



Designation: D 4322 – 96

Standard Test Method for Residual Acrylonitrile Monomer Styrene-Acrylonitrile Copolymers and Nitrile Rubber by Headspace Gas Chromatography¹

This standard is issued under the fixed designation D 4322; 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 is suitable for determining the residual acrylonitrile (RAN) content of styrene-acrylonitrile (SAN) copolymer, rubber-modified acrylonitrile-butadiene-styrene (ABS) resins, and nitrile rubber (NBR).

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 precautionary statements are given in Section 9.

NOTE 1—Although the packed column option of this test method and ISO 4581:1994 (E) differ in some details, data obtained using either test method should be technically equivalent. There is no equivalent ISO standard for the capillary column option of this test method.

2. Referenced Documents

2.1 ASTM Standards:

D 4526 Practice for Determination of Volatiles in Polymers by Headspace Gas Chromatography²

E 380 Practice for Use of the International System of Units³

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method³

3. Terminology

3.1 Units and Symbols used in this test method are those recommended in Practice E 380.

3.2 Abbreviations:

3.2.1 AN—acrylonitrile.

3.2.2 RAN—residual acrylonitrile.

3.2.3 SAN—styrene-acrylonitrile copolymer.

3.2.4 ABS—acrylonitrile-butadiene-styrene copolymer.

3.2.5 NBR—butadiene-acrylonitrile rubber.

3.2.6 DMAC—*N,N*-dimethylacetamide.

3.2.7 PN—propionitrile (internal standard).

¹ This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.

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This revision includes the addition of an ISO equivalency statement and a suitable capillary column headspace GC test method.

² Annual Book of ASTM Standards, Vol 08.03.

³ Annual Book of ASTM Standards, Vol 14.02.

3.2.8 PC—propylene carbonate.

3.2.9 ppm— μg RAN/g polymer (parts per million).

4. Summary of Test Method

4.1 A dispersion of the polymer in a suitable solvent is prepared in a headspace vial and sealed. The vial is thermally equilibrated in a constant temperature bath.

4.2 After equilibrium, a given portion of the sample headspace is injected into a gas chromatographic column packed with porous polymer beads or a capillary column coated with an appropriate liquid phase. Sample injection is achieved using available commercial automatic equipment or a manual syringe injection technique. Passing through the column in a stream of carrier gas, acrylonitrile is separated from other components that may be present. The response of acrylonitrile is measured by a nitrogen-specific detector for packed column analysis or a flame ionization detector for capillary column analysis and this signal is recorded to indicate the retention time and relative concentration of acrylonitrile.

5. Significance and Use

5.1 For various reasons one may wish to measure the amount of unreacted or residual acrylonitrile monomer in styrene-acrylonitrile copolymers, nitrile rubbers, or ABS terpolymers.

5.2 Under optimum conditions, the lowest level of detection of AN in SAN or ABS copolymers and NBR rubbers is approximately 0.5 ppm for the packed column test method and 3 ppm for the capillary test method.

6. Interferences

6.1 The nitrogen-specific detector eliminates interference from all but compounds containing nitrogen or phosphorus. Any such material eluting at or near the AN or PN retention times will cause erroneous RAN results. The headspace above a polymer solution containing no internal standard should be analyzed to determine that no sample peaks coincide with the PN retention time for the packed column test method. The capillary column test method specifies use of a flame ionization detector. It is an external standard test method, therefore, concern with sample peaks coinciding with the retention time of the internal standard peak is not an issue.

6.2 Normally the headspace will contain only air, RAN, PN,

water, solvent, and any other volatile compounds used during polymerization. Such impurities at concentrations of 0 to 100 ppm will have negligible effect on the equilibrium relationship upon which this test method is based.

7. Apparatus

7.1 *Gas Chromatograph*, equipped with nitrogen-phosphorus specific detector, and backflush valve, that is capable of automatically and sequentially sampling and analyzing the headspace vapors contained in sealed vials.

7.1.1 If packed column analysis is preferred, the gas chromatography should be equipped with a packed column inlet, a nitrogen-phosphorous specific detector, and a backflush valve.

NOTE 2—The Perkin-Elmer Model HS40XL Headspace Autosampler coupled with a Perkin-Elmer AutoSystem XL Gas Chromatograph⁴ can fulfill these requirements.

7.1.2 If capillary column analysis is preferred, the gas chromatograph should be equipped with a capillary column inlet, and a flame ionization detector.

NOTE 3—The Hewlett-Packard Model HP7694 Headspace Sampler coupled with a Hewlett-Packard Model HP6890 Gas Chromatograph⁵ can fulfill these requirements.

NOTE 4—Another suitable detector may be utilized (for example, nitrogen-phosphorus specific detector), however, the operating procedures in Section 12 would have to be altered to suit the equipment used.

NOTE 5—If “manual” analysis is to be performed (that is, syringe injection into other chromatographs), then the following additional equipment is needed.

- (1) *Constant-Temperature Bath*, capable of maintaining $90 \pm 1^\circ\text{C}$.
- (2) *Gastight Gas Chromatographic Syringes* for sampling and injection.
- (3) *Septa, Butyl Rubber, and Aluminum Vial Seals*, if headspace vials are used.
- (4) *Valve*, 6-port for backflush.

7.2 Chromatographic Columns:

7.2.1 *Packed Column Analysis*—80/100-mesh Chromosorb 101 or 0.2 % Carbowax 1500/Carbopack C (80/100), 3.2-mm outside diameter by 1 m and 3.2-mm outside diameter by 2 m, stainless steel.⁶

7.2.2 *Capillary Column Analysis*—Quadrex 007-2, 25 m \times 0.32-mm internal diameter fused silica, coated with a 5- μm film of 5 % phenyl/95 % methylsilicone liquid phase.⁷

NOTE 6—Other column packings may be used after suitable evaluation to determine that no interfering peaks elute at the AN or PN retention times. If column packings other than those listed in 7.2 are used, then the settings recommended in Sections 11 and 12 may have to be modified.

7.3 *Recorder*, 5-mV full-scale or computing integrator, or appropriate computer data station and software.

7.4 *Vial Sealer*, for vials.

7.5 *Analytical Balance*, capable of weighing to ± 0.0001 g.

7.6 *Pressure Regulators*, for all required gas cylinders.

7.7 *Filter-Drier Assemblies*, for each required GC gas cylinder.

7.8 *Soap Film Flowmeter*, if the gas chromatograph used is not capable of electronic flow programming.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise stated, 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.⁸ 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 *Acrylonitrile Standard*.

8.3 *Internal Standard*, propionitrile (PN) for packed column analysis.

8.4 *N, N-Dimethylacetamide (DMAC) or Propylene Carbonate (PC)* are suitable solvents for the packed column test method, and *o*-Dichlorobenzene is suitable for the capillary column test method.

NOTE 7—A solvent blank headspace must be chromatographed to ensure the absence of interferences at the AN or PN retention times.

8.5 *Hydrogen Cylinder*, prepurified.

8.6 *Helium or Nitrogen Cylinder*, prepurified.

NOTE 8—Either nitrogen or helium may be used as the carrier gas for the packed column test method. The capillary test method is written for use with helium as the carrier gas. Nitrogen may be substituted for helium, however, the number of effective theoretical plates may be altered. It may be necessary to adjust the head pressure and column flow to obtain comparable chromatographic peak retention times.

NOTE 9—Helium may also be used as the carrier gas.

8.7 *Air*, breathing or water-pumped.

8.8 Certified, low-residual ABS, SAN, or nitrile rubber material of known AN concentration to be used as a standard for the capillary column test method or combination thereof.⁹

9. Safety Precautions

9.1 Do not release acrylonitrile to the laboratory atmosphere. Prepare standards and handle samples in a well-ventilated hood. Dimethylacetamide and *o*-dichlorobenzene are absorbed through the skin, so avoid contact.

9.2 Be careful not to come into contact with heated chromatographic parts such as the detector, column, rotating sample tray, hot sample vials, etc. involving manual injections (see Note 4). Once heated, sample vials are under pressure. After analysis, vent the pressure with a hypodermic syringe needle into a charcoal slug or vent tube leading to a hood *before* removing vials from the water bath.

10. Sampling and Storage

10.1 Keep all samples in tightly sealed jars. Analyze sample solutions within 24 h. If 24 h are exceeded, report the age of the sample solution.

⁸ *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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

⁹ Available from Scientific Polymer Products, Inc., 6265 Dean Parkway, Ontario, NY 14519.

⁴ Available from Perkin-Elmer Corp., 761 Main Ave., Norwalk, CT 06859.

⁵ Available from Hewlett-Packard Co., 2850 Centerville Road, Wilmington, DE 19808.

⁶ Column packing available from Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048.

⁷ Column available from Quadrex Corp., P.O. Box 2881, New Haven, CT 06525.

11. Preparation of Gas Chromatograph for Packed Column Analysis

NOTE 10—All conditions outlined in this section refer to the Perkin-Elmer Model HS40XL Headspace Autosampler and Perkin-Elmer Auto-System XL Gas Chromatograph. If equivalent equipment is used or if analyses are performed “manually,” then alter operating procedures to suit equipment used.

11.1 Connect 1 m and 2-m chromatographic columns with a low dead volume “tee.” Install in the chromatograph oven with a 1-m length connected to the injection port and the “tee” outlet attached to the backflush exit port. Do not connect the exit end of the column to the detector.

NOTE 11—For manual injections, one method of achieving backflush of the solvent is shown schematically in Fig. 1. For this backflush mode, connect a 3-m column to the valve ports as shown. Attach an auxiliary carrier gas line and vent line to the appropriate valve ports. The “B” carrier gas line of dual-injector instruments is a convenient source for this auxiliary flow.

11.2 Adjust the carrier gas flow to 25 to 35 mL/min that is optimum for minimum peak broadening consistent with fast

analysis time. Use this flow rate for both the analysis and backflush mode. If electronic flow programming is not available, adjust the carrier gas pressure and use a soap film flowmeter to measure column flow.

NOTE 12—For the manual injection backflush system shown in Fig. 1, switch the valve to the VENT position. Adjust the auxiliary flow at the vent port to the same rate as established in 11.2.

NOTE 13—Switch the valve to the VENT position to begin backflush 1 min after elution of the internal standard peak. Backflush should be four times as long as the forward flow time. Vent backflushed products into a hood.

11.3 Condition the column overnight at 200°C. Hydrogen and air to the detector should be turned off while the column is conditioning.

11.4 Set the detector air flow and pressure at the optimum conditions for the make and model of the chromatograph being used.

11.5 Set the detector bead hydrogen flow and pressure at the optimum conditions for the make and model of the chromatograph being used.

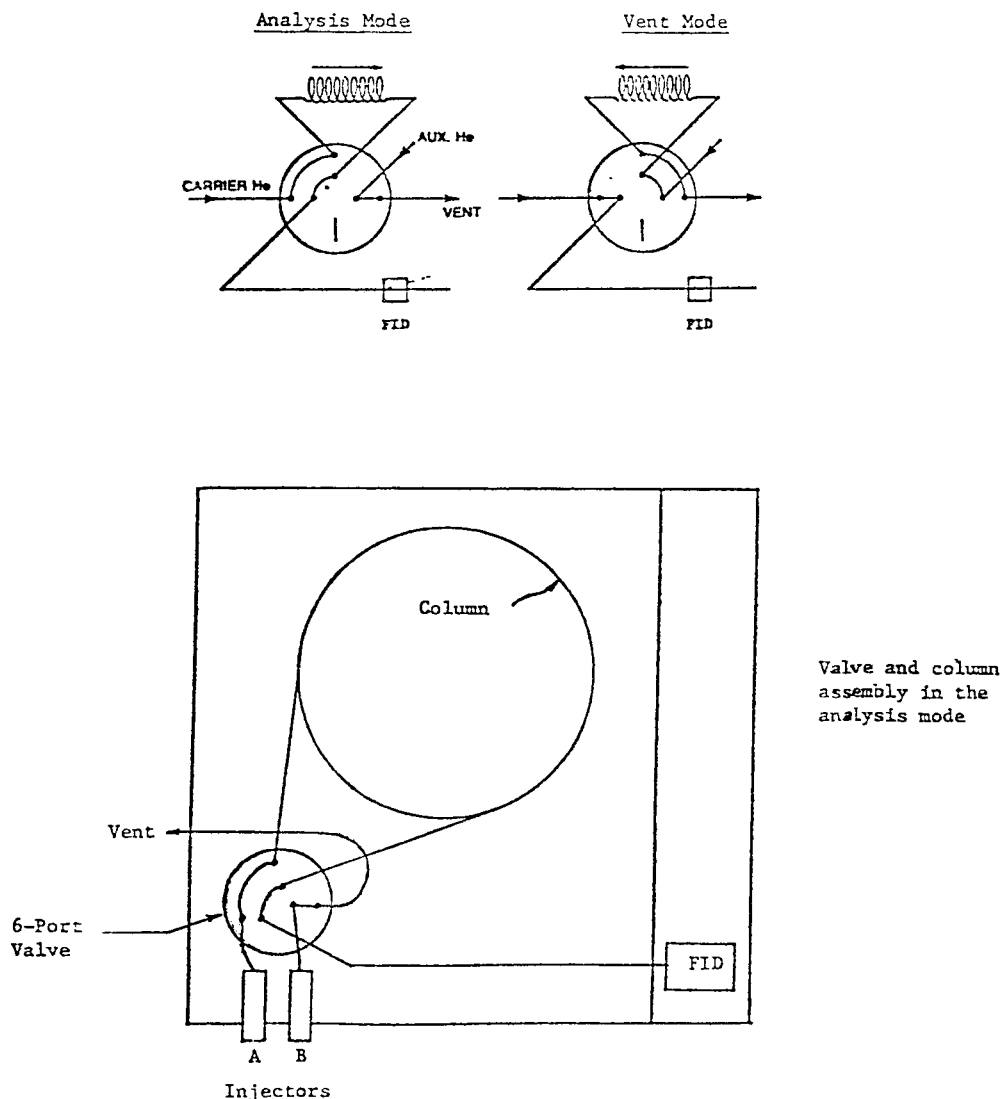


FIG. 1 Typical 6-Port Valve Backflush Assembly

NOTE 14—As a general rule, the lowest bead temperature that will produce adequate sensitivity should be used. By turning the bead setting off or to 2.5 between usages, bead life will be prolonged.

11.6 Set temperatures as follows:

11.6.1 *Chromatograph Oven (Column)*—130°C.

11.6.2 *Dosing Needle*—150°C.

11.6.3 *Injection Block*—180°C.

11.6.4 *Detector*—180°C.

11.6.5 *Autosampler Heated Zone*—90°C.

11.6.6 *Constant Temperature Bath (for Equilibration of Manually Injected Samples)*—90°C.

11.7 Set the headspace analyzer parameters as follows:

11.7.1 *Injection Time*—9 s,

11.7.2 *Analysis Time*—3 min,

11.7.3 *Backflush Time*—3.5 min, and

11.7.4 *Equilibration Time*—1 to 2 min.

12. Preparation of Gas Chromatograph for Capillary Column Analysis

NOTE 15—All conditions outlined in this section refer to the Hewlett-Packard HP7694 Headspace Sampler and HP6890 gas chromatograph. If equivalent equipment is used or if analyses are performed “manually,” then alter operating procedures to suit the equipment used.

12.1 Install the column in the chromatographic oven. Do not connect the exit end of the column to the detector.

12.2 Enter a column flow rate of approximately 2 mL/min helium at 8.1-psi (60-kPa) head pressure. If electronic flow programming is not available, adjust carrier gas pressure and use a soap film flowmeter to measure column flow.

12.3 Adjust additional flows to the following rates:

12.3.1 *Split Flow*—3.2 mL/min (no flow from headspace unit).

12.3.2 *Total Flow*—25 mL/min (includes flow from headspace unit).

12.3.3 *Septum Purge Rate*—2 to 3 mL/min.

12.4 Condition column overnight at 250°C. Hydrogen and air to the detector should be turned off while the column is conditioning.

12.5 Connect the column to the detector inlet and set the flame ionization detector gas flows as follows:

12.5.1 *Hydrogen*—Approximately 40 mL/min.

12.5.2 *Air*—Approximately 300 mL/min.

12.5.3 *Make-Up Gas*—Approximately 40 mL/min.

12.6 Set the instrument temperatures as follows:

12.6.1 *Injection Port*—200°C.

12.6.2 *Detector*—250°C.

12.6.3 *Oven*—60°C for 5 min, 10°C/min to 140°C, hold for 3 min, 3°C/min to 200°C.

12.7 Set the headspace analyzer parameters as follows:

12.7.1 *Carrier Pressure*—0.9 bar.

12.7.2 *Auxiliary Pressure*—1.0 bar.

12.7.3 *Servo Pressure*—4.0 bar.

12.7.4 *Heated Sample Zone Temperature*—90°C.

12.7.5 *Loop Temperature*—95°C.

12.7.6 *Equilibrium Time*—1 h.

12.7.7 *Sample Loop Volume*—3 mL.

12.7.8 *Timetable of Events*:

12.7.8.1 *Pressure Start*—03 s,

12.7.8.2 *Pressure Stop*—13 s,

12.7.8.3 *Fill Loop Start*—23 s,

12.7.8.4 *Fill Loop Stop*—33 s,

12.7.8.5 *Injection Start*—34 s, and

12.7.8.6 *Injection Stop*—74 s.

13. Calibration by Standard Addition for Packed Column Analysis

13.1 Pipet 10.0 mL of solvent into a 3-dram (12-mL) vial. Seal with Mininert® septum cap and weigh. Using a 10-μL syringe, add 5.0 μL acrylonitrile to this vial through the septum and reweigh. Shake well to mix and label Solution A. This stock standard should contain AN at a concentration of about 400 μg/mL.

13.2 To each of 5 headspace vials, weigh 0.5 ± 0.005 g of polymer. Using a pipet, add 5.0 mL solvent to each vial. Cover vials with butyl rubber septa and crimp seal with aluminum caps. Place vials on a mechanical shaker and mix until dispersed (approximately 1 h).

13.3 Using a 10-μL syringe, add 2, 5, 10, and 15-μL aliquots of stock Solution A to four polymer dispersions prepared in 12.2. These spikes, added through the septa, must be shaken again to ensure thorough mixing. Do not add AN to Vial 5.

NOTE 16—Standard addition is recommended for unknown systems, particularly if matrix effects are significant. For systems known to be interference-free at the internal standard retention time, the procedure of Section 14 is preferable.

NOTE 17—Concentration of Solution A from 12.1 should be such that spikes are in the same RAN concentration range expected for samples. The amount added should vary from 0.5 to 4 times the concentration of AN expected in samples.

14. Calibration with an Internal Standard for Packed Column Analysis

14.1 Prepare a polymer solvent solution containing a known amount of internal standard (PN) as follows:

14.1.1 Partially fill a 100-mL volumetric flask with solvent. Weigh a syringe containing approximately 10 mg PN. Transfer syringe contents to the flask and immediately reweigh. Dilute to volume with solvent, mix, and calculate the solution concentration.

14.1.2 Partially fill a 500-mL volumetric flask with solvent. Using a pipet, transfer 10.0 mL of solution from 14.1.1 to this flask and immediately dilute to volume. Calculate the concentration of this solution as follows:

$$\text{mg Propionitrile (PN)/5 mL} = (\text{mg PN from 14.1.1}) (0.1)/(100) \quad (1)$$

14.1.3 Store this internal standard solution in an amber Repipet® dispenser. Label the bottle Solution B and prepare a new solution monthly.

14.2 Weigh a 25-mL volumetric flask partially filled with solvent. Using a 50-μL syringe, transfer 25 μL AN to the flask and immediately reweigh. Dilute to volume with solvent and calculate the solution concentration (μg AN/mL). Identify this as Solution C and prepare fresh on a monthly basis.

14.3 Transfer 5.0 mL of internal standard Solution B into each of three vials and seal with butyl septa.

14.4 Using a 25-μL syringe, inject 10 μL of Solution C through the septa into each vial to give a working standard containing approximately 8 μg AN and 10 μg PN per 5 mL.

Calculate the exact concentration of AN in these standards as follows:

$$\mu\text{g AN} = \text{volume (mL)} \times \text{concentration } (\mu\text{g/mL}) \text{ Solution C}$$

14.5 Equilibrate standard vials in the 90°C water bath for at least 45 min. Obtain standard chromatograms using the operating conditions described in Section 11 and the procedure outline of Section 16.

14.6 Determine a response factor (R_f) as follows from AN and PN peak heights or areas and their known weights:
 $R_f = (\mu\text{g PN} \times \text{peak height (or area) AN}) / \mu\text{g AN} \times \text{peak height (or area) PN}$

<i>Example:</i>	Weight	Height
AN	8 μg	25 mm
PN	10 μg	35 mm

$$R_f = (10 \times 25) / (8 \times 35) = 0.893$$

NOTE 18—The average of a minimum of three calibration standards should be used for accurate daily determination of the response factor. Intersperse standards and samples in the analysis sequence. The standards prepared in 14.4 are equivalent to about 16 ppm AN based on a 500-mg sample. For significantly higher (or lower) AN levels, prepare additional standards and redetermine the response factor frequently to correct for any change in detector response.

15. Calibration with an External Standard for Capillary Column Analysis

NOTE 19—To avoid polymer matrix effects on detector response, an external standard of AN in polymer should be used as described in 15.2. The response of AN in solvent alone may not equal the response of the same amount of AN in extracted polymer.

NOTE 20—The capillary column test method has been validated using an external standard. A standard addition test method such as is described in Section 13 should give accurate results, as well, although this capillary test method has not been tested using standard addition and precision and bias data are not available using standard addition.

15.1 Verify that the instrument conditions are set as described in Section 12. Also, verify that baseline is stable by pressing the START button on the gas chromatograph. Observe the baseline for 5 min. When it is stable press the STOP button. If the idle oven temperature is set at 100°C overnight, the baseline should be stable at 60°C. Flame ionization detector response has been determined to be linear from 5 to 2100 ppm for acrylonitrile in SAN copolymers (see Fig. 2).

15.2 Weigh 0.500 ± 0.005 g of low-residual resin of known

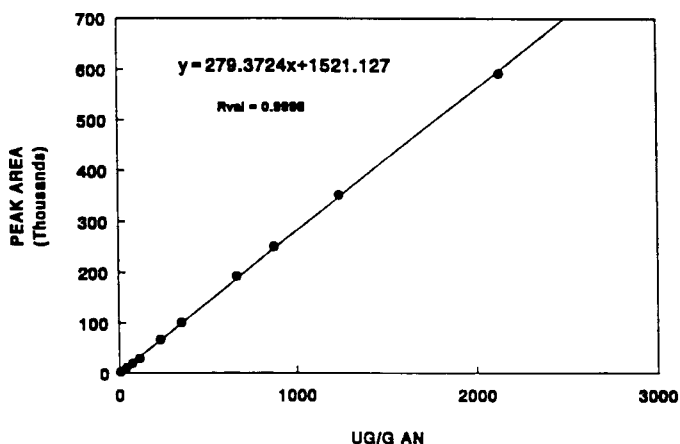


FIG. 2 Linearity Plot of Acrylonitrile in Styrene-Acrylonitrile Copolymers

acrylonitrile concentration (see 8.8) into a 20-mL headspace vial.

15.3 Using a 5-mL syringe, add 5 mL of *o*-dichlorobenzene to the vial in 15.2.

15.4 Shake the resulting solution in 15.3 on a flat-bed shaker at ambient temperature until dissolved or rubber is quite swollen. If desired, dissolution/swelling time may be decreased by placing the vial in a heated shaker at 85°C.

15.5 Place the vial containing the calibration solution (see 15.4) in the headspace analyzer, and analyze in accordance with the conditions summarized in Section 12.

15.6 Set the last vial parameter on the headspace analyzer to "1" and depress the START button on the headspace unit. At the completion of the run, a chromatogram should be obtained.

15.7 Repeat the process in accordance with 15.1-15.7 on every new day of analysis.

15.8 Calculate the response factor for acrylonitrile as follows:

$$Rf_{(AN)} = \frac{C_{(AN)}}{Area_{(AN,c)}} \quad (2)$$

where:

- $Rf_{(AN)}$ = response factor for acrylonitrile,
- $C_{(AN)}$ = concentration (ppm; wt/wt) of acrylonitrile in the calibration standard (see 15.4), and
- $Area_{(AN,c)}$ = peak area obtained for acrylonitrile during analysis of the calibration solution (see 15.6).

16. Manual Sample Analysis Procedure for Packed Column Analysis

16.1 Sample Preparation:

16.1.1 Mix the sample to be analyzed so that the portion selected will be as representative as possible. Weigh 0.5 ± 0.005 -g sample into a headspace vial and record the weight.

16.1.2 Pipet 5.0 mL of solvent or internal standard Solution B into the vial, cover with a butyl rubber septum, and seal.

16.1.3 Place the vial on a mechanical shaker and mix until completely dispersed. Shaking times average from 1 to 4 h depending on the sample. Nitrile rubber and ABS samples generally take the longer time to dissolve.

16.2 Place the sample vial into 90°C constant temperature bath and equilibrate for at least 45 min. Longer equilibration, not to exceed 5 h, can be used.

NOTE 21—Dissolution rate can be increased by placing the vial into the 90°C water bath, than removing periodically for manual shaking.

16.3 Using a warm gas syringe, inject 2.0 mL of equilibrated sample headspace into the gas chromatograph with parameters set in accordance with Section 11.

NOTE 22—The syringe can be kept warm in a 90°C oven between samplings.

16.4 At the predetermined time (Section 11, Note 12), switch valve to the vent position.

16.5 At the end of the predetermined backflush time, return valve to the ANALYSIS position.

16.6 Allow at least 2 min for baseline to equilibrate. Make additional injections as soon as normal baseline is established after backflush is ended.

17. Automated Sample Analysis Procedure for Packed Column Analysis

17.1 Weigh, disperse, and equilibrate sample as described in 16.1.1-16.2.

17.2 Set headspace analyzer parameters as recommended in 11.7. Equip the analyzer with a 2.0-mL sample loop.

17.3 Inject a sample and observe to ensure the automated versions of 16.4-16.6 occur at the appropriate times.

18. Automated Sample Analysis Procedure for Capillary Column Analysis

18.1 *Sample Solution:*

18.1.1 Weigh (and record to the nearest 0.0001 g) 0.500 ± 0.005 g of sample into a 20-mL headspace vial.

18.1.2 Add 5 mL of *o*-dichlorobenzene into the vial in 18.1.1.

18.1.3 Shake the resulting solution in 18.1.2 on a flatbed shaker at ambient temperature until dissolved or rubber is quite swollen. If desired, a heated shaker at 85°C may be used to decrease dissolution time.

18.1.4 Verify that the instrument and integrator conditions are set as described in Section 12. Also, verify that the baseline

is stable by pressing the START button on the gas chromatograph. Observe the baseline for 5 min. When it is stable press the STOP key.

18.1.5 Place the vial containing the sample solution (see 18.1.3) in the headspace analyzer and analyze according to the conditions summarized in Section 12. Set the last vial parameter equal to the number of samples that are to be analyzed. Depress the START button on the headspace unit.

19. Calculations—Standard Addition Method for Packed Column Analysis

19.1 Calculate ppm AN spiked into each standard from 13.3, using the following:

$$\text{ppm AN} = (\mu\text{g AN in aliquot spiked}) / (\text{g polymer sample}) \quad (3)$$

19.2 Plot ppm AN versus detector response (peak height corrected to attenuation or area) for the unspiked and spiked sample solutions of 12.3 to obtain a curve similar to Fig. 3. Nonlinearity suggests coeluting interferences that must be identified and eliminated by changes in the chromatographic system.

19.3 Calculate the response factor, *F*, from the slope of this curve, using the following:

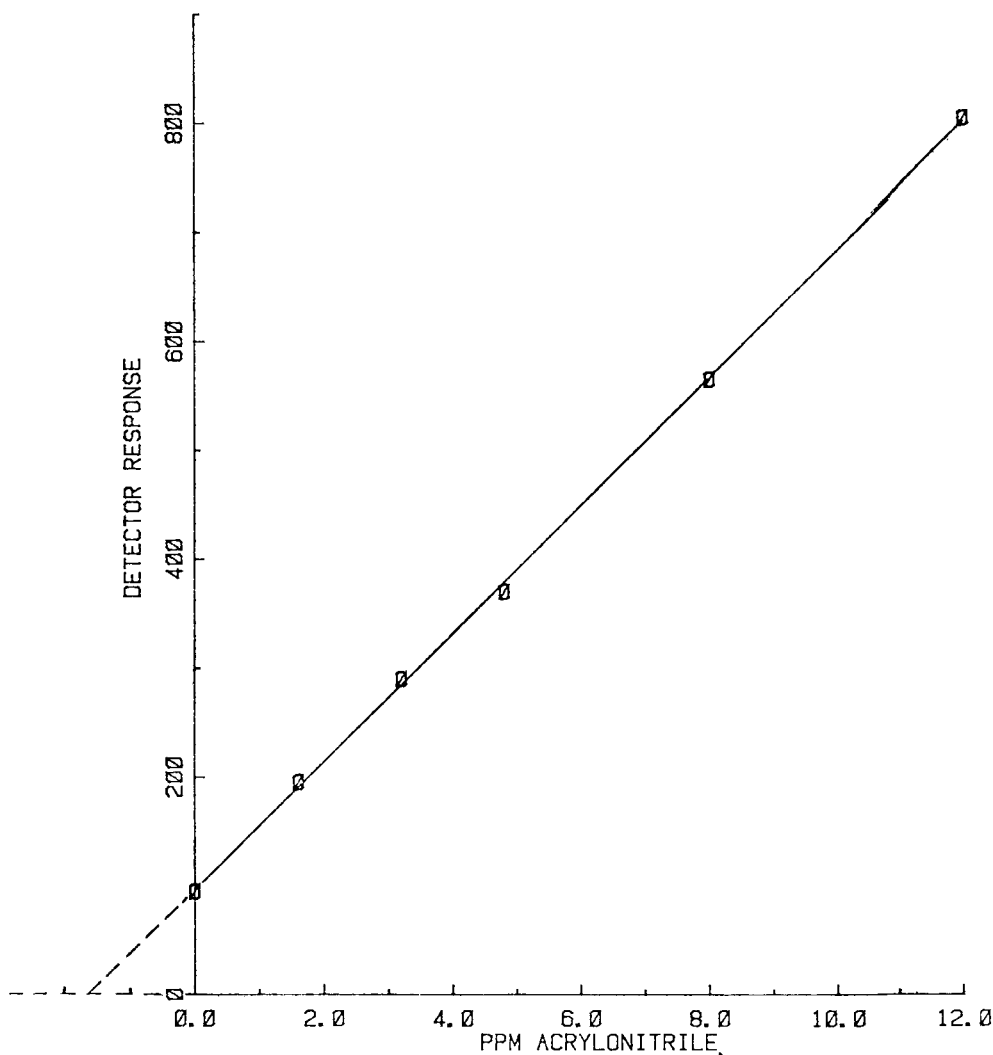


FIG. 3 Plot of Response versus ppm Acrylonitrile Added

$$F = (\text{AN (height)(area) at 10 ppm} - \text{AN height (area) at 0 ppm}) / (10)$$

19.4 Calculate the RAN content of samples in ppm by dividing the recorder response corrected for attenuation (height or area) by this response factor that is:

$$\text{RAN (ppm)} = (\text{AN height or area}) / (F) \quad (4)$$

This calculation assumes a constant weight as specified in 16.1.1.

20. Calculations—Internal Standard Method for Packed Column Analysis

20.1 Using the response factor, R_f , calculated in 14.6, calculate ppm RAN from the following equation for each sample:

$$\begin{aligned} \text{ppm RAN} &= (\text{AN response (height or area)} \\ &\times \mu\text{g PN}) / (\text{PN response (height or area)} \\ &\times \text{g sample} \times R_f) \end{aligned} \quad (5)$$

Example: Weight PN in sample = 10 μg
 $R_f = 0.893$
 Sample weight = 0.5 g
 Sample AN height = 30 mm
 Sample PN height = 35 mm
 $\text{ppm RAN} = (30 \times 10) / (35 \times 0.5 \times 0.893) = 19.2$

21. Calculation—External Standard Method for Capillary Column Analysis

21.1 Determine the concentration (ppm; wt/wt) of acrylonitrile in the original sample as follows:

$$S_{(AN)} = Rf_{(AN)} \times \text{area}_{(AN,s)} \times \frac{0.5 \text{ g}}{W_{(s)}} \quad (6)$$

where:

- $S_{(AN)}$ = concentration (ppm; wt/wt) of acrylonitrile in the original sample,
- $Rf_{(AN)}$ = response factor for acrylonitrile (see 15.8),
- $\text{area}_{(AN,s)}$ = peak area obtained for acrylonitrile during analysis of the sample solution (see 18.1.5), and
- $W_{(s)}$ = weight (g) of sample added to the sample solution (see 18.1.1).

22. Precision and Bias

NOTE 23—**Caution:** The following explanations of r (22.1-22.5) is only intended to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 and Table 2 should not be rigorously applied to acceptance or rejection of material, as those data are specific to the round robin and may not be representative of other lots,

TABLE 1 Summary of Packed Column Method Precision

Materials	Nominal ppm RAN	Expressed as % of the Average	
		V_r^A	r^B
San resin	1 to 2	20.2	56.6
	10	10.4	29.1
ABS resin	33	3.9	10.9
Nitrile rubber	1 to 2	7.7	21.6
	6	11.4	31.9

^A V_r = within laboratory coefficient of variation for the indicated material. It is obtained by pooling the within laboratory standard deviations of the test results

$$S_r = [(\sum(s_1)^2 + (s_2)^2 \dots + (s_n)^2) / n]^{1/2} \quad (7)$$

$$V_r = 100 \times (S_r \text{ divided by the overall average for the material})$$

^B r = within laboratory repeatability limit = $2.8 \times V_r$.

TABLE 2 Summary of Capillary Column Method Precision

Materials	Nominal ppm RAN	Expressed as % of the Average	
		V_r^A	r^B
San resin	78	1.9	5.3
ABS resin	75	1.9	5.3

^A V_r = within laboratory coefficient of variation for the indicated material. It is obtained by pooling the within laboratory standard deviations of the test results

$$S_r = [(\sum(s_1)^2 + (s_2)^2 \dots + (s_n)^2) / n]^{1/2} \quad (8)$$

$$V_r = 100 \times (S_r \text{ divided by the overall average for the material})$$

^B r = within laboratory repeatability limit = $2.8 \times V_r$.

conditions, materials, or laboratories. In particular, with data from less than six laboratories, the between-laboratories results are likely to have a very high degree of error. Users of this test method should apply the principles outlined in Practice E 691 to generate data specific to their laboratory and materials, or between specific laboratories. The principles of 22.1-22.5 would then be valid for such data.

22.1 Packed Column Test Method:

22.1.1 Table 1 is based on a round robin¹⁰ conducted in 1979 in accordance with Practice E 691, involving five materials tested by five laboratories. For each material, all the samples were prepared at one source, but the individual specimens were prepared at the laboratories which tested them. Each “test result” was the average of two individual determinations. Each laboratory obtained one test result for each material.

22.1.2 *Concept of r* —If V_r has been calculated from a large enough body of data, and for test results that were averages from testing two specimens then 22.3-22.5 apply.

22.2 Capillary Column Test Method:

22.2.1 Table 2 is based on a within-laboratory study conducted in 1995, involving two materials tested.¹¹ For each material, all the samples were prepared at one source. Each “test result” was the average of ten individual determinations. One test result was obtained for each material.

22.2.2 *Concept of r* —If V_r has been calculated from a large enough body of data, and for test results that were averages from testing ten specimens then 22.3-22.5 apply.

22.3 *Repeatability*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the r value for that material. The r value is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

22.4 No valid statement of between-laboratories reproducibility may be made for data from less than 6 laboratories.

22.5 Any judgment in accordance with 22.3 would have an approximate 95 % (0.95) probability of being correct.

22.6 There are no recognized standards by which to estimate bias of this test method.

23. Keywords

23.1 headspace gas chromatography; nitrile rubber; residual acrylonitrile; styrene-acrylonitrile copolymers

¹⁰ Supporting data are available from ASTM Headquarters. Request RR: D20-1111.

¹¹ Supporting data are available from ASTM Headquarters. Request RR: D20-1187.

 **D 4322**

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