target components.

3.2.1.1 *Discussion*—The effluent from the first-dimension column is collected, focused, and injected into the second-dimension column via a flow modulator. The effluent from the second-dimension is then directed into an FID. Using the two columns of different polarity allows the separation of the specified compounds into compound classes and several individual compounds.

3.2.2 *first-dimension column, n*—*in this test method*, a polar column used to separate components based on differences in polarity of the compounds being separated.

3.2.3 *flow modulator, n*—GCxGC system in which the interface device operates by a flow switching mechanism.

3.2.4 *GCxGC orthogonality, n*—two chromatographic dimensions that employ different separation mechanisms to determine elution times for the purpose of component identification and in which each dimension can be treated as statistically independent; in this test method, orthogonality is achieved by using two column phases that are different in polarity, such as a polar and non-polar column, to attain the required resolution of the components.

3.2.5 *hydrocarbon liquids, n*—*in this test method*, fuels or process streams primarily composed of hydrogen and carbon, with a boiling point in the range of approximately 36 °C to 343 °C and containing <1 % by volume total olefins, such as aviation fuels and kerosenes.

3.2.5.1 *Discussion*—Applicable fuels and processed streams may contain compounds of oxygen, nitrogen, or sulfur, or combinations thereof; however, these compounds, if present, usually are spread over a wide range of boiling point and in very low concentrations (for example, mg/kg) that cannot be detected and do not interfere with this test method. More specialized techniques may be required for their detection.

3.2.6 *injection time, n*—the time that the valve is switched to the second-dimension column.

3.2.7 *modulation, n*—the process of continuously collecting and reinjecting per modulation period onto the second-dimension column each fraction eluting from the first-dimension column.

3.2.8 *modulation delay, n*—the time between the start of the analysis and the first modulation.

3.2.9 *modulation period, n*—the duration of a complete cycle of modulation, i.e., the time between two successive injections into the second column.

3.2.10 *modulator, n*—interface device between the two columns in a comprehensive two-dimensional separation system that accumulates eluate of the first column for a brief period, typically on the order of seconds, for fast reinjection into the second column.

3.2.11 *monitor column, n*—a column allowing recording the chromatogram from the first-dimension column.

3.2.12 *peak or blob, n*—a graphical representation in the two-dimensional chromatogram of a component eluting from the GCxGC system; it is the sum of all the individual modulated cycles for that component.

3.2.13 *second-dimension column or secondary column, n*—*in this test method*, a non-polar "boiling point" column used to acquire the second-dimension separation data based upon differences in boiling point of the components.

3.2.14 *separation space, n*—the plane region within the two-dimensional GCxGC plot in which compounds are, or may be, distributed.

3.2.15 *template, n*—a graphical object applied to a two-dimensional GCxGC image that is used to identify the boundaries between different hydrocarbon types.

3.2.16 *wrap-around, n*—the occurrence or appearance of second dimension peaks in consecutive modulation cycles, caused by second-dimension retention times that exceed the modulation period.

4. Summary of Test Method

4.1 A representative sample is injected into a gas chromatograph that is equipped with a two-stage flow modulator system, first-dimension and second-dimension capillary GC columns, and a flame ionization detector (FID). The flow modulator serves as an interface between the two GC columns. The first-dimension column in the series is a high-resolution capillary GC column coated with a polar stationary phase. The second-dimension GC column is a non-polar capillary. The modulator repetitively accumulates and re-injects fractions eluting off the first-dimension column onto the second-dimension column, which is connected to the FID. The outcome is a series of high-speed two-dimensional chromatograms from the second-dimension column from which peak data are collected, and then transformed into two-dimensional output by GCxGC software.

NOTE 1—This test method uses flow modulation and intermediate precision is based on such modulation. Precision and bias compared to other modulators, such as thermal modulation, has not been determined. Such other modulations may be tested in a future ILS to determine bias and precision.

4.1.1 The GCxGC software is used to identify the boundaries between the different hydrocarbon types or the separated components, or both. The mass percent composition of the sample is obtained by using FID response factors and normalization.

4.2 Tuning of the modulator is essential for proper operation. To facilitate the system's optimization, the chromatographic system may be equipped with a monitor column and a second FID. This monitor column allows recording the chromatogram from the first-dimension column and aids in determining the optimum modulation period. The apparatus preparation (Section 9) is based on a configuration including a monitor column. For configurations without a monitor column, we refer to the instrument manufacturer's guidelines.

4.3 The application is validated by compliance with known QC standards and samples.

5. Significance and Use

5.1 Accurate quantitative compositional information on hydrocarbon types can be useful in determining the effects of processes in the production of various finished fuels. Producers may require additional determinations such as n-paraffins, i-paraffins, naphthenes, and aromatics for process optimization. This information also may be useful for indicating the quality of fuels and for assessing the relative combustion properties of finished fuels. This test method can be used to make such determinations.

6. Interferences

6.1 Olefins (for example, alkenes, cycloalkenes, and dienes) are known interferences that can be misidentified as naphthenes by this test method. Test method is limited to total olefins content of <1 % by volume as determined by Test Method D1319.

7. Apparatus

7.1 *Gas Chromatograph,* capable of operating at the conditions given in Table 1.

7.1.1 The typical system configuration includes a flow modulator, a first-dimension column and a second-dimension column (Fig. 1).

7.1.2 To achieve optimum separation for the different group types, column dimensions and polarity must be selected such that sufficient orthogonality is achieved. Various column configurations have been found satisfactory. Suitable non-polar column phases are dimethylpolysiloxane or similar phases. Polyethylene glycol, cyanopropyl/cyanopropyl phenyl, or equivalents are examples of suitable polar column phases.

7.2 *Gas Flow and Pressure Controllers,* with adequate precision to provide reproducible flow and pressure of the carrier gas to the chromatographic system and meet quality control requirements of the test method.

7.3 *Sample Introduction System*—Using an automatic liquid injector, the injection volume shall be chosen in a way such that the capacity of the column is not exceeded, and that the linearity of the detector is valid and meets quality control requirements of the test method.

TABLE 1 Typical Chromatographic Operating Parameters Used in Developing the Test Method

	Description			
Inlets	Front	S/SL Inlet		
	Heater	325 °C		
	Carrier Gas	Helium		
	Split ratio	1:200		
Columns	**1st dimension polar column**			
	30 m x 250 µm polar column (e.g., polyethylene glycol)			
	Flow	1 mL/min		
	2nd dimension non-polar column			
	10 m x 320 µm non-polar column (e.g., polydimethylsiloxane)			
	Flow	35 mL/min		
	Monitor column			
	Deactivated Fused Silica			
	Flow	1 mL/min		
Oven	Temperature	40 °C		
	Equilibration time	1 min		
		°C/min	Next °C	Hold min
			40	7.5
	Oven Ramp	3.2	45	0
		4.2	120	0
		4.7	165	0
		5.2	200	0
		5.7	270	3
	Total run time			57.5
Detector	Front	Front FID	Back FID	
	Heater	325 °C	325 °C	
	H2 flow	35.0 mL/min	35.0 mL/min	
	Air flow	350.0 mL/min	350.0 mL/min	
	Make-up flow	20.0 mL/min	20.0 mL/min	
Flow Modulator	Valve Idle State	Off		
	Modulation delay	0.1 min		
	Modulation period	3.5 s		
	Inject time	0.1 s		

7.3.1 An injection volume of 0.1 µL has been found satisfactory.

7.4 *Electronic Data Acquisition System,* shall meet or exceed the specifications required by the GC×GC software. X1.2 contains information as guidelines.

7.5 *GC×GC Flow Modulator*—A device which precisely transfers effluent from the first column to the second column with high repeatability. Precision for this test method uses flow modulation; other modulation types have not been tested.

7.6 *Gas Purifiers,* to remove moisture and oxygen from helium, moisture and hydrocarbons from hydrogen, and moisture and hydrocarbons from air.

8. Reagents and Materials

8.1 *Air,* compressed, <10 mg/kg each of total hydrocarbons and water. (**Warning**—Compressed gas under high pressure that supports combustion.)

8.2 *Carrier Gas,* Helium, 99.995 % pure, <0.1 mg/kg water. (**Warning**—Compressed gas under high pressure.)

8.3 *Make-up Gas,* Nitrogen, 99.995 % pure.

8.4 *Hydrogen,* 99.995 % pure, <0.1 mg⁄kg water. (**Warning**—Extremely flammable gas under high pressure.)

8.5 *Blank Run*—An instrument blank under same operating conditions as used for the analysis of the samples, except either using an empty GC vial or set the autosampler to "no injection" mode if software allows it.
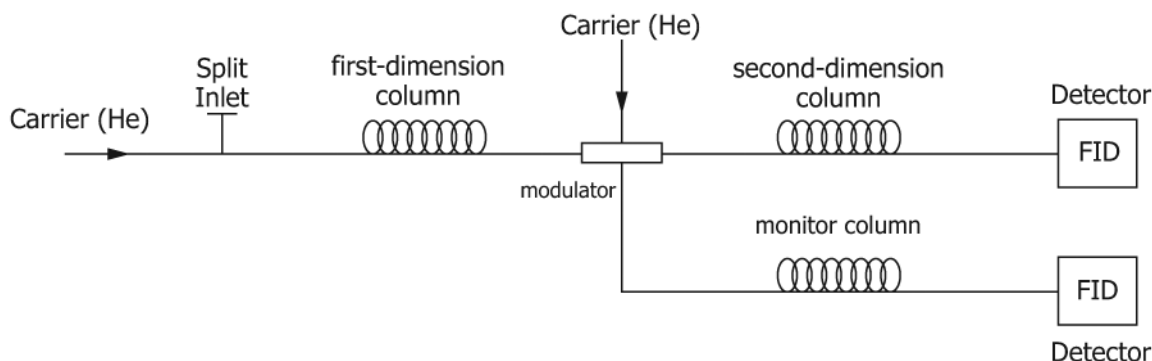
FIG. 1 Typical Instrument Configuration for a Flow Modulator used in this Test Method

8.6 *Gravimetric Blend*[2]—A quantitative blend containing paraffins, naphthenes, and aromatic hydrocarbons prepared gravimetrically in accordance with Practice D4307. Each component used in the test mixture preparations shall have a minimum purity of 99 %. The actual concentration levels are not critical, but the accepted reference values (ARV) shall be computed as per Practice D4307. A typical blend is shown in Table 2 and Fig. 2.

8.7 *Reference Check Sample(s)*[2], a known commercial or equivalent sample(s) for which the accepted average values (ARV) have been determined. Example is shown in Fig. 3 and Table 3.

NOTE 2—The blobs or peaks in Fig. 2 and Fig. 3 with a dot indicator are the blobs or peaks counted. Appendix X2 gives more information on the data acquisition and rejection of blobs or peaks.

9. Preparation of Apparatus

9.1 Install and place the system in service in accordance with the manufacturer's instructions.

9.2 Impurities in the carrier gas, hydrogen, or air will have a detrimental effect on the performance of the columns. Therefore, it is important to install efficient gas purifiers in the gas lines as close to the system as possible and to use good quality gases. The carrier gas and hydrogen gas connection lines shall be made of metal. Check that all gas connections, both exterior and interior to the system, are leak tight.

9.3 *System Conditioning*—When gas connections have been disconnected or the flow turned off, as on initial start-up, condition the system by permitting carrier gas to flow through the system for at least 30 min while the system is at ambient temperature.

9.4 Set the flow and temperatures. Table 1 contains typical settings.

9.5 Tuning the modulator to ensure full transfer of all analytes.

9.5.1 Using a monitor column:

---

[2] The sole source of supply of the commercial gravimetric blend and reference materials used in the development of this method known to the committee at this time is PAC, 8824 Fallbrook Drive, Houston, TX, 77064. PAClp.com. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee which you may attend.
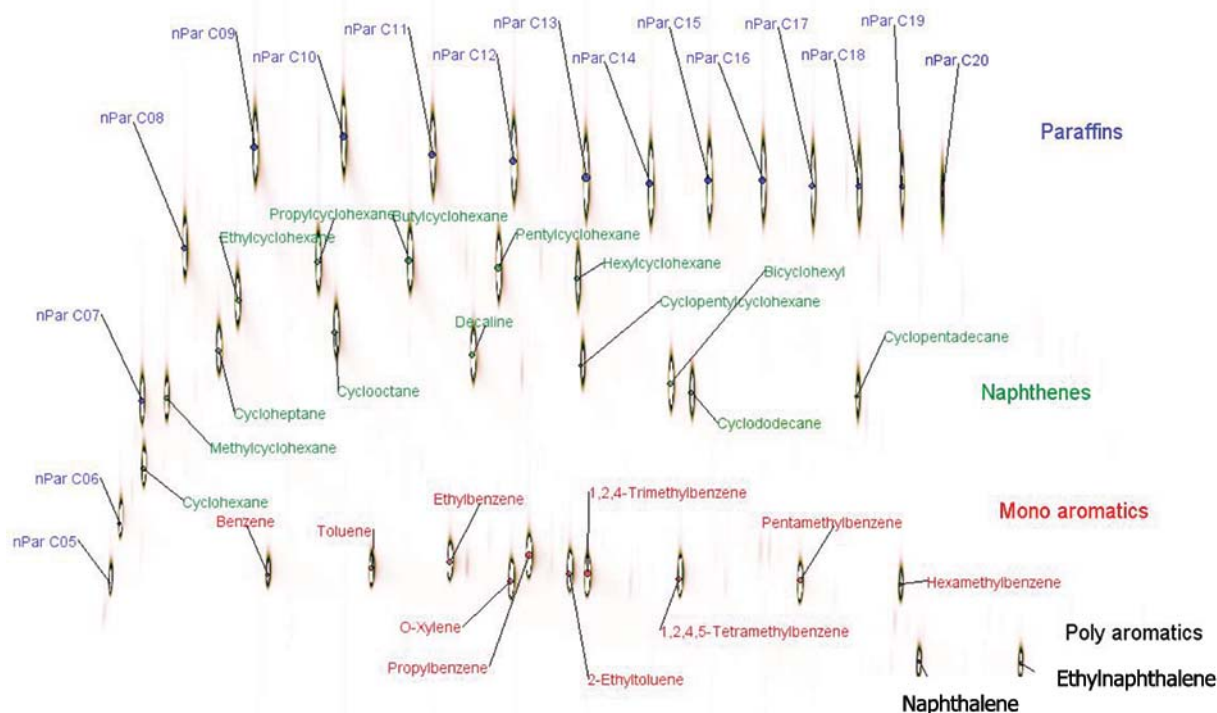
TABLE 2 Typical Content of a Gravimetric Blend

Component Name	Type	Mass Percent
n-Pentane	C5 nP	0.50
n-Hexane	C6 nP	1.00
n-Heptane	C7 nP	2.00
n-Octane	C8 nP	2.50
n-Nonane	C9 nP	3.50
n-Decane	C10 nP	4.00
n-Undecane	C11 nP	4.75
n-Dodecane	C12 nP	5.25
n-Tridecane	C13 nP	5.50
n-Tetradecane	C14 nP	5.00
n-Pentadecane	C15 nP	4.25
n-Hexadecane	C16 nP	3.50
n-Heptadecane	C17 nP	2.75
n-Octadecane	C18 nP	2.00
n-Nonadecane	C19 nP	1.00
n-Eicosane	C20 nP	0.50
Benzene	C6 A	0.50
Toluene	C7 A	1.05
Ethylbenzene	C8 A	2.00
o-Xylene	C8 A	2.75
2-ethyltoluene	C9 A	3.00
n-Propylbenzene	C9 A	4.00
1.2.4-Trimethylbenzene	C9 A	3.50
1.2.4.5-Tetramethylbenzene	C10 A	2.75
Pentamethylbenzene	C11 A	2.00
Hexamethylbenzene	C12 A	0.50
Naphthalene	C10 2-ring A	0.55
2-Ethylnaphthalene	C12 2-ring A	0.55
Methylcyclohexane	C7 N	1.25
Ethylcyclohexane	C8 N	2.00
Propylcyclohexane	C9 N	2.75
Butylcyclohexane	C10 N	3.50
Pentylcyclohexane	C11 N	4.00
Hexylcyclohexane	C12 N	1.50
Cyclohexane	C6 N	1.25
Cycloheptane	C7 N	2.00
Cyclooctane	C8 N	2.75
Cyclododecane	C12 N	1.25
Cyclopentadecane	C15 N	0.75
trans-Decahydronaphthalene	C10 2-ring N	2.75
Cyclopentylcyclohexane	C11 2-ring N	0.75
Bicyclohexyl	C12N 2-ring N	2.35
Total paraffins		48.00
Total naphthenes (cycloparaffins or cycloalkanes)		28.85
Total aromatics		23.15
Totals		100.00

FIG. 2 Gravimetric Blend for Analysis by GCxGC – FID
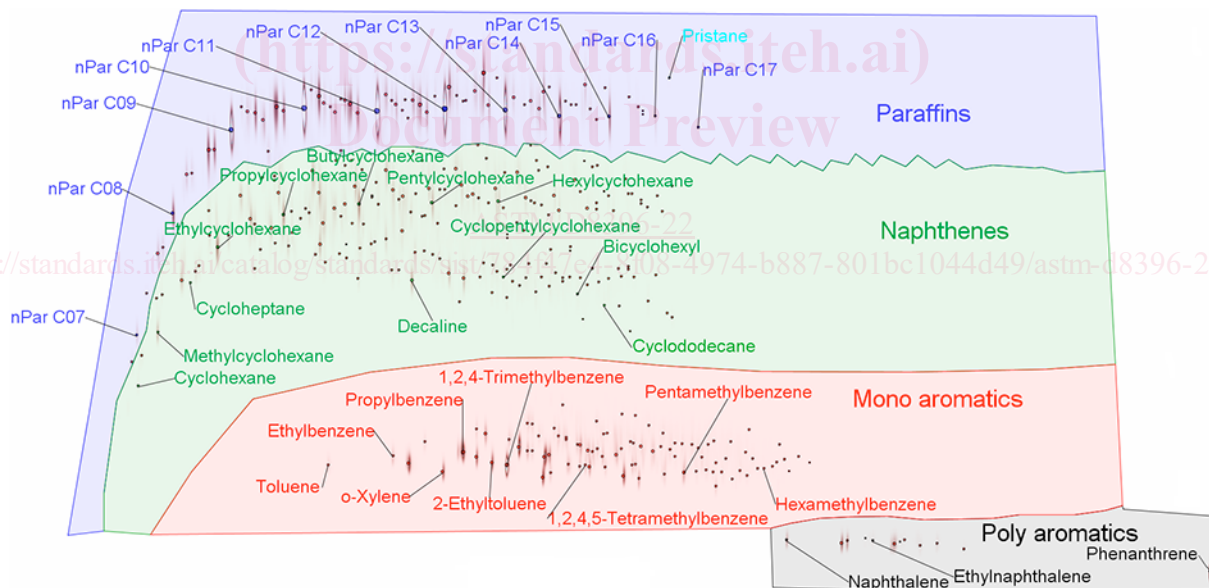

FIG. 3 GCxGC Chromatogram of Reference Check Sample by GCxGC-FID

9.5.1.1 Tune the length of the monitor column such that all components in the gravimetric blend (8.6) elute from the monitor column when the modulator is directing the flow from the first-dimension column to the monitor column.

NOTE 3—When the instrument is equipped with one detector, the tuning of the modulator requires changing the column connected to the FID. During the tuning of first-dimension column the monitor column is connected to the FID, during all other operations, including sample analysis, the second-dimension column is connected to the FID. 9.5.2 is carried out with the monitor connected to the FID, 9.6 is carried out with the second-dimension column connected to the FID, and 9.6.1 shall be

TABLE 3 Typical Content of a Reference Check Sample

Hydrocarbon Type	ARV[A] (mass percent)
Total i-paraffins	24.04
Total n-paraffins	21.50
Total naphthenes (cycloparaffins)	34.47
Total 1R aromatics	18.26
Total 2R+ aromatics	1.74

[A]The ARV's of the reference material are based on the results of six instruments. Reference material according to Practice D6299 will be developed during the pilot study or ILS, or both.

carried out twice, first with the monitor column connected, and then a second time with the second-dimension column connected. The requirements for the output as described in these sections remains equal.

9.5.2 Analyze the gravimetric blend (8.6) to confirm a correct length of the monitor column. Fig. 4 shows the correct monitor column length. All components appear in the monitor column chromatogram under normal operating conditions.

9.5.3 Fig. 5 shows a too-long monitor column, some of the components are also directed to the second-dimension column. The components are visible in both chromatograms. Shorten the column until all components elute from the first-dimension column.

9.6 Tuning the modulation period. Set the modulation delay to a time period in which all components elute from the first-dimension column to the second-dimension column.

9.6.1 Use the known gravimetric blend (8.6) to test the modulation setting. When using a monitor column, no components shall elute from the monitor column thus ensuring that all modulated fractions are retained prior to being injected into the second-dimension column; if the modulation period is too short, fractions may enter into the monitor column and be detected. Fig. 6 shows a correct modulation period; the upper chromatogram is from the second-dimension column and shows all components from the gravimetric blend. The lower chromatogram is from the monitor column and shows no peaks from the gravimetric blend.

9.7 Optimizing the oven temperature program: The optimum temperature program uses all separation space while avoiding wrap-around (Fig. 7). Fig. 8 is an example of a too-fast oven temperature program, and Fig. 9 is an example of a too-slow oven temperature program.

Note 4—Wrap-around is explained with the red arrow in Fig. 7 and Fig. 9. A too-slow oven temperature program causes too-late elution from the second-dimension column, and the peaks elute in the next modulation period. The red arrow in Fig. 7 shows the position where the band of n-paraffin peaks should appear with a correct oven temperature program. The arrow in Fig. 9 illustrates a too-slow oven temperature program, the band of n-paraffins elutes in the next modulation period.

9.7.1 Use the gravimetric blend (8.6) and the reference check sample (8.7) to check the temperature program. Fig. 2 and Fig. 3 are examples of a correct temperature program.

9.7.2 Verify the isothermal time. The isothermal time is set at the elution time of the first component.

9.8 Set the templates in the GCxGC software using vendor's recommendations. Fig. 3 shows the boundaries and fingerprint obtained. This method allows the use of any combination of data handling and/or instrument control software capable of generating the necessary data and data handling to present results in the GCxGC format (Appendix X1).

10. Standardization

10.1 Using the procedure outlined in Section 11, analyze the gravimetric blend (8.6). Each individual component should be presented as a single (blob) peak by the GCxGC software (Fig. 2).

10.1.1 Using the relative response factors in Table 4 or calculated from Eq 1, compare the reported values with the accepted reference values (ARV). The maximum acceptable
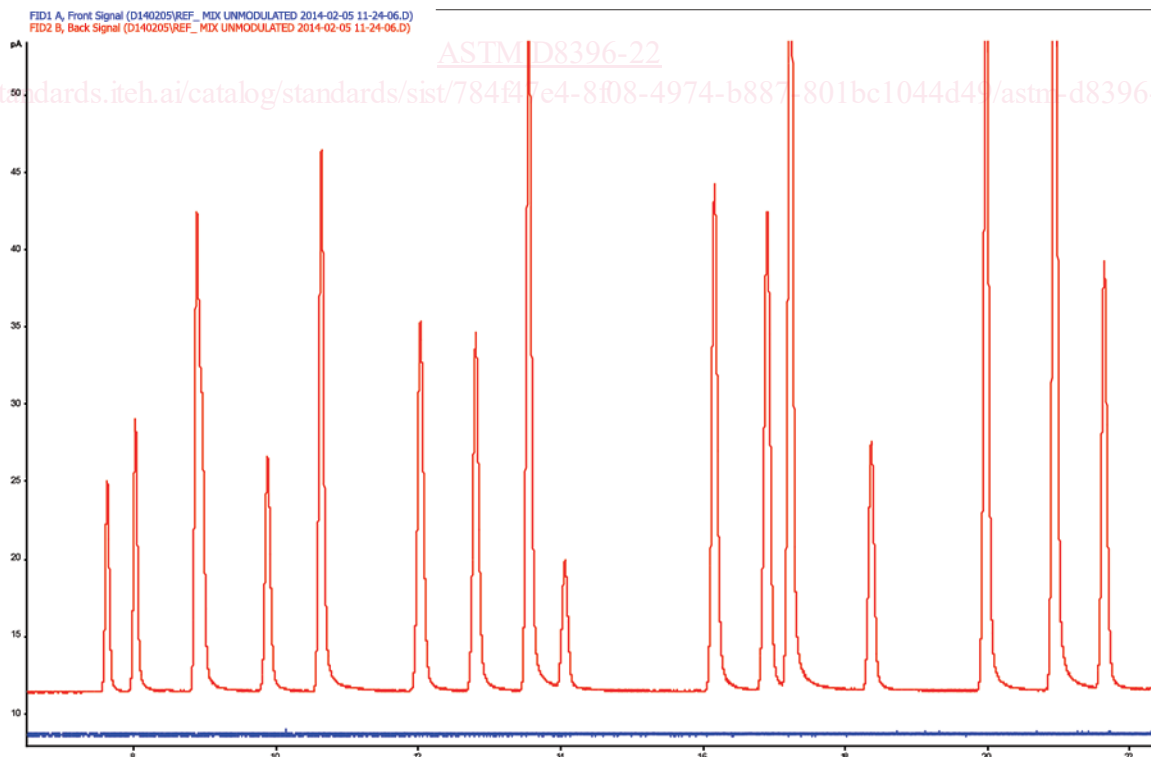

FIG. 4 All Gravimetric Standard Components Elute from the Monitor Column, Peaks are only Appearing in 1-Dimension Chromatogram (Red)
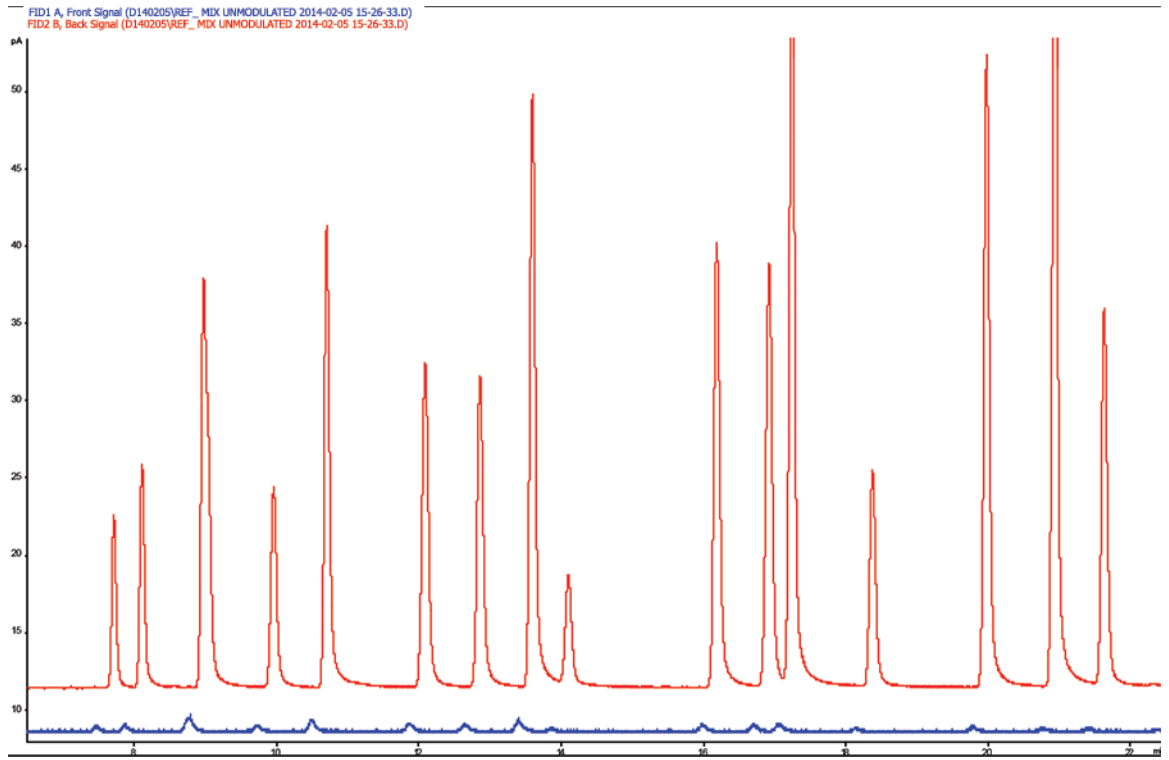
FIG. 5 Incorrect Monitor Column Length, Components Elute from both, the Monitor Column and the Second-Dimension Column
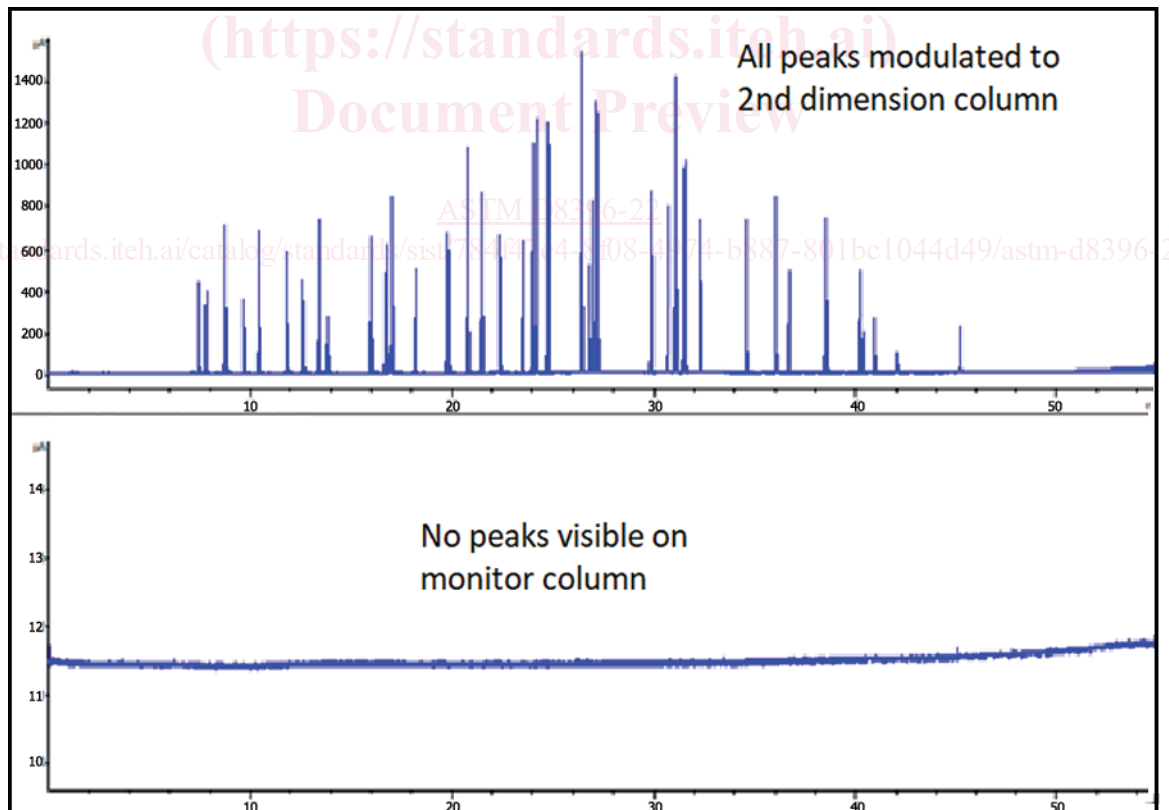

FIG. 6 Chromatogram Example of a Correct Modulation Period: All Components Modulated to and Eluted from the Second-Dimension Column
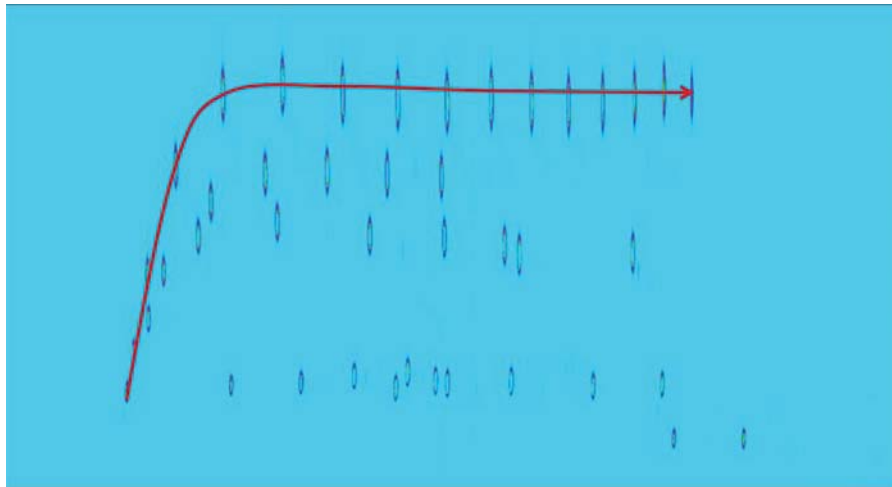
FIG. 7 Example of Optimal Use of the Separation Space

FIG. 8 Example of a Too-fast Oven Temperature Program

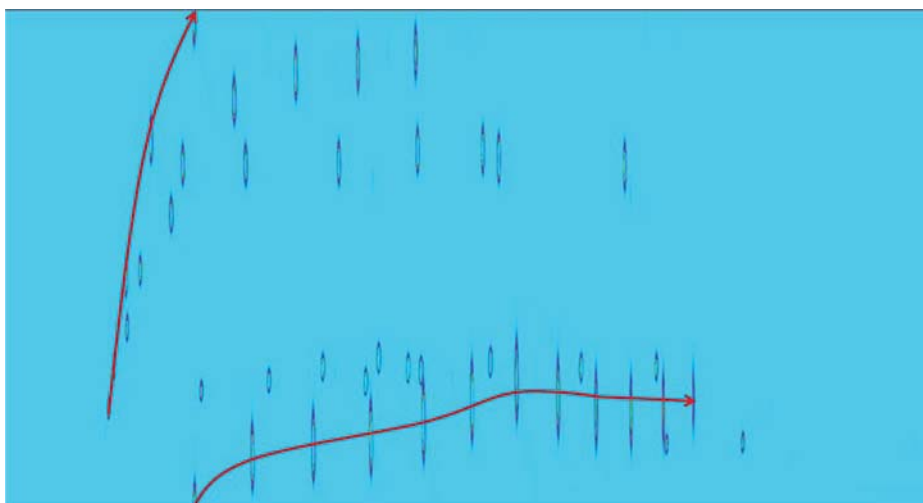**FIG. 9 Example of a Too-slow Oven Temperature Program (Wrap-Around)**

deviation for any n-Paraffin is 0.3 % mass absolute; the maximum acceptable deviation for each group is 1.0 % mass absolute.

NOTE 5—The quantification of n-paraffins is important because this result is subtracted from the total paraffins to determine the iso-paraffin content. The total paraffins do not contain the naphthenes (cycloparaffins).

TABLE 4 Calculated Relative Response Factors

Component	RRF	1/RRF
n-Paraffin 05	1.0080	0.9920
n-Paraffin 06	1.0034	0.9967
n-Paraffin 07	1.0000	1.0000
n-Paraffin 08	0.9975	1.0025
n-Paraffin 09	0.9955	1.0045
n-Paraffin 10	0.9940	1.0061
n-Paraffin 11	0.9927	1.0074
n-Paraffin 12	0.9916	1.0085
n-Paraffin 13	0.9907	1.0094
n-Paraffin 14	0.9899	1.0102
n-Paraffin 15	0.9893	1.0108
n-Paraffin 16	0.9887	1.0114
n-Paraffin 17	0.9882	1.0120
n-Paraffin 18	0.9877	1.0124
n-Paraffin 19	0.9873	1.0129
n-Paraffin 20	0.9869	1.0133
Methylcyclohexane	0.9799	1.0205
Ethylcyclohexane	0.9799	1.0205
Propylcyclohexane	0.9799	1.0205
Butylcyclohexane	0.9799	1.0205
Pentylcyclohexane	0.9799	1.0205
Hexylcyclohexane	0.9799	1.0205
Cycloheptane	0.9799	1.0205
Cyclooctane	0.9799	1.0205
Cyclohexane	0.9799	1.0205
Cyclopentadecane	0.9799	1.0205
Decalin	0.9658	1.0354
Cyclopentylcyclohexane	0.9671	1.0340
Bicyclohexyl	0.9681	1.0329
Benzene	0.9095	1.0995
Toluene	0.9195	1.0875
o-Xylene	0.9271	1.0787
Ethylbenzene	0.9271	1.0787
2-EthylToluene	0.9329	1.0719
Propylbenzene	0.9329	1.0719
1.2.4-trimethylbenzene	0.9329	1.0719
1.2.4.5-tetramethylbenzene	0.9376	1.0665
pentamethylbenzene	0.9415	1.0622
hexamethylbenzene	0.9447	1.0586
naphthalene	0.8954	1.1168
2-Ethylnaphthalene	0.8919	1.1213
Total Paraffins	0.9899	1.010
Total Naphthenes	0.9658	1.035
Total 1R-Aromatics	0.9446	1.059
Total 2R+-Aromatics	0.8850	1.125

10.2 Using the procedure outlined in Section 11, analyze the reference check (8.7) sample to test the analytical performance of the system (Fig. 3). Compare the reported values with the reported accepted reference values (ARV). The maximum acceptable deviation is 0.3 % mass absolute per component and 1.0 % mass absolute per group.

10.2.1 If the specifications in 10.1.1 and 10.2 are not met, adjust GC and modulator settings and parameters according to the manufacturer's guidelines and reanalyze the gravimetric blend (8.6) and reference check sample (8.7) until the specifications are met.

11. Procedure

11.1 Load the analysis conditions as determined in Section 9 into the instrument.

11.2 When all temperatures have stabilized at the analysis conditions, inject a representative aliquot of sample (or test mixture) and start the analysis. Typically, 0.1 µL has been found to be suitable.

11.3 Starting the analysis should begin the data acquisition and should begin the timing function that controls all the various programmed temperature changes and modulator switching.

11.4 Analyze a blank (8.5) (non-sample) analysis.

11.5 Analyze the gravimetric blend (8.6) and reference sample (8.7).

11.5.1 To ensure that the full range of 2-ring aromatic hydrocarbons are detected, analyze a sample spiked with a small amount (for example, 0.3 % to 0.5 % by mass) of phenanthrene. See Fig. 3. This method combines any detected 3-ring+ components with the 2-ring aromatics. Generally, 3-ring aromatics are expected to be in very low or nondetectable concentration in the applicable boiling point range of this test method.

11.6 Upon completion of its programmed cycle, generate for the sample(s) a chromatogram, and print a report of concentrations. Verify that QC sample(s) meet the specified requirements. Data processing may be conducted either automatically using appropriate software or processed off-line using appropriate software. If the results of the reference material differ more than the maximum acceptable deviation as defined in 10.2, verify the boundary settings between the groups or verify system optimization, or both. Appendix X2 gives information of testing the linearity of the system, if necessary, to aid in the troubleshooting.

11.6.1 Use the GCxGC software for the identification of the groups and calculation of the results in percent m/m.

12. Calculation

12.1 Calculations are based on relative response factors and produce results that are reported in mass percent.

12.2 The relative response factors of the components present in the gravimetric blend are given in Table 4; they are calculated relative to heptane using Eq 1.

NOTE 6— Since a RRf cannot be calculated for a group, the RRf for hydrocarbon types are equated to a representative hydrocarbon of the group. Given the uniform within-group response characteristics of a FID, the theoretical relative error, resulting from differences in carbon number distribution of typical samples, is <2 %. The precision of this test method is determined with the RRf's for the hydrocarbon types as indicated in Table 4.

$$RRf = \frac{[(C_{aw} \times C_n) + (H_{aw} \times H_n)] \times 0.83905}{(C_{aw} \times C_n)} \quad (1)$$

where:
RRf = relative response factor for a component,
C_{aw} = atomic mass of carbon, 12.011.
C_n = number of carbon atoms in the component,
H_{aw} = atomic mass of hydrogen, 1.008.
H_n = number of hydrogen atoms in the component, and
0.83905 = factor to normalize the result to a heptane response of unity, (1).

12.3 Calculate the concentration in mass percent of each identified component or hydrocarbon type according to Eq 2.

$$M = [(A_i / F_i) \times 100]/\Sigma A_x/F_x \quad (2)$$

9

where:

M = mass percent of an identified component or hydrocarbon type,
A_i = integrated area of the component or hydrocarbon type,
A_x = all individual integrated peaks or blobs,
F_i = relative response factor for the component or hydrocarbon type, RRF or 1/RRf, calculated using Eq 1 or from Table 4,
F_x = RRF or 1/RRF for all integrated peaks or blobs, and
100 = factor to normalize corrected area to 100 %.

12.4 The total paraffins and n-paraffins are calculated according to 12.3. The total of i-paraffins is calculated by subtracting the n-paraffin mass percent from the total paraffin mass percent.

13. Report

13.1 Report the mass percent for each hydrocarbon type total i-paraffins, total n-paraffins, total naphthenes, total 1R-aromatics, total 2R+ to the nearest 0.1 %.

14. Precision

14.1 The repeatability and reproducibility will be determined by an interlaboratory study in accordance with ASTM methodology within 5 years after publication using various sample types in the 36 °C to 343 °C range. This section reports interim, single-laboratory repeatability standard deviations for the quantities listed in Table 5.

14.1.1 To illustrate repeatability, tests were carried out by a single laboratory on three commercial aviation turbine fuel samples. Table 5 shows the percent mass values of the various

parameters for the three samples. The standard deviation was calculated for all five parameters in accordance with 6.2.1 of Practice D6300, and the results are given in Table 5.

15. Quality Control Checks

15.1 Once the test method has been set-up, it is recommended that the precision and accuracy of the analysis are monitored as follows:

15.1.1 *Precision:*

15.1.1.1 Quality control sample(s) as defined in D6299 may include typical production fuels in the concentration range(s) of interest and used as a daily standard to verify performance of the instrument. One or more QC samples may be used to span the concentration range of interest and variations in fuel compositions.

15.2 *Accuracy:*

15.2.1 Gravimetric standards and check or reference standards of known ARV (Average Reference Values) as described in this test method may be used. These standards may be analyzed periodically (for example, when instrument is first placed in service and/or after performing instrument maintenance and thereafter) and monitored by SQC as described in D6299.

16. Keywords

16.1 aromatics; comprehensive two-dimensional gas chromatography; cycloparaffins; gas chromatography; GCxGC; hydrocarbon type; i-paraffins; mid-distillates; multidimensional gas chromatography; naphthenes; n-paraffins

APPENDIXES

(Nonmandatory Information)

X1. GENERAL INFORMATION ON DATA ACQUISITION AND SETTING THE TEMPLATE

X1.1 This appendix is intended to give some guidelines on data acquisition and setting the template. These guidelines may not be applicable to all commercially available GCxGC software packages. For detailed operation of the GCxGC software

refer to the manufacturers' instructions. For the data handling, generally two software packages are needed to handle the GCxGC 3-D output.

TABLE 5 Single Laboratory Percent Mass Standard Deviations, Determined According to Practice D6300 Section 6.2.1

	Sample 1		Sample 2		Sample 3	
	Average (percent mass)	St. dev.	Average (percent mass)	St. dev.	Average (percent mass)	St. dev.
Total i-Paraffins	22.0	0.21	24.3	0.07	23.7	0.10
Total n-Paraffins	19.0	0.03	20.7	0.03	21.9	0.04
Total Naphthenes	36.7	0.22	34.3	0.05	34.8	0.12
Total 1R Aromatics	21.8	0.03	18.7	0.03	18.0	0.01
Total 2R+ Aromatics	0.5	0.05	1.9	0.01	1.5	0.04

X1.2 Electronic Data Acquisition System

X1.2.1 The chromatographic system shall be able to scan the column effluent with a frequency of at least 200 Hz. The raw data are further treated in the dedicated GCxGC software.

X1.3 GCxGC Software

X1.3.1 A typical processing sequence to analyze raw data produced by this test method, identifying and quantifying chemicals in a sample:

(1) Import a raw data file to create a chromatographic image (X1.4).

(2) Phase shift, to correctly align the chromatogram (X1.5).

(3) Detect the blob peaks in the chromatogram (X1.6).

(4) Load / apply Template (X1.7).

(5) Apply Calibration file (RRf) (X1.8).

(6) Report results (X1.9).

X1.4 Import a Raw Data File

X1.4.1 The sample datafile for processing in the GCxGC software shall be corrected for any signal from a blank analysis. The blank analysis (a run with no or an empty vial) shall be subtracted in either the data acquisition software or the GCxGC software.

X1.5 Phase Shift

X1.5.1 Phase shift is a tool for shifting the image with respect to the start time of the second-dimension, see Fig. X1.2.

X1.6 Detect the Blobs

X1.6.1 Identify the blobs, using the gravimetric blend. Blobs are rejected when they do not comply with minimum requirements for area, volume, or the peak, or combinations thereof. This method is developed with a minimum area of 15, a minimum volume of 250 (which is lower than the volume of a blob of 0.03 % mass), and a minimum peak of 1.

X1.6.1.1 Verify these minimum requirements by examining the 3-D output on the screen.

X1.6.1.2 Make sure to exclude sample analysis artifacts such as column bleed or other excessive detector noise.

X1.7 Load or Apply the Template

X1.7.1 Templates are patterns of peaks and graphic objects observed in image(s) used to recognize similar patterns of blobs in subsequent image(s). Once recognized, the metadata (including chemical name, group name, and internal standard association) for the blobs in the target image can be set from the template. Fig. X1.3 is an example of a template applied to an image of the gravimetric blend. The known blobs are marked.

X1.7.2 The known blobs are used to set the boundaries for the hydrocarbon types. For this test method, boundaries are set for paraffins, naphthenes, 1-R aromatics, 2-R aromatics plus 3-R aromatics.

X1.7.3 Quantification is based on the blobs, the area, or a combination of both.

X1.7.4 Fig. X1.4 is an example of the boundaries for paraffins, naphthenes, 1-R aromatics, 2-R aromatics. The correct determination of the boundaries can be checked using the 3-D plot on the computer screen, especially for the boundary between paraffins and naphthenes.

X1.8 Apply the Calibration File

X1.8.1 This test method uses theoretical response factors relative to n-heptane. The relative response factors can be calculated according to Section 12 or taken from Table 4. The interim precision of this test method has been determined by
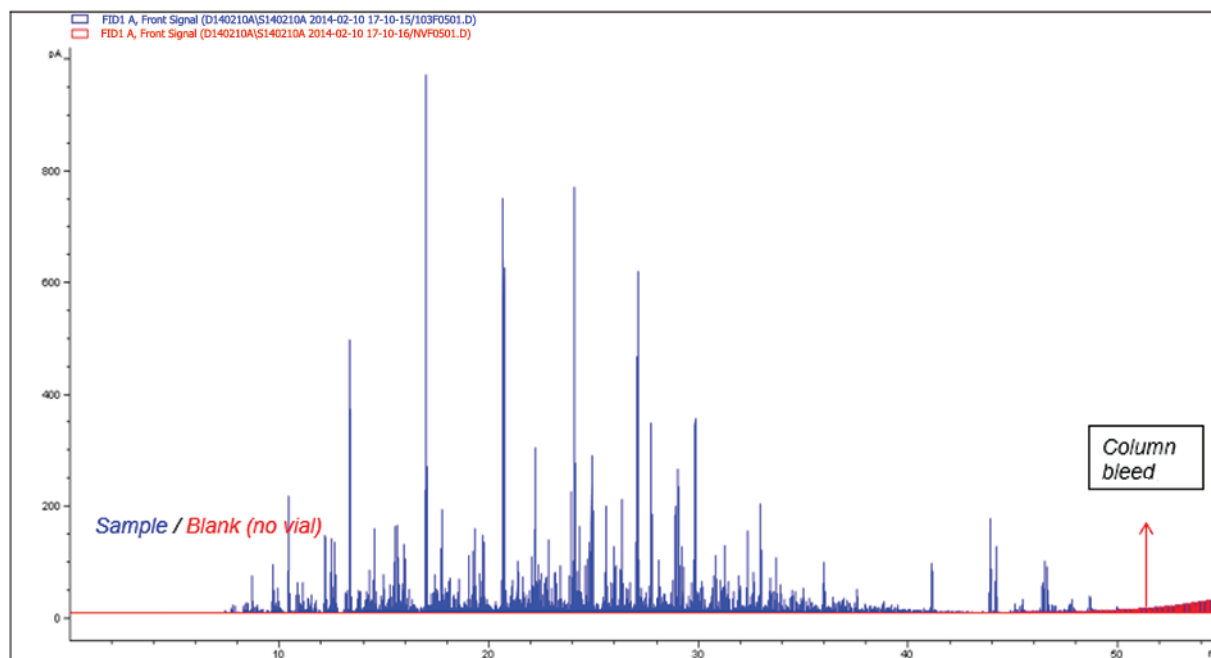

FIG. X1.1 Overlay of a Sample Analysis and a Blank Run