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

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.

ε[1] NOTE—Unit of measurement statement added to the Scope Section editorially in May 1997.

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 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 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 Materials[2]

E 260 Practice for Packed Column Gas Chromatography[3]

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 replacable 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 ⅛-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 ±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.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be

[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.

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[2] *Annual Book of ASTM Standards*, Vol 06.01.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[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

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 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 is 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.

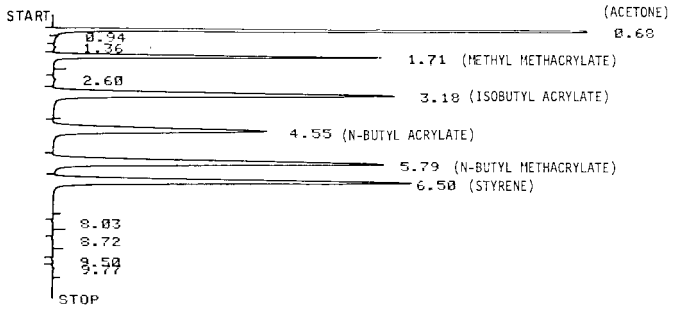
9.2 *Standardization*—Determine in duplicate the relative response of the monomers of interest to the isobutyl acrylate internal standard as follows:

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:



HP RUN # 26
AREA %

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

[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."

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

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 (9.2.1), and
W_s = weight of internal standard (9.2.1).

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 2-µL aliquot into the chromatographic 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 (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 the method is used.

10.3 Weigh to 0.1 mg an appropriate amount of sample into a septum vial using Table 2 as a guide to specimen size. Also weigh to 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.

10.4 Inject 2 µL of the prepared solution (10.3) into the chromatographic column and record the chromatogram using the conditions as in 10.1. Measure the peak areas (Note 3) of the internal standard and relevant monomers, multiplying each area by the appropriate 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 of Section 12. Electronic integration is recommended for best results.

TABLE 2 Suggested Dilutions

NOTE 1—This table shall 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 Free 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

10.5 Repeat procedure in 10.3 through 10.4 and calculate the mean values.

11. Calculations

11.1 The weight of the internal standard present in the diluted specimen (10.3) is calculated as follows:

$$W_4 = (W_5/W_6)W_7 \quad (1)$$

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

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

$$C = [(A_3 \times W_4 \times RF)/(W_8 \times A_4)] \times 10^6 \quad (2)$$

where:
C = concentration of free monomer, µg/g,
A_3 = peak area produced by the monomer,
A_4 = peak area produced by the internal standard,
RF = relative response factor for each monomer (9.2.4),
W_4 = weight of internal standard (11.1), and
W_8 = specimen weight (10.3).

12. Precision and Bias [6]

12.1 *Precision*—In an interlaboratory study of the method by five laboratories using four samples, the within-laboratory coefficient of variation was found to be 16.8 % relative at 11 degrees of freedom and the between-laboratories coefficient of variation was 18.1 % relative at 8 degrees of freedom. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level (see Practice D 3980 and Note 4).

12.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 52 % relative.

12.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 59 % relative.

NOTE 4—Variation in results may be due to the changing composition of the samples used for the study. This precision statement should be used only as a guide, since it represents only 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*—Bias cannot be determined for this test method.

[6] Supporting data are available from ASTM Headquarters. Request RR: D01–1055.

13. Keywords

13.1 acrylic latexes chromatography (subheading gas chromatography); gas chromatography; analysis of monomers; latex paints; latex vehicles; styrene; trace monomers; unreacted monomers in latexes