



Standard Test Methods for Analysis of Acrylonitrile¹

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1. Scope

- 1.1 These test methods cover the analysis of acrylonitrile.
- 1.2 The analytical procedures appear in the following order:

	Sections
Color	7 to 9
Hydrogen Cyanide	10 to 18
<i>p</i> -Methoxyphenol	19 to 28
Water	29 to 32

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.* See Section 5 for specific hazards statements.

1.4 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
 - D 1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)³
 - E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals⁴
 - E 180 Practice for Determining Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁵
 - E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis⁵
 - E 203 Test Method for Water Using Karl Fischer Reagent⁵

3. Significance and Use

3.1 These test methods provide for the determination of color and various impurities in acrylonitrile. Color and impurity levels are important factors in many uses of acrylonitrile.

¹ This specification is under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E 15.58 on Acrylonitrile.

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

³ *Annual Book of ASTM Standards*, Vol 06.04.

⁴ *Annual Book of ASTM Standards*, Vol 03.05.

⁵ *Annual Book of ASTM Standards*, Vol 15.05.

4. Purity of Reagents

4.1 *Purity of Reagents*—Use reagent grade chemicals 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,⁶ where such specifications are available. 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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water conforming to Specification D 1193.

5. Hazards

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

5.2 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.

5.3 Acrylonitrile liquid and vapor are absorbed readily 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.

6. Photometers and Photometric Practice

6.1 The photometers and photometric practice described in these test methods shall conform to Practice E 60.

COLOR

7. Procedure

7.1 Determine the color of the acrylonitrile in accordance with Test Method D 1209.

8. Report

8.1 Estimate and report the color of the acrylonitrile to the

⁶ *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.

nearest 1 Pt-Co unit, absolute.

9. Precision and Bias

9.1 The precision and bias of this test method have not been determined.⁷

HYDROGEN CYANIDE

10. Scope

10.1 This test method covers the determination of HCN over the concentration of 0.5 to 10 ppm in acrylonitrile.

11. Summary of Test Method

11.1 Hydrogen cyanide (HCN) is extracted from the sample as a water soluble salt by means of a solution containing sodium hydroxide, ammonium hydroxide, and potassium iodide. The aqueous extract is then titrated with standard silver nitrate until all the cyanide is complexed as soluble $\text{Ag}(\text{CN})_2^-$. The first excess of silver, the end point, is indicated visually with the formation of insoluble silver iodide (turbidity). The HCN content is calculated from the quantity of silver nitrate consumed.

12. Significance and Use

12.1 The level of HCN in product acrylonitrile is an indication of product quality and stability. Knowledge of the HCN content can be used in judging quality and monitoring stability.

13. Apparatus

13.1 *Buret*, micro, 10-mL capacity, graduated in 0.02 mL subdivisions.

13.2 *Separatory funnels*, 250-mL capacity.

14. Reagents

14.1 *Potassium Iodide* (KI), crystal.

14.2 *Ammonium Hydroxide* (NH_4OH), concentrated.

14.3 *Sodium Hydroxide* (NaOH), pellets.

14.4 *Caustic Iodide Reagent*—Dissolve 3.6 g of potassium iodide crystals and 44.1 g of sodium hydroxide pellets in approximately 700 mL of water contained in a 1-L volumetric flask. Add 180 mL of concentrated NH_4OH and swirl to mix. Dilute to volume with water, mix thoroughly, and store in a plastic screw-capped bottle. This solution is stable for at least 6 months.

14.5 *Standard Silver Nitrate Solution*, 0.1 N—Prepare and standardize as described in Practice E 200.⁸

14.6 *Standard Silver Nitrate Solution*, 0.01 N—Pipet 50.0 mL of standard 0.1 N AgNO_3 solution into a 500-mL volumetric flask. Dilute to volume with water and mix thoroughly.

15. Procedure

15.1 Add 100 mL of caustic iodide to each of three 125-mL Erlenmeyer flasks using a graduated cylinder.

15.2 Slowly titrate each solution with standard 0.01 N AgNO_3 to the same slight persistent opalescence.

15.3 Transfer the contents of two of the flasks into glass-stoppered 250-mL separatory funnels. Retain the third flask for reference. Add 100 mL of sample to each separatory funnel using a graduated cylinder.

15.4 Stopper and shake the separatory funnels for 1 min \pm 10 s, then allow the layers to separate.

15.5 Drain the lower aqueous layers into the original 125-mL Erlenmeyer flasks.

15.6 Titrate each solution with standard 0.01 N AgNO_3 until an opalescence is obtained that matches the reference solution. Record the volume of 0.01 N AgNO_3 required for each titration and calculate the duplicate values for HCN content.

16. Calculation

16.1 Calculate the HCN content of the sample as follows:

$$\text{HCN, ppm (w/w)} = \frac{(\text{mL AgNO}_3)(N \text{ AgNO}_3)(0.054) \times 10^6}{(\text{mL sample})(0.806)} \quad (1)$$

where:

0.054 = meq weight of HCN, and

0.806 = density acrylonitrile, g/mL.

$$\text{or HCN, ppm (w/w)} = \frac{(\text{mL AgNO}_3)(N \text{ AgNO}_3)(66914)}{(\text{mL sample})} \quad (2)$$

17. Report

17.1 Report the parts per million of HCN to two significant figures.

18. Precision and Bias

18.1 The following criteria should be used for judging the acceptability of results (Note 1):

18.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 17.6 % relative at 12 df. The 95 % limit for the difference between two such runs is 49 % relative.

18.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability (formerly called repeatability))*—The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 12.4 % relative at 4 df. The 95 % limit for the difference between two such averages is 35 % relative.

18.1.3 *Reproducibility (multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 39.1 % relative at 3 df. The 95 % limit for the difference between two such averages is 109 % relative.

NOTE 1—The above precision estimates are based on an interlaboratory study of analyses performed in 1986 on one sample of acrylonitrile containing approximately 0.81 ppm HCN. One analyst in each of 5 laboratories performed duplicate determinations and repeated one day later, for a total of 20 determinations. One outlying laboratory (four determinations) was excluded from the calculations.⁹ Practice E 180 was used in developing these precision estimates.

⁷ A round-robin test was conducted with acrylonitrile for color. In each case the value reported was <5 Pt-Co units which is typical for industrial grade acrylonitrile.

⁸ This solution may be purchased from Fisher Scientific Co., No. 5572, or an equivalent.

⁹ Supporting data are available from ASTM Headquarters. Request RR: E15 - 1038.

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

p-METHOXYPHENOL

19. Scope

19.1 This test method covers the determination of *p*-methoxyphenol (MEHQ) in acrylonitrile. MEHQ is added to acrylonitrile to prevent polymerization during storage and shipment.

20. Summary of Test Method

20.1 The absorbance of MEHQ is measured directly in acrylonitrile at 295 nm using UV spectrophotometry. The ppm MEHQ is determined from the absorbance by use of a standard curve prepared from known concentrations of MEHQ in pure acrylonitrile.

21. Significance and Use

21.1 Knowledge of the inhibitor content of product acrylonitrile is essential for proper stability during storage and shipment of this material. The MEHQ prevents premature polymerization of the monomer.

22. Interferences

22.1 Any impurity which absorbs at 295 nm will interfere. Experience has shown that some impurities produced in aged acrylonitrile absorb in this region. The test method should, therefore, be applied only to acrylonitrile which is within the color specification.

23. Apparatus

- 23.1 *UV Spectrophotometer*.
- 23.2 *Absorption Cells*, 1 cm, matched, silica, with caps.
- 23.3 *Buret*, 25-mL capacity, graduated in 0.1 mL subdivisions.
- 23.4 *Separatory Funnel*, 500-mL capacity.

24. Reagents

- 24.1 *p*-Methoxyphenol (monomethyl ether hydroquinone, MEHQ).
- 24.2 *Sodium Hydroxide* (1 *N*)—Dissolve 40 g of NaOH in about 500 mL of water. Cool, then dilute to 1-L with water and mix.¹⁰

25. Standardization and Calibration

- 25.1 Prepare inhibitor-free acrylonitrile as follows:
 - 25.1.1 Shake 200 mL of 1 *N* NaOH with 100 mL of acrylonitrile in a 500-mL separatory funnel. Draw off and reserve the acrylonitrile layer. Repeat the extraction until 500 mL of inhibitor-free acrylonitrile has been accumulated.
 - 25.1.2 Alternately, distill 750 mL of acrylonitrile retaining the 500 mL heart-cut.
- 25.2 Prepare calibration curve as follows:

25.2.1 Quantitatively transfer 0.160 g of MEHQ to a 100-mL volumetric flask. Add 50 mL inhibitor-free acrylonitrile and swirl to dissolve. Dilute to volume with inhibitor-free acrylonitrile and mix well. This solution contains 2000 ppm MEHQ.

25.2.2 Pipet 10 ml of this solution (25.2.1) into a second 100-mL volumetric flask, dilute to volume with inhibitor-free acrylonitrile and mix well. This solution contains 200 ppm MEHQ.

25.2.3 Using a buret, deliver 5.0, 7.5, 10.0, and 12.5 mL of the 200 ppm standard solution into separate 50.0 mL volumetric flasks. Dilute each to the mark with inhibitor-free acrylonitrile and mix well. These solutions contain 20, 30, 40, and 50 ppm MEHQ respectively.

25.2.4 Measure the absorbance of each of the standards at 295 nm using 1-cm cells and inhibitor-free acrylonitrile as the reference.

25.2.5 Construct a calibration curve by plotting the absorbance of each standard (ordinate) versus the ppm MEHQ (abscissa). Draw the best straight line through the plotted prints.

25.2.6 Reinhibit any remaining inhibitor-free acrylonitrile by adding at least 35 ppm MEHQ to prevent premature polymerization of the monomer.

26. Procedure

26.1 Measure the absorbance of the product acrylonitrile sample at 295 nm using 1-cm cells and inhibitor-free acrylonitrile as a reference.

NOTE 2—Air can be used as the reference in place of inhibitor-free acrylonitrile.

26.2 Determine the ppm MEHQ present in the sample by reference to the standard calibration curve.

27. Report

27.1 Report the parts per million of *p*-methoxyphenol to two significant figures.

28. Precision and Bias

28.1 The following criteria should be used for judging the acceptability of results (Note 3):

28.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 0.91 % relative at 12 df. The 95 % limit for the difference between two such runs is 2.5 % relative.

28.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability (formerly called repeatability))*—The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 1.02 % relative at 6 df. The 95 % limit for the difference between two such averages is 2.9 % relative.

28.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 2.79 % relative at 5 df. The 95 % limit for the difference between two such averages is 7.8 % relative.

NOTE 3—The above precision estimates are based on an interlaboratory study of analyses performed in 1986 on one sample of acrylonitrile

¹⁰ This solution may be purchased from Fisher Scientific Co., No. 55266, or the equivalent.

containing approximately 44.9 ppm *p*-methoxyphenol. One analyst in each of six laboratories performed duplicate determinations and repeated one day later, for a total of 24 determinations.⁹ Practice E 180 was used in developing these precision estimates.

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

WATER

29. Scope

29.1 This test method covers the determination of water in the concentration of 0.05 to 3.0 weight percent in product acrylonitrile.

30. Procedure

30.1 Determine the water in the acrylonitrile sample as described in Test Method E 203.¹¹

31. Report

31.1 Report the percentage of water to two significant figures.

32. Precision and Bias

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

32.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 3.07 % relative at 12 df. The 95 % limit for the difference between two such runs is 8.6 % relative.

32.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability (formerly called repeatability))*—The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 2.70 % relative at 6 df. The 95 % limit for the difference between two such averages is 7.6 % relative.

32.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 4.39 % relative at 5 df. The 95 % limit for the difference between two such averages is 12.3 % relative.

NOTE 4—The above precision estimates are based on an interlaboratory study of analyses performed in 1986 on one sample of acrylonitrile containing approximately 0.22 % water. One analyst in each of six laboratories performed duplicate determinations and repeated one day later, for a total of 24 determinations.⁹ Practice E 180 was used in developing these precision estimates.

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

33. Keywords

33.1 absorbance; acrylonitrile; color; end point; HCN; MEHQ; spectrophotometer; titration; water

¹¹ Fisher Scientific Co. Karl Fischer Reagent No. So-K-3 has been found satisfactory for use as titrant.

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