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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.~~ 1—This standard and ISO 6401:2008 address the same subject matter, but differ in technical content.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

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

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

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

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[3]

29 CFR 1919.1017 Vinyl Chloride for Regulated Levels of Exposure[4]

2.3 *ISO Standard:*

~~ISO 6401-1985~~ISO 6401:2008 Determination of Residual Vinyl Chloride Monomer in Homopolymers and Copolymers by Gas Chromatography[5]

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[1] This test method 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] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* ~~, Vol 06.03.~~volume information, refer to the standard's Document Summary page on the ASTM website.

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

[3] Available from United States Environmental Protection Agency (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

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

[4] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

~~[5] Available from the U.S. Environmental Protection Agency, Research Triangle Park, NC27711.~~

[5] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

***A Summary of Changes section appears at the end of this standard.**

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 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[6] 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. 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~~shall be ~~desirable~~used for ~~a~~ detection limits less than 2 ppm.

[6] Available from the Superintendent of Documents, Government Printing Office, Washington, DC20402.

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