Designation: D 4827 – 93 (Reapproved l998)

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Determining the Unreacted Monomer Content of Latexes Using Capillary Column Gas Chromatography[1]

This standard is issued under the fixed designation D 4827; 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 for the determination of the unreacted monomer content of acrylic latexes. Monomers that have been successfully determined by this procedure include *n*-butyl methacrylate, *n*-butyl acrylate, styrene, and methyl methacrylate. The determination of other monomers has not been evaluated, but this test method is believed to be applicable. The established working range of this test method is from 100 to 1000 µg/g, but there is no reason to believe it will not work outside of this range, provided that appropriate dilutions and adjustments in specimen size are made.

1.2 The unreacted monomer in acrylic latexes is expected to change with time and environmental factors. This time dependence of the determination may be seen as an artificially large deviation of results, making the test method mostly applicable for in-house quality control, where sampling and analysis conditions can be better controlled.

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.* For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

3. Summary of Test Method

3.1 A suitable aliquot of the latex is internally standardized with isobutyl acrylate, diluted with water, and then injected onto a capillary gas chromatographic column containing a stationary phase that separates the internal standard and monomers in question from each other and from other volatile compounds.

4. Significance and Use

4.1 Excessive amounts of unreacted monomer may cause concerns relating to toxicity and odor. This test method is designed to measure the unreacted monomer content of latexes. The results may be used to monitor the extent of polymerization during manufacture, as well as to establish maximum unreacted monomer content for regulatory purposes.

5. Apparatus

5.1 *Gas Chromatograph*—Any gas-liquid chromatographic instrument having a flame ionization detector and linear temperature programming and a capillary column inlet capable of split operation. The split liner should be constructed of glass and be replaced or cleaned as needed. On-column injection into a wide bore capillary column was not evaluated but is expected to also be satisfactory for this procedure.

5.2 *Column*—30-m by 0.25-mm inside diameter fused silica coated with a 1 µm thick film of a phenyl methyl silicone polymer. A bonded phase is preferred. Other columns having equivalent or superior performance may also be used.

5.3 *Recorder*—A recording potentiometer with a full-scale deflection of 10 mV, a full-scale response time of 2 s or less, and a maximum noise level of ±0.03 % of full scale. The use of a recording integrator or other data-handling device is preferred.

5.4 *Liquid Charging Devices*—A microsyringe, 1.0-µL capacity, or an automatic liquid sampling device using a suitable syringe and appropriate change in split ratio.

5.5 *Dropper Pipettes*, glass, disposable.

5.6 *Vials*, approximately 7 mL capacity, with caps. Open top screw-cap vials fitted with PTFE/silicone septa are preferred.

5.7 *Autosampler Vials*, 2 mL capacity (optional).

5.8 *Analytical Balance*, accurate to 0.1 mg.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be

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[1] This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials.

Current edition approved May 15, 1993. Published July 1993. Originally published as D 4827 – 88. Last previous edition D 4827 – 88.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

6.3 *Carrier Gas*—Helium of 99.995 % or higher purity. High purity nitrogen may also be used.

6.4 *Acetone*.

6.5 *Isobutyl Acrylate* (internal standard), 99 + % pure.

NOTE 1—Isobutyl acrylate was found to be a suitable internal standard, but any other monomer not found in the sample may be substituted. The internal standard chosen should yield a clear chromatographic separation, and should be free of interferences.

6.6 *Monomers of Interest*, 99+ % pure.

6.7 *Methanol*.

7. Hazards

7.1 Acrylic and methacrylic monomers are considered hazardous. All sample preparations should be done in a well ventilated area, such as a fume hood.

8. Preparation of Apparatus

8.1 *Column Conditioning*—Attach one end of the column to the inlet side of the instrument leaving the exit end of the column disconnected. This prevents the contamination of the detector due to column bleed. Set the helium flow rate at 0.5 mL/min (approximately equivalent to a linear velocity of 20 cm/s) and purge the column at 220°C for 1 h.

8.2 After conditioning, connect the exit end of the column to the detector and establish the operating conditions required to give the desired separation (see Table 1). Allow sufficient time for the instrument to reach equilibrium as indicated by a stable baseline.

8.3 Control the detector temperature so that it is constant to within 1°C without thermostat cycling which causes an uneven baseline. Adjust the carrier gas flow rate to a constant value.

TABLE 1 Instrument Conditions

Detector	flame ionization
Airflow, mL/min	240[A]
Hydrogen flow, mL/min	30
Makeup gas	30
Helium	
Column:[B]	
Length, m	30
Inside diameter, mm	0.25
Film thickness, µm	1
Carrier gas	helium
Flow rate	0.5 mL/min
Temperatures:	
Injection port, °C	220
Detector block, °C	250
Column:	
Initial, °C	60
Hold time, min	4
Program rate, °C/min	8
Final, °C	200 (or higher as needed)
Final hold, min	10 (or longer)
Injection volume, µL	0.5
Split ratio	20:1

[A] Set at recommended flow according to the instrument manufacturer.

[B] Cross-linked 50 % phenyl 50 % methyl silicone. A column of equivalent or better performance may also be used.

9. Calibration

9.1 Determine the retention time of each component expected to be present by injecting small amounts either separately or in known mixtures. Retention times should be determined each day that the test method is used.

9.2 *Standardization*—Determine in duplicate the relative response of the monomers of interest to the isobutyl acrylate internal standard as follows:

9.2.1 Weigh to within 0.1 mg about 0.05 g of isobutyl acrylate and each monomer of interest into a vial (see 5.6). Weigh approximately 5 g of acetone into the vial and mix well.

9.2.2 Weigh approximately 0.05 g of the solution prepared in 9.2.1 into another vial, add approximately 5 g of acetone, and mix well.

9.2.3 Inject a 0.5-µL aliquot of the solution from 9.2.2 onto the column and record the chromatogram. The elution order for acetone and each of the monomers using the conditions given in Table 1 is shown in Fig. 1.

9.2.4 Measure the peak areas of the individual components and calculate the relative response factor, *RF*, for the monomers of interest as follows:

$$RF = (W_1 \times A_s)/(W_s \times A_1) \quad (1)$$

where:

RF = relative response factor for each monomer,
A_1 = peak area produced by the monomer,
A_s = peak area produced by the internal standard,
W_1 = weight of monomer used for calibration (see 9.2.1), g, and
W_s = weight of internal standard (see 9.2.1), g.

10. Procedure

10.1 If the composition of the latex is not known or if the approximate *level* of monomers in the latex is not known, a preliminary analysis must be performed by diluting approximately 0.5 g of latex with approximately 5 g of water and injecting a 0.5 µL aliquot into the chromatographic

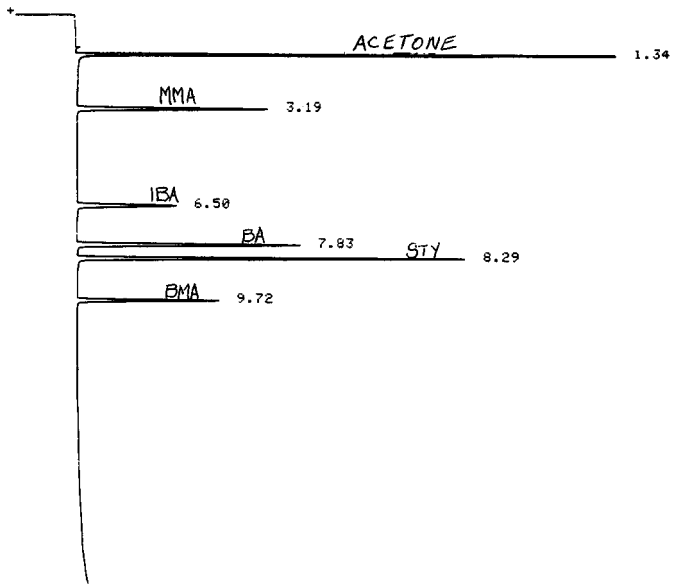

FIG. 1 Typical Chromatogram

column. Using the same conditions as for standardization, record the peaks of all components at attentuation settings that provide maximum peak heights. Use the relative retention times to identify the monomers present. If the specimen has a component eluting at the same retention time as isobutyl acrylate, choose a different internal standard (see Note 1).

10.2 Prepare a dilute solution of the internal standard by weighing to 0.1 mg about 0.05 g of isobutyl acrylate and 5 g of acetone into a septum vial. Take care to minimize losses due to evaporation. Prepare this solution fresh each day that the test method is used.

10.3 Weigh to within 0.1 mg an appropriate amount of sample into a septum vial using Table 2 as a guide to specimen size. Also weigh to within 0.1 mg 50 mg of the dilute solution prepared in 10.2 into the vial. Add about 3 to 5 g of water or acetone. Shake the vials on a wrist action shaker or other suitable device for 15 min.

NOTE 2—The viscosity of a number of latexes increases upon the addition of an organic solvent. If acetone (or another organic solvent) is found to be compatible with the specimen, it should be used as the diluent instead of water. It should be kept in mind that some organic solvents may interfere with the chromatographic separation. A 50:50 water/methanol mixture was also found to work well as a diluent for a number of specimens.

10.4 Inject 0.5 µL of the solution prepared in 10.3 and record the chromatogram using the conditions given in 10.1. Measure the peak areas (Note 3) of the internal standard and relevant monomers, multiplying each area by the appropriate attenuation factor to express the peak areas on a common basis.

NOTE 3—Peak areas may be determined by any method that meets the precision requirements given in Section 12. Electronic integration is recommended for best results.

10.5 Repeat 10.3 and 10.4 and calculate the mean values.

11. Calculations

11.1 Calculate the weight of the internal standard present in the diluted specimen (see 10.3) as follows:

TABLE 2 Suggested Dilutions

NOTE 1—This table is to be used only as a guide. If the monomer concentrations are outside the range given, appropriate adjustments must be made in terms of specimen size, dilution, and amount of internal standard added.

Level of Unreacted Monomer Expected, µg/g	Specimen Size, g	Diluent, g
250	2	3
500	1	4
750	0.7	4.3
1000	0.5	4.5

$$W_4 = (W_5/W_6)W_7 \quad (2)$$

where:

W_4 = weight of internal standard in diluted specimen prepared in 10.3, g,
W_5 = weight of internal standard used to prepare solution in 10.2, g,
W_6 = weight of acetone plus weight of internal standard used to prepare solution in 10.2, g, and
W_7 = weight of the dilute internal standard solution in 10.2 added to the specimen in 10.3, g.

11.2 Calculate the concentration of each monomer present in the latex specimen from the results obtained in 10.5 as follows:

$$C = [(A_3 \times W_4 \times RF)/(W_8 \times A_4)] \times 10^6 \quad (3)$$

where:

A_3 = peak area produced by the monomer,
A_4 = peak area produced by the internal standard,
C = concentration of unreacted monomer, µg/g,
RF = relative response factor for each monomer calculated in 9.2.4,
W_4 = weight of internal standard calculated in 11.1, g, and
W_8 = weight of specimen prepared in 10.3, g.

12. Precision and Bias [4]

12.1 In an interlaboratory study of this test method by five laboratories using four specimens, each containing variable concentrations of four different monomers, the following duplicates, repeatability, and reproducibility coefficients of variation were obtained for each monomer:

	Precision, %		
Monomer	Duplicates	Repeatability (Single Laboratory)	Reproducibility (Between Laboratory)
Methyl methacrylate (MMA)	11.7	34.3	86.2
n-Butyl acrylate (BA)	13.3	21.7	49.2
Butyl methacrylate (BMA)	14.5	33.5	96.5
Styrene (STY)	11.3	30.5	71.5

NOTE 4—Variation in results may be due to the changing composition of the specimens used for the study. This precision statement should only be used as a guide since it only represents the magnitude of variation that is possible, which will vary with time depending on the latex and the particular monomers being determined.

12.2 Bias cannot be determined for this test method.

13. Keywords

13.1 gas chromatography; gas chromatography (capillary column); latex paints; latex vehicles; monomer (unreacted); unreacted monomer content

[4] Supporting data is available from ASTM Headquarters. Request RR: D01-1059.