Designation: ~~D8368 – 22~~ D8368 – 22a

Standard Test Method for Determination of Totals of Aromatic, Polyaromatic and Fatty Acid Methyl Esters (FAME) Content of Diesel Fuel Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)[1]

This standard is issued under the fixed designation D8368; 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 a standard procedure for the determination of group type totals of aromatic, polyaromatic, and FAME content in diesel fuel using gas chromatography and vacuum ultraviolet absorption spectroscopy detection (GC-VUV).

1.1.1 Polyaromatic totals are the result of the summation of diaromatic and tri-plus aromatic group types. Aromatics are the summation of monoaromatic and polyaromatic group types. FAME content is the result of summation of individual fatty acid methyl esters.

1.1.2 This test method is applicable for renewable diesel fuels from hydrotreated vegetable oil (HVO) or animal fat, gas to liquid (GTL) diesel, light cycle oil, wide boiling range aromatic solvents and biodiesel blends.

1.2 Concentrations of group type totals are determined by percent mass or percent volume. The applicable working ranges are as follows:

Total Aromatics %Volume	0.088 to 77.000
Total Aromatics %Mass	0.104 to 79.451
MonoAromatics %Mass	0.076 to 67.848
Diaromatics %Mass	0.027 to 34.812
Tri-plus aromatics %Mass	0.45 to 6.77
PAH %Mass	0.028 to 41.586
FAME %Volume	1.08 to 21.67

1.3 Diesel fuel containing biodiesel, (FAME, that is, fatty acid methyl esters including soy methyl esters, rapeseed methylesters, tallow methylesters and canola methylesters) can be analyzed by this test method. The FAME component completely elutes from the analytical column independent of feedstock.

1.4 Individual hydrocarbon components are not reported by this test method; however, any individual component determinations are included in the appropriate summation of the totals of aromatic, polyaromatic, monoaromatic, diaromatic, tri-plus aromatic, or FAME groups.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

Current edition approved ~~Feb. 1, 2022~~Oct. 1, 2022. Published ~~March 2022~~November 2022. Originally approved in 2021. Last previous edition approved in ~~2021~~2022 as ~~D8368 – 21.~~D8368 – 22. DOI: ~~10.1520/D8368-22.~~10.1520/D8368-22A.

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

1.4.1 Individual components are typically not baseline-separated by the procedure described in this test method. The coelutions are resolved at the detector using VUV absorbance spectra and deconvolution algorithms.

1.5 This test method may apply to other hydrocarbon streams boiling between heptane (98 °C) and triacontane (450 °C), but has not been extensively tested for such applications.

1.6 *Units*—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 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.*

1.8 *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]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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

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

3. Terminology

3.1 *Definitions:*

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

3.1.2 *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.

3.1.3 *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.

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

3.1.4.1 *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 *diaromatic hydrocarbons, n*—hydrocarbon compounds containing two aromatic rings; this group includes naphthalene, biphenyls, acenaphthene, acenaphthylene and alkylated derivatives of these hydrocarbons.

3.2.2 *monoaromatic hydrocarbons, n*—hydrocarbon compounds containing one aromatic ring; including benzene, alkylsubstituted benzenes, indans, tetralins, alkyl-substituted indans, and alkyl-substituted tetralins.

[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.

3.2.3 *polyaromatic hydrocarbons, n*—all hydrocarbon compounds containing two or more aromatic rings, including diaromatics and tri plus aromatics.

3.2.4 *relative response factor, n—in vacuum ultraviolet spectroscopy*, the relative response factor for a given compound is calculated from the compound's absorption cross section (expressed in cm^2/molecule) and methane's cross section.

3.2.4.1 *Discussion—*

The absorption cross section is averaged over the 125 nm to 240 nm wavelength region.

3.2.4.2 *Discussion—*

A compound's relative response factor is a function of the type and number of chemical bonds.

3.2.4.3 *Discussion—*

A compound's relative response factor is relative to the response of methane, which is taken to have a relative response factor of 1.

3.2.5 *tri plus aromatic hydrocarbons, n*—hydrocarbon compounds containing three aromatic rings; this group includes phenanthrene, anthracene and alkylated derivatives of these hydrocarbons.

3.3 *Abbreviations:*

3.3.1 *ARV*—accepted reference value

3.3.2 *AU*—absorbance units

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

3.3.4 *LTL*—lower 95 % confidence/99 % coverage tolerance level

3.3.5 *PAH*—polyaromatic hydrocarbons

3.3.6 *RI*—retention index

3.3.7 *RRF*—relative response factor

3.3.8 *UTL*—upper 95 % confidence/99 % coverage tolerance level

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.[3,4] 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 Total response areas are determined for sequential time intervals over the entire chromatogram. The calculation of the results is based on the ~~determination of the total~~ deconvoluted response areas of each of the classes of saturate, aromatic, monoaromatic, diaromatic, tri-plus aromatic, and fatty acid methyl ~~ester compounds.~~ esters. The total aromatics class includes the summation of monoaromatics, diaromatics, and tri-plus aromatics. The total polyaromatics class includes a summation of the diaromatics and tri-plus aromatics. The percent mass concentrations are calculated from the response areas using specific component or class and

[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, which you may attend.~~[1]

[4] 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, which you may attend.[1]

carbon number based relative response ~~factors, as appropriate.~~ factors. The volume percent concentrations are calculated from the mass concentrations by applying specific component or class and carbon number based density ~~values as appropriate.~~values. The mass
and volume percent calculations are software automated, whereby the RRFs and densities are a function of elution time in a static database library.

NOTE 1—Appendix X1 and Appendix X2 provide further RRF details.

TABLE 1 Typical Instrument Settings

Column Dimensions	Capillary, 30 m × 0.25 mm ID × 0.25 µm film thickness
Column phase[A]	Nonpolar (for example, 100 % dimethyl polysiloxane)
~~Injector temperature~~	~~250 °C~~
Injector temperature	300 °C
Injection volume[B]	1.0 µL
Split ratio[B]	100:1
Column flow (constant flow mode)	2.0 mL/min
Oven initial temperature	50 °C
Initial hold time	0.1 min
Oven ramp	15 °C/min
Final oven temperature	260 °C
Final hold time	10.9 min
Detector makeup gas pressure (gauge)	as per manufacturer's instructions
Data scan rate	7.0 Hz
Detector flow cell temperature	275 °C
Transfer line 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 and split ratios may be used to achieve the required naphthalene response (see 13.2).

5. Significance and Use

5.1 The determination of group type composition of diesel fuel is useful for evaluating quality and expected performance. Aromatics and polyaromatics, in particular, are related to combustion characteristics, cetane number, energy content, lubricity, water solubility and exhaust emissions.

5.1.1 Aromatic hydrocarbon type analysis may be useful for evaluating refinery processes.

5.1.2 The ability to determine aromatics content in the presence of FAME may be useful to users of diesel fuel.

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.

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 (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 30 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. Data processing system shall include a database library[3] 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.

7.7.1 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.

7.7.2 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.

7.7.3 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.[5] 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.

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 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.

8.5.1 The components of the system validation mixture may be modified to include other components of particular relevance to this test method.

8.5.2 The components of the system validation mixture must include linear alkanes in a continuous series from C7 to C30 at the nominal concentrations in Table 2.

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

8.5.2.2 The system validation mixture is used to determine split linearity (see 13.4).

8.6 A quality control (QC) sample, similar in characteristics to samples that are to be routinely analyzed such as diesel fuel or biodiesel blend. See Section 18 Quality Control Monitoring.

8.7 Check standard VUVCSD S1,[6] with accepted reference values (ARV) and tolerance limits as listed in Table 3.

NOTE 2—VUVCSD S1 is one of the samples included in the ILS for the determination of method precision.

9. Hazards

9.1 Many of the compounds in diesel 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.

---

[5] *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.

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

TABLE 2 System Validation Mixture

Component	Concentration (percent mass)
Hexane	0.25
Heptane	0.25
Octane	0.25
Nonane	0.25
Decane	0.25
Undecane	0.25
Dodecane	0.25
Tridecane	0.25
Tetradecane	0.25
Pentadecane	0.25
Hexadecane	0.25
Hexadecanoic methyl ester C16:0	0.25
Heptadecane	0.25
Octadecane	0.25
Linoleic acid methyl ester C18:2	0.25
Nonadecane	0.25
Eicosane	0.25
Heneicosane	0.25
Docosane	0.25
Tricosane	0.25
Tetracosane	0.25
Pentacosane	0.25
Hexacosane	0.25
Heptacosane	0.25
Octacosane	0.25
Nonacosane	0.25
Triacontane	0.25
Naphthalene	0.25
2-Methylnaphthalene	0.25
1,2,4-Trimethylbenzene	0.25
Phenanthrene	0.25
Methylene Chloride	Balance

10. Sampling

10.1 Refer to Practice D4057 for guidelines on obtaining samples.

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 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 (see 8.5) run. 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 GC-VUV apparatus, or after a significant method change,

TABLE 3 Check Sample VUVCSD S1 95 % Confidence/99 % Coverage Tolerance Intervals[A]

Aromatics	ARV	LTL	UTL
Total Aromatics %Volume	23.349	22.259	24.439
Total Aromatics %Mass	25.224	24.035	26.413
Monoaromatics %Mass	23.282	22.348	24.216
Diaromatics %Mass	1.466	1.302	1.631
Tri-plus aromatics %Mass	0.47	0.03	0.90
FAME %Volume	5.06	4.22	5.90
PAH %Mass	1.930	1.587	2.273

[A] Consensus results for Check Sample VUVCSD S1 obtained from 21 laboratories in 2021. Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-2027. Contact ASTM Customer Service at service@astm.org.

establish a retention index file. Run the system validation 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 C7 through C30 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 changing or trimming the analytical column.

12.2 A list of retention times and retention indices for the linear alkanes is used to estimate elution times of other compounds in the VUV library according to an interpolation scheme. The retention index scheme sets the linear alkane retention indices to multiples of 100 according to carbon number: nonane RI = 900, decane RI = 1000, etc. 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 class-based 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 ~~Examples of relative response factors~~ Relative response factor ranges 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.~~. The relative response factor(s) used within each time interval are fixed and invariable and are determined by the defined software algorithms.

12.7 Relative response factors may alternatively be refined or determined as described in Appendix X1~~.~~; however, precision may be affected.

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.

TABLE 4 Relative Response Factors for Bulk ~~Hydrocarbon Classes~~Group Types

~~Hydrocarbon Class~~ Group Type	~~Relative Response Factor C7 to C30[A]~~ Relative Response Factor Range[A]
Saturates	0.587 – 0.796
Monoaromatics	0.267 – 0.540
Diaromatics	0.190 – 0.254
Tri-plus aromatics	0.213 – 0.262
FAMEs	0.454 – 0.825

[A] A compound's relative response factor is a function of the type and number of chemical bonds. See Appendix X2.

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

Compound	Relative Response Factor
Toluene	0.267
Ethylbenzene	0.284
Xylenes	0.284
1,2,4-trimethylbenzene	0.279
Naphthalene	0.198
Methylnaphthalenes	0.202
Phenanthrene	0.231

13.2 Verify that the total response for naphthalene is 3.25 ± 0.25 in the system validation mixture (see 8.5).

13.2.1 Otherwise adjust the detector make-up gas pressure in 0.14 kPa increments and reanalyze the system validation mixture, checking the naphthalene response until it is in the specified range. Increasing the detector make-up gas pressure will decrease the naphthalene 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 8.5) and verify the total response for naphthalene (see 13.2).

13.3 The system validation mixture (see 8.5) serves as a verification of the analytical system.

13.3.1 *System Accuracy*—The system validation mixture percent by mass results for individual components shall be within ±10 % relative of the certified concentration values.

13.4 *Split Linearity*—The experimentally determined ratio of C30 to C7 shall be within ±10 % relative of each of the certified percent by masses in the system validation mixture. For example; the lower limit of this ratio is [0.9 multiplied by the certified percent by mass C30] divided by [1.1 multiplied by the certified percent by mass C7].

13.4.1 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.

13.5 Analyze the quality control sample defined in 8.6.

13.6 If the specifications in 13.3 or control limits in 13.5 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 13.5 are met before proceeding.

13.7 It is strongly recommended that the system validation mixture and or the QC sample 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.~~stop. From this point up to and including the reporting of the measurement results, the apparatus automatically controls all operations.

14.5.1 Process the recorded absorbance spectra in order to obtain response areas for each of the hydrocarbon classes and individual compounds being monitored.

14.5.2 Calculate percent mass for each hydrocarbon group; saturates, aromatics, monoaromatics, diaromatics, tri plus aromatics, and FAME.

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

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 ±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_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:

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

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 5. If an individual compound in Table 5 also belongs to a compound class in Table 4 (for example, naphthalene), 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,