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Standard Test Method for
Determination of Hydrocarbon Group Types and Select Hydrocarbon and Oxygenate Compounds in Automotive Spark-Ignition Engine Fuel Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)[1]

This standard is issued under the fixed designation D8071; 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 is a standard procedure for the determination in percent mass or percent volume of hydrocarbon group types (paraffins, isoparaffins, olefins, naphthenes, aromatics), methanol, ethanol, benzene, toluene, ethylbenzene, xylenes, naphthalene, and methylnaphthalenes in automotive spark-ignition engine fuels using gas chromatography and vacuum ultraviolet detection (GC-VUV).

1.1.1 The concentration ranges for which precision has been determined are as follows:

Property	Units	Applicable Range
Paraffins	% Volume	3.572 to 23.105
Isoparaffins	% Volume	22.697 to 71.993
Olefins	% Volume	0.011 to 44.002
Olefins	% Mass	0.027 to 41.954
Naphthenes	% Volume	0.606 to 18.416
Aromatics	% Volume	14.743 to 58.124
Methanol	% Volume	0.063 to 3.426
Ethanol	% Mass	0.042 to 15.991
Benzene	% Volume	0.09 to 1.091
Toluene	% Volume	0.698 to 31.377
Ethylbenzene	% Volume	0.5 to 3.175
Xylenes	% Volume	3.037 to 18.955
Naphthalene	% Volume	0.019 to 0.779
Methylnaphthalenes	% Volume	0.21 to 1.484

1.1.2 This test method may be applicable to other concentration ranges, to other properties, or to other hydrocarbon streams, however precision has not been determined.

1.2 Individual hydrocarbon components are typically not baseline-separated by the procedure described in this test method, that is, some components will coelute. The coelutions are resolved at the detector using VUV absorbance spectra and deconvolution algorithms.

1.3 While this test method reports percent mass and percent volume for several specific components that may be present in automotive spark-ignition engine fuel, it does not attempt to speciate all possible components that may occur in automotive spark-ignition engine fuel. In particular, this test method is not intended as a type of detailed hydrocarbon analysis (DHA).

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

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use. See specific hazard statements in subsection* 8.4 *and Section* 9.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

D3606 Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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

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

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

D5769 Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasolines by Gas Chromatography/Mass Spectrometry

D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement

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

D6550 Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

D6730 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre Capillary (with Precolumn) High-Resolution Gas Chromatography

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *integration filter, n*—a mathematical operation performed on an absorbance spectrum for the purpose of converting the spectrum to a single-valued response suitable for representation in a two-dimensional chromatogram plot.

3.1.2 *library reference spectrum, n*—an absorbance spectrum representation of a molecular species stored in a library database and used for identification of a compound/compound class or deconvolution of multiple coeluting compounds.

3.1.3 *response area, n*—generally refers to a response summed over a given time interval and has units of absorbance units (AU).

3.1.3.1 *Discussion*—A time factor necessary to convert a response area to a true mathematical area cancels out of all critical calculations and is omitted.

3.2 *Abbreviations:*

3.2.1 AU—absorbance units

3.2.2 DHA—detailed hydrocarbon analysis

3.2.3 GC-VUV—gas chromatography with vacuum ultraviolet spectroscopy detection

3.2.4 RI—retention index

3.2.5 RRF—relative response factor

4. Summary of Test Method

4.1 An automotive spark-ignition fuel sample is introduced to a gas chromatographic (GC) system. After volatilization, the effluent is introduced onto a GC column for separation, and then detected by a vacuum ultraviolet absorption spectroscopy detector.[3] The separation is accomplished using a 30 m, nonpolar phase capillary column and a moderately fast temperature ramp (typical operating parameters of this test method are given in Table 1). Coelutions are resolved by the detector using vacuum ultraviolet absorbance spectra and deconvolution.

4.2 The result of the measurement is the determination of the total response areas of the five hydrocarbon classes of paraffins, isoparaffins, olefins, naphthenes, and aromatics, in addition to several individual species components. The percent mass concentrations are calculated from the response areas using class-based or compound-specific relative response factors, as appropriate. The percent volume concentrations are calculated from the mass concentrations.

5. Significance and Use

5.1 The determination of class group composition of automotive spark-ignition fuels as well as quantification of various individual species such as oxygenates and aromatics in automotive fuels is useful for evaluating quality and expected performance, as well as compliance with various governmental regulations.

6. Interferences

6.1 Interferences with this test method, if any, have not been determined.

7. Apparatus

7.1 *Gas chromatograph,* equipped with automated oven temperature control and split/splitless inlet.

7.1.1 *Flow Controllers*—The gas chromatograph must be equipped with mass flow controllers capable of maintaining carrier gas flow constant to ±1 % over the full operating temperature range of the column. The inlet pressure of the carrier gas supplied to the gas chromatograph must be at least 485 kPa. This will ensure that the minimum pressure needed to compensate for the increase in column back-pressure as the column temperature is maintained.

TABLE 1 Typical Instrument Settings for GC-VUV Automotive Spark-Ignition Fuel Measurement

Column dimensions	Capillary, 30 m × 0.25 mm ID × 0.25 µm film thickness
Column phase[A]	Nonpolar (for example, 100 % dimethyl polysiloxane)
Inlet temperature	250 °C
Injection volume[B]	1.0 µL
Split ratio[B]	300:1
Column flow[C]	1.0 mL/min
Oven initial temperature	35 °C
Initial hold time	10 min
Oven ramp	7 °C/min
Final oven temperature	200 °C
Final hold time	0 min
Detector makeup gas pressure (gauge)	2.1 kPa
Detector scan rate	4.5 Hz
Detector flow cell temperature	275 °C
Transfer tube temperature	275 °C

[A] Columns with low bleed phases such as MS grade have been successfully used for this application (see 11.6)
[B] Other injection volumes (see 7.1.2) and split ratios may be used to achieve the required benzene response (see 13.2)
[C] Gas chromatograph manufacturer's column flow systems must be set to maintain constant flow or gas velocity throughout the temperature ramp. Do not use constant pressure.

7.1.2 *Autosampler*—It is highly recommended that the gas chromatograph is equipped with an autosampler. All precision data were obtained using a GC equipped with an autosampler.

7.2 *Purge/Makeup Gas,* for detector: nitrogen or argon (see 8.3).

7.3 *Oxygen, Water, Hydrocarbon Filters,* to further purify GC carrier gas and detector purge/makeup gas.

7.4 *Capillary Analytical Column,* nonpolar (for example, dimethyl polysiloxane) phase, dimensions 30 m length, 0.25 mm internal diameter, 0.25 µm film thickness.

7.5 *Vacuum Ultraviolet Absorption Spectroscopy Detector,* capable of measuring 125 nm to 240 nm absorbance spectra with a wavelength resolution of 1 nm or better.

7.5.1 The detector shall be able to interface with a gas chromatographic system and measure an eluent with a scan frequency of at least 4.5 Hz with a baseline peak-to-peak noise width over a 10 s interval no greater than 0.002 AU when averaged over the following wavelength regions: 125 nm to 240 nm, 170 nm to 200 nm, 125 nm to 160 nm, and 0.001 AU when averaged over the 140 nm to 160 nm wavelength region.

7.5.2 The detector shall be equipped with a shutter or equivalent mechanism that allows the detector array to be blocked from the light source in order to perform a "dark" measurement of electronic noise level.

7.5.3 The detector shall be equipped with a flow cell capable of being heated to at least 275 °C.

7.5.4 The detector shall have an independently controlled makeup gas capability, capable of providing up to 5 mL ⁄ min additional flow of nitrogen, helium, or argon to the flow cell.

7.6 *Data Processing System,* capable of storing and processing absorbance scan data and corresponding time.

7.6.1 Data processing system shall include a database library of vacuum ultraviolet reference spectra, compound class information, carbon number, density, and approximate retention index values. Data processing system shall also store relative response factors for each hydrocarbon class in addition to relative response factors for individually reported compounds.

7.6.2 Data processing system shall be capable of implementing equations and fit procedures that result in deconvolution of absorbance spectra that contain contributions from multiple species.

7.6.3 Data processing system shall be capable of binning and storing response contributions from each deconvolution analysis and reporting a combined total response at the end of the analysis.

7.6.4 Data processing system shall be capable of implementing equations to convert response areas to percent mass and further convert percent mass to percent volume.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where

such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 Helium carrier gas for gas chromatograph, 99.999 % pure.

NOTE 1—Test method performance has not been studied for other carrier gases such as hydrogen or nitrogen.

8.3 Nitrogen, helium, or argon purge/makeup gas for vacuum ultraviolet detector, 99.999 % pure.

8.4 Methylene chloride, reagent grade, used as a solvent test sample and GC rinse solvent. (**Warning—**Toxic material. May be combustible at high temperatures.)

8.5 Retention time standard consisting of isobutane (iC4), butane (C4), isopentane (iC5), and pentane through pentadecane linear alkanes, approximately 1 % by mass each, in suitable solvent such as methylene chloride, used as retention time markers.

8.6 A system validation mixture prepared in compliance with Practice D4307, having the components and approximate concentrations given in Table 2. The concentrations of the

TABLE 2 System Validation Mixture

Component	Concentration (percent mass)
Cyclopentane	1.1
n-Pentane	1.1
Cyclohexane	2.1
2,3-Dimethylbutane	2.1
n-Hexane	2.1
1-Hexene	1.5
Methylcyclohexane	4
4-Methyl-1-hexene	1.6
n-Heptane	3.5
1,2-Dimethylcyclohexane	5
*Iso*octane	5
n-Octane	5
1,2,4-Trimethylcyclohexane	4
n-Nonane	4.5
n-Decane	4.5
n-Undecane	3.5
n-Dodecane	3.5
Benzene	2.2
Toluene	2.2
trans-Decahydronaphthalene	4
n-Tetradecane	4.5
Ethylbenzene	4.5
o-Xylene	4
n-Propylbenzene	5
1,2,4-Trimethylbenzene	4.5
1,2,3-Trimethylbenzene	5
1,2,4,5-Tetramethylbenzene	5
Pentamethylbenzene	5
Total Paraffins	32.2
Total Isoparaffins	7.1
Total Olefins	3.1
Total Naphthenes	20.2
Total Aromatics	37.4
Total Xylenes	4.0

prepared system validation mixture should be close to those in Table 2.

8.7 Check standard VUVCS S24,[5] with accepted reference values (ARV) and tolerance limits as listed in Table 3.

NOTE 2—VUVCS S24 is one of the samples included in the ILS for the determination of method precision as described in Research Report RR:D02-1909.

9. Hazards

9.1 Many of the compounds in automotive spark-ignition engine fuel or other test samples used in this test method are toxic, flammable, or both. Safety and sample-handling procedures appropriate for working with such materials shall be in place before attempting to use this test method.

9.2 Hydrogen is flammable and potentially explosive if not properly used. Use of hydrogen as a GC carrier gas shall only be done at laboratories experienced with its use, with proper safety procedures in place.

10. Sampling

10.1 Refer to Practices D4057 and D5842 for guidelines on obtaining automotive spark-ignition engine fuel samples for analysis. Samples should be kept refrigerated at approximately 4 °C until ready to be analyzed.

11. Preparation of Apparatus

11.1 Ensure that all gas connections are properly made, without leaks.

11.2 Install oxygen, moisture, and hydrocarbon filters in gas lines upstream of GC and detector. Maintain gas filters as instructed by manufacturer.

11.3 Install the 30 m column in the GC inlet. Condition the column according to the column manufacturer's recommendations prior to installation in the detector.

11.4 Perform maintenance on the GC as suggested by manufacturer, such as replacing septum and liner.

11.5 Configure the injector, carrier gas, and other GC parameters according to Table 1.

11.6 Inject the solvent test sample defined in 8.4 and run the GC-VUV apparatus through a full oven ramp and cool-down cycle. Repeat.

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[5] Available from Spectrum Quality Standards, 17360 Groeschke Rd., Houston, TX 77084, https://spectrumstandards.com.

TABLE 3 Check Sample VUVCS S24 Tolerances[A]

Property	Sample	95 % conf. /99 % coverage tolerance interval
Aromatics, vol%	VUVCS-S24	15.346 to 18.078
Benzene, vol%	VUVCS-S24	0.616 to 0.712
Olefins, vol%	VUVCS-S24	9.15 to 10.925
Ethanol, mass%	VUVCS-S24	10.203 to 11.678
Paraffins, vol%	VUVCS-S24	9.486 to 11.003

[A] Consensus results for Check Sample VUVCS S24 obtained from 21 laboratories in 2019. Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1909. Contact ASTM Customer Service at service@astm.org.

11.6.1 Assess the baseline on either a solvent test sample or a system validation mixture (see 8.6) run. The average absorbance value (125 nm to 240 nm) of the last 1.0 min section of the baseline at the end of the oven ramp shall be no more than ±0.0035 AU of the average value (125 nm to 240 nm) of the initial 1.0 min to 2.0 min range.

12. Calibration and Standardization

12.1 On installation of GC-VUV apparatus, after significant maintenance of GC-VUV apparatus, or after a significant method change, establish a retention index file. Run the retention index sample (see 8.5) using the same flow conditions and oven ramp profile as measured samples (see Table 1 for recommended run conditions). Record the retention times of iC4, C4, iC5, and C5 through C15 linear alkanes. These will serve as retention time markers.

12.1.1 Significant method changes include changing the GC, column type, carrier gas type, or oven ramp profile. Significant maintenance of the GC-VUV apparatus includes changing or trimming the analytical column.

12.2 A list of retention times and retention indices for the linear alkanes is used to estimate rough elution times of other compounds in the VUV library according to an interpolation scheme. The most convenient retention index scheme sets the linear alkane retention indices to multiples of 100 according to carbon number: butane RI = 400, pentane RI = 500, etc. Each compound entry in the VUV library shall have an associated retention index generated using the same RI scheme. Otherwise, the associated retention indices do not need to be particularly accurate. The RI values for nonpolar capillary chromatography found in the literature or other ASTM test methods, such as Test Method D6730, may be used.

12.2.1 Once updated, the same retention time marker list is used for all subsequent automotive spark-ignition fuel measurements until the next modification or maintenance of the GC-VUV instrumentation.

12.3 The conversion from response areas to percent mass uses class-based or compound-specific relative response factors. The relative response factors account for the differing areal response per unit mass for the various hydrocarbon classes.

12.4 For the purpose of this calculation, the response at a given elution time refers to the absorbance averaged over the 125 nm to 240 nm wavelength region. The response area refers to the sum of the response over all detector scans within a given time region. A true area can be generated by multiplying this quantity by the time interval between scans. However, this step is unnecessary when the scan rate is kept constant throughout a given measurement. For the purposes of this test method, the response area is taken to be a sum having units of absorbance units.

12.5 The response factors are relative to the response of methane, which is taken to have a relative response factor of 1.

12.6 Relative response factors used to obtain the precision data in this test method are given in Table 4 and Table 5, and are suitable for use with this test method.

TABLE 4 Relative Response Factors for Bulk Hydrocarbon Classes

Hydrocarbon Class	Relative Response Factor
Paraffin	0.769
Isoparaffin	0.781
Olefin	0.465
Naphthene	0.786
C_9+ Aromatics	0.296

TABLE 5 Relative Response Factors for Specific Individual Compounds and Compound Groups

Compound	Relative Response Factor
Ethanol	1.029
Methanol	1.211
*Iso*octane	0.674
Benzene	0.258
Toluene	0.267
Ethylbenzene	0.284
Xylenes	0.284
Naphthalene	0.207
1-Methylnaphthalene, 2-Methylnaphthalene	0.250

13. Pre-Measurement Validation

13.1 Before proceeding with measurements after a significant change or maintenance of the GC-VUV system, the procedures in Section 11 shall have been completed, and a retention index file generated or verified following the procedure in 12.1 and 12.2.

13.2 Analyze the system validation mixture (8.6) and verify that the total response for benzene is 3.5 ± 0.25.

13.2.1 If the total response is outside the required range, adjust the detector make-up gas pressure and reanalyze the system validation mixture, checking the benzene response until it is within the specified range. Increasing the detector make-up gas pressure will decrease the benzene response. Do not adjust the make up gas pressure to less than 1.0 kPa or to more than 4.1 kPa.

13.2.2 If the detector make-up gas pressure has been changed, reanalyze the retention index sample (12.1 and 12.2) and establish a new retention index file. Adjusting the detector make-up gas pressure will change retention times. Reanalyze the system validation mixture (8.6) and verify the total response for benzene (13.2).

13.3 Verify that the system validation mixture results are within tolerance limits.

13.3.1 The group totals for paraffins, isoparaffins, olefins, naphthenes, and aromatics shall be within ±1.0 % by mass of the known totals.

13.3.2 The benzene, toluene, ethylbenzene, total xylenes, and *iso*octane shall be within ±0.5 % by mass of their known values.

13.3.3 The ratio of tetradecane to pentane shall be between 3.8 and 4.5.

13.4 Analyze the check sample VUVCS S24 as defined in 8.7. Results shall be within the tolerances stated in Table 3.

13.5 If the tolerances in 13.3 or 13.4 are not met, verify functionality of all GC-VUV components, validity of retention time marker list, and validity/quality of the check sample or system validation mixture, or both. Repeat setup methodology

in Sections 11, 12, and 13 as necessary to ensure tolerances in 13.3 or 13.4 are met before proceeding.

14. Procedure

14.1 Inject the sample into the GC inlet port. Typical GC method and detector conditions are given in Table 1.

14.2 The system shall record a dark scan immediately after start.

14.3 The system shall record a reference scan immediately after the dark scan.

14.3.1 The reference scan refers to an initial detector scan used as a reference to convert subsequent detector scans to absorbance scans, and is defined in Annex A1. It is not a library reference spectrum.

14.4 The system shall record 125 nm to 240 nm absorbance spectra and time of scan for each detector scan. Conversion of recorded intensity data to absorbance is given in Annex A1.

14.5 At the end of the GC run, the data collection shall automatically stop, and the recorded absorbance spectra processed in order to obtain response areas for each of the hydrocarbon classes and individual compounds being monitored.

14.5.1 Calculate percent mass for each hydrocarbon group and each of the individual compounds/compound groups ethanol, methanol, *iso*octane, benzene, toluene, ethylbenzene, and total xylenes.

14.5.2 Calculate percent volume results from the percent mass results and class/compound densities.

14.6 Generate a report displaying the information calculated in 14.5.

15. Calculation

NOTE 3—See pertinent information on modeling absorbance data in Annex A2.

15.1 Divide the measured chromatogram into time slices of a given width, Δt. Define the following parameters:

15.1.1 A retention index (RI) window,

15.1.2 A chi-squared iteration threshold, expressed as a percentage,

15.1.3 An R^2 threshold,

15.1.4 A saturation threshold, and

15.1.5 An initial background time region (optional).

15.2 If an initial background time region is defined, calculate a background spectrum from the average of the absorbance scans over the background time region.

15.3 Analyze each time slice using the following algorithm:

15.3.1 Calculate the total absorbance from the sum of the absorbance scans within the time slice.

15.3.1.1 If a background spectrum is defined, subtract the background spectrum from each of the individual absorbance spectra within the time slice. Sum the resulting background-subtracted spectra to obtain the total absorbance spectrum for the time slice.

15.3.1.2 If the absorbance value at a given wavelength exceeds the saturation threshold for any of the absorbance scans within the time slice, remove the data at that wavelength

value from the total absorbance and library reference spectra used in subsequent fits for that time slice.

15.3.2 Calculate the average retention index of the time slice using the average elution time of the time slice and the list of retention time markers. A linear interpolation scheme is sufficient.

15.3.3 Construct a list consisting of all compounds in the VUV reference library within $\pm$RI window of the average retention index of the time slice.

15.3.4 Perform a tiered search on the total absorbance spectrum, drawing from the constructed list of compounds:

15.3.4.1 Construct Eq A2.1 (see Annex A2) assuming a single component contributes to the total absorbance. Select a compound from the list and assign its library reference spectrum to $A_{1,ref}$ in Eq A2.1. Fit the total absorbance to Eq A2.1 using general linear least squares. Calculate a metric, such as the chi-squared statistic:

$$x^2 = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{\sigma_i^2}(A_{i,meas} - A_{i,calc})^2 \qquad (1)$$

where:

N = the number of data points in an absorbance spectrum fit,
$A_{i,meas}$ = the measured total absorbance at data point i,
$A_{i,calc}$ = the calculated total absorbance at data point i, and
σ_i = the uncertainty of measured data point i, expressed as a standard deviation

If the uncertainty in the measured data have not been estimated, the σ_i may be set to 1. Normalization by the number of data points, N, is also optional.

15.3.4.2 Repeat the fit for each compound in the list and retain the fit yielding the best chi-square value, along with the best-fit compound's fit value f_1.

15.3.4.3 Construct Eq A2.1 assuming two compounds contribute to the total absorbance spectrum. Populate $A_{1,ref}$ and $A_{2,ref}$ in Eq A2.1 with library reference spectra for each possible pair of compounds from the compound list. Fit the total absorbance to Eq A2.1 for each pair. Retain the pair resulting in the best chi-squared value along with their fit values, f_1 and f_2. Compare the chi-squared value from the best two-component fit to the chi-squared value from the best one-component fit. If the percent improvement of the chi-squared value for the best two-component fit over the best one-component fit is greater than the chi-squared iteration threshold, retain the two-component result. Otherwise, reject the two-component result and retain the one-component result.

15.3.4.4 Construct Eq A2.1 assuming three compounds contribute to the total absorbance spectrum. Populate $A_{1,ref}$, $A_{2,ref}$, and $A_{3,ref}$ with library reference spectra for each possible triplet of compounds from the compound list. Fit the total absorbance to Eq A2.1 for each triplet. Retain the triplet resulting in the best chi-squared value along with the fit values, f_1, f_2, and f_3. Compare the chi-squared value from the best three-component fit to the chi-squared value from the best two-component fit. If the percentage improvement of the chi-squared value for the best three-component fit over the best two-component fit is greater than the chi-squared iteration threshold, retain the best three-component result. Otherwise,

reject the three-component result and retain the best two-component result, unless the best two-component result was also rejected, in which case retain the best one-component result.

15.3.5 The result of the tiered search procedure is a prediction of the number of compounds that contribute to the total absorbance spectrum, their likely identities, as well as the best-fit values. "Integrate" the library reference spectra of the best-fit compounds by averaging them over the 125 nm to 240 nm region, generating an integration factor for each compound. Multiply the best-fit values, f_i, by the corresponding integration factors. These are the compounds' contributions to the response area of the time slice.

15.3.6 If the R^2 value, determined from

$$R^2 = 1 - \frac{\sum_{i=1}^{N}(A_{i,meas} - A_{i,calc})^2}{\sum_{i=1}^{N}\left(A_{i,meas} - \bar{A}\right)^2} \qquad (2)$$

is less than the R^2 threshold value, reject the analysis results for the time slice (optional). Otherwise, add the compound contributions to the total class response areas according to their class, or to an individual compound's response area if a compound is one of the speciated compounds given in Table 5. If an individual compound in Table 5 also belongs to a compound class in Table 4 (for example, *iso*octane), add its response to the individual compound response area and not to the class response area. In Eq 2, $\bar{A}$ is the wavelength average of the measured total absorbance spectrum.

15.3.7 Iterate the algorithm until all of the time slices have been analyzed.

15.4 Implementation of an analysis criterion for determining whether to analyze a time slice and a background subtraction is permissible. If a background subtraction is used, a criterion for automatically determining that a time region should be used as a background spectrum may be defined.

15.4.1 *Absorbance Check 1*—Compare the change of a response filter over a time slice. If the response filter changes by more than the absorbance threshold, then analyze the time slice. Otherwise, skip the time slice.

15.4.1.1 If a time slice is skipped, the background threshold may be checked and if the response change over the time slice is less than the background threshold, update the background spectrum using the average absorbance spectrum over the time slice.

15.4.2 *Absorbance Check 2*—If the maximum response of the four filters consisting of average 125 nm to 240 nm absorbance, average 170 nm to 200 nm absorbance, average 125 nm to 160 nm absorbance, and average 140 nm to 160 nm absorbance exceeds the maximum response of the same four filters applied to the current background spectrum by more than three times the absorbance threshold, then analyze the time slice (and do not update the background spectrum) regardless of the outcome of Absorbance Check 1.

15.4.3 Other threshold criteria may be used, provided it is first determined that use of alternative threshold criteria does not lessen the accuracy or precision of the test method.

15.5 Due to the similarities of absorbance spectra of compounds belonging to the same class, as well as the similarities of relative response factors among compounds belonging to the same class, it is not necessary to have an explicit representation of all compounds in the VUV reference library. The following substitutions for an uncharacterized compound are permissible and will generally automatically be made by the algorithm:

15.5.1 Library reference spectra of similar compound class and similar carbon number.

15.5.2 Linear combinations of spectra of similar compound class and similar carbon number.

15.6 If an R^2 threshold is applied, record the amount of response area rejected by implementation of the R^2 threshold. Compare the rejected amount to the total response area at the end of the analysis. If more than 3 % of the response area was rejected, the analysis should be flagged, and the measurement data and GC-VUV instrumentation should be inspected.

15.7 Table 6 lists values for analysis parameters used in the statistical study given in Section 17, and are suitable for use with this test method.

15.8 The result of the measurement and analysis procedure are total response areas for each of the hydrocarbon classes and each individually speciated compound. For a given class or specific compound, a, calculate the percent mass from

$$M_a = 100 \times \frac{A_a \times RRF_a}{\sum\limits_{i=1}^{n} A_i \times RRF_i} \tag{3}$$

where:

M_a = percent mass for analyte or analyte class a,
A_a = total response area for analyte or analyte class a, and
RRF_a = relative response factor for analyte or analyte class a.

The sum runs over all hydrocarbon classes and speciated compounds.

15.8.1 Calculate the total aromatics percent mass by adding the percent mass for the individual mono-aromatics in Table 5 to the C_9+ aromatics class percent mass.

15.8.2 Calculate total isoparaffins percent mass by adding the percent mass for *iso*octane to the percent mass for the isoparaffins class.

15.9 Calculate total saturate content by summing the percent mass values of the hydrocarbon classes of paraffins, isoparaffins, and naphthenes.

15.10 Convert the percent mass result for analyte or analyte class, a, to percent volume using:

$$V_a = 100 \times \frac{\dfrac{M_a}{\rho_a}}{\sum\limits_{i=1}^{N}\left(\dfrac{M_i}{\rho_i}\right)} \tag{4}$$

where:

M_a = percent mass for analyte or analyte class a,
M_i = percent mass for analyte or analyte class i,
V_a = percent volume for analyte or analyte class a,
ρ_i = liquid density for analyte or average relative density for analyte class i, and
ρ_a = liquid density for analyte or average relative density for analyte class a.

The liquid density values may be obtained from various literature or ASTM publications. For example, densities for many relevant compounds are given in Test Method D6730 and in ASTM publication DS4A, *Physical Constants of Hydrocarbons C^1 to C^{10}*. Average density values may be used for densities of bulk PIONA classes or for PIONA classes at various carbon numbers. Recommended densities for use with this test method are given in Table 7.

15.10.1 Eq 4 shall be applied to percent mass values before the individually speciated aromatics percent mass values are added to the C_9+ aromatics percent mass, and before the

TABLE 6 Parameters Used in Analysis of GC-VUV Scan Data

Parameter	Value
Time slice width	0.02 min
RI window	±25
Initial background region	1.6 min to 1.8 min
Saturation threshold	0.8 AU
R^2 Threshold	0.4
Background scalar	1.5
Absorbance threshold	0.0005 AU
Background threshold	0.00025 AU
Response filter to apply Absorbance Check 1	Average 140 nm to 160 nm absorbance
Response filter to apply background check	Average 140 nm to 160 nm absorbance
Response filter(s) to apply Absorbance Check 2	Average 125 nm to 240 nm absorbance
	Average 170 nm to 200 nm absorbance
	Average 125 nm to 160 nm absorbance
	Average 140 nm to 160 nm absorbance
Chi-square iteration threshold	60 %
Area reject (15.6)	Max 3 %