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.

Designation: D8369 – 21

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

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

1. Scope

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

[1] 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. Referenced Documents

2.1 *ASTM Standards:*[2]

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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

D4814 Specification for Automotive Spark-Ignition Engine Fuel

D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement

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

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

D6729 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography

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

D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories

D7372 Guide for Analysis and Interpretation of Proficiency Test Program Results

D7900 Test Method for Determination of Light Hydrocarbons in Stabilized Crude Oils by Gas Chromatography

3. Terminology

3.1 *Definitions:*

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

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

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

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

3.2 *Definitions of Terms Specific to This Standard:*

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

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

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

3.3 *Abbreviations:*

3.3.1 *AU*—absorbance units

3.3.2 *DHA*—detailed hydrocarbon analysis

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

3.3.4 *RI*—retention index

3.3.5 *RRF*—relative response factor

4. Summary of Test Method

4.1 A sample is introduced to a gas chromatographic (GC) system. After volatilization, the effluent is introduced onto a GC column for separation, and then detected by a vacuum ultraviolet absorption spectroscopy detector.[3] The separation is accomplished using a 60 m, nonpolar phase capillary column and a moderately fast temperature ramp (typical operating parameters of this test method are given in Table 1). Coelutions are resolved by the detector using vacuum ultraviolet absorbance spectra and deconvolution.

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

5. Significance and Use

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

[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] The sole source of supply of the apparatus known to the committee at this time is VUV-Analytics, Cedar Park, Texas. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

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

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

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

[A] Alternate instrument settings are presented in Appendix X3.
[B] Columns with low bleed phases such as MS grade have been successfully used for this application (see 11.6).
[C] The typical flow rate is for helium carrier gas, other carrier gases may be utilized (see 8.2).
[D] Other injection volumes and split ratios may be used to achieve the required benzene response (see 13.2).

6. Interferences

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

7. Apparatus

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

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

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

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

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

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

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

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

7.6.1 The detector shall be able to interface with a gas chromatographic system and measure an eluent with a scan frequency of at least 5 Hz with a baseline peak-to-peak noise width over a 10 s interval no greater than 0.002 AU when averaged over the following wavelength regions: 125 nm to 240 nm, 170 nm to 200 nm, 125 nm to 160 nm, and 0.001 AU when averaged over the 140 nm to 160 nm wavelength region.

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

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

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

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

7.7.1 Data processing system shall include a database 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.

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

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

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

8. Reagents and Materials

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

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

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

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