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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Practice for Determination of Volatiles in Polymers by Static Headspace Gas Chromatography¹

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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 Column*—Common 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.

4.3 *Integrator*, capable of measuring and storing peak area data.

¹ This practice 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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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.

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