



Designation: D8564 – 24

Standard Test Method for Determination of Phenolic Antioxidants and Fuel System Icing Inhibitors in Aviation Turbine Fuels¹

This standard is issued under the fixed designation D8564; 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 determination, in the interim precision ranges, of hindered phenolic antioxidants from approximately 1 mg/L to 50 mg/L and fuel system icing inhibitors from approximately 450 mg/L to 4500 mg/L in aviation turbine fuels by solid phase extraction (SPE) with gas chromatography-mass spectrometry detection (SPE-GC/MS).

1.1.1 Higher concentrations can be determined, but the interim precision of the test method has not been determined.

1.2 This test method is applicable to aviation turbine fuels that meet several international aviation turbine fuel specifications including, but not limited to, petroleum based, such as specified in Specification [D1655](#), and synthetic aviation turbine fuels (SAF), such as specified in Specification [D7566](#), and a blend of such fuels.

1.3 The test method does not purport to identify all of the individual antioxidants and fuel system icing inhibitors. The interim precision estimates have been determined in accordance with Practice [D6300](#) for the following:

1.3.1 *Phenolic Antioxidants*—2,6-di-tert-butyltert-butylphenol; 2,4,6-tri-tert-butylphenol; 2,6-di-tert-butyl-4-methyl phenol; 4-sec-butyl-2,6-di-tert-butylphenol; 2-tert-butyl-4,6-dimethylphenol; 2-tert-butylphenol; 4-tert-butyl-2-methylphenol; and

1.3.2 *Fuel System Icing Inhibitors*—Diethylene glycol monomethyl ether (DiGME) and ethylene glycol monomethyl ether (EGM) (2-methoxyethanol).

1.3.3 Not all of the above antioxidants and/or fuel system icing inhibitors may be listed in all aviation turbine fuel specifications. User should consult the pertinent specification(s) for testing requirements.

1.4 [Appendix X1](#) presents information on the data such as accuracy recovery studies and application to several types of aviation turbine fuels.

1.5 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

[D1655](#) Specification for Aviation Turbine Fuels

[D4057](#) Practice for Manual Sampling of Petroleum and Petroleum Products

[D4171](#) Specification for Fuel System Icing Inhibitors

[D4175](#) Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

[D4177](#) Practice for Automatic Sampling of Petroleum and Petroleum Products

[D4307](#) Practice for Preparation of Liquid Blends for Use as Analytical Standards

[D5006](#) Test Method for Measurement of Fuel System Icing Inhibitors (Ether Type) in Aviation Fuels

[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

[D7566](#) Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons

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

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

E355 Practice for Gas Chromatography Terms and Relationships

2.2 Other Standards:

DEF-STAN 91-091 Turbine Fuel, Kerosene Type, Jet A-1; NATO Code: F-35; Joint Service Designation: AVTUR (Def Stan 91-091)³

GB 6537 No. 3 Jet Fuel Specification⁴

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology **D4175** and Practice **E355**.

3.1.2 *aviation turbine fuel, n*—refined distillate, generally used as a fuel for aviation turbines.

3.1.2.1 *Discussion*—Different grades are characterized by volatility ranges, freeze point and by flash point. In this test method, it refers both to petroleum-based aviation turbine fuels and synthetic aviation turbine fuels such as produced according to Specification **D7566**. The fuels have specific properties that meet specifications, for example, Specification **D1655**, GB 6537, and DEF-STAN-091. The test method also may be applicable to other international aviation turbine fuel specifications.

3.1.3 *antioxidants, n*—hindered phenolics which can improve the oxidation stability of the fuels.

3.1.3.1 *Discussion*—The determined antioxidants are listed in this test method.

3.1.4 *fuel system icing inhibitors, n*—additives which, when added to aviation turbine fuel, preferentially dissolve in water to reduce its freeze point, thereby inhibiting the formation of ice crystals in jet fuels in cold conditions.

3.1.4.1 *Discussion*—The fuel system icing inhibitors additives are listed in this test method. The use of such fuel system icing inhibitors is also described in Specification **D4171**.

3.1.5 *selected ion monitoring (SIM), n*—an MS selective scanning mode in which only a limited mass-to-charge ratio (m/z) targeted range is filtered and detected by the MS, in contrast to full scan mode in which all the ions are detected in a single scan; results in significantly increased sensitivity.

3.2 Acronyms:

3.2.1 *GC*—gas chromatography

3.2.2 *MS*—mass spectrometry

3.2.3 *PTV*—programmed temperature vaporizer

3.2.4 *SIM*—single ion monitoring

3.2.5 *SPE*—solid phase extraction

3.2.6 *WCOT*—wall coated open tubular

4. Summary of Test Method

4.1 The sample is separated using a small SPE column into a saturates plus aromatics fraction and an additives fraction. A known amount of an internal standard is added to the additives

fraction and analyzed by a gas chromatograph equipped with a mass spectrometer (GC/MS) detection. The content of the antioxidants and fuel system icing inhibitors are calculated based on the peak areas of additives and the internal standard and respective calibration curves.

5. Significance and Use

5.1 Antioxidants are added to the aviation turbine fuels as protection against oxidation and formation of gums. Fuel system icing inhibitors are used to avoid ice formation in jet fuel under cold environment. The concentration of antioxidants and fuel system icing inhibitors is very important for the storage, trade and use of aviation turbine fuel. A standard test method for accurately measuring their contents and determination of specification limits is required to protect the fuels and engine performance. Test Method **D5006** describes the analysis of one icing inhibitor; however, Test Method **D5006** is more for field use and does not selectively identify or quantify the individual fuel system icing inhibitors. Several aviation turbine fuels specifications, such as Specification **D1655**, GB 6537, DEF-STAN 91-091 do not specify selective test method(s) for the listed additives.

6. Interferences

6.1 The use of SPE, GC separation and SIM significantly reduce interferences from many other compounds, such as hydrocarbons, etc., present in aviation turbine fuels or possible contaminants of the aviation turbine fuel(s). However, the test method has not been tested on all possible interferences or potential contaminants in aviation turbine fuels. It is possible that certain polar compounds containing nitrogen, oxygen, etc., may have similar SPE adsorption and SIM responses at same gas chromatographic retention time windows; therefore, user should be cautious in the interpretation of the results obtained. For the fuels tested in the development of this test method, interferences were minimal or not detectable. The future interlaboratory testing (ILS) will conduct a more extensive fuel type testing for possible interferences.

7. Apparatus

7.1 Solid Phase Extraction Separation System:

7.1.1 *Solid Phase Extraction (SPE) Column*, approximately 4 cm³ column packed with 2 g (approximately 3 cm³) of stationary phase. The dimensions ($\pm 10\%$) of the column are given in **Fig. 1**. The aluminum oxide (see Section 8) is activated by heating in a muffle furnace or equivalent at 400 for two hours, then cooled to room temperature and stored in a desiccator. The required verification of the separation efficiency and activity of new batches of SPE columns or alumina, before using for the analysis of the fuels, is described in **12.1**. A new SPE column is used for each analysis.

7.2 *Erlenmeyer flask*, 10 mL and 25 mL.

7.3 *Syringe*, 1 mL and 5 mL.

7.4 *Pipet*, 100 μ L and 1 mL.

7.5 *Desiccator*, 500 mL.

7.6 *Analytical balance*, capable of weighing to the nearest 0.0001 g (0.1 mg).

³ Available from U.S. Government Publishing Office (GPO), 732 N. Capitol St., NW, Washington, DC 20401, <http://www.gpo.gov>.

⁴ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

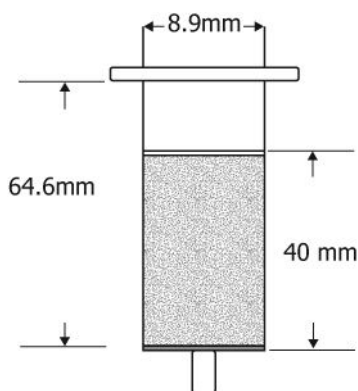


FIG. 1 Specifications of the Solid Phase Extraction (SPE) Column

7.7 GC/MS System:

7.7.1 The GC/MS system shall be equipped with sample inlet system, capillary (WCOT) column, column temperature programmer, a mass spectrometer capable of working in the SIM mode and data acquisition system. This method was developed using a quadrupole GC/MS system; other GC/MS systems may be used if all the requirements in this method are met.

7.7.2 Recommended GC/MS operating conditions are given in Table 1. Tables 2 and 3 provide additional requirements.

7.7.3 The GC/MS system and operating conditions shall ensure baseline separation of the solvent, sample and internal standard as shown in Fig. 2. Other GC/MS operating conditions capable of yielding equivalent results and meeting all the requirements in this test method may be used.

7.7.4 Sample Introduction System—An automated liquid sample injection system (autosampler) with a split/splitless inlet is required. The inlet is used in the split mode.

7.7.4.1 A cool-on-column or PTV inlet capable of yielding equivalent results and meeting all the requirements in this test method may be used. This test method was developed using split/splitless injection system.

7.7.5 Data Acquisition System—A computerized data acquisition and reporting system is required to acquire, display, and process the GC/MS/SIM data. The areas of the SIM chromatogram peak may be determined through either manual or automated peak integration. Ensure that the peaks are properly integrated.

8. Reagents and Materials

8.1 Purity of Reagents—Analytical reagent grade ($\geq 95\%$ purity) chemicals shall be used in this test method. Other grades of reagents may be used, provided it is first ascertained that the reagent is of sufficiently high purity ($\geq 95\%$ purity) to permit its use without lessening the accuracy of the determination.

8.2 Diethyl ether, (CAS 60-29-7), analytical reagent. (**Warning**—highly flammable, and may cause irritation by inhalation, ingestion, or skin contact.)

8.3 *n*-Hexane, (CAS 110-54-3), analytical reagent. (**Warning**—Highly flammable, and high potential toxicity, may cause irritation by inhalation, ingestion, or skin contact.)

8.4 Methanol, (CAS 56-1), analytical reagent. (**Warning**—Highly flammable, and may cause irritation by inhalation, ingestion, or skin contact.)

8.5 4-Methoxy-benzenemethanol, (CAS 105-13-5), analytical reagent. Used as the internal standard. (**Warning**—Highly flammable, may cause irritation by inhalation, ingestion, or skin contact.)

8.5.1 4-methoxy-benzenemethanol—Internal Standard Solution, dissolved in dichloromethane, to obtain the mass concentrations of 2000 mg/L. Table 4 gives a recommended procedure for its preparation.

8.6 Dichloromethane, (CAS 75-09-2), analytical reagent. (**Warning**—Toxic fumes may be generated during combustion; may cause irritation by inhalation, ingestion, or skin contact.)

8.7 Diethylene Glycol Monomethyl Ether (DiGME), (CAS 111-77-3), analytical reagent. (**Warning**—May cause irritation by inhalation, ingestion, or skin contact.)

8.8 Ethylene Glycol Monomethyl Ether (EGME) (2-methoxyethanol), (CAS 109-86-4), analytical reagent. (**Warning**—Flammable, high potential toxicity, may cause irritation by inhalation, ingestion, or skin contact.)

8.9 2,6-Di-*tert*-butylphenol, (CAS 118-82-1) and other antioxidants listed in 1.3.1, analytical reagent. (**Warning**—May cause irritation by inhalation, ingestion, or skin contact.)

8.10 Cyclohexane, (CAS 110-82-7), analytical reagent. (**Warning**—Highly flammable, may cause irritation by inhalation, ingestion, or skin contact.)

TABLE 1 Typical Operating Conditions of GC/MS

GC Column	Fused silica WCOT capillary column, FFAP, 30 m $\times$ 320 μ m $\times$ 0.5 μ m
GC Oven	Initial oven temperature 40 $^{\circ}$ C, initial hold 5 min, program rate 10 $^{\circ}$ C/min, final oven temperature 240 $^{\circ}$ C, final hold 5 min
GC Inlet	300 $^{\circ}$ C
GC Inlet Split Ratio	80:1
GC Injection sample and calibration standards size	1 μ L
Carrier gas	He, 2 mL/min, constant flow mode
Mass spectrometer (MS) Quadrupole	Transfer line temperature: 280 $^{\circ}$ C Source temperature: 230 $^{\circ}$ C Quadrupole temperature: 150 $^{\circ}$ C Ionization: EI, 70 eV Solvent delay: 5.0 min SIM parameters (see Table 2) SIM Ion Dwell time: 100 ms for each ion

TABLE 2 GC and SIM Parameters for Operating Conditions in Table 1

Additives in Internal Standard	Primary SIM Ion (m/z)	Secondary SIM Ion (m/z)	Approximate percent abundance of secondary ion vs. primary ion: Ratio Secondary SIM/Primary SIM ^A	SIM Ions Scan Time Windows (min) ^B	Retention Time of Additives using the Typical Operating Conditions of the Test Method (min) ^B
Ethylene glycol monomethyl ether (2-methoxyethanol) (fuel system icing inhibitor) (CAS 109-86-4)	45	76	6	7.5.0 to 9.5	(8.6)
Diethylene glycol monomethyl ether (fuel system icing inhibitor) (CAS 111-77-3)	45	90	15	14.0 to 16.0	(15.0)
2,6-di-tert-butylphenol (CAS 118-82-1)	191	206	19	17.0 to 18.2	(18.0)
2,4,6-tri-tert-butylphenol (CAS 732-26-3)	247	262	14	18.2 to 18.6	(18.3)
2,6-di-tert-butyl-4-methylphenol (CAS 128-37-0)	205	220	22	18.6 to 20.0	(18.6)
4-sec-butyl-2,6-di-tert-butylphenol (CAS 17540-75-9)	233	247	25	18.6 to 20.0	(18.7)
2-tert-butyl-4,6-dimethylphenol (CAS 1879-09-0)	163	178	32	20.0 to 21.0	(20.2)
2-tert-butylphenol (CAS 88-18-6)	135	150	36	21.0 to 21.6	(21.3)
4-tert-butyl-2-methylphenol (CAS 98-27-1)	149	164	48	21.6 to 22.0	(21.7)
4-methoxy-benzenemethanol (internal standard) (CAS 105-13-5)	138	109	78	22.0 to 30.0	(22.3)

^A These percent abundances are approximate; determine appropriate abundances for a specific GC/MS instrument using calibration standard components. A mid-range concentration of the calibration standards may be an initial starting point.

^B The time ranges indicated (and retention times) represent the retention time window for the detection of the indicated compound using the typical operating conditions described in this method. Some adjustment in the windows may be required to ensure the compound is properly detected. Using the calibration standard(s), the windows for the GC/MS elution may be established.

TABLE 3 Instructions for Use of the Quantitative Primary Mass (m/z) SIM Ions

Mass m/z	Uses
45	quantitate ethylene glycol monomethyl ether (2-methoxyethanol) and diethylene glycol monomethyl ether from its calibration curve. Ignore any other mass 45 peaks
191	quantitate 2,6-di-tert-butyl-tert-butylphenol from its calibration curve. Ignore any other mass 191 peaks
247	quantitate 2,4,6-tri-tert-butylphenol from its calibration curve. Ignore any other mass 247 peaks
205	quantitate 2,6-di-tert-butyl-4-methylphenol from its calibration curve. Ignore any other mass 205 peaks
233	quantitate 4-sec-butyl-2,6-di-tert-butylphenol from its calibration curve. Ignore any other mass 233 peaks
163	quantitate 2-tert-butyl-4,6-dimethylphenol from its calibration curve. Ignore any other mass 163 peaks
135	quantitate 2-tert-butylphenol from its calibration curve. Ignore any other mass 135 peaks
149	quantitate 4-tert-butyl-2-methylphenol from its calibration curve. Ignore any other mass 149 peaks
138	quantitate 4-methoxy-benzenemethanol (internal standard) from its calibration curve. Ignore any other mass 138 peaks

8.11 *Aluminum oxide*⁵ (neutral), (CAS 1344-28-1), particle size range 75 µm to 150 µm, surface area range 132 m²/g to 350 m²/g. (**Warning**—Avoid inhalation of dust particles.)

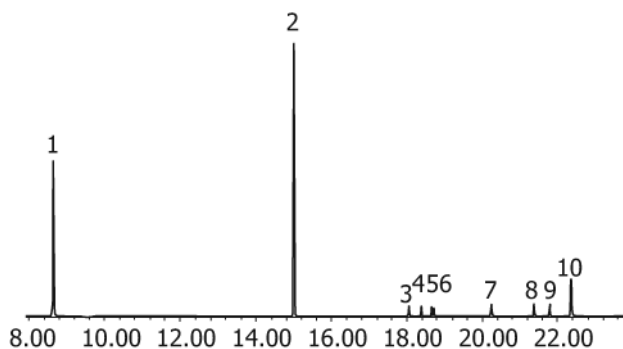
8.12 *Carrier gas*, helium, 99.99 % pure. (**Warning**—Compressed gas under high pressure; may displace oxygen and cause rapid suffocation).

8.13 Calibration Standards of the Additives:

8.13.1 Calibration standards are used to establish the standard response curves of the additives relative to the internal standard 4-methoxy-benzenemethanol.

8.13.2 At least five calibration solutions shall be prepared in cyclohexane by mass containing all the specified additives in 1.3. Adjust these concentrations, as necessary, to ensure that the concentrations of the components in the fuel samples are bracketed by the calibration concentrations. Table 4 gives a recommended procedure for the preparation of the calibration standards.

⁵ The sole source of supply of the apparatus known to the committee at this time is Sinopharm Chemical Reagent Co. Ltd China (Catalog number 20002361). 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.



1. Ethylene glycol monomethyl ether (2-Methoxyethanol);
2. Diethylene glycol monomethyl ether;
3. 2,6-Di-tert-butyl-tert-butylphenol;
4. 2,4,6-Tri-tert-butylphenol;
5. 2,6-Di-tert-butyl-4-methylphenol;
6. 4-sec-Butyl-2,6-di-tert-butylphenol;
7. 2-tert-Butyl-4,6-dimethylphenol;
8. 2-tert-Butylphenol;
9. 4-tert-Butyl-2-methylphenol;
10. 4-methoxy-benzenemethanol (internal standard)

FIG. 2 Typical Mass Spectrum of Antioxidants and Fuel System Icing Inhibitors in a Petroleum Base Aviation Turbine Fuel

TABLE 4 Recommended Preparation of the Calibration Standards and Internal Standard

1. <i>Preparation of Calibration Standards</i> —Multicomponent calibration standards are prepared by mass and fixed volumes using all the compounds listed in Table 2 following Practice D4307. For convenience, the standards may be prepared initially by combining the specified individual additives into a single mixture.
2. Cap and record the tare weight of a 50 mL vial with cap to 0.1 mg.
3. Remove the cap and carefully add 1 g each of 2-methoxyl ethanol and diethylene glycol dimethyl ether and 14 g of cyclohexane. Cap the vials and record the net mass of each icing inhibitor and cyclohexane to 0.1 mg for each addition. Mix the solution well to make stock solution Mixture C.
4. Cap and record the tare weight of a 50 mL vial with cap to 0.1 mg.
5. Remove the cap and carefully add 0.1 g each of the antioxidants and 15 g of cyclohexane. Cap the vials and record the net mass of each antioxidant and cyclohexane to 0.1 mg. Mix the solution well to make stock solution Mixture D.
6. Cap and record the tare weight of a 25 mL volumetric flask to 0.1 mg. Transfer 0.08 g of Mixture C and 0.02 g of Mixture D to the volumetric flask, cap and weigh to 0.1 mg then add cyclohexane to the mark. Mix well the solution and label as calibration standard #1. The calibration standard solution contains about 200 mg/L each of the ice inhibitors and 5 mg/L each of the antioxidants.
7. Cap and record the tare weight of a 25 mL volumetric flask to 0.1 mg. Transfer 0.16 g of Mixture C and 0.06 g of Mixture D to the volumetric flask, cap and weigh to 0.1 mg, then add cyclohexane to the mark. Mix well the solution and label as calibration standard #2. The calibration standard solution contains about 400 mg/L each of icing inhibitors and 15 mg/L each of antioxidants.
8. Cap and record the tare weight of a 25 mL volumetric flask to 0.1 mg. Transfer 0.24 g of Mixture C and 0.10 g of Mixture D to the volumetric flask, cap and weigh to 0.1 mg then add cyclohexane to the mark. Mix well the solution and label as calibration standard #3. The calibration standard solution contains about 600 mg/L each of icing inhibitors and 25 mg/L each of antioxidants.
9. Cap and record the tare weight of a 25 mL volumetric flask to 0.1 mg. Transfer 0.8 g of Mixture C and 0.14 g of Mixture D to the volumetric flask, cap and weigh to 0.1 mg then add cyclohexane to the mark. Mix well the solution and label as calibration standard #4. The calibration standard solution contains about 2000 mg/L each of icing inhibitors and 35 mg/L each of antioxidants.
10. Cap and record the tare weight of a 25 mL volumetric flask to 0.1 mg. Transfer 3.2 g of Mixture C and 0.2 g of Mixture D to the volumetric flask, cap and weigh to 0.1 mg then add cyclohexane to the mark. Mix well the solution and label as calibration standard #5. The calibration standard solution contains about 8000 mg/L each of icing inhibitors and 50 mg/L each of antioxidants.
11. <i>Preparation of the Internal Standard Solution</i> —The internal standard is prepared by first taring a 50 mL volumetric flask and cap to 0.1 mg. Transfer 0.1 g of 4-Methoxy-benzenemethanol to the 50 mL volumetric flask. Cap and weigh the flask to 0.1 mg. Then, fill the volumetric flask with dichloromethane to the mark. The latter prepares a 2000 mg/L internal standard.
12. <i>Addition of the Internal Standard to the Calibration Standards</i> —The calibration standard with the added internal standard is prepared by adding 0.1 mL of the internal standard solution (prepared in step 11) using a pipette with a tip volume of 100 µL into 2 mL of each calibration standard prepared according to steps 6 to 10. Using a pipette with a tip of 1000 µL transfer the standard with the added internal standard into a 5 mL GC vial and mix well the resulting solution. Transfer to a 2 mL GC vial for GC/MS analysis. The resulting concentration of the internal standard in each of the calibration standards is approximately 100 mg/L.

8.13.3 In the development of this test method, the five concentrations of each antioxidant were approximately 5 mg/L, 15 mg/L, 25 mg/L, 35 mg/L and 50 mg/L. The five concentrations of each of the fuel system icing inhibitors were approximately 200 mg/L, 400 mg/L, 600 mg/L, 2000 mg/L, and 8000 mg/L.

8.13.4 To each of the calibration standards, 0.1 mL of the internal standard solution is added to 2.0 mL of each standard. Table 4 gives a recommended procedure.

8.13.5 Commercially prepared NIST traceable standards using reagents that meet or exceed the purity requirements of this test method may be used as an alternative to the in-house prepared standards. Such standards must be prepared and stored in glass and may be glass sealed for stability and to prevent evaporation.

8.14 SPE Column Fractionation Efficiency Evaluation Mixtures (CFEEM):

8.14.1 The separation efficiency (effectiveness and accuracy of the SPE column) is confirmed by using an aviation turbine fuel (Mixture A) to which additives have not been added (non-spiked low or non-detectable concentration of additives) and a Mixture B (spiked) prepared by adding the additives to be tested for recovery into same fuel as Mixture A.

8.14.1.1 Mixture B is prepared by adding 8 g diethylene glycol monomethyl ether and 0.015 g 2,6-di-tert-butylphenol to 1 L of Mixture A (aviation turbine fuel). The resulting concentrations of diethylene glycol monomethyl ether and 2,6-di-tert-butylphenol in Mixture B are approximately 8000 mg/L and 15 mg/L, respectively.

8.14.1.2 Mixture A (non-spiked) and Mixture B (spiked) are analyzed separately by the SPE procedure described in 12.1 and the collected SPE additive fractions analyzed by GC/MS.

8.14.1.3 The recovery of diethylene glycol monomethyl ether and 2,6-di-tert-butylphenol is calculated as described in 13.2. A recovery of greater or equal to 90 % of the two compounds is required to be able to use the SPE column batch for the analysis of the fuels.

9. Sampling

9.1 Use only representative samples obtained as described in Practices D4057 or D4177 or equivalent, unless otherwise specified. The additives, because of their polar nature, may adsorb readily on container surfaces; the use of inert or deactivated containers is recommended to minimize loss of the additives.

10. Preparation of Apparatus

10.1 *Gas Chromatograph/Mass Spectrometer (GC/MS)*—Before initiating the calibration procedure, tune the mass spectrometer according to manufacturer's instructions. Set the mass spectrometer data system to acquire primary and secondary ion data in the SIM mode. Typical operating conditions are shown in Table 1 and Table 2.

10.1.1 The GC capillary WCOT shall meet the resolution requirements described in 10.4 when installed in the GC/MS system.

10.2 Preparation of SPE Columns:

10.2.1 Add 100 g of neutral aluminum oxide⁵ to a 25 mL Erlenmeyer flask.

10.2.2 Place the Erlenmeyer flask into a muffle furnace (or equivalent) to activate the aluminum oxide at 400 °C for 2 h.

10.2.3 After the activation process, transfer the sample to a desiccator and cool to room temperature.

10.2.4 The activated aluminum oxide is now ready for preparation of the SPE column described in 7.1.

10.2.5 Commercially pre-packaged SPE columns may be used provided they meet the specifications of this test method.

10.2.6 Each sample or blank analysis shall use a new or newly prepared SPE column.

10.3 *Capillary Column WCOT*—This test method is limited to the use of polar fused silica WCOT capillary columns capable of separating all the additives and the internal standard. In the development of this method, FFAP stationary phase was used successfully.

10.3.1 The column and conditions shall provide separation of typical compounds in order of increasing polarity. Fig. 2 shows a chromatogram of a typical separation.

10.3.2 Resolution (R) between 2,6-tert-butyl-4-methyl phenol and 4-sec-butyl-2,6-di-tert-butylphenol (both at 25 mg/L) shall be equal to or greater than 1.5.

$$R = \frac{2 \times (t_2 - t_1)}{1.699 \times (w_2 + w_1)} \quad (1)$$

where:

t_2 = retention time of 4-sec-Butyl-2,6-di-tert-butylphenol, min,

t_1 = retention time of 2,6-Di-tert-butyl-4-methyl phenol, min,

w_2 = peak width at half height of 4-sec-Butyl-2,6-di-tert-butylphenol, min, and

w_1 = peak width at half height 2,6-Di-tert-butyl-4-methyl phenol, min.

10.4 *MS Detection of the Additives and Internal Standard*—The MS detector shall have enough sensitivity, linearity, and stability to meet performance requirements. The SIM primary selective target ions that are used for quantification of the additives are summarized in Tables 3 and 4. The secondary ion for each compound is used to further identify the compound.

10.4.1 The various additives components in the calibration standards and fuel samples are identified from their retention times and the SIM mass spectrum from calibration standard(s). A mid-concentration standard may be used initially to establish the relative intensities (abundance) of the secondary to the primary ions. Table 2 gives an approximate abundance obtained during the development of this test method using a quadrupole mass spectrometer using the operating conditions in Table 1.

10.4.1.1 The two characteristic primary and secondary ions for the compound shall be found to maximize in the same or within one spectrum or scan of each other.

10.4.1.2 The percent abundance (percent ratio of the intensities of the secondary ion to the primary ions) of the compound must agree within $\pm 30\%$, $\pm 50\%$, and $\pm 100\%$ relative for ions with relative intensities of $>50\%$, 20% to 50% , and $<20\%$, respectively, when compared to the percent relative ion intensity ratios obtained for calibration standard(s) or average relative intensities from such standards.

10.4.1.3 The GC/MS retention time at the maximum intensity scan shall be within ± 15 s of the retention time of the authentic compound from the calibration analyses.

11. Calibration

11.1 Prepare calibration standards of the additives and the internal standards as described in 8.13 and 8.5.

11.2 Quantitatively add 0.1 mL internal standard solution (8.5) to 2 mL of each additive standard (8.13). Inject and analyze 1 μ L of the standards prepared.

11.3 Obtain the response ratio of the internal standard to additives by integrating the primary ion SIM chromatograms as described in 10.4 and construct calibration curves for each of the additives.

11.3.1 Plot as follows: x -coordinate is the area ratio of the primary ion additive compound to the primary ion of the internal standard, and y -coordinate is the concentration of the additive compound in the standard. The formula of concentration content is obtained by the slope of internal standard calibration curve according to Eq 2.

$$y_i = a_i x_i + b_i \quad (2)$$

where:

y_i = concentration content of additive compound in i in mg/L,

x_i = area ratio of additive compound to i to internal standard, a_i = the slope of the internal standard curve of additive compound i , and

b_i = the intercept of the internal standard curve of additive compound i .

Typical examples of the internal standard calibration curves of the additives are shown in Fig. 4. The correlation r^2 value for the calibration line obtained shall be at least 0.997 or better.

12. Procedure

12.1 *Verification of the Separation Efficiency of the SPE Column:*

12.1.1 For non-certified or newly prepared batches of SPE columns or aluminum oxide stationary phase, it is necessary to determine the separation efficiency.

12.1.2 Use the separation efficiency evaluation mixtures (CFEEM) A and B prepared in 8.14 to evaluate the SPE column following the sample fractionation procedure in 12.2.

12.1.2.1 The recovery of diethylene glycol monomethyl ether and 2,6-di-tert-butyl-tert-butylphenol is calculated as described in 13.2. A recovery of greater or equal to 90 % of the two additive compounds is required to be able to use the SPE column batch for the analysis of the fuels.

12.2 *Fuel Sample Fractionation Procedure using Solid Phase Extraction (SPE) and GC/MS Analysis of Sample:*

12.2.1 Add 0.5 mL mixture of diethyl ether and n -hexane (10 % to 90 % by volume) to the top of the SPE column to pre-wet the adsorbent.

12.2.2 Add 2.0 mL of sample to the top of the column and wait until it is completely adsorbed.

12.2.3 Place a 10 mL Erlenmeyer flask beneath the column to collect the eluate. Sequentially add 3 mL mixture of diethyl ether and n -hexane (10 % to 90 % by volume) to the top of the column to elute the combined saturates and aromatics fraction. The flow rate should be approximately 1 mL/min.