Designation: D4094 – 07

Standard Test Method for Acid Content of Ethylene-Acrylic Acid Copolymers[1]

This standard is issued under the fixed designation D4094; 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 the acid content of ethylene-acrylic acid (EAA) copolymers containing 2.5 to 25 weight % of acrylic acid.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parenthesis are for information only.

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 hazards statements are given in Section 8.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

IEEE/ASTM SI-10 Standard for Use of the International System of Units (SI): The Modern Metric System

3. Terminology

3.1 Units and symbols used in this test method are those recommended in IEEE/ASTM SI-10. Additional acronyms unique to this test method are defined in the text.

4. Summary of Test Method

4.1 In this test method, a weighed specimen is dissolved in a suitable hot solvent and titrated while hot with standard base to a visual equivalence point.

5. Significance and Use

5.1 EAA copolymers possess unusual chemical and physical properties because they contain free acid groups. Since polymer performance in end-use applications is a function of the amount of copolymerized acrylic acid, it is important that acid contents be determined quantitatively by a suitable method, such as that described herein.

6. Apparatus

6.1 *Balance*, analytical, with precision of 0.0001 g.

6.2 *Buret*, 25-mL, 0.1-mL subdivisions, Class A, polytetrafluoroethylene stopcock.

6.3 *Flask*, Erlenmeyer, 250-mL, female standard-taper joint, with condenser, reflux, matching male standard-taper joint.

6.4 *Stirrer/Hotplate*, magnetic.

6.5 *Stirrer*, magnetic.

6.6 *Stirring Bar*, magnetic, 40 mm (1.5 in.) long, polytetrafluoroethylene-encased.

7. Reagents and Materials

7.1 *Xylene*, reagent-grade.

7.2 *n-Butanol*, reagent-grade.

7.3 *Mixed Solvent*—Mix 3 volumes of xylene with 1 volume of *n*-butanol.

7.4 *Tetrabutylammonium Hydroxide (TBAH)*, solution in methanol, in 1 M concentration.

7.5 *Standard Base* (0.1 *N*)—Mix 1 volume of 1 *M* TBAH solution with 9 volumes of mixed solvent.

7.6 *Benzoic Acid*, primary standard.

7.7 *Thymol Blue (TB) Indicator (Formula Weight of 466.58)*—Prepare 0.5 % solution by weighing 0.125 g of reagent-grade TB (acid form) into a small beaker, adding 25 mL of mixed solvent, and adding 0.268 milliequivalents of 0.1 *N* base to form a clear, red-orange solution. Transfer to a glass-dropping bottle.

8. Hazards

8.1 Solvents and titrants are odorous and flammable and can cause burns to skin, eyes, and lungs. Wear proper body and eye protection when handling these materials and conduct all operations in a fume hood from which all possible sources of ignition have been removed.

[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 D20.70.11).

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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.

***A Summary of Changes section appears at the end of this standard.**

9. Test Specimen

9.1 Analyze samples in the form as received. Pellets or powder are suitable.

9.2 Analyze samples in duplicate.

10. Standardization

10.1 Weigh out 0.2 to 0.3 g of benzoic acid and record its weight to 0.0001 g. Transfer to a flask containing a stirring bar, add 100 mL of mixed solvent, and stir at room temperature until dissolved.

10.2 Add 6 drops of TB indicator and titrate with 0.1 *N* TBAH solution to the yellow-to-green-to-blue color change. Record the titrant volume, V_1, to 0.01 mL.

10.3 Make a second standardization by repeating 10.1 and 10.2.

10.4 Determine a solvent blank by following 10.1 and 10.2 except omit the benzoic acid. Record the value, V_2, to 0.01 mL.

10.5 Calculate titrant normality for each replicate determination as follows:

$$N = \frac{(W/E)}{(V_1 - V_2)} \quad (1)$$

where:

N = normality, meq/mL,
W = benzoic acid, g,
V = titrant for benzoic acid, mL,
V = titrant for blank, mL, and
E = benzoic acid factor = 0.1221 g/meq.

10.6 Average the two values for titrant normality and record to 0.0001 meq/mL.

10.7 Since solvent loss from titrant can occur readily, restandardize weekly.

10.8 Whenever new batches of solvent are ready to use, redetermine the solvent blank.

11. Conditioning

11.1 Samples need not be conditioned.

11.2 Conduct all titrations at the standard laboratory temperature of 23 ± 2°C (73.4 ± 3.6°F).

12. Procedure

12.1 Weigh out a specimen to a weight is within ± 10 % of the applicable nominal weights given below and record to 0.0001 g.

Expected % Acid	Specimen Weight, g
<8	2.0
8–25	0.65

NOTE 2—Below 8 % acid, it may be possible to achieve greater precision and better-defined end points by using a specimen weighing more than 2 g, provided the specimen dissolves completely and stays in solution during titration.

NOTE 3—At 8 % acid and above, increased precision can be achieved by adjusting specimen weight within the 0.65 to 2.0-g limits, according to expected acid content.

12.2 Transfer the weighed specimen to a flask containing a stirring bar and add 100 mL of mixed solvent. Connect the flask to a condenser and begin stirring and rapid heating. When boiling begins, reduce the heat to produce a steady moderate stream of reflux from the condenser tip. Reflux until specimen is dissolved (for 30 min, or longer if necessary).

TABLE 1 Acrylic Acid Content

Materials	Average	S_r	S_R	r	R
6.6 %	6.6833	0.0370	0.0769	0.1035	0.2153
9.5 %	9.4467	0.1252	0.1477	0.3505	0.4136
20.1 %	20.2344	0.1044	0.3083	0.2923	0.8632
20.2 %	20.4150	0.1772	0.3549	0.4961	0.9937

12.3 Stop stirring and heating. Transfer flask containing dissolved specimen to an unheated stirrer, begin stirring, add 6 drops of TB indicator, and titrate while hot from a yellow color through an intermediate green to a final blue color which persists for 30 s. Record the final titrant volume, V_3, to 0.01 mL.

12.4 Analyze a second specimen by following 12.1-12.3 above.

13. Calculation

13.1 Calculate acid content for each specimen as follows:

$$A = \frac{(V_3 - V_2)\,(N)\,(E)}{W} \times 100 \quad (2)$$

where:

A = acid content as acrylic acid, weight %,
N = titrant normality, meq/mL,
W = specimen weight, g,
V_3 = base for specimen, mL,
V_2 = base for solvent blank, mL, and
E = factor for acrylic acid = 0.07206 g/meq.

13.2 Average the two values for *A*, for reporting as the acrylic acid content of the sample.

14. Report

14.1 Sample identification.

14.2 Acid content, as acrylic acid, weight %, to three significant figures.

15. Precision and Bias [3]

15.1 *Precision*:

15.1.1 Table 1 is based on a round-robin test conducted in 2000, in accordance with Practice E691, involving four materials, tested by six laboratories, in the shortest possible time, typically 1 to 2 days. Each test result is the average of three individual determinations. This study has been submitted to ASTM to be filed as a research report.

15.1.2 The repeatability standard deviation and the reproducibility standard deviation are shown in Table 1.

15.1.3 S_r, or the repeatability, is the within-laboratory standard deviation of the average; r is 2.8 times S_r and is the 95 % confidence level for the data. Repeatability is a measure of the precision within-laboratory, obtained by a single operator using the same equipment to obtain the result on the same day.

15.1.4 S_R, or the reproducibility, is the between-laboratory standard deviation of the average; R is 2.8 times S_R and is the 95 % confidence level for the data. Reproducibility is a

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1216.

measure of the between-laboratory standard deviation obtained by different operators on different equipment on different days.

15.2 *Bias*—No information can be presented on the bias of this test method because no material having an accepted reference value is available.

16. Keywords

16.1 acid content; ethylene-acrylic acid copolymers; titration

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D4094 – 00) that may impact the use of this standard. (November 1, 2007)

(*1*) Removed references to ASTM D1898.
(*2*) Changed balance requirements from "accuracy" to "precision."
(*3*) Removed use of benzene as alternative solvent.