Designation: D4827 – 03 (Reapproved 2015)

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 D4827; 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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:*[2]

D1193 Specification for Reagent Water

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).

[1] This test method is under the jurisdiction of ASTM Committee D01 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.

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

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 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 D1193.

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.

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.

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.

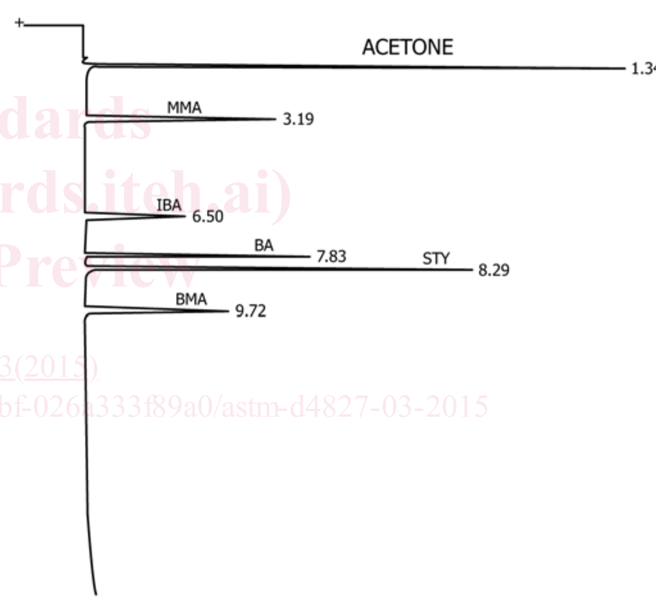

FIG. 1 Typical Chromatogram

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

[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.