



## Standard Test Methods for Assay of Organic Peroxides<sup>1</sup>

This standard is issued under the fixed designation E 298; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 These test methods cover the assay of organic peroxides. Two procedures are given, depending upon the ease of reduction:

1.1.1 *Sodium Iodide, Room Temperature Test Method*, for organic peroxides easy to reduce, and

1.1.2 *Sodium Iodide, 60°C Test Method*, for organic peroxides that are moderately stable.

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.*

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

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>3</sup>

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis<sup>3</sup>

### 3. Significance and Use

3.1 Organic peroxides are widely used as chemical intermediates, catalysts, and initiators. These test methods provide procedures for assaying organic peroxides to determine if they are suitable for their intended use.

### 4. Purity of Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used 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.<sup>4</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water conforming to Specification D 1193.

### SODIUM IODIDE, ROOM TEMPERATURE TEST METHOD

#### 5. Scope

5.1 This test method covers the assay of organic peroxides that are easily reduced, such as hydroperoxides and diacyl peroxides. Dialkyl peroxides do not react, while peresters and bridge-type peroxides like ascaridole react slowly and incompletely.

5.2 Specific peroxides that can be analyzed by this procedure include the following:

5.2.1 *Diacyl Peroxides*—Benzoyl 2,4-dichlorobenzoyl, *p*-chlorobenzoyl, lauroyl, acetyl, and decanoyl peroxides.

5.2.2 *Dibasic Acid Peroxide*—Succinic acid peroxide.

5.2.3 *Ketone Peroxides*—Cyclohexanone peroxide and methyl ethyl ketone peroxide.

5.2.4 *Alkyl Hydroperoxides*—*tert*-Butylhydroperoxide and 2,5-dimethylhexane-2,5-dihydroperoxide.

#### 6. Summary of Test Method

6.1 A sample is dissolved in a mixture of methylene chloride and acetic acid. A saturated solution of sodium iodide is added and the mixture is allowed to react in the dark at room temperature for 15 min. The liberated iodine is then titrated with standard sodium thiosulfate solution.

#### 7. Interferences

7.1 Conjugated diolefins interfere by absorbing iodine.

#### 8. Apparatus

8.1 *Iodine Flasks, 250-mL, with stoppers.*

NOTE 1—All glassware should be thoroughly cleaned before use.

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and are the direct responsibility of Subcommittee E15.01 on General Standards.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 15.05.

<sup>4</sup> *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

## 9. Reagents

9.1 *Acetic Acid, Glacial.*

9.2 *Carbon Dioxide*, cylinder.

9.3 *Methylene Chloride.*

9.4 *Sodium Iodide, Saturated Solution*—Prepare a saturated solution of sodium iodide (NaI) in de-aerated water. This solution should be prepared just prior to use and kept in a brown bottle.

9.5 *Sodium Thiosulfate, Standard Solution (0.1 N)*—Prepare and standardize a 0.1 N solution of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) in accordance with the appropriate sections of Practice E 200.

9.6 *Starch Indicator Solution (10 g/L)*, Prepare as described in the appropriate sections of Practice E 200.

9.7 *Water, De-aerated*—Pass carbon dioxide ( $\text{CO}_2$ ) through distilled water for several minutes prior to use.

## 10. Procedure

10.1 Add 20 mL of acetic acid to a 250-mL iodine flask and sparge with a rapid flow of  $\text{CO}_2$  for 2 min. Stopper the flask and reserve for the sample.

10.2 Accurately weigh a sample containing 3 to 4 meq of active oxygen to the nearest 0.1 mg and transfer to the flask. Volatile liquid peroxides may be diluted to a known volume with acetic acid and aliquots taken for analysis.

NOTE 2—The approximate weight of the sample to be used in the analysis may be calculated as follows:

$$\text{Sample weight, g} = 3.5M/2C \times 1000 \quad (1)$$

where:

$M$  = molecular weight of the compound, and

$C$  = number of peroxide groups in the molecule.

10.3 Add 10 mL of methylene chloride and restopper. Swirl briefly to dissolve the sample.

10.4 Add 5 mL of freshly prepared saturated NaI solution. Restopper and swirl. Place a few millilitres of water in the well of the flask and allow to stand in the dark at room temperature for 15 min.

10.5 Add 50 mL of de-aerated water and titrate with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution until the solution is a pale straw color. Add 1 to 2 mL of starch solution and continue the titration to the sharp disappearance of the blue color. Record the number of millilitres required for titration.

10.6 Subtract the number of millilitres required for titration of a blank carried through the entire procedure and calculate the assay value of the sample.

NOTE 3—The blank titration should normally require 0.05 mL or less of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The results should be discarded and the analysis repeated if high blank values are obtained.

## 11. Calculation

11.1 Calculate the assay as follows:

$$\text{Assay, as percent compound} = (A - B) \times N \times M \times 100/W \times 2C \times 1000 \quad (2)$$

where:

$A$  = mL of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the sample,

$B$  = mL of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the blank,

$N$  = normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution,

$C$  = number of peroxide groups in the molecule,

$M$  = molecular weight of the compound, and

$W$  = grams of sample used.

11.2 Calculate the percent active oxygen in the compound as follows:

$$\text{Active oxygen, \%} = (A - B) \times N \times 0.008 \times 100/W \quad (3)$$

11.3 If required, the percent active oxygen can be converted to a specific peroxide using the appropriate conversion factor.

$$\text{Peroxide } X, \% = \% \text{ Active Oxygen in Peroxide } X \times F \quad (4)$$

where:

$F$  = conversion factor for Compound  $X$ .

11.3.1 Conversion Factors for some common peroxides are as follows:

Cumene Hydroperoxide	= 9.5125
Benzoyl Peroxide	= 15.140
<i>t</i> -Butyl Hydroperoxide	= 5.6328
Lauroyl Peroxide	= 24.915

## 12. Report

12.1 Report the assay value of the compound to the nearest 0.01%.

## 13. Precision and Bias <sup>5</sup>

13.1 The following criteria shall be used for judging the acceptability of results (Note 4):

13.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.047 % absolute at 36 df. The 95 % limit for the difference between two such determinations is 0.13 % absolute.

13.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability, Formerly Called Repeatability)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst on different days, has been estimated to be 0.010 % absolute at 18 df. The 95 % limit for the difference between two such averages is 0.028 % absolute.

13.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be 0.035 % absolute at 5 df. The 95 % limit for the difference between two such averages is 0.10 % absolute.

NOTE 4—These precision estimates are based on an interlaboratory study in which 3 samples were analyzed. One analyst in each of 6 laboratories performed duplicate determinations and repeated them on a second day, for a total of 72 determinations. Practice E 180 was used in developing these statements.

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

## SODIUM IODIDE, 60°C TEST METHOD

### 14. Scope

14.1 This test method covers the assay of organic peroxides

<sup>5</sup> Supporting data are available from ASTM Headquarters. Request RR: E15-1001.

that are moderately stable, such as peresters, di-*n*-alkyl peroxides, and *n*-alkyl peroxides. These peroxides react slowly with sodium iodide at room temperature, but do not require the use of hydriodic acid.

14.2 Specific peroxides that can be analyzed by this procedure include the following: *t*-butyl peracetate, *t*-butyl peroxyisobutyrate, di-*t*-butyl diperphthalate, *t*-butyl perbenzoate, and 2,2-*bis*(*t*-butylperoxy) butane.

## 15. Summary of Test Method

15.1 A sample is dissolved in glacial acetic acid. Saturated sodium iodide solution is then added and the mixture is allowed to react for 1 h at 60°C. The liberated iodine is titrated with standard sodium thiosulfate solution.

## 16. Interferences

16.1 Conjugated diolefins interfere under the conditions of analysis by absorbing iodine.

## 17. Apparatus

17.1 *Iodine Flasks*, 250-mL with stopper (Note 1).

17.2 *Water Bath*, maintained at 60 ± 1°C.

## 18. Reagents

18.1 *Acetic Acid, Glacial*.

18.2 *Carbon Dioxide*, cylinder.

18.3 *Sodium Iodide, Saturated Solution*—See 9.4.

18.4 *Sodium Thiosulfate, Standard Solution* (0.1 *N*)—See 9.5.

18.5 *Starch Indicator Solution*—See 9.6.

18.6 *Water, De-aerated*—See 9.7.

## 19. Procedure

19.1 Add 20 mL of acetic acid to a 250-mL iodine flask and sparge with a rapid flow of carbon dioxide (CO<sub>2</sub>) for 2 min. Stopper the flask and reserve for the sample.

19.2 Accurately weigh a sample containing 3 to 4 meq of active oxygen to the nearest 0.1 mg and transfer to the flask (Note 2).

19.3 Add 5 mL of freshly prepared saturated NaI solution (Note 5). Restopper tightly and swirl. Place a few millilitres of water in the well of the flask and allow the flask to stand partially submerged in a water bath maintained at 60°C for 1 h.

NOTE 5—Some peroxides may require the addition of a small amount of hydrochloric acid (HCl) to react completely in a reasonable time. In this case 1 mL of concentrated HCl shall be added to the solution just before it is placed in the water bath.

19.4 Remove the flask from the bath and cool to room temperature.

19.5 Add 60 mL of de-aerated water and titrate with 0.1 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution until the solution is a pale straw color. Add 1 to 2 mL of starch solution and continue the titration to the sharp disappearance of the blue color. Record the number of millilitres required for titration.

19.6 Subtract the number of millilitres required for titration of a blank carried through the entire procedure and calculate the assay value of the sample.

NOTE 6—The blank titration should normally require about 0.10 mL of 0.1 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. The results should be discarded and the analysis

repeated if high blank values are obtained.

## 20. Calculation

20.1 Calculate the assay as follows:

Assay, as percent compound

$$= (A - B) \times N \times M \times 100/W \times 2C \times 1000 \quad (5)$$

where:

*A* = mL of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required for titration of the sample,

*B* = mL of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required for titration of the blank,

*N* = normality of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution,

*C* = number of peroxide groups in the molecule,

*M* = molecular weight of the compound, and

*W* = grams of sample used.

20.2 Calculate the percent of active oxygen in the compound as follows:

$$\text{Active oxygen, \%} = (A - B) \times N \times 0.008/W \times 100 \quad (6)$$

20.3 If required, the percent active oxygen can be converted to a specific peroxide using the appropriate conversion factor. See 11.3.

## 21. Report

21.1 Report the assay value of the compound to the nearest 0.01 %.

## 22. Precision and Bias<sup>5</sup>

22.1 The following criteria should be used in judging the acceptability of results (Note 7):

22.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.080 % absolute at 24 df. The 95 % limit for the difference between two such determinations is 0.23 % absolute.

22.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability, Formerly called Repeatability)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst on different days, has been estimated to be 0.055 % absolute at 12 df. The 95 % limit for the difference between two such averages is 0.15 % absolute.

22.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be 0.126 % absolute at 5 df. The 95 % limit for the difference between two such averages is 0.35 % absolute.

NOTE 7—These precision estimates are based on an interlaboratory study conducted in which 2 samples were analyzed. One analyst in each of 6 laboratories performed duplicate determinations and repeated them on a second day, for a total of 48 determinations. Practice E 180 was used in developing these statements.

22.2 *Bias*—The bias of this test method has not been determined due to the lack of suitable reference materials or methodology.

## 23. Keywords

23.1 assay; iodometric; organic peroxide; peroxides

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