



Designation: D8369 – 21

Standard Test Method for Detailed Hydrocarbon Analysis by High Resolution Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy (GC-VUV)¹

This standard is issued under the fixed designation D8369; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the use of gas chromatography and vacuum ultraviolet absorption spectroscopy (GC-VUV) for the determination of individual compounds and compound classes by percent mass or percent volume with a final boiling point as defined by Test Method **D86** up to 225 °C.

1.1.1 Typical products encountered in petroleum refining or biofuel operations, such as blend stocks; naphthas, reformates, alkylates, FCC gasoline, liquefied petroleum gas (LPG), alcohols and ethers may be analyzed.

1.1.2 Spark-ignition engine fuels including those with commonly blended oxygenates may also be analyzed.

1.2 Individual compounds are spectrally verified and speciated. Compounds that are not spectrally verified and speciated are identified by carbon number, based on retention index, and by class type, based on spectral response. The resulting verified hydrocarbon analysis therefore identifies, classifies, and reports 100 % of the spectral responses.

1.2.1 This test method may not be applicable to all concentrations of individual hydrocarbons; the user must evaluate the spectral response of the hydrocarbon of interest, the amount and proximity of co-eluting hydrocarbons, and detector saturation. Quantitation of individual hydrocarbons with concentrations less than 0.1 % or greater than 30 % by mass may require validation.

1.2.2 This test method can be used to determine methanol in the range of 0.05 % to 3 % by mass, ethanol in the range of 0.05 % to 25 % by mass, butanols in the range of 0.5 % to 10 % by mass, methyl t-butyl ether (MTBE) in the range of 0.5 % to 22 % by mass, ethyl t-butyl ether (ETBE) in the range of 0.5 % to 22 % by mass, and t-amyl methyl ether (TAME) in the range of 0.5 % to 22 % by mass in spark-ignition engine fuels.

NOTE 1—Applicable ranges of individual components and precision will ultimately be defined by an interlaboratory study.

¹ This test method is under the jurisdiction of ASTM Committee **D02** on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee **D02.04.01** on Gas Chromatography Methods.

Current edition approved April 1, 2021. Published May 2021. DOI: 10.1520/D8369-21.

1.2.3 Other compounds containing oxygen, sulfur, nitrogen, and so forth, may also be present, and may co-elute with the hydrocarbons. If determination of other specific compounds is required, supplementation of the spectral library may be necessary.

1.3 Class-type composition – paraffins, iso-paraffins, olefins, naphthenes, aromatics and oxygenates are reported. The class composition totals are the sum of speciated individual compounds and spectrally classed compounds.

1.3.1 The class types may optionally be sub classed by carbon number.

1.3.2 Olefins may optionally be sub classed into mono-olefins, non-conjugated diolefins, conjugated diolefins, and cyclic olefins.

1.3.3 Aromatics may optionally be sub classed into mono-aromatics, diaromatics, and naphtheno-aromatics (indans and indenenes).

NOTE 2—Interim precision for optional sub class reporting is not determined.

1.4 Individual compounds may not be baseline-separated by the procedure described in this method; that is, some compounds will coelute. The coelutions are resolved at the detector using VUV absorbance spectra and deconvolution algorithms.

1.5 This test method is intended as a type of detailed hydrocarbon analysis (DHA). Incorporation of the GC-VUV data report into commercial DHA software packages with subsequent physical and chemical property calculations and correlations is the responsibility of the DHA software vendor.

1.6 Temporary precision has been determined on a limited subset of samples and compounds given in Table 6 and Table 7.

1.7 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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:²

- D86** Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure
- D4057** Practice for Manual Sampling of Petroleum and Petroleum Products
- D4307** Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D4814** Specification for Automotive Spark-Ignition Engine Fuel
- D5842** Practice for Sampling and Handling of Fuels for Volatility Measurement
- 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
- D6729** Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography
- D6730** Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre Capillary (with Precolumn) High-Resolution Gas Chromatography
- D6792** Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories
- D7372** Guide for Analysis and Interpretation of Proficiency Test Program Results
- D7900** Test Method for Determination of Light Hydrocarbons in Stabilized Crude Oils by Gas Chromatography

3. Terminology

3.1 Definitions:

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).

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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 Definitions of Terms Specific to This Standard:

3.2.1 *retention index, n*—linear alkane retention indices are assigned as multiples of 100 according to carbon number.

3.2.1.1 *Discussion*—A linear interpolation scheme between *n*-alkanes along with retention index windows is sufficient to narrow the search in the library database.

3.2.2 *verified hydrocarbon analysis, n*—the summed result of spectrally verified, library matched components and components identified by carbon number and class type.

3.3 Abbreviations:

3.3.1 *AU*—absorbance units

3.3.2 *DHA*—detailed hydrocarbon analysis

3.3.3 *GC-VUV*—gas chromatography with vacuum ultraviolet absorption spectroscopy

3.3.4 *RI*—retention index

3.3.5 *RRF*—relative response factor

4. Summary of Test Method

4.1 A 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 60 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 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 volume percent concentrations are calculated from the mass concentrations by applying specific component or class-based density values as appropriate.

5. Significance and Use

5.1 The determination of class group composition of hydrocarbon streams and automotive spark-ignition fuels as well as quantification of various individual species such as oxygenates and aromatics is useful for evaluating quality and expected performance.

³ The sole source of supply of the apparatus known to the committee at this time is VUV-Analytics, Cedar Park, Texas. 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,¹ which you may attend.

The vacuum ultraviolet absorption apparatus is covered by a patent. Interested parties are invited to submit information regarding the identification of an alternative(s) to this patented item to the ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

TABLE 1 Typical Instrument Settings for GC-VUV Sample Measurement^A

	Standard Conditions
Column Dimensions	Capillary, 60 m × 0.25 mm ID × 0.25 µm film thickness
Column phase ^B	Nonpolar (for example, 100 % dimethyl polysiloxane)
Carrier Gas ^C	Helium
Injector temperature	250 °C
Injection volume ^D	1.0 µL
Split ratio ^D	300:1
Column flow (constant flow mode)	2.0 mL/min
Oven initial temperature	5 °C
Hold time	4 min
Oven ramp 1	18 °C/min
Oven temperature 1	50 °C
Hold time	14 min
Oven ramp 2	5.5 °C/min
Final oven temperature	200 °C
Final Hold	0 min
Detector makeup gas pressure (gauge)	as per manufacturer's instructions
Data scan rate	5.0 Hz
Detector flow cell temperature	275 °C
Transfer line temperature	275 °C

^A Alternate instrument settings are presented in [Appendix X3](#).

^B Columns with low bleed phases such as MS grade have been successfully used for this application (see [11.6](#)).

^C The typical flow rate is for helium carrier gas, other carrier gases may be utilized (see [8.2](#)).

^D Other injection volumes and split ratios may be used to achieve the required benzene response (see [13.2](#)).

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 $\pm 1\%$ 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.

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

7.2 *Carrier Gas*, for gas chromatograph: helium, nitrogen, or hydrogen (see [8.2](#)).

7.3 *Purge/Makeup Gas*, for detector: helium, nitrogen, or argon (see [8.3](#)).

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

7.5 *Capillary Analytical Column*, nonpolar (for example, dimethyl polysiloxane) phase, dimensions 60 m length, 0.25 mm internal diameter, 0.25 µm film thickness.

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

7.6.1 The detector shall be able to interface with a gas chromatographic system and measure an eluent with a scan frequency of at least 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.

7.6.2 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.

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

7.6.4 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.

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

7.7.1 Data processing system shall include a database library³ of vacuum ultraviolet absorption 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.

7.7.2 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.

7.7.3 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.

7.7.4 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 shall 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 Nitrogen, helium, or hydrogen carrier gas for gas chromatograph, 99.999 % pure.

NOTE 3—Helium carrier gas was used to develop temporary precision statement.

⁴ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.3 Nitrogen, helium, or argon purge/makeup gas for vacuum ultraviolet absorption spectroscopy 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 mixture consisting of iC4, C4, iC5, and C5 through C15 linear alkanes, approximately 1 % by mass each, in suitable solvent such as methylene chloride.

8.5.1 The retention time mixture is used to determine a retention time marker list (see 12.1 and 12.2).

8.5.2 The retention time mixture is used to determine splitter linearity (see 13.3.2).

8.6 A system validation mixture that complies with Practice D4307, having the components and approximate concentrations given in Table 2. The concentrations of the prepared system validation mixture should be close to those in Table 2 and shall otherwise be accurately known.

8.7 A quality control (QC) sample, similar in characteristics to samples that are to be routinely analyzed. Examples include automotive spark-ignition fuel, naphtha, reformat, alkylate and FCC gasoline. See Section 18 Quality Control Monitoring.

NOTE 4—Refer to Practices D6299 and D6792 for guidance on quality assurance (QA) practices.

8.8 A hydrocarbon stream standard used to set up the spectrally verified peak table and define the report method (see 12.8). The QC sample (8.7) can also be used as a hydrocarbon

stream standard. See Table 3. A typical chromatogram and an example of a report are shown in Appendix X1.

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.

10. Sampling

10.1 Refer to Practices D4057 and D5842 for guidelines on obtaining volatile samples including 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 60 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 apparatus through a full oven ramp and cool-down cycle. Repeat.

11.6.1 Assess the baseline on either a solvent test sample or a system validation mixture run (see 8.6). The average absorbance value (125 nm to 240 nm) of at least a 0.1 min section of the baseline near 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 0.5 min to 1.0 min range.

12. Calibration and Standardization

12.1 On installation of apparatus, after significant maintenance of apparatus, or after a significant method change, establish a retention index file. Run the retention time mixture (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, make-up gas pressure, or oven ramp profile. Significant maintenance of the apparatus includes replacing or trimming the analytical column.

12.2 A list of retention times and retention indices for the branched and linear alkanes is used to estimate elution times of other compounds in the VUV library³ according to an interpolation scheme. The retention index should be used to

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	4.0
4-Methyl-1-hexene	1.6
n-Heptane	3.5
1,2-Dimethylcyclohexane	5.0
Isooctane	5.0
n-Octane	5.0
1,2,4-Trimethylcyclohexane	4.0
n-Nonane	4.5
n-Decane	4.5
n-Undecane	3.5
n-Dodecane	3.5
Benzene	2.2
Toluene	2.2
trans-Decahydronaphthalene	4.0
n-Tetradecane	4.5
Ethylbenzene	4.5
o-Xylene	4.0
n-Propylbenzene	5.0
1,2,4-Trimethylbenzene	4.5
1,2,3-Trimethylbenzene	5.0
1,2,4,5-Tetramethylbenzene	5.0
Pentamethylbenzene	5.0
Total Paraffins	32.2
Total Isoparaffins	7.1
Total Olefins	3.1
Total Naphthenes	20.2
Total Aromatics	37.4

TABLE 3 Report Method Component Data

Component	Class	Carbon Number	Retention Index	Density at 20 °C g/mL	RRF	Gasoline D4814	Petrol EN228	Alkylate	Reformate	Virgin Naphtha	Pyrolysis Gas	Naphtha Coker	Naphtha FCC
Propene	Olefin	3	297.3	0.505	0.363								
Propane	Paraffin	3	300.0	0.501	0.872								
Isobutane	Isoparaffin	4	360.0	0.557	0.700		X				X	X	X
Methanol	Oxygenate	1	370.4	0.792	1.299		X						
Isobutylene	Olefin	4	386.9	0.595	0.387							X	X
1-Butene	Olefin	4	388.3	0.595	0.387							X	X
1,3-Butadiene	Olefin	4	393.3	0.621	0.340							X	X
n-Butane	Paraffin	4	400.0	0.579	0.800		X	X					
Methyl mercaptan	Sulfur	1	405.2	0.960	1.350							X	X
trans-2-Butene	Olefin	4	407.5	0.604	0.387		X				X	X	X
cis-2-Butene	Olefin	4	419.2	0.621	0.387		X				X	X	X
1,2-Butadiene	Olefin	4	433.0	0.676	0.370								
Ethanol	Oxygenate	2	445.6	0.789	1.013		X						
3-Methyl-1-butene	Olefin	5	449.5	0.627	0.380		X						
Isopentane	Isoparaffin	5	470.4	0.620	0.740		X	X				X	X
1,4-Pentadiene	Olefin	5	474.4	0.661	0.370								
Dimethylacetylene	Alkyne	4	477.0	0.678	0.400								
1-Pentene	Olefin	5	487.1	0.641	0.380		X						
Isopropanol	Oxygenate	3	489.1	0.786	0.863								
Ethyl mercaptan	Sulfur	2	490.0	0.862	0.735								
2-Methyl-1-butene	Olefin	5	495.1	0.650	0.380		X					X	X
n-Pentane	Paraffin	5	500.0	0.626	0.730		X		X			X	X
2-Methyl-1,3-butadiene	Olefin	5	503.7	0.681	0.340								
trans-2-Pentene	Olefin	5	506.9	0.648	0.380		X						
cis-2-Pentene	Olefin	5	513.4	0.656	0.380		X						
tert-Butanol	Oxygenate	4	514.4	0.789	0.746								
2-Methyl-2-butene	Olefin	5	517.7	0.662	0.380		X						
trans-1,3-Pentadiene	Olefin	5	520.0	0.676	0.340								
Cyclopentadiene	Olefin	5	528.0	0.650	0.465								
2,2-Dimethylbutane	Isoparaffin	6	530.3	0.649	0.740		X	X					
cis-1,3-Pentadiene	Olefin	5	530.8	0.682	0.340								
Isopropyl mercaptan	Sulfur	5	540.5	0.820	0.600								
Cyclopentene	Olefin	5	546.3	0.772	0.465		X						
n-Propanol	Oxygenate	3	549.6	0.804	0.937								
4-Methyl-1-pentene	Olefin	6	551.5	0.667	0.400		X						
3-Methyl-1-pentene	Olefin	6	552.4	0.664	0.400		X						
Cyclopentane	Naphthene	5	556.6	0.745	0.828								
2,3-Dimethylbutane	Isoparaffin	6	559.9	0.662	0.740		X	X					
Methyl tert-butyl ether	Oxygenate	5	560.9	0.740	0.819								
2,3-Dimethyl-1-butene	Olefin	6	561.8	0.678	0.400		X						
cis-4-Methyl-2-pentene	Olefin	6	563.7	0.674	0.400		X						
trans-4-Methyl-2-pentene	Isoparaffin	6	565.6	0.653	0.740		X	X					
3-Methylpentane	Olefin	6	567.4	0.674	0.400		X	X					
1,5-Hexadiene	Isoparaffin	6	580.1	0.664	0.740		X						
2-Methyl-1-pentene	Olefin	6	582.0	0.692	0.370								
1-Hexene	Olefin	6	586.2	0.685	0.400		X						
2-Butanol	Olefin	4	587.6	0.678	0.400		X						
trans-1,4-Hexadiene	Oxygenate	6	590.9	0.808	0.905								
n-Propyl mercaptan	Olefin	3	592.0	0.710	0.370								
2-Ethyl-1-butene	Sulfur	6	593.6	0.841	0.600		X						
n-Hexane	Olefin	6	599.4	0.689	0.400		X						
DIPE	Paraffin	6	600.0	0.659	0.785		X		X				
trans-3-Hexene	Oxygenate	6	601.9	0.725	0.837								
cis-3-Hexene	Olefin	6	602.2	0.682	0.400		X						
	Olefin	6	602.9	0.685	0.400		X						

TABLE 3 Continued

Component	Class	Carbon Number	Retention Index	Density at 20 °C g/mL	RRF	Gasoline D4814	Petrol EN228	Alkylate	Reformate	Virgin Naphtha	Pyrolysis Gas	Naphtha Coker	Naphtha FCC
trans-2-Hexene	Olefin	6	604.2	0.683	0.400	X	X				X	X	X
2-Methyl-2-pentene	Olefin	6	606.2	0.691	0.400	X	X				X	X	X
cis-2-Hexene	Olefin	6	611.8	0.692	0.400	X	X				X	X	X
Ethyl tert-butyl ether	Oxygenate	6	617.2	0.736	0.766		X						
trans-3-Methyl-2-pentene	Olefin	6	617.2	0.702	0.400	X	X				X	X	X
Isobutanol	Oxygenate	4	617.8	0.802	0.858								
Methylcyclopentane	Naphthene	6	620.8	0.749	0.805	X	X		X	X	X	X	X
2,4-Dimethylpentane	Isoparaffin	7	626.1	0.673	0.760	X	X	X	X	X	X	X	X
2,2,3-Trimethylbutane	Isoparaffin	7	629.4	0.693	0.760	X	X	X	X	X	X	X	X
1-Methyl-1,3-cyclopentadiene	Olefin	6	632.1	0.706	0.465								
1-Methylcyclopentene	Olefin	6	642.4	0.780	0.500	X	X		X	X	X	X	X
Benzene	Aromatic	6	642.4	0.879	0.258	X	X						
Thiophene	Sulfur	4	646.6	1.051	0.260								
sec-Butyl mercaptan	Sulfur	4	647.0	0.830	0.650								
3,3-Dimethylpentane	Isoparaffin	7	648.4	0.693	0.760	X	X		X	X	X	X	
n-Butanol	Oxygenate	4	649.4	0.810	0.926								
Cyclohexane	Naphthene	6	651.0	0.779	0.805	X	X			X	X	X	X
1,3-Cyclohexadiene	Olefin	6	653.0	0.841	0.423								
tert-Amyl alcohol	Oxygenate	5	653.0	0.805	0.824								
4-Methyl-1-hexene	Olefin	7	658.4	0.705	0.455								
cis/trans-4-Methyl-2-hexene	Olefin	7	661.0	0.711	0.455	X	X					X	X
2-Methylhexane	Isoparaffin	7	663.0	0.679	0.760	X	X	X	X	X	X	X	X
2,3-Dimethylpentane	Isoparaffin	7	663.7	0.695	0.760	X	X	X	X	X	X	X	X
1,1-Dimethylcyclopentane	Naphthene	7	665.7	0.755	0.740					X			
tert-Amyl methyl ether	Oxygenate	6	667.0	0.766	0.877								
Cyclohexene	Olefin	6	667.9	0.811	0.500			X			X	X	X
3-Methylhexane	Isoparaffin	7	671.6	0.687	0.760	X	X		X	X	X	X	X
cis-3,4-Dimethyl-2-pentene	Olefin	7	675.3	0.718	0.455								
cis-1,3-Dimethylcyclopentane	Naphthene	7	677.6	0.745	0.740	X	X		X	X	X	X	X
trans-1,3-Dimethylcyclopentane	Naphthene	7	680.6	0.762	0.740	X	X		X	X	X	X	X
3-Ethylpentane	Isoparaffin	7	682.9	0.698	0.760	X	X		X	X	X	X	X
trans-1,2-Dimethylcyclopentane	Naphthene	7	683.6	0.751	0.740	X	X			X			
1-Heptene	Olefin	7	686.5	0.697	0.455								
Isooctane	Isoparaffin	8	686.9	0.692	0.674	X	X	X			X	X	X
cis-3-Methyl-3-hexene	Olefin	7	693.2	0.718	0.455	X	X				X	X	X
n-Heptane	Paraffin	7	700.0	0.684	0.780	X	X		X		X	X	X
trans-2-Heptene	Olefin	7	703.4	0.706	0.455	X	X						
cis-2-Heptene	Olefin	7	709.3	0.712	0.455								
cis-1,2-Dimethylcyclopentane	Naphthene	7	713.3	0.732	0.740					X		X	X
Methylcyclohexane	Naphthene	7	713.7	0.769	0.740	X	X		X	X	X	X	X
1,1,3-Trimethylcyclopentane	Naphthene	8	716.4	0.748	0.680					X		X	X
Ethylcyclopentane	Naphthene	7	723.3	0.766	0.740	X	X		X	X	X	X	X
2,5-Dimethylhexane	Isoparaffin	7	725.2	0.694	0.720	X	X	X	X	X	X	X	X
2,4-Dimethylhexane	Isoparaffin	8	726.7	0.700	0.720	X	X	X	X	X	X	X	X
cto-1,2,4-Trimethylcyclopentane	Naphthene	8	731.1	0.743	0.680					X		X	X
cto-1,2,3-Trimethylcyclopentane	Naphthene	8	737.8	0.754	0.680					X		X	X
2,3,4-Trimethylpentane	Isoparaffin	8	740.8	0.719	0.720	X	X		X	X	X	X	X
Toluene	Aromatic	7	744.5	0.867	0.263	X	X	X	X				
2,3,3-Trimethylpentane	Isoparaffin	8	744.9	0.726	0.720	X	X	X					
2-Methylthiophene	Sulfur	5	745.8	1.014	0.270								
2,3-Dimethylhexane	Isoparaffin	8	751.6	0.712	0.720				X	X		X	X
1-Methylcyclohexene	Olefin	7	754.6	0.811	0.500							X	X
3-Methylthiophene	Sulfur	5	754.6	1.027	0.270							X	X
2-Methylheptane	Isoparaffin	8	758.2	0.698	0.720	X	X		X	X		X	X
3-Methylheptane	Isoparaffin	8	766.5	0.706	0.720	X	X		X	X		X	X



TABLE 3 Continued

Component	Class	Carbon Number	Retention Index	Density at 20 °C g/mL	RRF	Gasoline D4814	Petrol EN228	Alkylate	Reformate	Virgin Naphtha	Pyrolysis Gas	Naphtha Coker	Naphtha FCC
1c,2t,3-Trimethylcyclopentane	Naphthene	8	767.6	0.763	0.680					X		X	X
trans-1,4-Dimethylcyclohexane	Naphthene	8	769.1	0.763	0.680	X	X			X		X	X
1,1-Dimethylcyclohexane	Naphthene	8	775.5	0.781	0.680					X		X	
2,2,5-Trimethylhexane	Isoparaffin	9	779.3	0.707	0.850	X	X	X		X		X	X
3c-Ethylmethylcyclopentane	Naphthene	8	780.2	0.767	0.680					X		X	X
3t-Ethylmethylcyclopentane	Naphthene	8	782.7	0.767	0.680					X		X	X
1-Octene	Olefin	8	784.5	0.765	0.451					X		X	X
2t-Ethylmethylcyclopentane	Naphthene	8	784.3	0.769	0.680					X		X	X
1-Ethyl-1-methylcyclopentane	Naphthene	8	786.7	0.777	0.680					X		X	X
trans-1,2-Dimethylcyclohexane	Naphthene	8	790.2	0.776	0.680					X		X	X
n-Octane	Paraffin	8	800.0	0.703	0.771	X	X		X	X	X	X	X
trans-2-Octene	Olefin	8	803.2	0.720	0.451					X	X	X	X
cis-2-Octene	Olefin	8	810.0	0.720	0.451					X		X	
cis-1,2-Dimethylcyclohexane	Naphthene	8	820.2	0.796	0.680					X		X	X
1,1,4-Trimethylcyclohexane	Naphthene	9	825.6	0.772	0.800					X		X	X
Ethylcyclohexane	Naphthene	8	831.1	0.784	0.680					X		X	X
Ethylbenzene	Aromatic	8	845.3	0.867	0.272	X	X		X	X	X	X	X
ctt-1,2,4-Trimethylcyclohexane	Naphthene	8	848.2	0.780	0.800					X		X	X
m-Xylene	Aromatic	8	855.9	0.870	0.272	X	X		X	X	X	X	X
p-Xylene	Aromatic	8	857.1	0.870	0.272	X	X		X	X	X	X	X
2-Methyloctane	Isoparaffin	9	868.9	0.713	0.850	X	X		X	X		X	X
ctc-1,2,3-Trimethylcyclohexane	Naphthene	9	872.1	0.758	0.800	X	X		X	X		X	X
Aromatic	Aromatic	8	873.7	0.909	0.270					X		X	X
Isoparaffin	Isoparaffin	9	875.3	0.721	0.850	X	X		X	X		X	X
3-Methyloctane	Aromatic	8	878.1	0.870	0.272	X	X		X	X		X	X
o-Xylene	Aromatic	9	890.5	0.768	0.490					X		X	X
1-Nonene	Olefin	9	900.0	0.718	0.780	X	X		X	X		X	X
n-Nonane	Paraffin	9	903.9	0.734	0.490					X		X	X
trans-2-Nonene	Olefin	9	909.4	0.862	0.280	X	X		X	X		X	X
Isopropylbenzene	Aromatic	9	942.0	0.862	0.280	X	X		X	X		X	X
n-Propylbenzene	Aromatic	9	950.4	0.865	0.280	X	X		X	X		X	X
1-Methyl-3-ethylbenzene	Aromatic	9	952.2	0.861	0.280	X	X		X	X		X	X
1-Methyl-4-ethylbenzene	Aromatic	9	957.9	0.865	0.280	X	X		X	X		X	X
1,3,5-Trimethylbenzene	Aromatic	9	966.2	0.881	0.280	X	X		X	X		X	X
1-Methyl-2-ethylbenzene	Aromatic	9	980.4	0.876	0.280	X	X		X	X		X	X
1,2,4-Trimethylbenzene	Aromatic	9	990.3	0.741	0.474					X		X	X
1-Decene	Olefin	10	993.6	0.853	0.290	X	X		X	X		X	X
Isobutylbenzene	Aromatic	10	995.9	0.862	0.290	X	X		X	X		X	X
sec-Butylbenzene	Aromatic	10	1000.0	0.730	0.765	X	X		X	X		X	X
n-Decane	Paraffin	10	1003.5	0.894	0.280	X	X		X	X		X	X
1,2,3-Trimethylbenzene	Aromatic	9	1007.1	0.861	0.290	X	X		X	X		X	X
1-Methyl-3-isopropylbenzene	Aromatic	10	1010.1	0.857	0.290	X	X		X	X		X	X
1-Methyl-4-isopropylbenzene	Aromatic	10	1012.4	0.986	0.500					X		X	X
Dicyclopentadiene	Olefin	10	1014.7	0.965	0.296	X	X		X	X		X	X
Indane	Aromatic	9	1021.4	0.996	0.265					X		X	X
Indene	Aromatic	9	1021.4	0.996	0.265					X		X	X
1,3-Diethylbenzene	Aromatic	10	1036.0	0.860	0.290	X	X		X	X		X	X
1-Methyl-3-n-propylbenzene	Aromatic	10	1038.8	0.861	0.290	X	X		X	X		X	X
1-Methyl-4-n-propylbenzene	Aromatic	10	1042.4	0.858	0.290	X	X		X	X		X	X
n-Butylbenzene	Aromatic	10	1043.4	0.861	0.290	X	X		X	X		X	X
1,3-Dimethyl-5-ethylbenzene	Aromatic	10	1045.9	0.88	0.290	X	X		X	X		X	X
1-Methyl-2-n-propylbenzene	Aromatic	10	1053.6	0.874	0.290	X	X		X	X		X	X
1,4-Dimethyl-2-ethylbenzene	Aromatic	10	1064.1	0.877	0.290	X	X		X	X		X	X
1,3-Dimethyl-4-ethylbenzene	Aromatic	10	1065.6	0.859	0.290	X	X		X	X		X	X
1,2-Dimethyl-4-ethylbenzene	Aromatic	10	1071.5	0.875	0.290	X	X		X	X		X	X
1-Undecene	Olefin	11	1089.4	0.750	0.484	X	X		X	X		X	X



TABLE 3 Continued

Component	Class	Carbon Number	Retention Index	Density at 20 °C g/mL	RRF	Gasoline D4814	Petrol EN228	Alkylate	Reformate	Virgin Naphtha	Pyrolysis Gas	Naphtha Coker	Naphtha FCC
n-Undecane	Paraffin	11	1100.0	0.740	0.755	X	X			X	X	X	X
1,2,4,5-Tetramethylbenzene	Aromatic	10	1100.8	0.888	0.290	X	X		X	X	X	X	X
1,2,3,5-Tetramethylbenzene	Aromatic	10	1104.6	0.89	0.290	X	X		X	X	X	X	X
Naphthalene	Aromatic	10	1160.6	1.025	0.198	X	X		X	X	X	X	X
n-Dodecane	Paraffin	12	1200.0	0.753	0.745	X	X			X	X	X	X
2-Methylnaphthalene	Aromatic	11	1274.3	1.010	0.202	X	X		X	X	X	X	X
1-Methylnaphthalene	Aromatic	11	1289.2	1.001	0.202	X	X		X	X	X	X	X
n-Tridecane	Paraffin	13	1300.0	0.756	0.735	X	X			X	X	X	X

alkane retention indices to multiples of 100 according to carbon number: butane RI = 400, pentane RI = 500, etc. Retention indices of compounds eluting between n-alkanes are linearly interpreted.

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

12.3 The conversion from response areas to percent mass uses compound specific response factors. The relative response factors account for the differing areal response per unit mass for the various compounds.

12.3.1 In cases where the identity of the specific compound is not known, the conversion from response areas to percent mass uses class-based and carbon number relative response factors. The relative response factors account for the differing areal response per unit mass for the various hydrocarbon classes and carbon number (Table 3).

NOTE 5—A compound's relative response factor is a function of the type and number of chemical bonds. See Appendix X4.

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, densities, and retention indices for individual components are given in Table 3. Hydrocarbon class relative response factors are given in Table 4.

12.6.1 Individual components listed in Table 3 have been spectrally verified, that is, the spectral response of the component is known. The retention index provides further component validation.

12.6.2 Other components of interest may be added to Table 3 provided that the spectral response and retention index are known.

12.6.2.1 Conversely, components not of interest may be deleted from Table 3.

12.7 The component's retention index specified in Table 3 and the retention index window specified in Table 5 shall be customized for different sample types. Larger retention index windows accommodate high concentration components ensuring

the entire peak is captured within the window and smaller windows facilitate improved component identification and data process speed.

12.7.1 A retention time window can be used in place of the retention index window.

12.8 Only the individual components defined in the customized peak table are reported as spectrally verified. All other components are reported based on class and carbon number. Customized peak tables are referred to as report methods.

12.8.1 Examples of individual components of the report method for different products are identified in Table 3 with an "X".

12.9 Each report method shall have a customized peak table and an associated hydrocarbon stream standard (8.8).

12.10 Relative response factors may alternatively be refined or determined as described in Appendix X2.

13. Pre-Measurement Validation

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

13.2 Verify that the total response for benzene is 4.25 ± 0.25 in the system validation mixture (see 8.6).

13.2.1 If the response is out of the specified range, adjust the detector make-up gas pressure in 0.14 kPa increments and reanalyze the system validation mixture, checking the benzene response until it is in 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 (see 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 (see 8.6) and verify the total response for benzene (see 13.2).

13.3 The system validation mixture (see 8.6) serves as a verification of the analytical system.

13.3.1 *System Accuracy*—The system validation mixture percent by mass results for total hydrocarbon group types (paraffins, isoparaffins, olefins, naphthenes, and aromatics) shall be within $\pm 10\%$ relative of the certified concentration values.

13.3.2 *Split Linearity*—The ratio of tetradecane to pentane shall be between 3.8 and 4.5.

13.3.2.1 If the split linearity results are unacceptable, verify that the inlet seals, liner, and column position are designed to minimize split inlet mass discrimination. A GC inlet liner packed with deactivated glass wool is recommended.

13.3.3 The benzene, toluene, ethylbenzene, total xylenes, and isooctane shall be within $\pm 0.2\%$ by mass of their known values.

13.4 Analyze the hydrocarbon stream standard (8.8 and 12.9). Verify the spectral response against the

TABLE 4 Relative Response Factors for Bulk Hydrocarbon Classes

Hydrocarbon Class	Relative Response Factor Range
Paraffin	0.697 – 1.00
Isoparaffin	0.713 – 0.850
Olefin	0.330 – 0.511
Naphthene	0.680 – 0.879
C9+ Aromatics	0.206 – 0.370



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

Analyte	VUVCS RFG		Gasoline 1		Gasoline 2		Gasoline 3		Gasoline 4		Gasoline 5		Gasoline 6		FCC Naphtha 1		Naphtha 1		Reformate		Alkylate		StdDev		F _{max} <4.85
	Average	StdDev	Average	StdDev	Average	StdDev	Average	StdDev	Average	StdDev	Average	StdDev	Average	StdDev	Average	StdDev	Average	StdDev	Average	StdDev	Average	StdDev			
Paraffin	8.65	0.21	5.64	0.16	10.2	0.26	14.0	0.09	9.36	0.13	9.33	0.26	5.14	0.10	3.47	0.03	21.6	0.1	9.68	0.10	0.763	0.03			
Isoparaffin	42.2	0.25	68.57	0.20	22.1	0.31	38.4	0.20	32.5	0.28	28.0	0.23	40.2	0.33	35.4	0.36	30.1	0.5	26.2	0.19	96.3	0.35			
OLEFIN	8.47	0.15	1.71	0.08	0.0843	0.02	5.18	0.08	10.6	0.14	6.33	0.11	6.86	0.09	17.1	0.25	0.178	0.020	0.261	0.03	0.0117	0.01			
Naphthene	7.59	0.30	2.89	0.23	5.78	0.09	12.0	0.19	6.31	0.13	4.00	0.13	6.02	0.29	12.7	0.26	34.1	0.4	2.74	0.14	2.96	0.35			
Aromatic	21.6	0.25	21.2	0.1	61.9	0.6	22.1	0.15	34.3	0.49	42.5	0.52	28.3	0.22	31.3	0.40	14.0	0.0	61.1	0.23	0.0008	0.00			
Isobutane			0.342	0.022	0.395	0.033	0.150	0.009	1.071	0.094	0.127	0.012							0.206	0.016					
n-Butane	1.202	0.072	3.626	0.152	2.376	0.136	0.930	0.035	2.005	0.121	3.259	0.207	1.171	0.063	0.135	0.009			0.831	0.044	0.275	0.017			
trans-2-Butene									0.200	0.009			0.105	0.006	0.308	0.017									
Ethanol	11.454	0.117							5.052	0.054	4.547	0.053													
Isopentane	6.716	0.144	5.515	0.104	7.778	0.201	6.918	0.091	11.600	0.231	8.788	0.213	8.040	0.169	10.615	0.252			2.101	0.051	5.063	0.134			
1-Pentene	0.217	0.006					0.149	0.003	0.512	0.010	0.140	0.003	0.188	0.006	0.611	0.017									
2-Methyl-1-butene	0.529	0.013					0.292	0.004	1.064	0.018	0.124	0.006	0.417	0.009	0.210	0.029									
n-Pentane	3.108	0.054	0.307	0.008	4.247	0.109	5.102	0.059	3.600	0.052	2.835	0.057	2.152	0.039	1.184	0.027			1.454	0.029	0.487	0.011			
trans-2-Pentene	1.000	0.020	0.167	0.004			0.416	0.009	1.360	0.019	1.562	0.030	0.753	0.014	1.799	0.034									
cis-2-Pentene	0.430	0.011					0.205	0.005	0.652	0.010	0.543	0.012	0.319	0.011	0.908	0.022									
2-Methyl-2-butene	1.351	0.024	0.218	0.004			0.584	0.006	1.958	0.025	0.603	0.012	0.930	0.018	2.484	0.044			0.267	0.005					
2,2-Dimethylbutane	0.427	0.006			0.117	0.004	0.254	0.006	1.996	0.011	1.467	0.016	0.158	0.003											
Cyclopentane	0.123								0.212		0.153				0.222										0.006
Cyclopentane	0.299	0.007			0.475	0.012			0.736	0.011	0.398	0.009	0.212	0.006	0.172	0.004	0.197	0.007							
2,3-Dimethylbutane	1.478	0.014	1.797	0.023	0.627	0.015	1.392	0.014	1.336	0.013	0.930	0.013	0.980	0.022	1.197	0.013			0.393	0.010	2.574	0.028			
Methyl tert-butyl ether							5.686	0.052	1.451	0.024	1.153	0.016	13.444	0.099											
2-Methylpentane	3.290	0.026	0.863	0.013	3.983	0.052	4.959	0.029	4.789	0.013	2.989	0.023	2.230	0.015	5.256	0.030	2.792	0.031	2.285	0.023	0.900	0.010			
trans-4-Methyl-2-pentene	0.166	0.004							0.154	0.002	0.119	0.004	0.108	0.004	0.266	0.005									
3-Methylpentane	1.929	0.011	0.441	0.005	2.038	0.026	2.822	0.015	2.690	0.009	1.640	0.013	1.208	0.010	3.092	0.017	2.111	0.023	1.636	0.016	0.364	0.006			
2-Methyl-1-pentene	0.202	0.012							0.191	0.006	0.107	0.005	0.127	0.009	0.396	0.004									
n-Hexane	2.043	0.014	0.149	0.005	2.129	0.023	4.413	0.024	1.723	0.006	1.657	0.008	0.913	0.008	0.829	0.005	6.357	0.063	2.406	0.020					
trans-3-Hexene	0.167								0.141				0.113		0.259										0.011
trans-2-Hexene	0.344	0.015							0.294	0.006			0.231	0.004	0.579	0.007									
2-Methyl-2-pentene	0.380	0.020						0.004	0.355	0.023	0.251	0.004	0.291	0.016	0.632	0.029									
cis-2-Hexene	0.149	0.002							0.134	0.004			0.107	0.005	0.302	0.005									
trans-3-Methyl-2-pentene	0.337	0.011					0.151	0.005	0.296	0.014	0.175	0.040	0.216	0.008	0.610	0.006									
Methylcyclopentane	1.378	0.014	0.258	0.006	3.602	0.042	2.702	0.020	1.882	0.029	1.144	0.028	0.836	0.021	2.541	0.015	3.118	0.050	0.832	0.034					
2,4-Dimethylpentane	1.119	0.011	4.514	0.022	0.589	0.008	0.853	0.006	0.329	0.005	0.375	0.006	1.340	0.008	0.429	0.026	0.341	0.010	0.529	0.012	9.055	0.030			
1-Methylcyclopentene	0.169	0.010							0.194	0.022			0.174	0.012	0.330	0.033									
Benzene	0.844	0.008	0.223	0.004	0.451	0.006	0.686	0.003	0.679	0.005	0.658	0.006	0.401	0.004	0.901	0.008	0.864	0.014	2.257	0.019					
Cyclohexane	0.412	0.012			0.546	0.012	1.268	0.011	0.618	0.017	0.646	0.010	0.181	0.011	0.169	0.011	2.777	0.026							
3-Methylhexane	1.721	0.046	2.516	0.538	1.929	0.056	1.727	0.036	1.284	0.024	1.400	0.030	0.926	0.121	2.768	0.022	2.812	0.029	3.428	0.033	0.845	0.497			
2,3-Dimethylpentane	0.832	0.060	8.886	0.572	0.501	0.057	0.761	0.037	0.359	0.020	0.460	0.036	1.411	0.118	0.409	0.020	0.601	0.031	0.723	0.032	10.605	0.520			
2-Methylhexane	1.543	0.011	1.398	0.011	1.672	0.005	1.644	0.007	1.317	0.010	1.484	0.006	0.854	0.005	2.132	0.013	2.885	0.014	3.621	0.017	0.364	0.011			
1,3-methylcyclopentane	0.341	0.011	0.109	0.006	0.370	0.003	0.584	0.006	0.259	0.010	0.132	0.008	0.245	0.005	0.947	0.008	1.129	0.007	0.149	0.008					
trans-1,3-methylcyclopentane									0.222	0.008	0.115	0.005	0.202	0.004	0.816	0.021	1.021	0.012	0.157	0.009					
2-methylcyclopentane	0.281	0.006			0.266	0.005	0.504	0.008	0.129	0.036	0.147	0.038			0.133	0.031	0.230	0.042	0.370	0.041					
3-ethylpentane	0.131	0.049	0.139	0.060	0.150	0.029																			

TABLE 5 Continued

Documents

Document Sharing Hub



TABLE 5 Continued

Naphthalene	0.207	0.004	0.469	0.008	0.180	0.001677	0.132	0.003	0.280	0.004	0.526	0.008	0.672	0.019							
2-Methylnaphthalene	0.168	0.004	0.295	0.006	0.179	0.00227			0.119	0.003	0.439	0.008	1.006	0.009							
1-Methylnaphthalene			0.148								0.130		0.442								
Total >>	87.018	0.292	86.850	0.228	95.930	0.177	93.579	0.200	93.880	0.186	87.675	0.319	80.244	0.296	81.224	0.412	88.727	0.210	84.428	0.279	0.004

spectrum for individual components of interest. Define a retention index window or alternatively a retention time window that will capture these individual components of interest in subsequent samples. A retention time window should be only large enough to capture all expected concentrations of the component in subsequent samples.

13.5 Analyze the quality control sample defined in 8.7.

13.6 If the specifications in 13.3 or control limits in Section 5 are not met, verify the functionality of all GC-VUV components, validity of retention time marker list, and validity/quality of the QC or system validation mixture or both. Repeat setup methodology in Sections 11, 12, and 13 as necessary to ensure specifications in 13.3 and Section 5 are met before proceeding.

13.7 It is recommended that the system validation mixture or the QC sample, or both, be run with every subsequent batch of 20 samples.

14. Procedure

14.1 Inject the sample into the GC injector 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 class and for individual compounds.

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

15. Calculation

NOTE 6—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 $A_{i,ref}$ 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:

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

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_j .

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:

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

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 3. If an individual compound in Table 3 also belongs to a compound class in Table 4, 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 alternate 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 1.5 % 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:

$$M_a = 100 \times \frac{A_a \times RRF_a}{\sum_{i=1}^n A_i \times RRF_i} \quad (3)$$

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 monoaromatics and diaromatics.

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

15.10 The percent mass result for analyte or analyte class may be converted to percent volume using