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Standard Test Methods for Assay of Organic Peroxides¹

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

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.

1.34 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:*²

D 1193 Specification for Reagent Water

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals

E 200 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.³ 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.

¹ 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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² Annual Book of ASTM Standards, Vol 11.01.

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 *Annual Book of ASTM Standards*, Vol 15.05-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 a brown amber bottle.

9.5 *Sodium Thiosulfate, Standard Solution* ($0.1 \text{ meq/mL } (N)$)—Prepare and standardize a $0.1 \text{ meq/mL } (N)$ 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 (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:

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

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 $0.1 \text{ meq/mL } (N) \text{ Na}_2\text{S}_2\text{O}_3$ 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 $0.1 \text{ meq/mL } (N) \text{ Na}_2\text{S}_2\text{O}_3$ 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,