Designation: D 3749 – 95 (Reapproved 2002)

# Standard Test Method for Residual Vinyl Chloride Monomer in Poly(Vinyl Chloride) Resins by Gas Chromatographic Headspace Technique[1]

This standard is issued under the fixed designation D 3749; 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 vinyl chloride monomer (RVCM) content of poly(vinyl chloride) (PVC) homopolymer and copolymer resins for uses other than food contact. The range for this test, based on interlaboratory evaluation, is from 0.1 to 400 ppm RVCM.

1.2 This test method can be adapted to determinations of RVCM in a PVC copolymer resin if the Henry's Law constant at 90°C for that copolymer is known.

1.3 This test method cannot be used for polymer in fused forms, such as cubes or sheets. Refer to Test Method D 4443 or Test Method D 3680 for these materials.

1.4 This test method is proposed as an alternative to EPA Method 107 for determination of vinyl chloride monomers in dry-resin samples.

1.5 The values stated SI units are to be regarded as the standard.

1.6 *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.*

NOTE 1—This test method is similar to ISO 6401-1985 in title only. The technical content is significantly different.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 3680 Test Method for Residual Vinyl Chloride Monomer Content of Poly(Vinyl Chloride) Resins, Compounds, and Copolymers by Solution Injection Technique[2]

D 4443 Test Method for Analysis for Determining Residual Vinyl Chloride Monomer Content in PPB Range in Vinyl Chloride Homo- and Co-Polymers by Headspace Gas Chromatography[3]

D 4526 Practice for Determination of Volatiles in Polymers by Headspace Gas Chromatography[3]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[4]

2.2 *Federal Standards:*

Environmental Protection Agency Method 107 Determination of Vinyl Chloride Content of In-Process Waste-Water Samples, and Vinyl Chloride Content of Poly(Vinyl Chloride) Resin, Slurry, Wet Cake, and Latex Samples[5]

29 CFR 1919.1017 Vinyl Chloride for Regulated Levels of Exposure[6]

2.3 *ISO Standard:*

ISO 6401-1985 Determination of Residual Vinyl Chloride Monomer in Homopolymers and Copolymers by Gas Chromatography[7]

## 3. Terminology

3.1 *Acronyms:* Acronyms:

3.1.1 *VCM*—Vinyl chloride monomer.

3.1.2 *RVCM*—Residual vinyl chloride monomer.

3.1.3 *PVC*—Poly(vinyl chloride).

3.1.4 *OSHA*—Occupational Safety and Health Agency.

3.1.5 *FID*—Flame ionization detector.

3.1.6 *PID*—Photoionization detector.

3.1.7 *HED*—Hall electroconductivity detector.

3.1.8 *MHE*—Multiple headspace extraction.

## 4. Summary of Test Method

4.1 The basis for this test method relates to the vapor equilibrium that is established between RVCM, PVC resin, and air in a closed system. The RVCM in a PVC resin will equilibrate in a closed vessel quite rapidly, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin type.

4.2 After sample equilibration, conventional gas chromatographic (GC) techniques are used. A constant amount of sample headspace vapor is injected into a GC column that is

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[2] *Annual Book of ASTM Standards*, Vol 06.03.

[3] *Annual Book of ASTM Standards*, Vol 08.03.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

[5] Available from the U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

[6] Available from the Superintendent of Documents, Government Printing Office, Washington, DC 20402.

[7] Available from American National Standards Institute, 25 W. 43rd St., 4th Floor, New York, NY 10036.

packed with a liquid-coated solid support or porous polymer beads. Sample injection is accomplished by available commercial automatic equipment. Passing through the column in a stream of carrier gas, the vinyl chloride monomer (VCM) is separated from other components which may be present and is detected by a standard sensing device. The signal is recorded to indicate the relative concentration of the VCM and its retention time.

4.3 Refer to Practice D 4526 for additional information on headspace gas chromatography.

## 5. Significance and Use

5.1 Poly(vinyl chloride) resins must contain a minimum possible amount of unreacted, or free, VCM.

5.2 This test method provides a measure of RVCM which is suitable for manufacturing control or specification acceptance purposes.

5.3 Under optimum conditions, a lower level of detection of 2 ppm by volume VCM can be detected in the headspace vapor. Using a 4-g sample, this is equivalent to about 0.02 ppm by mass RVCM in the PVC resin.

## 6. Interferences

6.1 Normally, the vapor above PVC resin will contain only air, VCM, water, small amounts of catalyst breakdown products, and any solvents or comonomers used in polymerization. Impurities in the 0 to 1000-ppm range will generally have only a very small influence on this equilibrium relationship.

6.2 Any material that elutes from the chromatographic column at approximately the same time as vinyl chloride will cause high RVCM results.

## 7. Apparatus

7.1 *Gas Chromatograph*, equipped with a flame ionization detector (FID), photoionization detector (PID), or a Hall electroconductivity detector (HED) and capable of heating, sampling, and analyzing the headspace vapors contained in sealed vials.

NOTE 2—Automatic backflushing capability may be a desirable option for some copolymer samples to reduce the time of analysis.

7.2 *Chromatographic Column*, 80/100-mesh[8] in 1-m by 3.2-mm stainless steel tubing.

NOTE 3—Any column that will resolve VCM from any interferences and will elute VCM between 1 and 4 min using a system pressure of 100 to 150 kPa is satisfactory. If an alternate column is used, the chromatographic conditions may need to be modified.

7.3 *Integrator*, or computerized data system for peak measurements.

7.4 *Balance*, capable of weighing to ±1 % of sample weight.

7.5 *Accessories*, for headspace samples, including vials, septa, seals, and crimper.

7.6 *Syringe*, 100-µL capacity, 24-gage needle.

7.7 *Programmable Calculator*, or computer.

[8] Porapak Q, available from Supelco, Inc., Supelco Park, Bellefonte, PA 16823 – 0048, has been found to be satisfactory for this purpose.

## 8. Reagents and Materials

8.1 *Standards*—Cylinders of known concentrations of vinyl chloride in nitrogen gas. Nominal concentrations of 5, 50, and 500 ppm by volume (vppm) are needed, unless multiple headspace extraction (MHE) is used. Lower concentration standards may be desirable for a detection limit less than 2 ppm.

8.2 *Nitrogen*, or helium, oxygen-free, carrier gas for chromatograph.

8.3 *Hydrogen*, prepurified for FID detector.

8.4 *Air*, breathing grade, for FID detector.

## 9. Hazards

9.1 Vinyl chloride monomer is a cancer-suspect agent and must never be released to the laboratory atmosphere, even at low ppm levels. Venting or purging of VCM mixtures must be held to a minimum and should be vented into a properly functioning fume hood. Refer to 29 CFR 1919.1017 for regulated levels of exposure.

9.2 Be careful not to come into contact with heated parts of the chromatograph, such as the detector, column, hot vials, etc. Handle all electrical connections with care.

9.3 Vials should be vented to atmospheric pressure after analysis and prior to removal from the thermostatted turntable. A hypodermic needle connected to a syringe containing a freshly activated charcoal is suitable for this operation.

## 10. Sampling and Storage

10.1 Weigh and seal resin samples in the headspace vials in accordance with 12.1 as soon as possible, not to exceed 24 h.

10.2 Resins may be stored in the sealed headspace vials for up to four weeks without loss of VCM if they are analyzed without being reopened.

## 11. Preparation of Gas Chromatograph

11.1 Connect carrier gas and detector gas cylinders to the chromatograph with the recommended filters and regulators as required by the manufacturer.

11.2 Establish correct control of the thermostatted headspace unit.

11.3 Install the chromatographic column connected to the injector only. Establish an appropriate flow rate, and condition the column overnight at 150°C. After conditioning, cool and connect the column exit to the detector.

NOTE 4—See Appendix XI for recommendations for particular instrument parameters.

11.4 Set the pressure and flow of hydrogen and air to the detector in accordance with the manufacturer's recommendations. Ignite the flame.

11.5 Set other chromatograph controls as necessary to obtain the desired resolution and sensitivity for the instrument used, as follows:

11.5.1 Analysis time (and backflush time, if used) as required, depending on the location time of VCM.

11.5.2 Detector, recorder, and integrator sensitivities as needed to detect the VCM levels in the samples. The system should be capable of producing a measurement for a 50-ppm