Designation: E1228 – 17

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 *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.

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]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

E298 Test Methods for Assay of Organic Peroxides

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

E755 Test Method for Dicumyl Peroxide, Assay (Liquid Chromatography) (Withdrawn 2016)[3]

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.

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.

[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 D16.15 on Industrial and Specialty General 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.

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

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

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.[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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or III 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.

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 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.

10.9 Subtract the number of millilitres required for titration of a blank carried simultaneously through the entire procedure and calculate the assay value of the sample. (See Warning note in 10.2.)

11. Calculation

11.1 Calculate the assay as follows:

$$\text{assay, as \% compound} = \quad (3)$$

$$[(A - B) \times N \times M \times 100]/(W \times 2C \times 1000)$$

where:

A = $Na_2S_2O_3$ solution required for titration of the sample, mL,
B = $Na_2S_2O_3$ solution required for titration of the blank, mL,
N = meq/mL, normality of the $Na_2S_2O_3$ solution,
C = number of peroxide groups in the molecule,
M = molecular weight of the ground, and
W = sample used, g.

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

[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.

$$\text{active oxygen, \%} = \frac{[(A - B) \times N \times 0.008] \times 100}{W} \quad (4)$$

NOTE 5—This assay is based on the determination of active oxygen under specified conditions. If other organic peroxides are present as impurities and release equivalent amounts of active oxygen under the same conditions, their concentrations must be determined by appropriate HPLC or GC procedures and the results corrected accordingly.

12. Report

12.1 Report the assay value of the compound to the nearest 0.1 %.

13. Precision and Bias[5]

13.1 *Precision*—The following criteria should be used for judging the acceptability of results: (see Note 6).

13.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.135 % at 14 DF. The 95 % limit for the difference between two such runs is 0.4 %.

13.1.2 *Laboratory Precision*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.141 % absolute at 6 DF. The 95 % limit for the difference between two such averages is 0.4 % 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 0.236 % absolute at 3 DF. The 95 % limit for the difference between two such averages is 0.7 %.

13.2 *Bias*—The bias of this test method cannot be determined due to the unavailability of suitable reference materials.

NOTE 6—The above precision estimates are based upon an interlaboratory study performed in 1987 on samples of *t*-butyl perbenzoate and *t*-butyl peracetate with manufacturer's assays of 98.3 % and 51.0 %, respectively. One analyst in each of four laboratories performed duplicate determinations and repeated one day later, for a total of 32 determinations. Practice E180 was used in developing these precision estimates.

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.

15. Keywords

15.1 active oxygen; iodometric; peroxides; peroxyesters

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1036. Contact ASTM Customer Service at service@astm.org.

SUMMARY OF CHANGES

Subcommittee D16.15 has identified the location of selected changes to this standard since the last issue (E1228–09) that may impact the use of this standard. (Approved June 1, 2017.)

(1) Added Section 14 Quality Guidelines.