



Standard Test Method for Total Peroxides in Acrylonitrile¹

This standard is issued under the fixed designation E 1784; 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 describes a procedure for determining the total peroxide content of acrylonitrile in the range of 0.1 to 0.6 mg H₂O₂/kg acrylonitrile (ppm). Peroxides are an undesirable impurity in acrylonitrile.

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.* Specific hazard statements are given in Section 7.

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 Water²

E 60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis⁴

3. Summary of Test Method

3.1 Peroxides in the sample react with potassium iodide to form the yellow I₃ ion. The intensity of the color, which is proportional to the concentration of the I₃ ion, is measured at 365 nm. Results are expressed as total peroxides as H₂O₂.

4. Significance and Use

4.1 This test method provides for the determination of total peroxide in acrylonitrile in the range of 0.1 to 0.6 ppm. Only peroxides or other oxidants that react under the conditions of this test method are measured.

5. Apparatus

5.1 *Spectrophotometer*, capable of measuring at 365 nm,

5.2 *Absorption Cells*, 1-cm, borosilicate, matched, and

5.3 *Buret*, 25-mL capacity.

NOTE 1—Photometers and photometric practice described in this test method shall conform to Practice E 60.

6. Reagents

6.1 *Purity of Reagents*—Unless otherwise indicated, 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water mean Type II or Type III reagent water conforming to Specification D 1193.

6.3 *Potassium Iodide*.

6.4 *Acetic Anhydride*.

6.5 *Hydrogen Peroxide, 30 %*.

6.6 *Acrylonitrile, Peroxide Free*—Prepare by passing acrylonitrile through a 2 cm × 40 cm glass column packed with 50 mL of activated alumina or acid form ion exchange resin.⁶

¹ This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.02 on Product Standards.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 03.05.

⁴ *Annual Book of ASTM Standards*, Vol 15.05.

⁵ *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.

⁶ Rohm and Haas Amberlyst 15 has been found to be suitable or an equivalent resin may be used.

Flow through the column should be approximately 8 to 10 bed volumes per h. The absorbance obtained by following 9.1 through 9.3 should be less than 0.01. Alternative means of preparation include extraction with 10 % NaOH followed by distillation. For the extraction technique, extract 100 mL of acrylonitrile with 50 mL of 10 % NaOH, follow with triple extraction with water. The volume of peroxide free acrylonitrile required for calibration is 500 mL.

6.7 *Sulfuric Acid Solution, 12 N*—Measure 360 mL of concentrated sulfuric acid (H_2SO_4 sp gr 1.84) into a 500-mL graduated cylinder and slowly add it to 400 mL of water in a 1000-mL beaker while stirring. Rinse the cylinder with water and add the washings to the beaker with water. Mix the acid-water mixture, allow to cool, and transfer to a 1-L volumetric flask. Dilute to volume with water, mix well, and store in a closed glass container.

6.8 *Ammonium Molybdate Solution, 3 %*—Dissolve 1.5 g of ammonium molybdate, $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ in water and dilute to 500 mL. Adjust the pH to 7.0 using 0.01 N NaOH or 0.01 N HCl as required.

6.9 *Sodium Thiosulfate Solution, 0.1 N*—Prepare and standardize in accordance with Practice E 200.

6.10 *Starch Indicator Solution, 1 %*—Prepare in accordance with Practice E 200.

7. Hazards

7.1 Acrylonitrile is potentially hazardous to human health if not properly handled. Acrylonitrile is a suspected human carcinogen. Use acrylonitrile in a well ventilated hood.

7.2 Acrylonitrile can contribute to a toxic condition in systems of the human body, from inhalation, swallowing, or contact with the eyes or skin. Direct contact with acrylonitrile can cause skin burns as well.

7.3 Acrylonitrile liquid and vapor are readily absorbed into shoe leather and clothing and will penetrate most rubbers, barrier fabrics, or creams. Contact lenses should not be worn in areas where eye contact with acrylonitrile could occur. Use impermeable protective clothing and consult the current MSDS for recommended materials.

8. Standard Solutions and Calibration

8.1 Pipet 0.5 mL of 30 % H_2O_2 into a 100-mL volumetric flask, dilute to volume with water, and mix thoroughly. This stock peroxide solution contains approximately 0.15 % H_2O_2 .

8.2 Standardization of the stock peroxide solution should be done in duplicate along with a reagent blank. Dissolve 2 g of potassium iodide in 100 mL of water in each of three 250-mL Erlenmeyer flasks. Add 25 mL of 12 N sulfuric acid and 3 drops of 3 % ammonium molybdate solution to each and swirl to mix. The ammonium molybdate solution is added to catalyze the reaction.⁷

8.3 Pipet 25 mL of the stock peroxide solution, as described in 8.1, into two of the flasks, pipet 25 mL of water into the flask used as the blank, stopper the flasks, and swirl to mix.

8.4 Allow to stand for 5 min, then titrate the liberated iodine with standard 0.1 N sodium thiosulfate until the color becomes pale yellow. Add 1 to 2 mL of starch indicator and continue the titration to the sharp disappearance of the blue color.

8.5 Correct the titer for a blank titration carried through the entire procedure and calculate the exact H_2O_2 concentration of the stock peroxide solution. The solution should contain about 1500 mg H_2O_2 /L of H_2O_2 .

$$\text{mg/L of H}_2\text{O}_2 = \frac{V \times N \times 17.08 \times 1000}{S} \quad (1)$$

where:

V = average volume sodium thiosulfate required for standardization, mL,

N = exact normality 0.1 N sodium thiosulfate titrant,

S = volume peroxide stock solution taken for standardization = 25 mL, and

17.08 = mg H_2O_2 /meq.

8.6 Pipet 1 mL of the assayed H_2O_2 stock solution into a 100-mL volumetric flask containing approximately 50 mL of acetic anhydride. Dilute to volume with acetic anhydride and mix well. The solution contains approximately 15 mg/L of H_2O_2 . Calculate the exact concentration.

8.7 Pipet 0.5, 1.0, 2.0, and 3.0 mL of the approximately 15 mg/L of H_2O_2 solution, as described in 8.6, into respective 100-mL volumetric flasks. Dilute each to volume with peroxide-free acrylonitrile and mix well. These standards contain approximately 0.07, 0.15, 0.30, and 0.45 mg/L of H_2O_2 . Calculate the actual concentrations, C , of H_2O_2 in AN in ppm (w/w) as mg H_2O_2 /kg AN as follows:

$$C = \frac{\text{mg/L of H}_2\text{O}_2}{0.806 \text{ g/mL}} \times \frac{\text{L}}{1000 \text{ mL}} \times \frac{1000 \text{ g}}{\text{kg}} \quad (2)$$

where:

0.806 g/mL = density of acrylonitrile.

For a 0.30 mg/L of H_2O_2 solution,

$$C = \frac{0.30 \text{ mg/L of H}_2\text{O}_2}{0.806 \text{ g/mL}} = \frac{0.37 \text{ mg H}_2\text{O}_2}{\text{kg AN}} \quad (3)$$

8.8 Pipet 5 mL of acetic anhydride into each of five 125-mL glass stoppered Erlenmeyer flasks. Add 0.5 g of potassium iodide to each. Pipet 25 mL of each of the four standards into the flasks. Pipet 25 mL of peroxide-free acrylonitrile into the fifth flask to serve as a blank. Stopper the flasks and swirl to dissolve the potassium iodide.

8.9 Allow the flasks to stand for 20 ± 1 min, then measure the absorbance of each solution at 365 nm using 1-cm cells and the blank as a reference.

NOTE 2—Protect from light by covering the flasks with aluminum foil or by using tinted glassware as described in 8.8.

8.10 Prepare a calibration curve by plotting the absorbance of each standard versus mg H_2O_2 /kg AN.

9. Procedure

9.1 Pipet 5 mL of acetic anhydride into each of two 125-mL glass stoppered Erlenmeyer flasks. Add 0.5 g of potassium iodide.

⁷ *Standard Methods of Chemical Analysis*, Wilfred W. Scott, Sc. D., 5th ed., D. Van Nostrand Co., Inc., New York, NY, 1939, p. 2180.

9.2 Pipet 25 mL of the acrylonitrile sample into one of the flasks. Pipet 25 mL of peroxide-free acrylonitrile into the second flask to serve as a blank. Stopper the flasks and swirl to mix.

NOTE 3—Protect from light by covering the flasks with aluminum foil or by using tinted glassware as described in 9.1.

9.3 Allow to stand for 20 ± 1 min, then measure the absorbance of the acrylonitrile sample solution at 365 nm under using 1-cm cells and the blank as a reference.

9.4 Determine the peroxide concentration of the sample, as mg H₂O₂/kg AN, by reference to the calibration curve.

10. Report

10.1 Report the concentration of total peroxides as H₂O₂ to the nearest 0.01 mg H₂O₂/kg AN (ppm).

11. Precision and Bias

11.1 Use the following criteria for judging the acceptability of results (see Note 4):

11.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0108 ppm absolute at 12 DF. The 95 % limit for the difference between two such runs is 0.03 ppm, absolute.

11.1.2 *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 0.0110 ppm absolute at 6 DF. The 95 % limit for the difference between two such averages is 0.03 absolute.

11.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories, has been estimated to be 0.0373 ppm absolute at 5 DF. The 95 % limit for the difference between two such averages is 0.10 ppm absolute.

NOTE 4—These precision estimates are based on an interlaboratory study of analyses performed in 1987 on one sample of acrylonitrile containing an average of 0.098 ppm peroxide. One analyst in each of seven laboratories performed duplicate determinations and repeated them one day later, for a total of 28 determinations. Data from one laboratory was omitted.⁸ Practice E 180 was used in developing these precision estimates.

11.2 *Bias*—The bias of this test method has not been determined because of the lack of acceptable reference material.

12. Keywords

12.1 absorbance; acrylonitrile; colorimeter; peroxide; spectrophotometer

⁸ Details of the interlaboratory study are available from ASTM International Headquarters. Request RR: E15 - 1048.

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