Designation: E755 – 08

Standard Test Method for Dicumyl Peroxide, Assay (Liquid Chromatography)[1]

This standard is issued under the fixed designation E755; 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 assay of dicumyl peroxide[2] in commercially available refined grades of dicumyl peroxide. Technical grades can also be assayed, provided that impurities that interfere chromatographically are absent (see Note 1). These materials nominally contain approximately 99 and 92 % of dicumyl peroxide, respectively.

NOTE 1—In the assay of technical grade dicumyl peroxide, errors are possible if the product contains an impurity that elutes with the same retention time as the internal standard. A chromatogram obtained under the test conditions minus the internal standard will determine whether an interference situation exists in the assay of a particular technical grade product. If an impurity is noted, and its retention time is slightly different from that of the internal standard, the interference can often be eliminated by the use of a column known to have a high plate count.

1.2 Review the current material safety data sheets (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

1.3 The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

1.4 *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.* Specific precautionary statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1193 Specification for Reagent Water

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[4]

E682 Practice for Liquid Chromatography Terms and Relationships

E685 Practice for Testing Fixed-Wavelength Photometric Detectors Used in Liquid Chromatography

E300 Practice for Sampling Industrial Chemicals

3. Summary of Test Method

3.1 A solution of sample and internal standard in methanol is chromatographed on a reversed-phase ODS column using 85/15 methanol/water as the mobile phase and an ultraviolet (UV) detector at 254 nm. The percent of dicumyl peroxide in the sample is determined by the internal standard technique, using the peak height ratios of standard and sample chromatograms.

4. Significance and Use

4.1 This test method provides a means for determining the percent of dicumyl peroxide in technical and refined grades of this material. This test method is specific for dicumyl peroxide. No interference is encountered from dimethylbenzyl alcohol, acetophenone, or other minor impurities normally associated with commercial dicumyl peroxide.

5. Apparatus

5.1 *Liquid Chromatograph,* equipped with a 254-nm UV detector, an injection valve, and an isocratic solvent delivery system capable of operating to a gage pressure of 3000 psi (21 MPa). The detector should be equipped with an attenuator switch to change the sensitivity range as required.

5.2 *Recorder,* 0 to 10-mV range, or an electronic integrator with printer-plotter, or both.

5.3 *Chromatographic Column,* reversed-phase C-18, 250 by 4.6-mm inside diameter, containing octadecyldimethylsilane chemically bonded to spherical, 5-µm microparticulate silica.[5]

[1] This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicalsand is the direct responsibility of Subcommittee E15.02 on Product Standards.

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[2] Dicumyl Peroxide; peroxide, *bis*(1-methyl-1-phenylethyl) $C_{18}H_{22}O_2$; CAS Registry No. 80-43-3.

[3] 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.

[4] The last approved version of this historical standard is referenced on www.astm.org.

[5] The commercial guard and analytical columns found to be most satisfactory for use with this test method are Zorbax Rx-18, Part Nos. 820764.914 and 880967.9002, respectively, available from Mac Mod, 127 Commons Court, Chadds Ford, PA 19317. This column was selected for its separation characteristics and linear response of the dicumyl peroxide and internal standard.

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

NOTE 2—Commercial HPLC columns vary in physical dimensions, degree of substrate loading, and size and type of support material. Some modification in the operating parameters may be required to achieve optimum separation for these reasons.

5.4 *Guard Column,* reversed-phase C-18, 12.5 by 4.0 mm, with an inline filter.[5]

5.5 *Precision Sample Injection Valve,* with a 10-µL loop and filler port.

5.6 *Syringe,* 250-µL capacity.

5.7 *Sample Filter,* consisting of a syringe and 0.2-µm filter assembly to remove microparticulate matter from the prepared sample solution.[6]

5.8 *Glass Bottles,* 120-mL, with polyethylene-lined screw caps.

6. Reagents

6.1 *Water*—Prepare ASTM Type II reagent water in accordance with Specification D1193, or distill deionized water. Filter through a 0.2-µm, Nylon-66 filter, and store in a glass container. Alternatively, commercial multicartridge systems that produce water meeting or exceeding the requirements of Type II can be used.

6.2 *Methanol,* chromatographic grade, distilled in glass.

6.3 *Methanol-Water Mobile Phase*, 85:15—Mix 8.5 volumes of methanol with 1.5 volumes of water.

6.4 *Di-n-Heptyl Phthalate,* purified.[7]

6.5 *Dicumyl Peroxide, Recrystallized*—Transfer 25.0 g of commercial refined dicumyl peroxide into a 100-mL Erlenmeyer flask. Add 8.0 mL of methanol, and gently warm the solution in a water bath while swirling to effect complete solution. Cool to 0°C in an ice bath. Transfer the contents to a medium-porosity sintered glass crucible and vacuum filter. Allow air to pass through the filter for 10 to 15 min to dry the peroxide. Repeat the crystallization twice using approximately 1 mL of methanol solvent for every 3 g of peroxide. Place the recrystallized dicumyl peroxide in a tightly capped bottle, and store in a refrigerator (see Section 7).

7. Safety Precautions

7.1 Small quantities of solid or molten dicumyl peroxide can be handled safely at temperatures up to 55°C. Dicumyl peroxide should not be heated above 55°C because the rate of peroxide decomposition increases rapidly with increasing temperatures above this point.

7.2 A recirculating water bath or a water bath that has been preheated to the desired temperature and removed from the heat source should be used for warming vessels containing dicumyl peroxide. Electrically heated water baths should not be used since they may cause localized hot spots. Other sources of heat considered unsafe for warming containers of dicumyl peroxide include ovens, hot plates, open flames, and direct steam.

7.3 Organic peroxides may ignite violently in contact with an open flame or electrical spark. These heat sources must be avoided for this reason.

8. Sampling

8.1 Prior to sampling technical and refined grades of dicumyl peroxide, it is essential that the sample be blended thoroughly after melting. This is best accomplished by placing the container in a 55°C water bath. After the sample has melted completely, mix thoroughly by swirling or stirring before withdrawing the sample for analysis (see 7.1 – 7.3). See Note 3.

NOTE 3—Refer to Practice E300 for guidelines on sampling.

9. Procedure

9.1 *Preparation of Standard Dicumyl Peroxide Solution:*

9.1.1 To the nearest 0.1 mg, weigh 0.40 ± 0.05 g of recrystallized dicumyl peroxide and 0.20 ± 0.05 g of di-n-heptyl phthalate (internal standard) into a tared 120-mL glass bottle.

9.1.2 Add 100 mL of methanol, and mix well until the sample and internal standard have dissolved completely.

9.1.3 Filter the solution through a 0.2-µm filter, collecting the filtrate in clean 17-mL vials equipped with PTFE-lined caps. Cap the vials and store in a cool, dark location. This solution should be used within 36 h, after which time a fresh solution should be prepared. Gradual peroxide decomposition will cause a change in the internal standard/dicumyl peroxide peak height ratio.

9.2 *Preparation of Sample Solution:*

9.2.1 To the nearest 0.1 mg, weigh 0.40 ± 0.05 g of melted dicumyl peroxide sample and 0.20 ± 0.05 g of di-n-heptyl phthalate (internal standard) into a tared 120-mL glass bottle.

9.2.2 Add 100 mL of methanol, and swirl until the sample and internal standard have dissolved completely.

9.2.3 Filter a portion of the solution through a 0.2-µm filter, collecting the filtrate in a 17-mL vial equipped with a PTFE-lined cap. Cap the vial and store in a cool, dark location. This solution should be used within 36 h, after which time a fresh solution should be prepared. Gradual peroxide decomposition will cause a change in the internal standard/dicumyl peroxide peak height ratio.

9.3 *Calibration:*

9.3.1 Adjust the liquid chromatograph in accordance with the following parameters, and allow the instrument to equilibrate until a stable baseline is obtained.

Column oven	40°C
Detector	UV, 254 nm
Mobile phase	methanol:water, 85:15
Flow rate	1.0 mL/min
Recorder chart speed	0.5 cm/min

NOTE 4—The parameters given above apply to a liquid chromatograph equipped with a Zorbax Rx-18 C-18 reversed-phase column, 4.6-mm diameter by 25 cm in length. Other columns may require some modification in the flow rate or mobile phase composition (see Note 2).

[6] Waters Associates Sample Clarification Kit, Catalog No. 26870, has been found to be satisfactory for this purpose.

[7] Di-n-heptyl phthalate, Lancaster Synthesis, Cat. No. 5396, has been found to be satisfactory for use as an internal standard.

NOTE 5—See Practice E682 for liquid chromatography terms and relationships. See Practice E685 for testing fixed-wavelength photometric detectors.

9.3.2 When the column is in equilibrium with the mobile phase, flush the sample loop with approximately 250 µL of the standard dicumyl peroxide solution and inject a 10-µL aliquot. Typical retention times for dicumyl peroxide and di-n-heptyl phthalate are 9 and 20 min, respectively.

9.4 *Analysis of Sample:*

9.4.1 Immediately after obtaining the chromatogram of the standard solution, flush the sample loop with approximately 250 µL of the prepared sample solution, and inject a 10-µL aliquot. A typical chromatogram of technical grade dicumyl peroxide obtained under the conditions outlined in 9.3.1 is shown in Fig. 1.

10. Calculation

10.1 Measure the heights of the dicumyl peroxide and di-n-heptyl phthalate peaks in the chromatogram of the standard solution.

10.2 Calculate the response factor, F_C, for dicumyl peroxide as follows:

$$F_C = \frac{W_C \times H_{IS}}{W_{IS} \times H_C} \quad (1)$$

where:

F_C = response factor,
W_C = mass of standard dicumyl peroxide, g, see 9.1,
W_{IS} = mass of di-n-heptyl phthalate, g, see 9.1,
H_{IS} = peak height of di-n-heptyl phthalate, and
H_C = peak height of dicumyl peroxide in standard.

10.3 Measure the heights of the dicumyl peroxide and di-n-heptyl phthalate peaks in the chromatogram of the sample solution.

10.4 Calculate the percent of dicumyl peroxide present in the sample as follows:

$$\%\,\text{mass (m/m) dicumyl peroxide} = \frac{W_{IS} \times H_C \times F_C \times 100}{W_S \times H_{IS}} \quad (2)$$

where:

F_C = response factor, see 10.2,
W_{IS} = mass of di-n-heptyl phthalate, g, see 9.2,
W_S = mass of sample, g, see 9.2,
H_{IS} = peak height of di-n-heptyl phthalate, and
H_C = peak height of dicumyl peroxide in sample.

11. Report

11.1 Report the percentage of dicumyl peroxide to the nearest 0.1 %.

12. Precision and Bias

12.1 *Precision*—The following criteria should be used for judging the acceptability of the results (Note 6):

12.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.418 % absolute at 14 DF. The 95 % limit for the difference between two such runs is 1.3 % absolute.

12.1.2 *Laboratory Precision (Within-Laboratory, Between Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.30 % absolute at 7 degrees of freedom. The 95 % limit for the difference between two such averages is 0.8 % absolute.

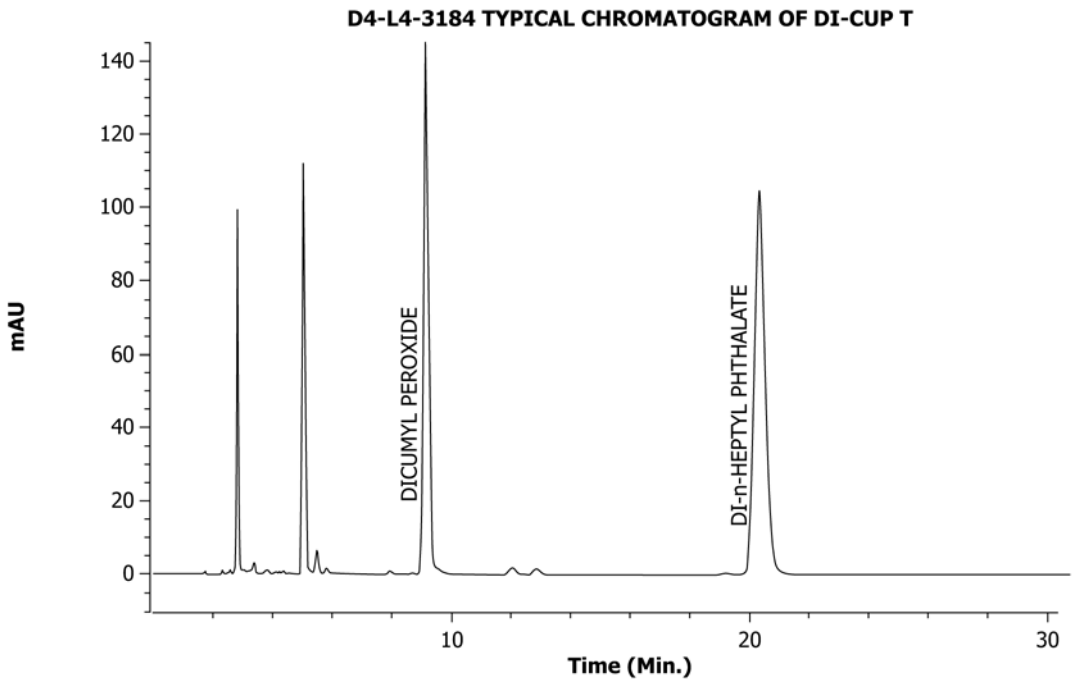

FIG. 1 Typical Chromatogram of Technical Grade Dicumyl Peroxide

12.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.58 % absolute at 6 degrees of freedom. The 95 % limit for the difference between two such averages is 1.6 % absolute.

NOTE 6—The above precision estimates are based on an interlaboratory study performed in 1992 on one sample containing approximately 99 % dicumyl peroxide. One analyst in each of seven laboratories performed duplicate determinations on each of two different days for a total of 28 determinations.[8] Practice E180 was used in developing these precision statements.

12.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

13. Keywords

13.1 assay; dicumyl peroxide; HPLC; liquid chromatography; peroxides

[8] Supporting data are available from ASTM Headquarters. Request RR:E15-1023.

SUMMARY OF CHANGES

Subcommittee E15.02 has identified the location of selected changes to this standard since the last issue (E755-94(2003)) that may impact the use of this standard.

(1) Updated units of measure to comply with the International System of Units (SI).
(2) Added numbered paragraph in Scope stating that the SI units are to be considered standard.
(3) Deleted (Formerly called Repeatability) from the Precision section.
(4) Added Summary of Changes section.