



Standard Test Method for Analysis of Acrylonitrile by Gas Chromatography¹

This standard is issued under the fixed designation E 1863; 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 determination of the impurities in, and the purity of, acrylonitrile by flame ionization detector gas chromatography. It is applicable to acrylonitrile in the range of 99 to 100 % purity.

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. Specific hazard statements are given in Sections 6 and 7.*

1.4 Review the current MSDS for detailed information concerning toxicity, first aid procedures, and safety precautions.

2. Referenced Documents

2.1 *ASTM Standards:*²

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

E 1178 Test Methods for Analysis of Acrylonitrile

3. Summary of Test Method

3.1 In this test method, a representative sample of acrylonitrile is introduced in a gas chromatograph equipped with a flame ionization detector and a capillary column where specific impurities are separated from the acrylonitrile. The chromatographic area for each impurity is compared to the area of the internal standard, toluene or other suitable known, added to the sample. From response factors of these impurities relative to that of the internal standard and the amount of the standard

added, the concentration of the impurities are calculated. Other impurities, such as water, are obtained by use of Test Methods **E 1178**. The acrylonitrile content is obtained by subtracting the total amount of all impurities from 100.0.

4. Significance and Use

4.1 This test method is designed to obtain acrylonitrile purity on the basis of impurities normally present in acrylonitrile and may be useful for final product inspection and process control.

4.2 This test method will measure the following impurities: acetone, acrolein, acetonitrile, and acetaldehyde. It also will allow calibration of other impurities including benzene, methacrylonitrile, oxazole, propionitrile, cis-crotonitrile, trans-crotonitrile, and others where specific impurity standards are available.

5. Apparatus

5.1 *Capillary Gas Chromatograph*—Any gas chromatograph equipped with a flame ionization detector and a split injection system for use with capillary columns that can be operated at the conditions given in **Table 1**.

5.2 *Column*—The column, such as Supelcowax 10,³ must give satisfactory resolution and proper peak shapes for the components listed in **Fig. 1**.

5.3 *Recorder/Integrator*—Electronic integration is recommended for this analysis.

5.4 *Syringe*, 10 µL capacity.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where

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 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 A Supelcowax 10 fused silica capillary column (60 m by 0.32 mm ID by 1 µm film thickness), has been found to be suitable, but similar polar wax columns from other vendors may be used after shown to be suitable.

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

TABLE 1 Typical Instrument Parameters

Detector:	Flame ionization
Column:	
length:	60 m
inside diameter:	0.32 mm
stationary phase:	Supelcowax 10
support:	Fused silica
film thickness, μm :	1.0
Temperature, $^{\circ}\text{C}$:	
injector:	225
detector:	350
oven:	50 initial, hold 25 min, rate $10^{\circ}/\text{min}$, 90 final, hold 20 min
Carrier Gas:	Helium
Flow:	20 cm/s
Total chromatograph run time:	54 min
Internal standard:	Toluene
Sample size, μL :	2.0
Split ratio:	1:100
Retention times, min (refer to Fig. 1 for typical chromatogram)	
Acetaldehyde	6
Acetone	9
Acrolein	10
Benzene	18
Methacrylonitrile	23
Oxazole	29
Propionitrile	29.5
Toluene	30
cis-Crotononitrile	38
trans-Crotononitrile	49

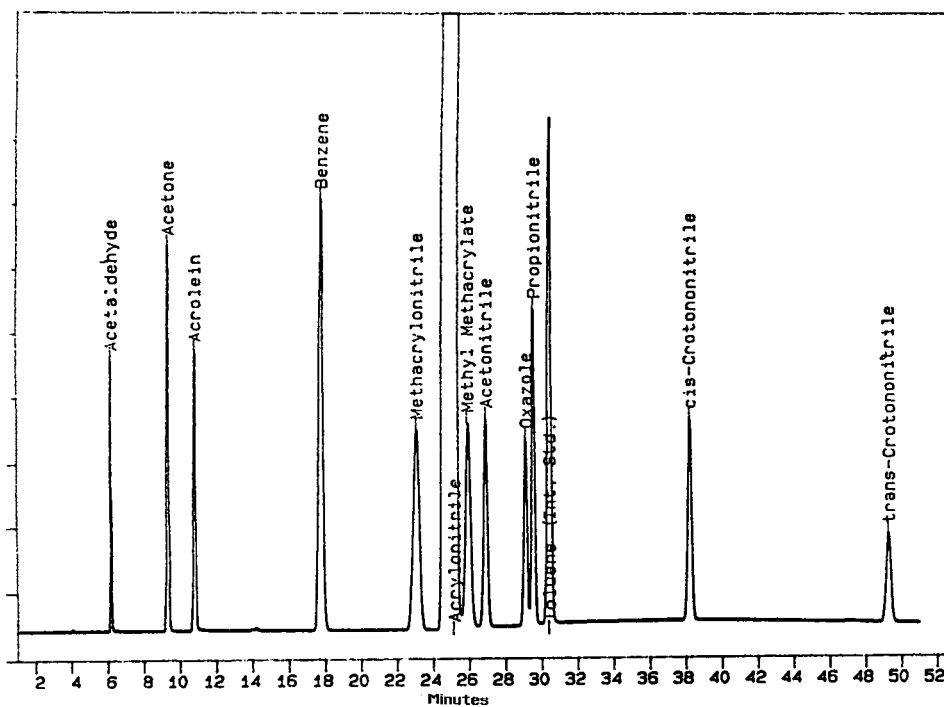


FIG. 1 Typical Chromatogram of Acrylonitrile Calibration Mixture

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.

6.2 *Carrier Gas*, helium minimum purity 99.995 mol %.

6.3 *Hydrogen*, high purity.

6.4 *Air*, hydrogen free, high purity.

6.5 *Toluene*, 99.0 % min purity or other internal standard, previously analyzed free of compounds coeluting with impurities in the sample.

6.6 *Acrylonitrile*, highest purity available.

NOTE 1—High purity acrylonitrile can be obtained by fractional distillation.

6.7 *Acetone*, at least 96 % pure.

6.8 *Acrolein*, at least 96 % pure.

6.9 *Acetonitrile*, at least 96 % pure.

6.10 *Acetaldehyde*, at least 96 % pure.

6.11 *Benzene*, at least 96 % pure.

6.12 *Methacrylonitrile*, at least 96 % pure.

6.13 *Propionitrile*, at least 96 % pure.

6.14 *Crotononitrile*, cis and trans, at least 96 % pure, available only as a mixture.

7. Hazards

7.1 Acrylonitrile potentially is 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 also can cause skin burns.

7.3 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. Impermeable protective clothing must be used. Consult the current MSDS for recommended materials.

8. Calibration and Standardization

8.1 Prepare a synthetic mixture containing approximately 99.4 mass % acrylonitrile and the expected significant impurities at their expected concentrations. Weigh all components to the nearest 0.1 mg. Fill a 100-mL volumetric flask about three fourths full of the synthetic mixture. With a microsyringe add 10 µL of toluene. Mix well. Add synthetic mixture to the mark and again mix well. If toluene is used as the internal standard, using a density of 0.867 for toluene and 0.806 for acrylonitrile, this solution will contain 0.011 mass % toluene.

8.2 Inject an appropriate amount of sample into the chromatograph and obtain a chromatogram. Approximate retention times are given in Table 1. A typical chromatograph is shown in Fig. 1.

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.

8.3 Measure the areas of all peaks, except the acrylonitrile peak, including the toluene (internal standard) peak.

8.4 Calculate the response factor for each impurity relative to the internal standard as follows:

$$Ri = \frac{As \times Fs \times Wi}{Ai \times Fi \times Ws} \quad (1)$$

where:

Ri = response factor relative to the internal standard,

As = area of internal standard peak,

Ai = area of impurity peak,

Fi = attenuation factor for impurity peak,

Fs = attenuation factor for internal standard peak,

Ws = internal standard in synthetic standard, mass %, and,

Wi = impurity in synthetic standard, mass %.

9. Procedure

9.1 Establish stable instrument operation at the prescribed or selected operating conditions. Reference should be made to the instructions provided by the manufacturer of the chromatograph.

9.2 Fill a 100-mL volumetric flask about three fourths full of sample. Mix well. With a microsyringe, add 10 µL of the internal standard. Add sample to mark and again mix well. If toluene is used as the internal standard, using a density of 0.867 for toluene and 0.806 for acrylonitrile, this solution will 0.011 mass % toluene.

9.3 Inject an appropriate amount of sample into the chromatograph and obtain the chromatogram.

10. Calculation

10.1 Measure the areas of all peaks, including the internal standard, except the acrylonitrile peak.

10.2 Calculate the mass percent of the individual impurities, I , as follows:

$$I = \frac{Ai \times Ri \times Fi \times Ws}{As \times Fs} \quad (2)$$

where:

Ai = area of impurity peak,

As = area of internal standard peak,

Ri = response factor for impurity, relative to the internal standard,

Ws = concentration of internal standard, mass %,

Fi = attenuation factor for impurity, and,

Fs = attenuation factor for internal standard.

For unknown impurities or for known impurities for which no response factor has been determined, a response factor (Ri) of 1.00 may be used.

NOTE 2—If an electronic integrator is used, Fs and Fi are usually 1.00.

10.3 Calculate the acrylonitrile content by subtracting the sum of all impurities from 100.00. Acrylonitrile mass % = 100.00 – sum of all impurities, whether measured by gas chromatography or by Test Methods E 1178.

11. Report

11.1 Report the concentration of each impurity to the nearest 1 mg/kg (ppm). Report any unidentified impurity or

any identified impurity for which a response factor has not been determined to the nearest 1 ppm (internal standard equivalent).

11.2 Report the sum of all impurities as total impurities to the nearest 0.01 % and the acrylonitrile assay (by difference) to the nearest 0.01 %.

12. Precision and Bias

12.1 The following criteria should be used for judging the acceptability of results for impurities (see **Note 3**):

12.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 5.8 % relative at 128 df. The 95 % limit for the difference between two such runs is 16 % relative.

12.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 4.2 % relative at 64 df. The 95 % limit for the difference between two such averages is 12 % relative.

12.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results, each the average of duplicates, obtained by analysts in different laboratories, has been estimated to be

9.4 % relative at 5 df. The 95 % limit for the difference between two such averages is 26 % relative.

NOTE 3—The above precision estimates are based on an interlaboratory study of analyses performed in 1988 on two samples of acrylonitrile containing approximately 18 and 82 mg/kg acetone, 164 and 443 mg/kg acetonitrile, 10 and 74 mg/kg benzene, 134 mg/kg cis-crotonitrile, 68 mg/kg trans-crotonitrile, 81 and 198 mg/kg methacrylonitrile, and 60 and 194 mg/kg propionitrile. The precision for other impurities should be determined as needed. One analyst in each of six laboratories performed duplicate determinations and repeated one day later, for a total of 48 determinations for each impurity. Practice **E 180** was used in developing these precision estimates.⁵

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

13. Keywords

13.1 acrylonitrile; capillary; gas chromatography; impurities; internal standard

⁵ Supporting data are available from ASTM International Headquarters as a research report. Request RR: E15 - 1059.

SUMMARY OF CHANGES

Committee E15.02 has identified the location of selected changes to this standard since the last issue (E 1863 - 97 (2002)) that may impact the use of this standard.

- (1) Updated units of measure to comply with the International System of Units (SI).
- (2) Added numbered paragraph in Scope stating that the SI units are to be considered standard.

- (3) Deleted (Formerly called Repeatability) from the title of **12.1.2**.
- (4) Added Summary of Changes section.

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