



Standard Practice for Determination of Volatiles in Polymers by Static Headspace Gas Chromatography¹

This standard is issued under the fixed designation D 4526; 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.

^{e1} NOTE—Several sections were changed and added editorially in March 2001.

1. Scope

1.1 Headspace gas chromatography (GC) involves the determination of volatile components in a polymer solution by gas chromatography of a vapor phase in thermal equilibrium with the sample matrix. Volatiles in finely ground insoluble polymers can also be determined with and without an extracting solvent.

1.2 This practice provides two procedures:

1.2.1 *Procedure A*—Automatic headspace analysis.

1.2.2 *Procedure B*—Manual injection headspace analysis.

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 precautionary statements are given in Section 6.

NOTE 1—There is no equivalent ISO standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 4322 Test Method for Residual Acrylonitrile Monomer in Styrene-Acrylonitrile Copolymers and Nitrile Rubber by Headspace Gas Chromatography²

E 260 Practice for Packed Column Gas Chromatography³

E 355 Practice for Gas Chromatography Terms and Relationships³

E 594 Practice for Testing Flame Ionization Detectors Used in Gas Chromatography³

3. Significance and Use

3.1 For various reasons, one may want to measure the level of unreacted or residual monomer, water, or other volatile components in a polymer sample.

3.2 Volatiles of interest are often at trace concentrations. Headspace analysis is suited for determination of these trace components which often cannot be determined by conventional gas chromatography because of sample decomposition or interferences.

3.3 For polymer analysis, sample treatment for headspace analysis is simpler than conventional gas chromatography, where precipitation steps may be required to prevent polymer contamination of the chromatographic column.

3.4 This headspace practice will be able to determine qualitatively any component with sufficient vapor pressure. It is capable of yielding semiquantitative results and can be used for relative comparisons between samples.

4. Apparatus

4.1 *Gas Chromatograph*, equipped with an appropriate detector and backflush valve.

4.1.1 For Procedure A, an *Automated Headspace Sampler*,⁴ including backflush capability, thermostated sample tray, and associated accessories fulfill these requirements while providing for automatic sequential sampling of headspace vapors.

4.1.2 Procedure B requires the following additional equipment:

4.1.2.1 *Constant-Temperature Bath*, capable of maintaining $90 \pm 1^\circ\text{C}$.

4.1.2.2 *Gas-Tight Gas Chromatographic Syringes*, which can be heated to 90°C for sampling and injection.

4.1.2.3 *Valve*, 6-port for backflush assembly.

NOTE 2—Appropriate detectors could include the following:

(a) Flame ionization (FID) for general organic volatiles,

(b) Electron capture (EC) for halogenated species,

(c) Nitrogen-phosphorous (NPD) for acrylonitrile,

(d) Thermal conductivity (TC) for water, and

(e) Hall electroconductivity or photoionization (PID) for vinyl chloride.

4.2 *Chromatographic Columns:*

¹ This practice is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.

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² *Annual Book of ASTM Standards*, Vol 08.02.

³ *Annual Book of ASTM Standards*, Vol 14.01.

⁴ Available from Perkin-Elmer Corp., Main Ave., Norwalk, CT 06856.

4.2.1 *Packed Column Analysis*—Column packings⁵ found to be useful for residual monomers (for example, acrylonitrile, vinyl chloride) include Chromosorb or Porapak porous polymer packings, 0.4 % Carbowax 1500 liquid phase on Carbopak C support, or 0.19 % picric acid on Carbopak C support. Other columns can be used after it is determined that they give the required resolution and accuracy for the component of interest.

4.2.2 *Capillary Column Analysis*—Choose a column capable of achieving the required resolution for the components of interest. For example, for acrylonitrile monomer, the column of choice is a Quadrex 007-2, 25m × 0.32-mm internal diameter fused silica.⁶

4.3 *Integrator*, recorder (5-mV full scale), computing integrator or appropriate computer data station and software capable of measuring and storing peak area data.

4.4 *Headspace Vials*, septa, ring closures, and vial sealer.

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

4.6 *Soap Film Flowmeter and Stopwatch*, or other means of measuring gas flow rates.

4.7 *Pressure Regulators* for all required gas cylinders.

4.8 *Filter-Dryer Assemblies* for each required gas cylinder.

5. Reagents and Materials

5.1 *Solvent, Reagent Grade, or Best Available*—The solvent should be free of interferences at the retention time of volatile compounds determined by this technique. Typical polymer solvents include water, dimethylformamide (DMF), dimethylacetamide (DMAC), propylene carbonate, and *o*-dichlorobenzene. These solvents are readily backflushed from most chromatographic columns.

NOTE 3—Volatile contaminants can often be removed by sparging with an inert gas for 24 to 48 h.

5.2 *Nitrogen*, oxygen-free.

NOTE 4—Helium may also be used as the carrier gas and argon/methane is the preferred carrier gas for use with electron capture detectors.

5.3 *Hydrogen*, prepurified, for use with flame ionization detectors.

5.4 *Air*, breathing or water pumped, for use with flame ionization or nitrogen-phosphorus detectors.

5.5 *Standards*, best available, for volatile compounds to be analyzed using this technique.

6. Safety Precautions

6.1 Volatiles such as vinyl chloride and acrylonitrile should not be released to the laboratory atmosphere. Prepare standards and handle samples in a well-ventilated fume hood.

6.2 Some of the recommended solvents are flammable. Dimethylacetamide is also absorbed through the skin, so avoid contact.

6.3 Be careful not to come into contact with heated chromatograph parts, such as the detector, column, rotating sample tray, hot sample bottles, etc.

6.4 Once heated, sample vials containing polymer volatiles are under pressure. After analysis, vent the pressure with a hypodermic syringe needle connected to a charcoal slug or vented hood *before* removing vials from the constant temperature bath.

7. Storage and Sampling

7.1 To prevent loss of volatiles from polymer pellets, or resin, store in tightly sealed jars with minimal headspace or heat-sealed pouches constructed of an outer polyester layer, an aluminum foil middle layer, and a polyolefin inner sealing layer.

7.2 For rolled polymer film samples, discard 3 to 5 m of film before taking the sample for headspace analysis because volatiles can be lost by diffusion through the outer film layers.

7.3 Powdered resin samples (for example, poly(vinyl chloride)) can be weighed directly into a tared headspace vial. A 4-g sample (weighed to the nearest 0.0001 g) should be adequate for determination of many volatiles at the parts per million (ppm) levels using sensitive ionization detectors.

7.4 Polymer pellets or granules and film samples can be dissolved, depending on chemistry of polymer, to facilitate attaining thermal equilibrium in a reasonable period of time. These samples are weighed (0.5 ± 0.001 g) into headspace vials, then dissolved in 10 mL of an appropriate solvent. Using ionization detection, these 5 % solutions provide sensitivity for many volatiles at ppm levels. Sample size can be increased to attain sensitivity at lower levels.

NOTE 5—Freeze grinding polymer pellets or granules with liquid nitrogen and screening through a thirty-mesh screen often works as well as testing powdered resin. However, some volatiles may be lost even at these low temperatures.

NOTE 6—This technique of sample preparation requires analysis of the solvent blank to ensure freedom from interferences at volatile component retention times.

NOTE 7—Increased sample sizes can result in viscous solutions. Warming these solutions is often necessary to ensure complete sample dissolution.

8. Preparation of the Gas Chromatograph

8.1 Refer to Recommended Practice E 260 and the operator and service manuals of the instrument being used for details regarding column installation, flow rate adjustment, and optimization of detector sensitivity.

8.2 Refer to Practices E 355 and E 594 for information on terms, relationships, and procedures for testing flame ionization detectors.

8.3 Install the chromatographic column in the instrument oven. If solvent backflush is to be used, the front portion of the column consists of a short length (3 ft) connected with a low dead volume tee to the longer analytical column section. Fig. 1 shows a typical backflush assembly for a gas chromatograph designed for manual headspace analysis.

8.4 Adjust the carrier gas flow rate to obtain the same column flow in the analysis and backflush chromatographic modes.

8.5 Switch off the detector combustion gases before disconnecting the column from the detector to avoid buildup of an explosive gas mixture in the GC oven.

⁵ Available from Supelco, Inc., P.O. Box 628, 146 S. Water St., Bellefonte, PA 16823.

⁶ Available from Quadrex Corp., P.O. Box 3881, Woodbridge, CT 06525.

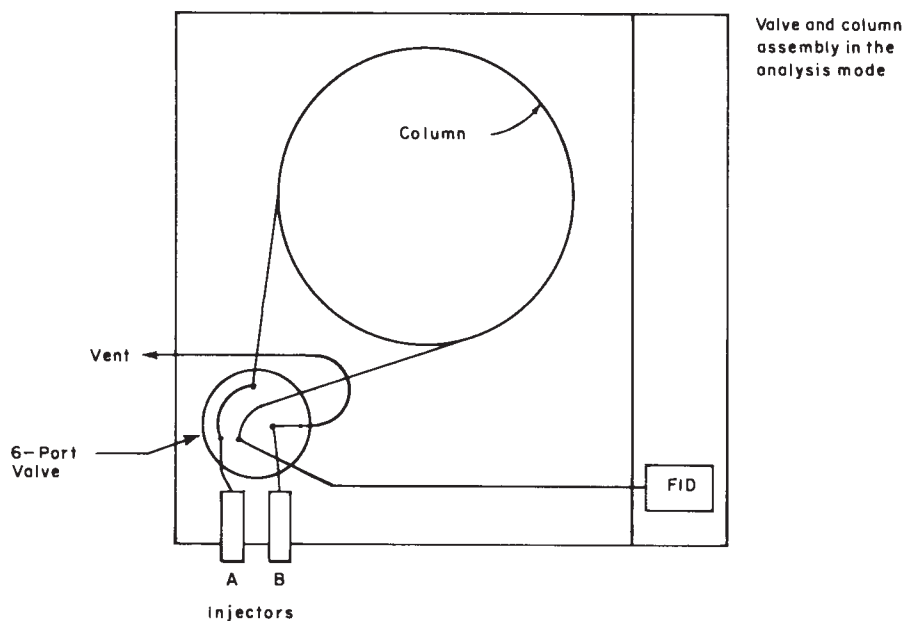
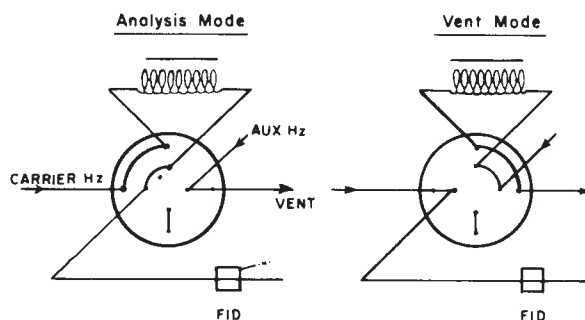


FIG. 1 Typical 6-Port Valve Backflush Assembly

8.6 Condition the column at a temperature that is 10 to 20°C above the expected operating temperature. With ionization detectors, the column should not be connected to the detector during the overnight conditioning period.

8.7 After conditioning, connect the column to the detector and optimize detector gas flow (air, hydrogen) for maximum sensitivity.

8.8 Set temperatures as follows:

8.8.1 *Chromatograph Oven (Column)*, as appropriate.

8.8.2 *Dosing Needle*, 10°C above column temperature.

8.8.3 *Injection Block*, 10°C above column temperature.

8.8.4 *Detector*, 10°C above column temperature.

8.8.5 *Temperature Bath*, 90 to 120°C (depending on component volatility and rated bath temperature).

9. Procedures

9.1 *Procedure A—Automated Sample Analysis:*

9.1.1 Prepare sample solutions in accordance with the criteria of Section 7, then equilibrate solutions for at least 1 h in the thermostatted sample tray.

9.1.2 Optimize analyzer injection time to give maximum signal. Injection times from 6 to 9 s are suitable for most determinations at the ppm level.

9.1.3 Adjust the analysis and backflush times consistent with fast analysis time and freedom from solvent interferences.

9.2 *Procedure B—Manual Injection:*

9.2.1 Prepare sample solutions in accordance with the criteria of Section 7, then equilibrate solutions for at least 1 h in a constant-temperature bath.

9.2.2 Using a warm gas syringe, inject 1.0 mL of the equilibrated sample headspace into the gas chromatograph prepared in Section 8.

NOTE 8—The syringe can be kept warm in a 90°C oven between samplings.

9.2.3 Switch backflush valve to VENT position 1 min after elution of the latest volatile component of interest. Backflush time should be four times as long as the forward flow time.

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

9.2.5 Allow at least 2 min for baseline equilibration between samples.

10. Report

10.1 Report the following information:

10.1.1 Sample identification,

10.1.2 Sample preparation; equilibration time and temperature,

10.1.3 Method of calibration, and

10.1.4 Concentration of desired volatile components.

11. Keywords

11.1 gas chromatography; headspace; polymers; volatiles

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D 4526 - 96) that may impact the use of this standard.

(1) Five year review with editorial changes.

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