Designation: E475 – 16

Standard Test Method for Assay of Di-*tert*-Butyl Peroxide Using Gas Chromatography[1]

This standard is issued under the fixed designation E475; 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 di-*tert*-butyl peroxide using gas chromatography. It is applicable to commercial di-*tert*-butyl peroxide which may contain small amounts of isobutylene, *tert*-butanol, *tert*-butyl hydroperoxide, triisobutylenes, and water as impurities.

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

1.3 *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 hazards statements are given in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E203 Test Method for Water Using Volumetric Karl Fischer Titration

3. Terminology

3.1 *Definitions:*

3.1.1 *active oxygen*—the oxidizing power present in organic peroxides expressed as oxygen (equivalent = 8.00).

4. Summary of Test Method

4.1 A sample is diluted in dodecane and injected into a gas chromatograph containing a wide-bore capillary column with a nonpolar stationary phase. A temperature program is used to separate di-*tert*-butyl peroxide from impurities using helium as a carrier gas. The flame ionization detector response, proportional to component concentration, is recorded and the peak areas are measured. The concentration of di-*tert*-butyl peroxide is determined by area normalization after correcting for the area of the solvent peak. The assay of di-*tert*-butyl peroxide is corrected for water, which is determined using a separate Karl Fischer titration since water is not detected using flame ionization detection. The area percent of di-*tert*-butyl peroxide is assumed to be equal to mass percent.

5. Significance and Use

5.1 Di-*tert*-butyl peroxide is widely used as a catalyst and reaction initiator. Knowledge of the peroxide content is important in such applications. This test method provides a procedure for determining the active peroxide content of commercial di-*tert*-butyl peroxide.

6. Interferences

6.1 Interferences will be encountered if other components are present in the sample that have the same retention time as di-*tert*-butyl peroxide.

7. Apparatus

7.1 *Instrumentation*—Gas chromatograph, capable of column oven temperature programming from 40 to 160°C at a rate of 10°C/min and from 160 to 240°C at a rate of 35°C/min.

7.2 *Injection System*—Glass-lined sample injection port, maintained at 150°C.

7.3 *Sample Introduction*—Microliter syringes or automatic syringe injectors, capable of delivering 0.5 µL of a liquid sample, have been used successfully.

7.4 *Detection*—Flame ionization detector, maintained at 250°C.

7.5 *Data Acquisition System*—Electronic data acquisition and area integration capabilities are recommended.

7.6 *Chromatographic Column*—30 m wide-bore capillary column (0.53 mm inside diameter) with a 5.0 µm dimethylpolysiloxane stationary phase.

8. Reagents and Materials

8.1 *Carrier Gas (Helium),* chromatographic grade.

8.2 *Hydrogen,* chromatographic grade.

8.3 *Compressed Air,* oil-free.

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.16 on Industrial and Specialty Product Standards.

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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.

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

8.4 *Dodecane,* for use as a sample diluent, 99 % or greater chromatographic purity.

9. Hazards

9.1 Organic peroxides are strong oxidizing agents and present potential fire and explosion hazards. While di-*tert*-butyl peroxide is one of the more stable peroxides, contact with reducing agents and sources of heat, sparks, or open flames must be avoided. Organic peroxides in general are irritating to the skin, eyes, and mucous membranes. Avoid bodily contact and handle only in a well-ventilated area.

9.2 Consult current OSHA regulations and supplier's Safety Data Sheets (SDS) for all materials used in this method.

10. Procedure

10.1 Install the column in the chromatograph. The operating conditions required to give the desired separation are given in Table 1. Set the helium flow to 10.0 mL/min and the oven temperature to 40°C and allow sufficient time for the instrument to equilibrate as indicated by a stable baseline.

10.2 Prepare test samples by transferring approximately 0.2 g of di-*tert*-butyl peroxide into a flask or vial and add approximately 10 mL of dodecane. Mix well.

10.3 Inject 0.5 µL of the sample solution into the chromatograph. A typical chromatogram is shown in Fig. 1 and Fig. 2.

10.4 Determine the water content of the sample using a Karl Fischer titration in accordance with Test Method E203.

NOTE 1—Water can be determined in samples of di-*tert*-butyl peroxide using Test Method E203 without pretreatment with SO_2 if the sample temperature is maintained below 20°C during the titration. If the sample temperature cannot be maintained below 20°C, the sample must be pretreated by bubbling SO_2 through the sample for several minutes prior to titrating.

11. Calculation

11.1 Measure the peak areas and calculate the total area by summing the individual areas for all peaks except for that of the solvent peak, as follows:

$$A_t = A_1 + A_2 + A_3 + \ldots + A_n \quad (1)$$

TABLE 1 Operating Conditions Required to Give the Desired Separation

Detector	flame ionization (FID)
Temperatures, °C	
Injection port	150
Detector	250
Column temperature program	
Initial temperature, °C	40
Initial time, min	3
Program rate, °C/min	10
Temperature 2, °C	160
Time 2, min	2
Program rate, °C/min	35
Final temperature, °C	240
Final time, min	2
Carrier gas	helium
Flow rate, mL/min	10.0
Injection volume, µL	0.5

where:

A_t = total area (excluding the solvent peak), and
$A_{1...n}$ = area of individual component peaks.

11.2 Calculate the area percent of di-*tert*-butyl peroxide as follows:

$$\text{di} - \textit{tert} - \text{butyl peroxide, area \%} = \frac{A_D\,(100 - W)}{A_t} \quad (2)$$

where:

A_D = area of the di-*tert*-butyl peroxide peak,
A_t = sum total of all component peaks (except solvent), and
W = mass percent of water in the sample, as determined in 10.4.

The area percent of di-*tert*-butyl peroxide is assumed to be equal to the mass percent.

11.3 If desired, calculate the mass percent of active oxygen due to di-*tert*-butyl peroxide as follows:

$$\text{active oxygen, mass \%} = \frac{C \times 8.000}{73.11} \quad (3)$$

where:

C = di-*tert*-butyl peroxide, mass %.

12. Report

12.1 Report the purity of the di-*tert*-butyl peroxide to the nearest 0.01 %.

13. Precision and Bias

13.1 *Precision:*

13.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 0.05 % relative at 18 degrees of freedom (df). The 95 % limit for the difference between two such runs is 0.13 % relative.

13.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability, Formerly Called Repeatability)*—The coefficient of variation of results (each the average of duplicates) obtained by the same analyst on different days has been estimated to be 0.04 % relative at 9 df. The 95 % limit for the difference between two such averages is 0.10 % relative.

13.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be 0.24 % relative at 8 df. The 95 % limit for the difference between two such averages is 0.67 % relative.

NOTE 2—The precision statements are based on an interlaboratory study[3] performed in 1995 on one sample of di-*tert*-butyl-peroxide.

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

14. Keywords

14.1 active oxygen; di-*tert*-butyl peroxide; gas chromatography; peroxides

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1044. Contact ASTM Customer Service at service@astm.org.

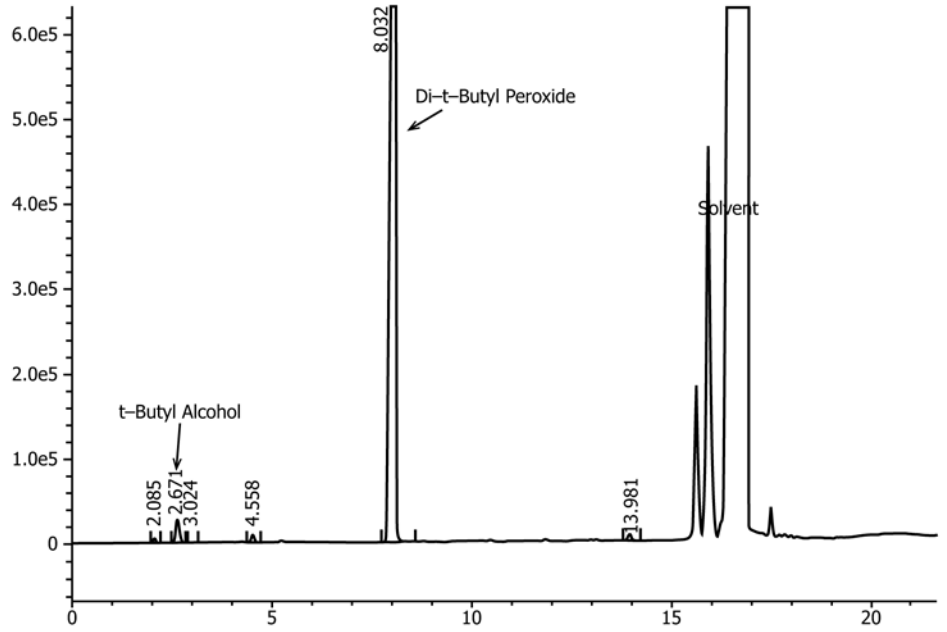

FIG. 1 Typical Chromatogram

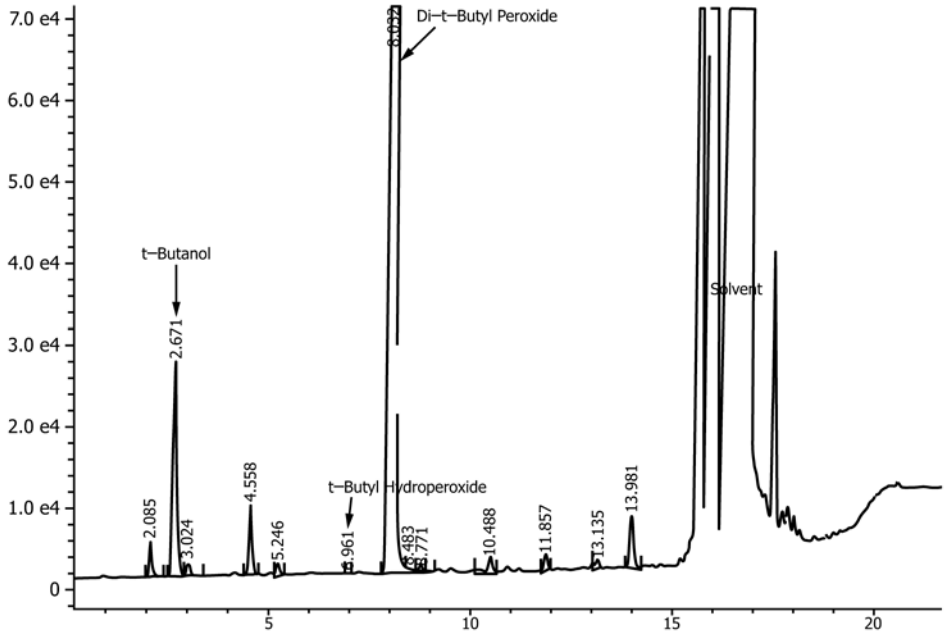

FIG. 2 Typical Chromatogram (Expanded View)

SUMMARY OF CHANGES

Subcommittee E15.02 has identified the location of selected changes to this standard since the last issue (E475-10) that may impact the use of this standard.

(1) Added reference to Safety Data Sheets (SDS) in 9.2.