Designation: D 4443 – 95 (Reapproved 2002)

Standard Test Method for Determining Residual Vinyl Chloride Monomer Content in PPB Range in Vinyl Chloride Homo- and Co-Polymers by Headspace Gas Chromatography[1]

This standard is issued under the fixed designation D 4443; 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 (RVM) content of homopolymer and copolymers of vinyl chloride down to a level of ~5 ppb.

1.2 This test method is applicable to any polymer form, such as resin, compound, film, bottle wall, etc. that can be dissolved in a suitable solvent.

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 hazard statements are given in Section 9 and Note 13.

NOTE 1—There is no similar or equivalent ISO standard.

2. Referenced Document

2.1 *OSHA Standard:*

29 CFR 1919.1017—Vinyl Chloride[2]

3. Terminology

3.1 *Abbreviations:Abbreviations:*

3.1.1 *DMAc*—N,N-dimethylacetamide.

3.1.2 *VCM*—Vinyl chloride monomer.

4. Summary of Test Method

4.1 Samples of vinyl chloride-containing polymers are dissolved in a suitable solvent in a closed system.

4.2 The polymer solution and headspace are equilibrated at an elevated temperature.

4.3 Aliquots of headspace gas are injected into a gas chromatograph and the vinyl chloride monomer is separated. The response of vinyl chloride monomer is determined by the use of one of several suggested detectors.

4.4 Calibration is accomplished using either *(a)* vinyl chloride monomer in nitrogen gas standards, *(b)* standard solutions containing known amounts of vinyl chloride monomer, or *(c)* a method of standard addition.

5. Significance and Use

5.1 Vinyl chloride-containing polymers are widely used to package a variety of materials, including foods.

5.2 Vinyl chloride monomer has been shown to be a human carcinogen. Threshold toxicity value has not been established.

5.3 Plastic manufacturers, food packagers, government agencies, etc. have a need to know the residual vinyl chloride monomer content of vinyl chloride-containing polymers.

6. Interferences

6.1 *N,N*- dimethylacetamide should be analyzed under identical conditions to determine the absence of interferences at the vinyl chloride monomer gas chromatography (GC) retention time.

6.2 Other solvents, monomers, or compounding aids may cause interference at the vinyl chloride monomer GC retention time.

7. Apparatus

7.1 *Gas Chromatography*, equipped with either a flame ionization detector (FID), a photo ionization detector (PID), or a Hall electroconductivity detector (HED), backflushing valve, and either automatic capability or manual sampling (Note 2) and ability to analyze the headspace vapors contained in a sealed vial.

NOTE 2—If the analyses are to be performed manually (that is, by syringe injection), then the following equipment will also be needed:

(*1*) Constant-temperature bath or oven capable of maintaining a temperature of 90 ± 1°C.

(*2*) Gas-tight GC syringes for sampling and injection.

(*3*) Sample bottles with fluoropolymer faces septa and caps (size optional).

(*4*) Gloves for handling hot syringes.

---

[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 (Section D20.70.03).

Current edition approved October 10, 1995. Published December 1995. Originally published as D4443 – 84. Last previous edition D 4443 – 84 (1989)$^{\epsilon 1}$.

This revision includes the addition of an ISO equivalency statement and a keywords section.

[2] Available from Superintendent of Documents, US Government Printing Office, Washington, DC 20402.

7.2 *Chromatographic Column,* 3 % OV-101 on 80/100[3] mesh Chromosorb WHP[3], ⅛-in. (3.2-mm) outside diameter by 2 ft (0.6 m), stainless steel connected through ⅛-in. "tee" to 0.19 % picric acid on 80/100 mesh Carbopack C[3], ⅛-in. outside diameter by 8 ft (2.4 m), stainless steel.

NOTE 3—Any column packing that will resolve VCM from interferences and elute VCM in a reasonable length of time (1 to 5 min) is satisfactory. For example, a 3-ft (0.9-m) by ⅛-in. (3.2-mm) outside diameter column containing 0.19 % picric acid on 80/100 mesh Carbopack C can replace the recommended 3 % OV − 101 column. Settings recommended in 11.3.1 may have to be modified to suit the packing material being used.

NOTE 4—The VCM peak must be kept on scale to manually measure the correct peak area or peak height. One method of achieving this without undue operator attention is to use a dual-channel recorder. One channel is set at a high sensitivity to obtain measurable small peaks for low-VCM samples. The other channel is set at a lower sensitivity to keep the larger peaks from high-VCM samples on scale. Most instruments will calculate peak height (or area) even if the peak goes off the scale on the recorder.

7.3 *Detector Output Filter/Amplifier*—The extreme sensitivity of this test method is best realized when the detector (usually operated at the maximum sensitivity) output is (*1*) filtered to remove the high-frequency noise and (*2*) amplified to give a visible or measurable signal. The filter/amplifier is connected in series between the detector and the recorder/computer.

NOTE 5—A Spectrum Scientific Model 1021A filter/amplifier[4] can fulfill these requirements. Other filter/amplifiers may be available that are suitable.

7.4 *Sample Headspace Vials*, glass, 23 mL, with fluoropolymer-lined septa and aluminum caps.

7.5 *Vial Sealer*.

7.6 *Analytical Balance*, capable of weighing to ±0.001 g.

7.7 *Statistical Programmable Calculator*.

NOTE 6—A programmable calculator is not absolutely necessary, but can save a considerable amount of time when large numbers of samples are being analyzed.

8. Reagents and Materials

8.1 *Vinyl Chloride Monomer (neat)*, pure, preferably in small cylinder.

8.2 *Standard Cylinders*, vinyl chloride monomer in nitrogen at 1 and 10 ppm by volume.

8.3 *Hydrogen Cylinder*, prepurified gas.

8.4 *Nitrogen*, oxygen-free.

NOTE 7—Helium may replace nitrogen as the carrier gas.

8.5 *Air*, breathing or water-pumped.

8.6 *N,N-Dimethylacetamide (DMAc)*, sparged with nitrogen gas for up to a week at room temperature to remove chromatographic interferences.

9. Hazards

9.1 *Safety Precautions*:

9.1.1 Vinyl chloride monomer is a carcinogen and exposure by inhalation or dermal contact, or both, is to be avoided. Refer to OSHA Standard 29 CFR 1919.1017 for regulated levels of exposure. *N,N*-dimethylacetamide is a teratogen. The use of a properly functioning hood and septum-sealed sample containers are recommended.

9.1.2 Avoid all contact with heated parts of the gas chromatograph, hot syringes, and sample bottles. Handle all electrical connections with care.

9.1.3 Once heated, sample vials are under pressure. After analysis, relieve the pressure with a hypodermic syringe needle vented into a charcoal slug or vent tube leading to a hood *before* removing vials from the water bath.

10. Sampling and Storage

10.1 Keep all polymer samples in tightly sealed jars or tightly wrapped aluminum foil prior to analysis. Dissolved polymer samples must be kept in septum-sealed vials or bottles until analyzed. Polymer solutions stored longer than 24 h should be maintained under refrigeration.

11. Preparation of Gas Chromatograph

NOTE 8—All conditions in this section refer to the Perkin-Elmer Headspace Analyzer. If analyses are performed manually, alter the operating procedures as required by the instrumentation.

11.1 Install the chromatographic column and condition overnight at 100°C, using normal carrier flow. Do not connect the exit end of the column to the detector *or* turn on detector gases during column conditioning.

11.2 Set the flow of detector gases as follows:

Detector	Gas	Flow
FID	Hydrogen	30 to 40 cm^3/min
	Air	300 to 400 cm^3/min
PID	Not required	
HED	Hydrogen	30 cm^3/min

11.3 Set other parameters as follows:

11.3.1 *Oven Temperature*—50 to 60°C.

NOTE 9—Higher oven temperatures may be required when other chromatographic columns are used, or when high-boiling solvents and late-eluting materials are being driven from the column.

11.3.2 *Dosing Needle*—150°C.

11.3.3 *Injection Block Temperature*—200°C.

11.3.4 *Constant-Temperature Bath*—90 ± 1.0°C.

11.3.5 *Carrier-Gas Flow Rate*—30 cm^3/min.

NOTE 10—Backflushing the carrier gas after VCM elutes can considerably shorten analysis time. After backflushing, allow adequate time for chromatographic conditions to stabilize before making another injection.

11.3.6 *Detector Temperature*:

11.3.6.1 *FID*—250°C.

11.3.6.2 *PID*—150°C.

11.3.6.3 *HED*—880°C.

11.3.7 *Filter/Amplifier*—Adjust as needed to remove high frequency noise and to provide adequate amplification of VCM signal. Typical settings: filter − 0.05 Hz and amplifier − 2×.

12. Calibration by Standard Addition

NOTE 11—The gas chromatograph is calibrated using either procedure: (*1*) VCM in nitrogen gas standards and a previously determined partition

[3] Column packing is available from Supelco, Inc., P.O. Box 628, 146 S. Water St., Bellefonte, PA 16823.

[4] Available from Spectrum Scientific Corp., 2401 Ogletown Rd., Newark, DE 19711.

coefficient for VCM between DMAc and headspace, (*2*) VCM solution standards, or (*3*) a method of standard addition of VCM to polymer solutions. Procedure (*3*) is preferred to correct for any contribution the polymer makes to partitioning of VCM. Therefore, only procedure (*3*) is described.

12.1 Accurately weigh headspace vial, cap, and septum using an analytical balance. Add 20 mL DMAc to weighed vial. Cap loosely, and reweigh. In hood, prepare VCM stock solution in this vial by quickly uncapping vial and adding 0.4 to 2 g liquid VCM from inverted freezer-cooled cylinder of VCM. Immediately cap vial tightly and mix well by shaking. Reweigh and calculate VCM concentration by weight (ca 20 000 to 80 000 ppm). Dilute this stock solution by withdrawing aliquots through the septum with a syringe and injecting into weighed, sealed vials of DMAc. Reweigh, and calculate VCM concentration (ca 50 ppm). This solution is similarly diluted to yield a solution containing 1 to 5 ppm. If refrigerated, these working standards are stable for several weeks. Multiple septum punctures shorten the working life of standards.

NOTE 12—Other methods of introducing VCM into the DMAc may be satisfactory. These should be shown to be accurate and safe.

12.2 Add known volumes (microlitres) of the 1 to 5-ppm VCM in the DMAc standard to the polymer solutions prepared as described in Section 13. Analyze solutions along with solvent blanks and the unknown, unspiked polymer solutions.

13. Procedure for Sample Analysis

13.1 Prepare two solvent blanks by adding 10.00 mL of DMAc to each of the two vials. Seal immediately with cap and septum.

13.2 Cut up polymer film and bottle samples into small (~5 by 5 mm) pieces. Use powder and pellet samples as received.

13.3 Prepare 8 vials, each containing the same weight, ±0.01 g, of polymer (1.00 to 4.00 g depending on previously determined solubility or desired sensitivity, or both). Add 10.00 mL of DMAc to each vial and seal immediately with cap and septum. Begin vigorously shaking vials *at once* to facilitate dissolution. Immerse vials in the constant-temperature bath (90 ± 1°C) until complete solution is effected. Vigorously shake vials occasionally to aid solution. Alternatively, (*1*) immediately add a magnetic stirring bar to the vials and effect solution in an 85 to 95°C water bath on a stirring-type hot plate or (*2*) place vials on/in a reciprocating shaker and heat with a heat lamp.

NOTE 13—**Precaution:** Vinyl chloride monomer may be present in the atmosphere of laboratories located in or near PVC manufacturing plants and PVC fabricating plants. Therefore, it may be necessary to prepare the sealed vials of solvent blanks and sample mixtures inside a nitrogen-flushed glove box or glove bag to avoid contamination by air-born VCM. Once sealed, the vials can be returned to the laboratory atmosphere for the remainder of the analysis.

13.4 After solution is attained (<5 h), spike vials accordingly, using syringe through thick portion of septum: Vials 1 and 2, no spike; Vials 3 and 4, × µL of 1 to 5 ppm VCM in DMAc standard (see 11.1) (× µL should give approximately double the GC response for VCM as in the unknown); Vials 5 and 6, 2 × µL of 1 to 5 ppm VCM standard; and Vials 7 and 8, 3 × µL of 1 to 5 ppm VCM standard.

13.5 Shake all vials to ensure homogeneity. Heat vials in constant-temperature bath (90 ± 1°C) for 1 h.

13.6 Adjust instrument injection time to inject maximum amount of headspace gas from each vial into the gas chromatograph in the following sequence: solvent blank, 8, 6, 4, 2, 1, 3, 5, 7 solvent blank.

NOTE 14—It may be useful to measure vial pressure after analysis but before removing the vial from the bath. This ensures that the vial was correctly pressurized and no leaks occurred, either of which will negate results.

NOTE 15—Experience with the method and system or development, or both, of response factors for one type of polymer may permit a reduction in the number of analyses of spiked unknowns during a determination.

NOTE 16—For manual injections, heat syringe to 90°C prior to withdrawing 1.0-mL headspace sample for injection. Wear gloves for protection.

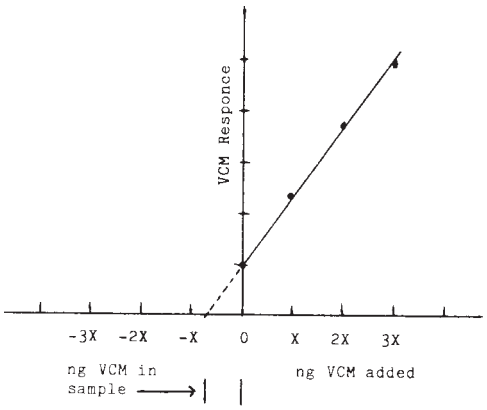

FIG. 1 Standard Additions Extrapolation Plot

13.7 Prior to plotting data points, construct two perpendicular axes on linear graph paper. The units of the *x*-axis should be in terms of X, from −3× or less to +3× or more. The units of the *y*-axis should be from 0 to a positive value at least as large as the net average response value for Vials 7 and 8.

13.8 Plot the net VCM response (average sample response for duplicate vials minus average blank response) for each vial pair on the *y*-axis versus the weight of VCM that was added to each member of the pair on the *x*-axis. Draw the best straight line through the four points and extrapolate the line to intersect the *x*-axis. The distance from this point of intersection to the Point X = 0 on the *x*-axis is a measure of the VCM content of the sample. See Fig. 1.

NOTE 17—A computer program can be used to plot and extrapolate the data.

14. Calculation

14.1 Calculate the VCM content in the unknown by determining the nanograms VCM obtained in the unknown (from the plot or computer) and dividing by the weight of polymer in the vial. Report findings in parts per billion (nanograms per gram).

15. Report

15.1 Report the VCM content in parts per billion as calculated in 14.1.

16. Precision and Bias [5]

16.1 The following values were determined for the coefficients of variation of this test method on the basis of an interlaboratory test program (1981–1982) involving 8 laboratories reporting results of at least duplicate analyses:

16.2 Coefficient of variation (CV) at a residual vinyl chloride monomer level of approximately 10 ppb:

	CV for Copolymer Film, %	CV for Homopolymer Pellets, %
Intralaboratory	33.5	14.9
Interlaboratory	37.7	34.8

16.3 *Bias*—Since no absolute method is available for comparison, no statement can be presented for this test method.

17. Keywords

17.1 copolymers: headspace gas chromatography; homopolomyer; ppb range; PVC; vinyl choride monomer

[5] Supporting data are available at ASTM Headquarters. Request RR: D20-1116.