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Standard Test Method for Determination of Hydrocarbon Types in Waste Plastic Process Oil Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)¹

This standard is issued under the fixed designation D8519; 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 hydrocarbon types (saturates, olefins, styrenes, aromatics and polyaromatics) of waste plastic process oil (WPPO) from chemical or thermal processes using gas chromatography and vacuum ultraviolet absorption spectroscopy detection (GC-VUV).

1.1.1 This test method is applicable for plastic recycling and circular schemes including wide range density material from polyethylene and polypropylene.

1.1.2 The test method is applicable to waste plastic process oil having a final boiling point of 545 °C or lower at atmospheric pressure as measured by this test or Test Method D2887. This test method is limited to samples having a boiling range greater than 36 °C, and having a vapor pressure sufficiently low to permit sampling at ambient temperature.

1.1.3 WPPOs with initial boiling points less than nC5 (36 °C) and final boiling point less than nC15 (271 °C) may be analyzed by Test Method D8369.

1.1.4 Appendix X3 is applicable to waste plastic process oils that are predominantly hydrocarbons in the boiling range of pentane, nC5 (36 °C) to tetrahexacontane, nC64 (629 °C).

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

Total Aromatics	%Mass	1 to 50
Monoaromatics	%Mass	1 to 50
Diaromatics	%Mass	1 to 15
Tri-plus aromatics	%Mass	0.5 to 5
PAH	%Mass	0.5 to 15
Saturates	%Mass	5 to 99
Olefins	%Mass	1 to 80
Conjugated diolefins	%Mass	0.2 to 5
Styrenes	%Mass	0.2 to 5

The final precision concentration ranges will be defined by a future ILS.

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.

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1.2.1 Saturates totals are the result of the summation of normal paraffins, isoparaffins, and naphthenes.

1.2.2 Aromatics are the summation of monoaromatic and polyaromatic group types. Polyaromatic totals are the result of the summation of diaromatic and tri-plus aromatic group types.

1.2.3 Olefin totals are the result of the sum of mono-olefins, conjugated diolefins, non-conjugated diolefins, and cyclic olefins.

1.2.4 Styrenes totals are the sum of styrene and alkylated styrenes. Styrenes are classified separately, neither as aromatic nor olefin.

1.3 Waste plastic process oil containing mixed plastic types such as polyethylene terephthalate PET and polyvinyl chloride or other material may yield compounds including hetero-compounds that are not speciated by this test method.

1.4 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 process oils from sources such as tires and bio-mass boiling between pentane (36 °C) and tetrahexacontane (545 °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, other than the boiling point of normal paraffins (°F) in Table 2 and Table X.3.1, 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

- D2887** Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography
- 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
- D7169** Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography
- D7213** Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100 °C to 615 °C by Gas Chromatography
- D7372** Guide for Analysis and Interpretation of Proficiency Test Program Results
- D8369** Test Method for Detailed Hydrocarbon Analysis by High Resolution Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy (GC-VUV)

3. Terminology

3.1 Definitions:

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

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *alpha olefins (or α -olefins)*, *n*—alkenes (also known as olefins) with a chemical formula C_xH_{2x} , distinguished by having a double bond at the primary or alpha (α) position.

3.2.1.1 *Discussion*— α -olefins in WPP0 are primarily straight chain hydrocarbons.

3.2.2 *alpha-omega olefins (or α - ω olefins)*, *n*—dialkenes (also known as diolefins) with a chemical formula $(CH_2)_n(CH=CH_2)_2$, distinguished by having a double bond at both the alpha (α) and omega (ω) positions.

3.2.2.1 *Discussion*— α - ω olefins in WPP0 are primarily straight chain hydrocarbons and are generally non-conjugated diolefins.

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

3.2.4 *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.

3.2.5 *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.

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

3.2.7 *olefins*, *n*—alkenes (also known as olefins) hydrocarbon with at least one carbon-to-carbon double bond.

3.2.7.1 *Discussion*—In the context of this method, olefins are the result of the sum of alpha olefins, other mono-olefins, conjugated diolefins, non-conjugated diolefins, and cyclic olefins.

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

3.2.9 *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.

3.2.9.1 *Discussion*—The absorption cross section is averaged over the 125 nm to 240 nm wavelength region.

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

3.2.9.3 *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.

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

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

3.2.11 *styrenes*, *n*—the chemical compound styrene CAS# 100-42-5 and alkyl-substituted styrenes.

3.2.11.1 *Discussion*—Styrenes may be attributed to polystyrene in the waste plastic feed.

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

3.2.13 *waste plastic process oil*, *n*—liquids from solid waste plastic produced by industrial processes such as pyrolysis, thermal cracking or chemical decomposition, depolymerization, which may include catalysis.

3.2.13.1 *Discussion*—Waste plastic used to produce WPP0

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.

may be homogeneous or non-homogeneous, containing a wide variety of common plastic types including polyethylene, polypropylene, polystyrene and may also contain minor amounts of polyethylene terephthalate, polyvinyl chloride, polycarbonate and other plastic or biobased material.

3.2.13.2 *Discussion*—WPPOs are mostly comprised of hydrocarbons and may contain hetero-compounds.

3.2.13.3 *Discussion*—WPPOs typically have a final boiling point of 545 °C (nC44) or lower at atmospheric pressure, however may reach a final boiling point of 629 °C (nC64). Waste plastic process oils usually have an initial boiling point greater than 36 °C (nC5), and have a vapor pressure sufficiently low to permit sampling at ambient temperature (adapted from Test Method D2887).

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

3.3.9 *WPPO*—waste plastic process oil

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 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 deconvoluted response areas of each of the classes of saturate, aromatic, monoaromatic, polyaromatic, styrenes, and olefin. 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 total olefins class is

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.

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

TABLE 1 Typical Instrument Settings

Column Dimensions	Capillary, 30 m × 0.32 mm ID × 0.10 μm film thickness
Column phase ^A	Nonpolar (for example, 100 % dimethyl polysiloxane)
Injector temperature	335 °C
Injection volume ^B	0.5 μL
Split ratio ^B	25:1
Column flow (constant flow mode)	1.8 mL/min
Oven initial temperature	35 °C
Initial hold time	5 min
Oven ramp 1	10 °C/min
Final oven temperature	200 °C
Final hold time	0 min
Oven ramp 2	15 °C/min
Final oven temperature	390 °C
Final hold time	0 min
Total run time (approx.)	34 min
Detector makeup gas pressure (gauge)	as per manufacturer's instructions
Data scan rate	7.1 Hz
Detector flow cell temperature	425 °C
Transfer line temperature	425 °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).

the summation of alpha olefins, mono-olefins, conjugated diolefins, non-conjugated diolefins, and cyclic olefins. The styrenes class is a summation of styrene and alkylated styrenes. Individual species compounds may be determined by summation of deconvoluted response areas of each time interval containing the compound. The percent mass concentrations are calculated from the response areas using specific component or class and carbon number based relative response factors. The volume percent concentrations are calculated from the mass concentrations by applying specific component or class and carbon number based density 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.

5. Significance and Use

5.1 The determination of WPPO composition is useful in optimization of process variables, diagnosing unit performance, and in evaluating the effect of changes in waste plastic composition on WPPO performance properties.

5.1.1 Aromatics and olefin hydrocarbon type analysis, including sub-classes, may be useful for evaluating suitability of WPPO as a feedstock for further processing.

6. Interferences

6.1 Interferences with this test method have not been assessed.

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, 0.32 mm internal diameter, 0.10 μm film thickness. Metal clad columns designed for high temperature applications are recommended.

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 425 °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 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.

7.7.1 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 Carbon Disulfide (CS_2), 99+ % pure. (**Warning**—Extremely flammable and toxic liquid.) Used as a solvent to dilute the sample and standards as well. Use gloves and safety glasses when handling the CS_2 in a well-ventilated area or fume hood. It is recommended to use adjustable-volume bottle dispensers and/or pipettors to minimize direct handling and avoid cross-contamination of CS_2 . Wash vials containing CS_2 should be capped with a solvent resistant septa (from Test Method D7169).

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.

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

8.6.2 The system validation mixture is used to determine make up gas pressure (13.2).

8.7 *Calibration Mixture*—An accurately weighed mixture of approximately equal mass quantities of n-hydrocarbons dissolved in carbon disulfide (CS_2). (**Warning**—Carbon disulfide is extremely volatile, flammable, and toxic.) The mixture shall cover the boiling range from n-C5 to n-C44, but does not need to include every carbon number (see Note 2).

8.7.1 At least one compound in the mixture must have a boiling point lower than the IBP of the sample and at least one compound in the mixture must have a boiling point higher than the FBP of the sample. Boiling points of n-paraffins are listed in Table 3.

8.7.1.1 If necessary, for the calibration mixture to have a compound with a boiling point below the IBP of the sample, propane or butane can be added to the calibration mixture,

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.

TABLE 2 System Validation Mixture

Retention Index	Compound	Type/Sub-Class	RRF	Concentration (% mass)
588	1-Hexene	Olefin/ Mono α Olefin	0.446	0.25
653	1,3-Cyclohexadiene	Olefin/Conjugated diolefin	0.423	0.10
687	Isooctane	Saturate/Isoparaffin	0.657	0.25
714	Methylcyclohexane	Saturate/Naphthene	0.756	0.25
800	Octane	Saturate/Paraffin	0.737	0.25
874	Styrene	Styrene	0.278	0.1
920	Isopropylcyclohexane	Saturate/Naphthene	0.790	0.25
980	1,2,4-Trimethylbenzene	Aromatic/Mono-Aromatic	0.277	0.10
1095	cis-Decalin	Saturate/Naphthene	0.785	0.25
1161	Naphthalene	Polyaromatic/Diaromatic	0.198	0.10
1500	Pentadecane	Saturate/Paraffin	0.722	0.25
1775	Phenanthrene	Polyaromatic/Tri-aromatic	0.231	0.10
	Methylene chloride	Solvent		Balance

TABLE 3 Boiling Points of Normal Paraffins^A

Carbon Number	Boiling Point, °C	Boiling Point, °F	Carbon Number	Boiling Point, °C	Boiling Point, °F
1	-162	-259	23	380	716
2	-89	-127	24	391	736
3	-42	-44	25	402	755
4	0	31	26	412	774
5	36	97	27	422	791
6	69	156	28	431	808
7	98	209	29	440	825
8	126	258	30	449	840
9	151	303	31	458	856
10	174	345	32	466	870
11	196	385	33	474	885
12	216	421	34	481	898
13	235	456	35	489	912
14	254	488	36	496	925
15	271	519	37	503	937
16	287	548	38	509	948
17	302	576	39	516	961
18	316	601	40	522	972
19	330	626	41	528	982
20	344	651	42	534	993
21	356	674	43	540	1004
22	369	695	44	545	1013

^A API Project 44, October 31, 1972 is believed to have provided the original normal paraffin boiling point data that are listed in Table 3. However, over the years some of the data contained in both API Project 44 (Thermodynamics Research Center Hydrocarbon Project) and Test Method D2887 have changed, and they are no longer equivalent. Table 3 represents the current normal paraffin boiling point values accepted by Subcommittee D02.04 and found in all test methods under the jurisdiction of Section D02.04.0H. B Test Method D2887 has traditionally used *n*-paraffin boiling points rounded to the nearest whole degree for calibration. The boiling points listed in Table 3 are correct to the nearest whole number in both degrees Celsius and degrees Fahrenheit. However, if a conversion is made from one unit to the other and then rounded to a whole number, the result will not agree with the table value for a few carbon numbers. For example, the boiling point of *n*-heptane is 98.425 °C, which is correctly rounded to 98 °C in the table. However, converting 98.425 °C gives 209.165 °F, which rounds to 209 °F, while converting 98 °C gives 208.4 °F, which rounds to 208 °F. Carbon numbers 2, 4, 7, 8, 9, 13, 14, 15, 16, 25, 27, and 32 are affected by rounding.

non-quantitatively, by bubbling the gaseous compound into the calibration mixture in a septum sealed vial using a gas syringe.

NOTE 2—Calibration mixtures containing normal paraffins with the carbon numbers 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18, 20, 24, 28, 32, 36, 40, and 44 have been found to be sufficient to generate a retention index file.

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

8.7.3 The calibration mixture is used to determine split linearity (see 13.4).

8.8 A quality control (QC) sample, similar in characteristics to samples that are to be routinely analyzed. See Section 18 on Quality Control Monitoring

9. Hazards

9.1 Many of the compounds in waste plastic process oil 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 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 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 Assess the baseline on either a solvent test sample run (see [8.4](#)) or a system validation mixture (see [8.5](#)) run.

11.6.1 Baseline drift can negatively impact the analysis results. In regions where no analytes are eluting, especially towards the end of the chromatogram, the intensity in the 140 nm to 160 nm filter shall be no greater than ± 0.0035 AU and the absorbance spectra shall show no evidence of oxygen or water absorbance. The presence of oxygen at the end of a chromatogram accompanied by a positive drift in the baseline indicates a leak in the system. The presence of water at the end of a chromatogram indicates either water accumulation on the column or water contamination in the VGA purge gas or GC carrier gas. Water build up on the GC column can be minimized by maintaining the GC oven at 100 °C while idle.

12. Calibration and Standardization

12.1 On installation of apparatus, after significant maintenance of GC-VUV apparatus, or after a significant method change, establish a retention index file. Run the calibration mixture (see [8.7](#)) using the same flow conditions and oven ramp profile as measured samples (see [Table 1](#) for recommended run conditions). Record the retention times of C5 through C44 linear alkanes. These will serve as retention time markers.

12.1.1 *Accuracy*—The experimentally determined % by mass of each component of the calibration mixture from C7 to C44 shall be ± 10 % relative of each of the certified percent by masses of the calibration mixture.

NOTE 3—The calibration mixture contains C5 and C6 which may be masked by the solvent.

12.1.2 *Split Linearity*—The experimentally determined ratio of C44 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 C44) divided by (1.1 multiplied by the certified percent by mass C7).

12.1.3 If the accuracy or 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.

12.1.4 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 Relative response factor ranges used to obtain the precision data in this test method are given in [Table 4](#). 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](#).

13.2 Verify that the total response for naphthalene is 3.25 ± 0.25 in the system validation mixture (see [8.6](#)).

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 calibration mixture 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 naphthalene (see [13.2](#)).

TABLE 4 Relative Response Factors for Bulk Group Types

Group Type	Relative Response Factor Range ^A
Saturates	0.564 – 0.811
Monoaromatics	0.244 – 0.565
Diaromatics	0.198 – 0.238
Tri-plus aromatics	0.213 – 0.286
Olefins	0.440 – 0.575
Conjugated diolefin	0.300 – 0.500
Styrenes	0.278 – 0.310

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

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

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

13.4 *Split Linearity*—The experimentally determined ratio of C44 to C7 shall be within $\pm 10\%$ 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 C44) 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.

13.4.2 *System Accuracy of Calibration Mixture*—The calibration mixture percent by mass results for individual components of C7 through C44 shall be within $\pm 10\%$ relative of the certified concentration values.

13.5 Analyze the quality control sample defined in 8.8.

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, calibration mixture or system validation mixture, or all. 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.

14.1.1 WPP0 may be non-homogeneous and contain solids, water and or waxy material. Sample filtration, centrifugation, heating, the addition of viscosity modifiers or solvents may be required prior to injection. Solvents or viscosity modifiers may mask early eluting peaks.

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. 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, styrenes, and olefins.

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

14.6 Check the chromatogram for saturation. If more than three consecutive time intervals have absorbance saturation in more than 80 % of their wavelength range then the software will alert the user and the sample shall be reanalyzed using $\frac{1}{2}$ of the original injection volume.

15. Calculation

NOTE 4—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 an individual compound 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 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 5** 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, diaromatics, and tri plus aromatics.

15.8.2 Calculate the total polyaromatics percent mass by adding the percent mass for the diaromatics and tri plus aromatics.

15.9 Calculate the total saturate percent mass content by summing the percent mass values of the speciated component or class of the saturate.

15.9.1 Calculate the total olefin percent mass content by summing the percent mass values of the specific speciated component or class and carbon number of the olefins.

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

$$V_a = 100 \times \frac{\frac{M_a}{\rho_a}}{\sum_{i=1}^N \left(\frac{M_i}{\rho_i} \right)} \quad (4)$$

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_a = liquid density for analyte or average liquid density for analyte class *a*, and
 ρ_i = liquid density for analyte or average liquid density for analyte class *i*.

The liquid density values may be obtained from various literature or ASTM publications. For example, liquid densities for many relevant compounds are given in Test Method **D6730** and in ASTM publication DS4A, *Physical Constants of Hydrocarbons C1 to C10*.⁶ Average liquid density values may be used for densities of bulk classes or for classes at various carbon numbers. Density ranges for use with this test method are given in **Table 6**. The density value(s) used within each time interval are fixed and invariable and are determined by the defined software algorithms.

15.10.1 **Eq 4** shall be applied to percent mass values. Calculate total aromatic percent volume by summing the percent volume values of the monoaromatics, diaromatics, and tri plus aromatics.

15.10.2 Calculate the total polyaromatics percent volume by adding the percent volume for the diaromatics and tri plus aromatics.

15.10.3 Calculate the total saturate percent volume content by summing the percent volume values of the speciated component or class of the saturate.

15.10.4 Calculate the total olefin percent volume content by summing the percent volume values of the specific speciated component or class and carbon number of the olefin.

16. Report

16.1 Report total aromatics, monoaromatics, diaromatics, and PAH to the nearest 0.001 % by mass.

16.2 Report total olefins content to the nearest 0.001 % by volume.

16.2.1 Olefins subclasses may be reported to the nearest 0.001 % by mass (optional).

16.3 Report tri-plus aromatics content to the nearest 0.01 % by mass.

⁶ Available from ASTM International, West Conshohocken, PA, www.astm.org.

TABLE 6 Average Liquid Density Value Ranges for Group Types

Group Type	Density Value Ranges
Saturates	0.673 to 0.897
Monoaromatics	0.853 to 0.996
Diaromatics	0.980 to 1.200
Tri-plus aromatics	1.060 to 1.280
Olefins	0.850 to 0.900
Styrenes	0.89 to 0.92

TABLE 5 Typical Parameters Used in Analysis of GC-VUV Scan Data

Parameter	Value
Time slice width	0.01 min
RI window	±25
Initial background region	0.8 min to 0.9 min
Saturation threshold	1.2 AU
R ² threshold	0.8
Absorbance threshold	0.0005 AU
Background threshold	0.0002 AU
Background Scalar	3.0
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
	40 %

16.4 Report styrenes content to the nearest 0.001 % by mass.

16.5 Reference this test method.

17. Precision and Bias

17.1 The repeatability and reproducibility will ultimately be determined by an interlaboratory study⁷ in accordance with ASTM methodology. This section reports temporary, single-laboratory repeatability standard deviations for the quantities listed in 1.2.

17.1.1 Repeatability tests were carried out by a single laboratory on five WPP0 samples. In order to mitigate effects of sample change during repeated measurement, each sample was split into fifteen vials. Each vial was measured one time, for a total of 15 measurements per sample using the standard conditions in Table 1. Hydrocarbon class type totals were determined during each measurement. Table 7 shows the average percent mass values of the various parameters for the five samples and the standard deviation in accordance with section 6.2.1 of Practice D6300.

17.1.2 *Bias*—Since there is no accepted reference material suitable for determining bias for the procedure in this test method, no statement of bias is being made.

18. Quality Control Monitoring

18.1 Confirm the test method performance procedure by regular analyzing testing of quality control (QC) sample(s) (see Practice D6299) (8.8).

18.2 Record QC sample test results and confirm the statistical control status (see Practice D6299) for the execution of the complete test method using control charts (see Practice

D6299). Investigate any out-of-control result for root cause(s). The outcome from this investigation may, but not necessarily, result in instrument re-calibration.

18.3 The frequency of QC testing is dependent on the criticality of the property being measured, the demonstrated stability of the testing process, and business requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ASTM International published method precision for consistency (see Practice D6792).

18.4 The QC sample material (see Practice D6299) that is regularly tested should be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

18.5 Participation in appropriate PT programs (if available) is recommended for monitoring performance relative to industry (see Guide D7372).

18.6 See Practices D6299 and D6792 and Guide D7372 for further guidance.

19. Keywords

19.1 aromatics; gas chromatography; PAH; plastic circularity; plastic recycling; polyaromatics; pyrolysis oil; saturates; styrenes; vacuum ultraviolet absorption spectroscopy; waste plastic process oil

⁷ An interlaboratory study of this test method is being conducted and a complete precision statement is expected to be available on or before 2029.

<https://standards.iteh.ai/catalog/standards/sist/a2a6f964-cbee-4789-9818-702f6e45bf9/astm-d8519-23>

TABLE 7 Single Laboratory Percent Mass Repeatability Standard Deviations, Determined According to Practice D6300 Section 6.2.1

		Saturates	Olefins	Dienes	Conjugated Dienes	Styrenes	Aromatics	Mono-Aromatics	PAHs	Di-Aromatics	Tri(+)-Aromatics
Sample 1	Average	20.411	68.557	13.062	4.367	1.340	9.693	7.095	2.597	2.161	0.437
	StdDev	0.275	0.241	0.206	0.052	0.022	0.092	0.060	0.081	0.054	0.031
Sample 2	Average	17.616	61.626	8.852	4.978	2.517	18.242	12.758	5.484	5.125	0.359
	StdDev	0.225	0.675	0.112	0.104	0.050	0.623	0.578	0.082	0.061	0.028
Sample 3	Average	59.782	15.678	1.605	0.947	0.928	23.612	20.950	2.661	2.626	0.035
	StdDev	0.326	0.339	0.054	0.059	0.020	0.094	0.084	0.058	0.050	0.009
Sample 4	Average	27.273	45.926	6.864	5.921	5.777	21.023	20.446	0.576	0.576	0.000
	StdDev	0.147	0.184	0.041	0.061	0.035	0.083	0.082	0.009	0.009	0.000
Sample 5	Average	44.897	40.695	2.183	0.688	1.094	13.314	12.177	1.137	1.116	0.021
	StdDev	0.404	0.608	0.162	0.035	0.036	0.263	0.175	0.106	0.088	0.022
	Min	17.6	15.7	1.6	0.7	0.9	9.7	7.1	0.6	0.6	0.0
	Max	59.8	68.6	13.1	5.9	5.8	23.6	21.0	5.5	5.1	0.4

ANNEXES

(Mandatory Information)

A1. GENERATING ABSORBANCE SPECTRA FROM INTENSITY SCAN DATA

A1.1 The following converts recorded scan intensity data to VUV absorbance spectra, assuming the availability of a previously recorded dark intensity scan, $I_d(\lambda)$, and reference intensity scan, $I_r(\lambda)$.

A1.1.1 The dark scan is collected at the beginning of the chromatogram with the lamp shutter closed. The dark scan is subtracted from all subsequent intensity scans. The reference scan is collected at the beginning of the chromatogram with the shutter open, but with only carrier/makeup gas flowing through the flow cell.

A1.1.2 After collecting dark and reference scans, the detector continues to collect intensity scans, $I(\lambda)$, at regular intervals. The detector array typically has settings for scan time, in ms, and number of averages per scan. The total time per scan is the scan time multiplied by the number of averages. For example, a scan time of 11 ms with 20 averages results in a scan rate of about 4.5 scans/s.

A1.1.3 The absorbance is given by:

$$A(\lambda) = \log_{10} \left(\frac{1}{\tau(\lambda)} \right) = \log_{10} \left(\frac{I_r(\lambda) - I_d(\lambda)}{I(\lambda) - I_d(\lambda)} \right) \quad (\text{A1.1})$$

A2. MODELING ABSORBANCE DATA

A2.1 The separation of diesel fuel samples will typically involve multiple cases of coelution, where more than one analyte compound can exist in the flow cell at any given time. The absorbance for a given number of compounds n can be written as:

$$A = \sum_{i=1}^n f_i A_{i,ref} = (f_1 A_{1,ref} + f_2 A_{2,ref} + \dots + f_n A_{n,ref}) \quad (\text{A2.1})$$

where:

$A_{i,ref}$ = a reference absorbance spectrum for molecule, i , and
 f_i = a weighting factor related to the amount of compound i present.

A2.2 The absorbances of multiple scans are summed over a time region, or “time slice.” The relationship between this total absorbance and the individual constituents is also given by **Eq A2.1**, which then includes one term for each compound that elutes within the time slice.

A2.3 A measured absorbance can be fit using **Eq A2.1** and a general linear least squares optimization procedure.⁸ The f_i are the parameters to be fit. Each of the reference spectra can be “integrated” using the same integration filter that generated the chromatogram response (in this case by averaging over 125 nm to 240 nm), resulting in an integration factor for each reference spectrum included in **Eq A2.1**. The fit f_i multiplied by the corresponding integration factors are the contributions from each of the coeluting compounds to the chromatogram response within the time slice.

⁸ Press, W. H., Flannery, B. P., Teukolsky, S. A., and Vetterling, W. T., *Numerical Recipes in C: The Art of Scientific Computing*, Second Edition, Cambridge University Press, Cambridge, UK, 1992.

APPENDIXES
(Nonmandatory Information)
X1. EXPERIMENTAL DETERMINATION OF RELATIVE RESPONSE FACTORS

X1.1 The relative response factor for a given compound may be determined from the compound's absorption cross section (expressed in $\text{cm}^2/\text{molecule}$) and methane's cross section by calculating:

$$RRF_a = \frac{\Sigma_{\text{methane}}}{MW_{\text{methane}}} \times \frac{MW_a}{\Sigma_a} \quad (\text{X1.1})$$

where:

RRF_a = relative response factor for compound a ,
 MW = molecular weight, and
 Σ = absorption cross section averaged over the 125 nm to 240 nm wavelength region.

X1.2 The relative response factor for a given compound may be determined from a prepared standard consisting of the compound and a second compound whose relative response factor is known. The relative amounts of the two compounds in the standard must be known:

$$RRF_2 = \frac{M_2}{M_1} \cdot \frac{A_1}{A_2} RRF_1 \quad (\text{X1.2})$$

where:

RRF_1 = relative response factor of known compound,
 RRF_2 = relative response factor of compound to be determined,
 A_1 = total measured response area of known compound,
 A_2 = total measured response area of compound to be determined,
 M_1 = percent mass of known compound in standard, and
 M_2 = percent mass of compound to be determined in standard.

X1.2.1 The standard does not have to be limited to two compounds. Any number of compounds may be included, as long as the relative response factor of one of them is known, and all amounts are known relative to the known compound.

X1.3 Class-based relative response factors may be determined by applying this test method to a standard having known class-based relative concentrations. To do this, follow the method procedure and calculation given in Sections 14 and 15 up to the point where class-based total response areas are obtained (prior to implementing Eq 3). Class-based relative response factors are obtained from the total class response areas and the known class percent mass concentrations of the standard by applying Eq X1.2, except in this case all quantities refer to class totals instead of individual compounds.

X1.3.1 If a standard consisting of known percent mass concentrations of the hydrocarbon classes of paraffins, isoparaffins, naphthenes, aromatics, diaromatics, tri plus aromatics, and olefin is used, this procedure will leave one of the class RRFs undetermined (whichever one is arbitrary). The relative response factor for the unknown class may be determined by averaging relative response factors of a selection of individual compounds belonging to that class by Eq X1.1. This is most easily applied to the paraffins class. Then apply Eq X1.2 using the response areas and relative response factor for paraffins (as RRF_1) to determine the other class-based relative response factors.

X1.3.2 If desired, the calibration procedure may use a standard sample where the percent mass values for each carbon number within each class are known. First, use Eq X1.1 to calculate the RRF for one of the paraffins relative to methane. Set that paraffin's RRF to RRF_1 , its known percent mass to M_1 , and its measured total area response to A_1 in Eq X1.2. Calculate each of the remaining compound class RRFs at each carbon number by making the appropriate substitutions for M_2 and A_2 in Eq X1.2.

X2. THE RELATIONSHIP OF MOLECULAR ABSORPTION CROSS SECTION TO RELATIVE RESPONSE FACTORS

X2.1 The Relative Response Factor (RRF) relationship to the molecular absorption cross-section, along with a description of the procedure to experimentally determine RRFs is described in Appendix X1. Additional details regarding the application of absorption cross-sections to specific component determinations as well as bulk property determinations in complex hydrocarbon streams are provided.

X2.2 The absorption cross-section is the ability of a molecule to absorb a photon of a particular wavelength, or the probability of particle-to-particle interactions causing absorption. In other words, the absorption cross-section is the affective area of a molecule that a photon must travel through to be absorbed. The larger the cross section, the easier it is for

a photon to be absorbed and excite bonds within that molecule.

X2.3 The absorption cross-section of a compound is a unique molecular physical property which is defined by the excitation of both the bonded and nonbonded electrons within the molecule. It is uniquely described by the electronic excitation energies (absorbed wavelengths), as well as the oscillator strengths which corresponds to the intensity of this absorption. The compound's absorption cross-section is not impacted by the power of the lamp, nor the matrix of the sample.

X2.4 As the electron configuration is unique for each molecule (apart from enantiomers) then all molecules exhibit