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Designation: D8267 - 19 <u>D8267 - 19a</u>

Standard Test Method for Determination of Saturated Hydrocarbon, Total Aromatic, <u>Monoaromatic</u> and Diaromatic Content of Aviation Turbine Fuels Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)¹

This standard is issued under the fixed designation D8267; 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 Scope*

1.1 This test method is a standard procedure for the determination of saturated, total aromatic, monoaromatic and diaromatic content in aviation turbine fuels using gas chromatography and vacuum ultraviolet detection (GC-VUV).

1.2 Concentrations of compound classes and certain individual compounds are determined by percent mass or percent volume.

1.2.1 This test method is developed for testing aviation turbine engine fuels having concentrations of approximately 70% to 99% by volume saturated compounds, 1.0% to 30% by volume aromatic compounds, and 0.1% to 5% concentration test results ranging from 0.487% to 27.876% by volume total aromatic compounds, 0.49% to 27.537% by volume monoaromatics and 0.027% to 2.523% by volume diaromatics. Pending confirmation by a full interlaboratory study, this test method is projected to be applicable to a wider range of concentrations and matrices. Temporary repeatability has been determined on a limited subset of samples given in 17.1.

NOTE 1—Samples with a final boiling point greater than 300 °C that contain triaromatics and higher polyaromatic compounds are not determined by this test method.

1.3 Individual hydrocarbon components are not reported by this test method, however, any individual component determinations are included in the appropriate summation of the saturate; total aromatic, monoaromatic or diaromatic groups.

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

1.4 This test method has been tested for aviation turbine engine fuels; this test method may apply to other hydrocarbon streams boiling between hexane (68 °C) and heneicosane (356 °C), including sustainable alternative jet fuels but has not been extensively tested for such applications.

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

1.6 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.

1.7 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

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

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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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.



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

D5186 Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels By Supercritical Fluid Chromatography

D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement

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

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants D6379 Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection

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 of Terms Specific to This Standard:

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

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

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

3.1.3.1 Discussion-

iTeh Standards

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

3.2 Abbreviations:

3.2.1 AU-absorbance units

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

3.2.3 *RI*—retention index

3.2.4 *RRF*—relative response factor

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4. Summary of Test Method

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

4.2 The result<u>calculation</u> of the measurement<u>results</u> is <u>based on</u> the determination of the total response areas of each of the reported classes of saturate, <u>aromatic, aromatic</u> and diaromatic compounds. The saturates class includes the summation of the paraffins, isoparaffins, and naphthenes. The <u>total aromatics class includes the summation of monoaromatics and diaromatics</u>. The percent mass concentrations are calculated from the response areas using class-based relative response factors, as appropriate. The volume percent concentrations are calculated from the mass concentrations by applying specific component or class-based density values as appropriate.

5. Significance and Use

5.1 The determination of class group composition of aviation turbine fuels is useful for evaluating quality and expected performance, as well as compliance with various industry specifications and governmental regulations.

6. Interferences

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

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.



TABLE 1 Typical Instrument Settings for GC-VUV Aviation Turbine Fuel Measurement

| Column Dimensions | Capillary, 30 m \times 0.25 mm ID \times 0.25 μm film thickness |
|---|--|
| Column phase ^A | Nonpolar (for example, 100 % |
| | dimethyl polysiloxane) |
| Injector temperature | 250 °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 | 0 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).

7. Apparatus

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

<u>7.1.1 Flow Controllers</u>—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: Heliumhelium (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.

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

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

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

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

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

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

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

8.5 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 C6 to C21 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 splitter linearity (see 13.3.2).

8.6 A quality control (QC) sample, similar in characteristics to samples that are to be routinely analyzed such as aviation turbine engine fuel. See Note 2. Section 18 on Quality Control Monitoring.

8.6.1 The use of a QC sample with accepted references values (ARV) from a proficiency test program (PTP) is recommended.

Note 2—Refer to Practices D6299 and D6792 for guidance on quality assurance (QA) practices.

9. Hazards

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

10. Sampling

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10.1 Refer to Practices Practice D4057 and D5842 for guidelines on obtaining aviation turbine engine fuel samples for analysis.

11. Preparation of Apparatus

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

| 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 |
| Heptadecane | 0.25 |
| Octadecane | 0.25 |
| Nonadecane | 0.25 |
| Eicosane | 0.25 |
| Heneicosane | 0.25 |
| Naphthalene | 0.25 |
| 2-Methylnaphthalene | 0.25 |
| 1,2,4-Trimethylbenzene | 0.25 |
| Methylene Chloride | Balance |

TABLE 2 System Validation Mixture

⁴ Reagent Chemicals, American Chemical Society Specifications, 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.



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

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

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

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

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

11.6.1 Assess the last baseline. 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 the last 1.0 minute at least a 0.1 min section of the baseline at 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 $\frac{1.0 \text{ min}0.5 \text{ min}}{1.0 \text{ min}1.0 \text{ min}}$ range.

12. Calibration and Standardization

12.1 On installation of GC-VUV apparatus, after significant maintenance of GC-VUV apparatus, or after a significant method change, establish a retention index file. Run the 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 C6 through C21 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 GC-VUV apparatus includes changing or trimming the analytical column.

12.2 A list of retention times and retention indices for the linear alkanes is used to estimate 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.

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

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

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

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

12.6 Relative response factors used to obtain the statistical precision data in this test method are given in Table 3 and Table 4, and are suitable for use with this test method.

12.7 Relative response factors may alternatively be refined or determined by one of as described in Appendix X2 the following procedures:

12.7.1 The relative response factor for a given compound may be determined from the compound's absorption cross section (expressed in cm²/molecule) and methane's cross section by calculating:

| TABLE 3 Relative | Response | Factors for | Bulk Hydr | ocarbon |
|------------------|----------|-------------|-----------|---------|
|------------------|----------|-------------|-----------|---------|

| Classes | | |
|---|---|--|
| Hydrocarbon Class | Relative Response Factor | |
| Saturates | 0.705 | |
| Monoaromatics | s 0.296 | |
| Diaromatics | 0.240 | |
| · (| , 196666 | |
| | 103363 | |
| Hydrocarbon Class | Relative Response Factor <u>C6 to C21⁴</u> | |
| Hydrocarbon Class Saturates | Relative Response Factor C6 to C21 ^A 0.811 to 0.683 | |
| Hydrocarbon Class Saturates Monoaromatics | Relative Response Factor C6 to C21 ^A 0.811 to 0.683 0.258 to 0.422 | |

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



TABLE 4 Relative Response Factors for Specific Individual Compounds and Compound Groups

| Compound | Relative Response Factor |
|------------------------|--------------------------|
| Benzene | 0.258 |
| Toluene | 0.267 |
| Ethylbenzene | 0.284 |
| Xylenes | 0.284 |
| 1,2,4-trimethylbenzene | 0.279 |
| Naphthalene | 0.207 |
| Naphthalene | 0.198 |
| Methylnaphthalenes | 0.202 |

$$\frac{RF_a}{MW_{\text{methane}}} \times \frac{MW_a}{\Sigma_a} \tag{1}$$

where:

Σ

 RRF_a = relative response factor for compound a,

MW = molecular weight, and

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

R

12.7.2 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:

$$RRF_2 = \frac{M_2}{M_1} \frac{A_1}{A_2} RRF_1 \tag{2}$$

where:

 RRF_2 = relative response factor of compound to be determined,

 $A_{\overline{I}}$ = total measured response area of known compound,

 A_2 = total measured response area of compound to be determined,

 M_{I} = percent mass of known compound in standard, and

 M_2 = percent mass of compound to be determined in standard.

12.7.2.1 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.

12.7.3 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 test 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 5). 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 2, except in this case all quantities refer to class totals instead of individual compounds.

12.7.3.1 If a standard consisting of known percent mass concentrations of the hydrocarbon classes of paraffins, isoparaffins, naphthenes, aromatics, and diaromatics 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 1. This is most easily applied to the paraffins class. Then apply Eq 2 using the response areas and relative response factor for paraffins (as RRF_1) to determine the other class-based relative response factors.

12.7.3.2 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 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 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 2.

13. Pre-Measurement Validation

13.1 Before proceeding with measurements or after a significant change or maintenance of the GC-VUV system, 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 $3.0\pm0.253.25\pm0.25$ 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.

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).