Designation: E1228 – 23

Standard Test Method for Assay of Peroxy Esters—Catalyzed Iodometric Procedure[1]

This standard is issued under the fixed designation E1228; 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 organic peroxides of the peroxy ester type.

NOTE 1—Other test methods for the assay of organic peroxides are given in Test Methods E298, E475, and E755.

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 the standard. No other units of measurement are included in this test method.

1.4 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in Section 9.

1.6 *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

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]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

E298 Test Methods for Assay of Organic Peroxides

E300 Practice for Sampling Industrial Chemicals

E475 Test Method for Assay of Di-*tert*-Butyl Peroxide Using Gas Chromatography

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E755 Test Method for Dicumyl Peroxide, Assay (Liquid Chromatography) (Withdrawn 2016)[3]

2.2 *Other Documents:*

OSHA Regulations, 29 CFR paragraphs 19100.1000 and 1910.1200[4] Air contaminates – table of exposure limits and Hazard Communication

3. Terminology

3.1 *Definitions:*

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

4. Summary of Test Method

4.1 A sample is dissolved in a mixture of isopropyl alcohol, acetic acid, and cupric chloride. A solution of potassium iodide is added and the mixture is briefly heated, then allowed to react in the dark at room temperature for 30 min. The cupric ion catalyzes the reduction of the peroxide and the liberated iodine is titrated with standard sodium thiosulfate solution.

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.12 on Caustics and Peroxides.

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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.

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

[4] Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

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

5. Significance and Use

5.1 Peroxy esters are widely used as chemical intermediates, catalysts, and initiators. This test method provides a procedure for assaying peroxy esters to determine if they are suitable for their intended use.

6. Interferences

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

7. Apparatus

7.1 *Iodine Flasks,* 250 mL capacity, with stoppers.

NOTE 2—All glassware should be cleaned thoroughly with dichromate cleaning solution before use.

7.2 *Beakers,* 1 mL capacity, glass or PTFE.

7.3 *Buret,* 50 mL capacity, graduated in 0.1 mL subdivisions.

7.4 *Water Bath,* maintained at 60 °C.

8. Reagents

8.1 *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.[5] 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type I or II reagent water conforming to Specification D1193.

8.3 *Acetic Acid,* glacial.

8.4 *Isopropyl Alcohol.*

8.5 *Hydrochloric Acid*, (1:100)—Dilute 1.0 mL of concentrated hydrochloric acid (HCl) to 100 mL with water.

8.6 *Cupric Chloride Solution,* 1 %—Dilute 1.0 g of anhydrous cupric chloride ($CuCl_2$) to 100 mL with water. Add 1.0 mL of 1:100 HCl and mix. The solution should be clear.

8.7 *Potassium Iodide Solution,* 50 %—Dissolve 25 g of potassium iodide (KI) in 25 mL of de-aerated water. This reagent should be freshly prepared just prior to use.

8.8 *Sodium Thiosulfate Standard Solution,* (0.1 meq/mL)—Prepare and standardize in accordance with the appropriate sections of Practice E200.

8.9 *Nitrogen Gas,* oxygen-free.

9. Hazards

9.1 Organic peroxides are strong oxidizing agents and present potential fire and explosion hazards. Avoid contact with reducing agents and sources of heat, sparks, or open flames. Reactivity varies widely and some compounds may explode when shocked. Organic peroxides 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 review the current Safety Data Sheets (SDS) for detailed information concerning toxicity, first aid procedures, handling, and safety precautions. Review local regulations for all materials used in this test method.

10. Procedure

10.1 Add 50 mL of isopropyl alcohol and 15 mL of acetic acid to a 250 mL iodine flask. A graduate can be used for these additions.

10.2 Pipet 1.00 mL of 1 % cupric chloride solution into the flask. (**Warning—**The quantity of the cupric chloride catalyst solution must be carefully measured in order to obtain reproducible results as the reagent also reacts with iodide to liberate iodine according to the following Eq 1:

$$2Cu^{++} + 4I^- \rightarrow 2\,CuI + I_2 \quad (1)$$

The blank titration should be approximately 1.0 mL. The results should be discarded and the analysis repeated if a significantly higher blank value is obtained.)

10.3 Sparge the solution with a rapid flow of nitrogen for 2 min, then stopper the flask and reserve.

10.4 Accurately weigh a sample containing 3 meq to 4 meq of active oxygen in a 1 mL beaker. Transfer the beaker containing the sample to the prepared flask and immediately restopper and mix. The approximate sample weight may be calculated as follows:

$$\text{Sample mass, g} = \frac{3.5\,M}{2C \times 1000} \quad (2)$$

where:

M = molecular weight of compound, and
C = number of peroxide groups in the molecule.

NOTE 3—Volatile liquid peroxides may be diluted to a known volume with isopropyl alcohol and aliquots taken for analysis.

10.5 While maintaining a flow of nitrogen over the solution, add 5 mL (graduate) of freshly prepared 50 % KI solution, and then immediately restopper and swirl to mix.

10.6 Place the flask in a water bath maintained at 60 °C for 20 s while gently swirling. The level of water in the bath should be above the level of solution in the flask.

NOTE 4—The reaction is temperature sensitive. If the temperature of the solution is above 25 °C, a 30 min reaction time is generally sufficient for most peresters. If the temperature of the solution is less than 25 °C, a longer reaction period may be required. By preheating the solution for 20 s at 60 °C, the solution temperature is high enough to obtain complete reaction in 30 min with minor variation in the ambient laboratory temperature.

10.7 Remove the flask from the bath and allow to stand in a dark location at room temperature for 30 min.

10.8 Add 50 mL of de-aerated water and titrate the solution with 0.1 meq/mL $Na_2S_2O_3$ solution to the colorless end point. Record the number of millilitres required for the sample titration.

[5] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.