Designation: D 4768 – ~~96~~03

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 D 4768; 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] This test method is under the jurisdiction of ASTM Committee D~~-~~27 on Electrical Insulating Liquids and Gases and is the direct responsibility of Subcommittee D27.0~~1~~3 on ~~Ph~~ Analys~~t~~ical Tests.

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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 D 3487, 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 923 Test Method for Sampling Electrical Insulating Liquids [2]

D 3487 Specification for Mineral Insulating Oil Used in Electrical Apparatus [2]

D 5222 Guide for High-Fire Point Electrical Insulating Oils of Petroleum Origin [2]

E 260 Practice for Packed Column Gas Chromatography [3]

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.

[2] *Annual Book of ASTM Standards*, Vol 10.03.

[3] *Annual Book of ASTM Standards*, Vol 14.01.

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.

NOTE 1—A 3 % OV-1 [4] on 100/120 Mesh Supelcoport, [5] 1.83 m (6 ft) long, 3.2 mm (0.125 in.) in outside diameter has 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 275 ± 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. [6] 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— [7])*—Also known as butylated hydroxytoluene (BHT).

6.4 *Glass Wool*.

6.5 *Aluminum Oxide* (Alumina), acid powder, ACS, Brockman Activity Grade 1, for chromatography. [8]

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 275°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_1) 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:

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

where:

[4] Registered trademark of Ohio Valley Specialty Co.

[5] Registered trademark of Supelco, Inc.

[6] *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.

[7] Registered Trademark of Rhone-Poulenc, Inc.

[8] Available from J.T. Baker Chemical Co., Phillipsburg, NJ 08865.

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
D_I = relative density (specific gravity) of oil used in working standard preparation.

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, collecting the eluate in a waste container. Remove as much of the solvent as possible by using pipet bulb pressure, but do not allow the column to dry out.

7.4.3 Elute the inhibitors from the column with three washes consisting of 1 mL of methanol each, collecting the eluate in a clean 5 mL volumetric flask. Dilute to 5 mL with methanol and mix well. These are the working standards.

7.5 *Working Standard Chromatography*— Inject a volume of the working standard solution into the equilibrated chromatograph as described in Section 8. Recommended injection volumes are 2 to 10 µL, depending on individual detector response. Measure the response, A_x, (peak height or area in integrator counts) for each peak (excluding the solvent front).

7.5.1 Perform separate linear regression analyses of the responses resulting from both DBPC and DBP working standards by plotting S_i versus area, *Ax* (or height) where:

$$S_i = \frac{\text{Concentration of Working Standard, weight \%}}{\text{Mass of Working Standard Used (7.4.1)}}$$

where:
S_i = weight normalized, %.

7.5.1.1 If the correlation coefficient for the regression analyses (7.5.1) is less than 0.995, prepare new working standards (7.4), repeat the chromatographic measurements (7.5) and perform the data analysis (7.5.1) on the new results alone. If the situation is not improved, repeat the procedure using working standards made from newly prepared standard solutions (7.2).

8. Chromatograph Operating Conditions

8.1 *General*—The characteristics of individual chromatographs and columns differ. Choose particular operating conditions to give a complete separation and good quantification of the peaks obtained. Temperatures and flow rates with which satisfactory separations have been obtained are listed in 8.2 through 8.5.

8.2 *Packed Column Temperature*—A column oven temperature held isothermally at 150°C for 5 min followed by temperature ramping at 20°C/min to 250°C and a hold period at that temperature for 2 min gives satisfactory results. Although the inhibitors are resolved by the isothermal portion of the run, higher temperatures are required to purge the column of interfering substances for successive runs.

8.3 *Detector Temperature*—A detector temperature of 300°C has been found to be satisfactory.

8.4 *Injector Port Temperature*—An injector port temperature of 275°C has been found to be satisfactory.

8.5 *Carrier Gas*—A carrier gas of high purity helium at a flow of 20 to 40 mL/min gives satisfactory results for packed columns.

9. Procedure

9.1 *Test Specimen Preparation*:

9.1.1 Accurately weigh a cleanup column to 0.001 g. Pipet 0.25 mL of the test specimen onto the top of the cleanup column. Weigh the cleanup column to 0.001 g. Record the difference as W_x.

9.1.1.1 Due to variances between different batches of alumina, care must be taken to prepare both the working standards and test specimens by using the same batch of cleanup columns. The same “batch” should be interpreted to mean the same lot number of alumina, preparation date, and conditioning time.

9.1.2 To remove nonpolar interferences, wash the test specimen with approximately 5 mL of hexane or heptane, collecting the eluate in a waste container. Remove as much of the solvent as possible by using pipet bulb pressure, but do not allow the column to dry out.

9.1.3 Elute the inhibitor(s) from the column with three washes consisting of 1 mL of methanol each, collecting the eluate in a clean 5-mL volumetric container. Dilute to 5 mL volume with methanol and mix well.

9.2 *Test Specimen Chromatography*—Inject a volume of test specimen into the chromatograph under the same chromatographic conditions used to analyze the working standard(s).

10. Calculation

10.1 Identify the type(s) of inhibitors present by comparing the retention time obtained from the test specimens to those obtained for the working standards.

10.2 Using the results of the regression analyses (7.5.1), determine the uncorrected weight percent (C_u) of the inhibitor in the test specimens. Calculate the inhibitor content(s) as follows:

$$C = C_u \times W_x$$

where:

C = weight of inhibitor in test specimen, %,
C_u = weight normalized, obtained from regression analyses of working standards, %, and
W_x = mass of 0.25 mL test specimen as recorded in 9.1.1.

11. Report

11.1 Report the following information:

11.1.1 Type and amount of each inhibitor found, and

11.1.2 Total amount of inhibitor as the sum of the individual inhibitors found.

12. Precision and Bias

~~12.1 An interlaboratory test is planned to determine the precision and bias~~

12.1 The single operator coefficient of ~~the test method and~~ variation has been found not to ~~verify the values~~ exceed 11 % for inhibitor content between 0.06 and 0.45 %. Therefore, the ~~efficiency~~ results of two tests conducted on the ~~column extraction and~~ same sample by the ~~correlation coefficient~~ same operator using the same equipment should not differ from each other by more than 30.8 % of the ~~regression analysis~~ average of the ~~calibration data. The values referenced in 7.3.5 and 7.5.1.1 have been consistently obtained in one laboratory.~~ two tests.

13. Keywords

13.1 2,6-ditertiary-butyl para-cresol; 2,6-ditertiary-butyl phenol; dbp; dbpc; inhibitor; mineral oil; transformer oil