



Standard Test Method for Residual Vinyl Chloride Monomer in Poly(Vinyl Chloride) Resins by Gas Chromatographic Headspace Technique¹

This standard is issued under the fixed designation D3749; 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 D4443 or Test Method D3680 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 standard and ISO 6401 address the same subject matter, but differ in technical content.

2. Referenced Documents

2.1 ASTM Standards:²

D3680 Test Method for Residual Vinyl Chloride Monomer Content of Poly(Vinyl Chloride) Resins, Compounds, and

Copolymers by Solution Injection Technique (Withdrawn 2005)³

D4443 Test Method for Determining Residual Vinyl Chloride Monomer Content in PPB Range in Vinyl Chloride Homo- and Co-Polymers by Headspace Gas Chromatography

D4526 Practice for Determination of Volatiles in Polymers by Static Headspace Gas Chromatography

E691 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 Samples⁴

29 CFR 1919.1017 Vinyl Chloride for Regulated Levels of Exposure⁵

2.3 ISO Standard:

ISO 6401 Determination of Residual Vinyl Chloride Monomer in Homopolymers and Copolymers by Gas Chromatography⁶

3. Terminology

3.1 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.

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.

Current edition approved Nov. 1, 2013. Published November 2013. Originally approved in 1978. Last previous edition approved in 2012 as D3749 - 12. DOI: 10.1520/D3749-13.

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* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ Available from United States Environmental Protection Agency (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

⁵ 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>.

⁶ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

- 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 **D4526** 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 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 *Balance*, capable of weighing to $\pm 1\%$ of sample weight.

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

7.5 *Syringe*, 100- μ L capacity, 24-gage needle.

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 shall be used for detection limits 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 shall 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 shall 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 It is possible to store resins 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.

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. Ensure that the system is capable of producing a measurement for a 50-ppm vinyl chloride standard that is at least 10 times the standard deviation of the system background noise level.

11.6 Establish the proper combination of oven temperature and carrier flow rate to obtain a resolved, symmetrical VCM peak eluting from the chromatographic column between 60 and 250 s after injection. Record the system head pressure under those conditions.

12. Calibration

12.1 Prepare calibration standards by filling vials with the VCM in nitrogen standards, rapidly seating the septum, sealing with the aluminum retainer, and injecting 100 μL of distilled water.

12.1.1 Purge the sample line from the cylinder into the hood prior to filling the vials. (Use 3.2-mm stainless steel, not rubber or plastic, sample lines.)

12.1.2 With a flow rate of 500 to 1000 cm^3/min , place the end of the tubing into a vial to the bottom. Position the septum on top of the vial, pressing it against the tube to minimize mixing air with the standard gas in the vial. Purge each vial with the standard for at least 60 s.

12.1.3 Gradually slide the tube to the top of the vial, simultaneously sealing the vial with the septum as the tube is withdrawn.

12.1.4 Crimp an aluminum retainer over the septum.

12.1.5 Inject 100 μL of organic-free water into the vial with a burr-free, 24-gage needle to ensure uniformity of water vapor contribution to the vial pressure.

12.2 For each series of samples to be tested, prepare two vials each of the three standard gases. These calibration standards will be analyzed along with the samples in exactly the same manner and at the same detector range.

13. Procedure

13.1 *Sample Preparation*—Add 0.2 to 4 g $\pm$ 10 % of resin to a tared vial. Record exact weight to ± 1 %. Add by pipet, 2 drops of organic-free water, and immediately seal the vial.

13.2 Place the vials in the analyzer turntable in the order required for the instrument in use.

13.3 Condition each vial in the 90°C bath for at least 1 h, but no more than 5 h, before analyzing.

13.4 Analyze the headspace in each equilibrated vial to determine the VCM peak area.

13.5 Depressurize each vial with a needle after analysis prior to removal from the turntable. (See 9.3.)

14. Calculation

14.1 Calculate the individual response factors for the standards as follows:

$$R_{fi} = (A_i)/(C_i) \quad (1)$$

where:

R_{fi} = response factor from standard in Vial i,

A_i = VCM peak area from Vial i, counts, and

C_i = concentration of VCM, ppm by volume, in standard gas in Vial i.

14.2 Calculate the average response factor for the six standards. (Compare the factors to each other and previously determined factors. Investigate any large differences.)

14.3 The generalized headspace equation for the VCM/PVC resin system is as follows:

$$C_{vcm} = \frac{A_s P_a}{R_f T_1} \left[\frac{M_v V_g}{mR} + K_p T_2 \right] \quad (2)$$

where:

C_{vcm} = concentration of residual vinyl chloride in resin, ppm by weight,

A_s = VCM peak area in sample, counts,

P_a = atmospheric pressure, mm Hg,

R_f = average response factor, counts per vppm,

T_1 = laboratory temperature, °K,

M_v = molecular weight of VCM (62.5 g/mole), and

V_g = free vapor volume of vial, cm^3 ,

$$\text{volume of empty vial} = (m)/(\text{density of polymer}) \quad (3)$$

where:

m = mass of sample, g,

R = gas constant (62 360 $\text{cm}^3 - \text{mm}/\text{mol} - ^\circ\text{K}$),

K_p = Henry's Law constant (7.52×10^{-6} /mm Hg for PVC homopolymer at 90°C), and

T_2 = equilibration temperature (363 K).

14.4 The generalized equation can be simplified for a particular set of conditions, assuming the following conditions are met:

14.4.1 A sample is a PVC homopolymer containing less than 1 % water ($K_p = 6.52 \times 10^{-6}$).

14.4.2 Vials have a total capacity of 23 ± 1 cm^3 ($V_g = 20.5$).

14.4.3 Laboratory temperature is $22 \pm 2^\circ\text{C}$ ($T_1 = 295$).

14.4.4 Ambient pressure is 750 ± 10 mm Hg ($P_a = 750$).

14.4.5 Equilibration temperature is $90 \pm 1^\circ\text{C}$ ($T_2 = 363$).

14.5 The equation in 14.3 under the conditions in 14.4.1 through 14.4.5 reduces to

$$C_{vcm} = \frac{2.54 A_s}{R_f} \frac{0.0205}{m} + 0.0024 \quad (4)$$

15. Report

15.1 Report the calculated residual vinyl chloride concentrations to two significant figures in parts per million by weight (mg/kg) of dry resin.

16. Precision and Bias⁷

16.1 *Precision*—Values were determined in accordance with Practice E691 using data from an interlaboratory evaluation of three materials analyzed in duplicate (same day) by six laboratories:

	Average RVCM (µg/g)	
	400	12 to 18
Within laboratory (S_r)	21.5	0.62
Between laboratories (S_R)	53.3	0.91

⁷ Supporting data are available from ASTM Headquarters. Request RR: D20 – 1140.

16.1.1 Another sample containing an average RVCM level of 0.13 ppm gave within-laboratory precision of 0.02 and between-laboratory precision of 0.1.

16.2 *Bias*—In the absence of any absolute standard or alternative test method, there is no estimate of bias.

17. Keywords

17.1 gas chromatography; headspace gas chromatography; poly(vinyl chloride); vinyl chloride monomer

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D3749 - 12) that may impact the use of this standard. (November 1, 2013)

- (1) Removed 7.3, *Integrator* and 7.7, *Programmable Calculator*.
- (2) Renumbered Section 7.

- (3) Removed footnote for 7.2
- (4) Remove Note 5.

Committee D20 has identified the location of selected changes to this standard since the last issue (D3749 - 08) that may impact the use of this standard. (October 1, 2012)

- (1) Removed year reference from ISO standard in Note 1.

- (2) Removed year reference from ISO standard in section 2.3.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the ASTM website (www.astm.org/COPYRIGHT/).