Designation: D 4322 – 96

Standard Test Method for Residual Acrylonitrile Monomer Styrene-Acrylonitrile Copolymers and Nitrile Rubber by Headspace Gas Chromatography[1]

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 Chromatography[2]

E 380 Practice for Use of the International System of Units[3]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

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).

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,

[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.

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 Chromatograph[4] 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 Chromatograph[5] 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 ± 1°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 × 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.

[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, Bellefont, PA 16823-0048.

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

[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 Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

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.

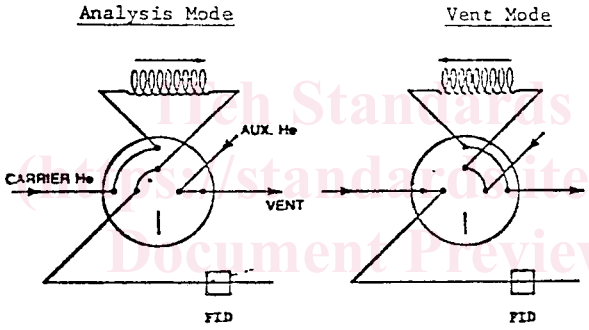
NOTE 12—For the manual injection backflush system shown in Fig. 1, switch the valve to the VENT position. Adjust the auxiliary flow at the vent port to the same rate as established in 11.2.

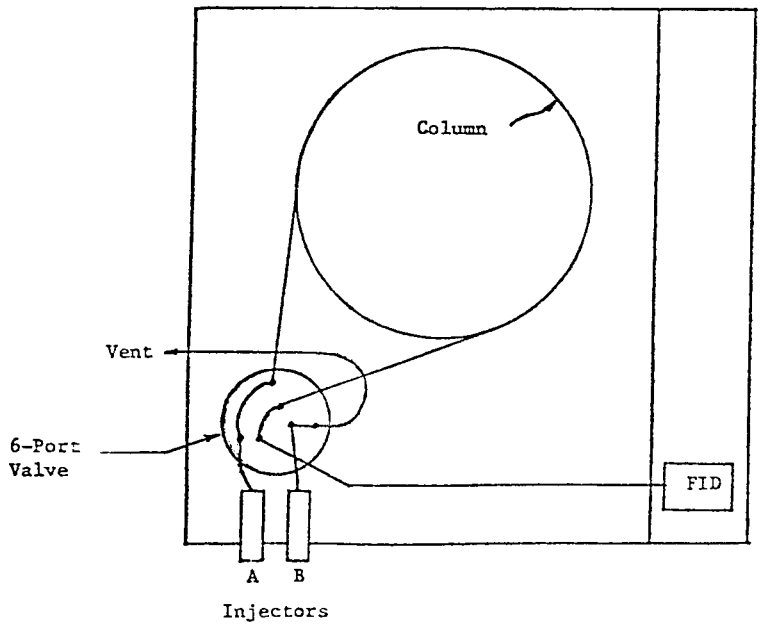
NOTE 13—Switch the valve to the VENT position to begin backflush 1 min after elution of the internal standard peak. Backflush should be four times as long as the forward flow time. Vent backflushed products into a hood.

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.





Valve and column assembly in the analysis mode

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.