Designation: E298 – 17a

Standard Test Methods for Assay of Organic Peroxides[1]

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 Review the current Safety Data Sheets (SDS) for detailed information concerning toxicity, first-aid procedures, and safety precautions.

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

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.*

1.5 *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]

D1193 Specification for Reagent Water

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

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.[4] 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 D1193.

SODIUM IODIDE, ROOM TEMPERATURE TEST METHOD

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.

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[1] These test methods are under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and are the direct responsibility of Subcommittee D16.15 on Industrial and Specialty General Standards.

Current edition approved July 1, 2017. Published July 2017. Originally approved in 1966. Last previous edition approved in 2017 as E298 – 17. DOI: 10.1520/E0298-17a.

[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.

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

[4] *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.

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

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.

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 an amber bottle.

9.5 *Sodium Thiosulfate, Standard Solution* (0.1 meq/mL*(N))*—Prepare and standardize a 0.1 meq/mL(*N*) solution of sodium thiosulfate ($Na_2S_2O_3$) in accordance with the appropriate sections of Practice E200.

9.6 *Starch Indicator Solution* (*10 g/L*), Prepare as described in the appropriate sections of Practice E200.

9.7 *Water, De-aerated*—Pass carbon dioxide (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 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:

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

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 meq/mL (*N*) $Na_2S_2O_3$ 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 meq/mL (*N*) $Na_2S_2O_3$ 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:

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

where:

A = mL of $Na_2S_2O_3$ solution required for titration of the sample,
B = mL of $Na_2S_2O_3$ solution required for titration of the blank,
N = meq/mL (*N*) of the $Na_2S_2O_3$ 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:

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

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

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

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
t-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[5]

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

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1001. Contact ASTM Customer Service at service@astm.org.

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)*—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 E180 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.

14. Quality Guidelines

14.1 Laboratories shall have a quality control system in place.

14.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

14.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

14.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

14.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

SODIUM IODIDE, 60°C TEST METHOD

15. Scope

15.1 This test method covers the assay of organic peroxides that are moderately stable, such as peresters, di-acyl peroxides, and n-alkyl peroxides. These peroxides react slowly with sodium iodide at room temperature, but do not require the use of hydroiodic acid.

15.2 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.

16. Summary of Test Method

16.1 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.

17. Interferences

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

18. Apparatus

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

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

19. Reagents

19.1 *Acetic Acid, Glacial.*

19.2 *Carbon Dioxide,* cylinder.

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

19.4 *Sodium Thiosulfate, Standard Solution* (0.1 meq/mL *(N))*—See 9.5.

19.5 *Starch Indicator Solution*—See 9.6.

19.6 *Water, De-aerated*—See 9.7.

20. Procedure

20.1 Add 20 mL of acetic acid to a 250-mL iodine flask and sparge with a rapid flow of carbon dioxide (CO_2) for 2 min. Stopper the flask and reserve for the sample.

20.2 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).

20.3 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.

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

20.5 Add 60 mL of de-aerated water and titrate with 0.1 meq/mL (*N*) $Na_2S_2O_3$ 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.

20.6 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 meq/mL (*N*) $Na_2S_2O_3$ solution. The results should be discarded and the analysis repeated if high blank values are obtained.

21. Calculation

21.1 Calculate the assay as follows:

$$\text{Assay, as percent compound} = (A - B) \times N \times M \times 100/W \times 2C \times 1000 \quad (5)$$

where:

A = mL of $Na_2S_2O_3$ solution required for titration of the sample,

B = mL of $Na_2S_2O_3$ solution required for titration of the blank,
N = meq/mL (N) of the $Na_2S_2O_3$ solution,
C = number of peroxide groups in the molecule,
M = molecular weight of the compound, and
W = grams of sample used.

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

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

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

22. Report

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

23. Precision and Bias[5]

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

23.1.1 *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.

23.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—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.

23.1.3 *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 E180 was used in developing these statements.

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

24. Quality Guidelines

24.1 Laboratories shall have a quality control system in place.

24.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

24.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

24.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

24.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

25. Keywords

25.1 assay; iodometric; organic peroxide; peroxides

SUMMARY OF CHANGES

Subcommittee D16.15 has identified the location of selected changes to this standard since the last issue (E298–17) that may impact the use of this standard. (Approved July 1, 2017.)

(1) Section 14 Quality Guidelines and Section 24 Quality Guidelines were added.

Subcommittee D16.15 has identified the location of selected changes to this standard since the last issue (E298–08) that may impact the use of this standard. (Approved February 1, 2017.)

(1) Removed “Material” from MSDS statement in Scope section 1.4.

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