



Designation: D 4747 – 02

Standard Test Method for Determining Unreacted Monomer Content of Latexes Using Gas-Liquid Chromatography¹

This standard is issued under the fixed designation D 4747; 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 covers the determination of free 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 $\mu\text{g/g}$, 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 volatile composition of 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 method mostly applicable for in-house quality control, where sampling and analysis conditions can be better controlled.

1.3 The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

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. See Section 7 for specific hazard statements.*

2. Referenced Documents

2.1 ASTM Standards:

D 3980 Practice for Interlaboratory Testing of Paint and Related Materials²

E 260 Practice for Packed Column Gas Chromatography³

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

into a gas chromatographic column containing a packing material coated with 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. An injection port using replaceable glass liners to facilitate periodic removal of accumulated residues is recommended.

5.2 *Column*, 2 by 2-mm inside diameter glass or 6 ft by 1/8-in. outside diameter steel tubing, packed with 10 % by weight of a 2-nitroterephthalic acid derivative of a synthetic polyester wax on 100/120 mesh acid washed, silane treated diatomaceous earth.⁴ A column of 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 $\pm 0.03\%$ of full scale (see Practice E 260).

5.4 *Liquid Charging Devices*, microsyringe, 10- μL capacity or an automatic liquid sampling device.

5.5 *Dropper Pipets*, glass, disposable.

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

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

5.8 *Analytical Balance*, accurate to 0.1 mg.

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 Discontinued—See 1999 Annual Book of ASTM Standards.

³ Annual Book of ASTM Standards, Vol 03.06.

⁴ Columns prepared from the stationary phases and supports have been found suitable for this purpose and are available from scientific supply houses.

TABLE 1 Instrument Conditions

Detector	flame ionization
Air flow	240 mL/min
Hydrogen flow	30 mL/min
Column (suggested)	2 by 2 mm inside diameter glass, packed with 10% of a 2-nitroterephthalic acid derivative of Carbowax 20M on 100/120 mesh acid washed, silane-treated diatomaceous earth.
Carrier gas, flow rate	Helium, 30 mL/min
Temperatures:	
Injection port	250°C
Detector block	250°C
Column	
Initial	80°C
Hold time	4 min
Program rate	8°C/min
Final	200°C, or higher as needed (see 8.1)
Final hold	10 min, or as needed
Injection volume	2 µL

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.⁵ 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 Carrier Gas, helium of 99.995 % or higher purity. High purity nitrogen may also be used.

6.3 Acetone, reagent grade.

6.4 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.

6.5 Monomers of Interest, 99+ % pure.

7. Hazards

7.1 Acrylic and methacrylic monomers are considered hazardous. Precautions should be taken to avoid inhalation and skin or eye contact with these chemicals. 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 30 mL/min and purge the column at ambient temperature for 30 min. Program the column oven from 50 to 220°C at 2°C/min

⁵ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

and maintain at 220°C overnight. In no case should the temperature of the column be allowed to exceed 275°C.

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. 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 of each component expected to be present by injecting small amounts either separately or in known mixtures. Retention times should be determined each day the 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:

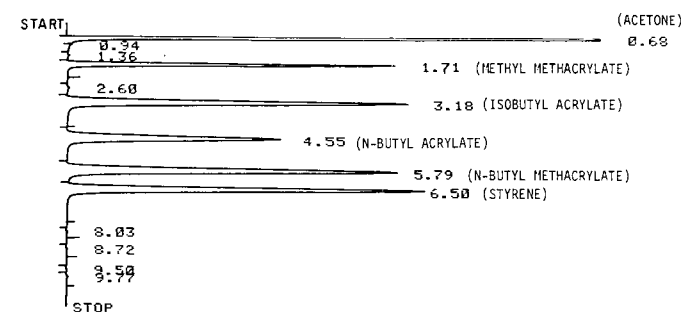
9.2.1 Weigh to 0.1 mg about 0.05 g of isobutyl acrylate and each monomer of interest into a vial (5.6). Weigh approximately 5 g of acetone into the vial and mix well.

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

9.2.3 Inject a 1-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:

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



RT	AREA	AREA %
0.68	4910000	24.005
0.94	33690	0.165
1.36	16450	0.080
1.71	1947000	9.519
2.60	17190	0.084
3.18	3542000	17.317
4.55	2565000	12.540
5.79	3780000	18.481
6.50	3625000	17.723
8.03	1189	0.006
8.72	3328	0.016
9.50	1478	0.007
9.77	11530	0.056

DIL FACTOR: 1.0000 E+ 0

FIG. 1 Typical Chromatogram