Designation: D4768 – 11 (Reapproved 2019)

Standard Test Method for Analysis of 2,6-Ditertiary-Butyl Para-Cresol and 2,6-Ditertiary-Butyl Phenol in Insulating Liquids by Gas Chromatography[1]

This standard is issued under the fixed designation D4768; 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 by gas chromatography of 2,6-ditertiary-butyl para-cresol and 2,6-ditertiary-butyl phenol in new and used insulating liquids at concentrations up to 0.5 %. It includes the determination in Type I and II insulating mineral oils as specified in Specification D3487, but has also been used to measure these inhibitors in other insulating liquids, such as esters and high fire-point hydrocarbons.

1.2 *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.*

1.3 *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]

D923 Practices for Sampling Electrical Insulating Liquids

D3487 Specification for Mineral Insulating Oil Used in Electrical Apparatus

D5222 Specification for High Fire-Point Mineral Electrical Insulating Oils

E260 Practice for Packed Column Gas Chromatography

3. Summary of Test Method

3.1 The test specimen is placed onto a column containing activated alumina and extracted to remove interfering substances. The inhibitors are then eluted from the column with suitable solvent and analyzed by gas chromatography. The inhibitor type and quantity are determined by comparison of each component with a working standard tested under similar conditions.

4. Significance and Use

4.1 In new electrical insulating oil, this test method provides a quantitative measure of the amounts of 2,6-ditertiary-butyl para-cresol and 2,6-ditertiary-butyl phenol that have been added to the oil. In a used oil, the test measures the amount of these inhibitors remaining in the oil. This test method is suitable for manufacturing control, specification acceptance, and service evaluation.

4.2 This test method is used to separate, identify, and quantify the inhibitors with minimal interference and matrix effects.

4.3 This test method has also been used successfully to determine the inhibitor concentrations in other insulating liquids such as esters and high-temperature hydrocarbons.

5. Apparatus

5.1 *Gas Chromatograph,* equipped with oven temperature control constant to 1 °C and with heated injector port.

5.1.1 *Means to Record the Chromatogram,* such as a pen recorder or a digital integrator to determine peak areas, is recommended. An automated sample injector may be used.

5.2 *Flame Ionization Detector,* with appropriate hydrogen/air gas flows, is preferred over a thermal conductivity detector to provide maximum sensitivity.

5.3 *Column,* a suitable stainless steel or glass column packed with a nonpolar silicone on an appropriate support or equivalent capillary column.

[1] This test method is under the jurisdiction of ASTM Committee D27 on Electrical Insulating Liquids and Gases and is the direct responsibility of Subcommittee D27.03 on Analytical Tests.

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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.

NOTE 1—A 3 % OV-1[3] on 100/120 Mesh Supelcoport,[4] 1.83 m (6 ft) long, 3.2 mm (0.125 in.) in outside diameter has been used successfully. A SPB-1[4] 30 m by 0.53 mm 1µm film column has also been used successfully.

5.3.1 Condition columns in accordance with manufacturer's recommendations. Disconnect columns from detector prior to conditioning and reconnect after conditioning.

5.4 *Precision Syringe,* glass, 10.0 µL.

5.5 *Volumetric Glassware,* appropriate for making dilutions.

5.6 *Pipets,* Pasteur, disposable, 146 by 7.5 mm.

5.7 *Analytical Balance.*

5.8 *Automatic Pipetter,* 1 mL calibrated, adjustable.

5.9 *Oven,* capable of maintaining a temperature of 325 ± 5 °C for conditioning extraction columns.

5.10 *Desiccator.*

6. Reagents and Materials

6.1 *Purity of Reagents*—Use reagent grade chemicals 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 sufficient purity to permit its use without lessening the accuracy of the determination.

6.2 *2,6-ditertiary-butyl phenol (DBP).*

6.3 *2,6-ditertiary-butyl para-cresol (DBPC [6])*—Also known as butylated hydroxytoluene (BHT).

6.4 *Glass Wool.*

6.5 *Aluminum Oxide* (Alumina), acid powder, ACS, Brockman Activity Grade 1, for chromatography.[7]

6.6 *Hexane or Heptane,* ACS reagent grade.

6.7 *Methanol,* anhydrous, ACS reagent grade.

6.8 *Mineral Oil,* inhibitor-free, transformer grade.

7. Calibration and Standardization

7.1 *Cleanup Column Preparation*—Prepare cleanup columns by inserting a small glass wool plug into the wide end of a Pasteur pipet and tamping down to the narrow end. Fill column to a height of approximately 35 mm (1.5 in.) with alumina and place a second glass wool plug on top of adsorbent. Activate column by placing in 325°C oven for a minimum of 12 h. Cool in a desiccator prior to use. After column has cooled, purge column with approximately 2 mL hexane or heptane. Do not allow column to dry out prior to use.

7.2 *Standard Solution Preparation*—Standard solutions are prepared containing both DBP and DBPC from inhibitor-free mineral oil. Prepare oil solutions of 0, 0.040, 0.080, 0.15, 0.30, and 0.40 % (w/w) of both DBP and DBPC. Determine the relative density (specific gravity) of the oil used in standard solution preparation (D_I) to 0.001.

7.3 *Column Extraction Efficiency*—Verify by the following procedure that the extraction efficiency of the prepared columns is acceptable.

7.3.1 Prepare a check standard containing 0.30 % (w/w) DBP and 0.30 % (w/w) DBPC in methanol. Dilute 0.25 mL of check standard to 5.0 mL with methanol.

7.3.2 Prepare a working standard in accordance with 7.4, using the 0.30 % (w/w) oil standard and the cleanup column whose efficiency is to be determined. Inject a volume of this working standard into the gas chromatograph.

7.3.3 Inject a volume (equal to that used in 7.3.2) of the diluted check standard into the chromatograph using the same chromatographic conditions used to analyze the working standards.

7.3.4 Calculate the extraction efficiency for both DBP and DBPC as follows:

$$\frac{\frac{A_I}{C_I \times W_{0.30}}}{\frac{A_C}{C_C \times V_C \times D_C}} \times 100 = \frac{A_I \times C_C \times V_C \times D_C}{A_C \times C_I \times W_{0.30}} = \textit{extraction efficiency, \%}$$

where:

A_I = area (or height) of 0.30 % working standard,
A_C = area (or height) of 0.30 % check standard,
C_I = known concentration of working standard,
C_C = known concentration of check standard,
D_C = relative density (specific gravity) of methanol used in check standard preparation, and
$W_{0.30}$ = weight of 0.30 % working standard as recorded in 7.4.1.
V_C = volume of check standard diluted to 5 mL in 7.3.1 (=0.25 mL)

7.3.5 The minimum acceptable extraction efficiency is 70 % for DBPC and 60 % for DBP. If the prepared columns do not achieve this level of efficiency, make and test new cleanup columns until acceptable extraction efficiency is achieved. If unable to obtain this, purchase a new lot of acid powder alumina or verify that extraction columns are being activated properly as in 7.1.

7.4 *Working Standard Preparation :*

7.4.1 Accurately weigh a cleanup column to 0.001 g. Pipet 0.25 mL of the 0 % standard solution onto the top of the cleanup column. Weigh the cleanup column to 0.001 g. Record the difference as $W_{0\,\%}$. Repeat for the remaining standard solutions utilizing different cleanup columns and recording weights as $W_{0.040\,\%}$, $W_{0.080\,\%}$, $W_{0.15\,\%}$, $W_{0.30\,\%}$ and $W_{0.40\,\%}$, respectively.

7.4.2 To remove nonpolar interferences, wash the standard solutions with approximately 5 mL of hexane or heptane,

[3] Registered trademark of Ohio Valley Specialty Co.
[4] Registered trademark of Supelco, Inc.
[5] *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 *"Reagent Chemicals and Standards,"* by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY and the" United States Pharmacopeia.
[6] Registered Trademark of Rhone-Poulenc, Inc.
[7] The sole source of supply of the apparatus known to the committee at this time is J.T. Baker Chemical Co., Phillipsburg, NJ 08865. 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.