Designation: D 4415 – 05

Standard Test Methods for Determination of Dimer in Acrylic Acid[1]

This standard is issued under the fixed designation D 4415; 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 *Test Method A*—Describes a chemical (titrametric) procedure for the determination of acrylic acid dimer in acrylic acid. This procedure may be applicable to other unsaturated organic acids.

1.2 *Test Method B*—Describes a gas chromatographic procedure for the determination of acrylic acid dimer in acrylic acid. Other impurities may also be determined simultaneously.

1.3 The following applies to all specified limits in this standard; for purposes of determining conformance with this standard, an observed value or a calculated value shall be rounded off "to the nearest unit" in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

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

1.5 *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 8.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 268 Guide for Sampling and Testing Volatile Solvents and Chemical Intermediates for Use in Paint and Related Coatings and Materials

D 1193 Specification for Reagent Water

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis

3. Summary of Test Methods

3.1 *Test Method A*—The acid specimen is neutralized and the dimer (Acrylic acid dimer, $CH_2 = CH - COO - CH_2- CH_2-COOH$) determined by saponification and titration. Purity of the acid can also be determined by carrying out the first neutralization, quantitatively, but this is not covered in this method.

3.2 *Test Method B*—An internal standard, *n*-dodecane, is added to the sample and then introduced into a gas chromatograph containing an appropriate capillary column for separation. The separated components are measured in the column effluent by a detector and recorded as a chromatogram. The peak areas are measured and the concentration of the components of interest are calculated by reference to the internal standard.

4. Significance and Use

4.1 These test methods provide a measurement of the dimer content of acrylic acid. The results of this measurement can be used for specification purposes but must be on an as-shipped basis since the dimer content will vary with the age and the storage temperature of the acrylic acid.

5. Interferences

5.1 *Test Method A*—If present, ester impurities present in the acrylic acid will be determined as dimer.

5.2 *Test Method B*—Impurities having the same or similar retention times as the acrylic acid on the column used may cause abnormally high results.

6. Apparatus

6.1 *Test Method A*:

6.1.1 *Pressure Bottle*, 200 to 350-mL capacity, with lever-type closure and made of heat-resistant glass.

6.1.2 *Container for Pressure Bottle*— A suitable safety device to contain the pressure bottle. A metal container with a hinged top and perforated bottom, a strong synthetic fabric or canvas bag, or a safety shield may be used.

6.1.3 *Open-Top Vial*, 3 to 5-mL capacity, of such diameter to fit the pressure bottle.

6.1.4 *Buret*, 100-mL capacity.

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[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 D01.35 on Solvents, Plasticizers and Chemical Intermediates.

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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.**

6.1.5 *Buret*, 50-mL capacity, calibrated.

6.1.6 *Boiling Water Bath*.

6.2 *Test Method B*:

6.2.1 *Gas Chromatograph*—Any gas chromatograph having a flame ionization detector (FID) or any other detector, provided the system has sufficient sensitivity and stability to obtain, for a 0.01 % impurity in the specimen, a recorder deflection of at least 20 mm at a signal to noise ratio of at least 5 to 1.

6.2.1.1 The chromatograph should be capable of temperature programming.

6.2.1.2 The injection port or system should be one suitable for the capillary column used. Split injection techniques should be used.

6.2.2 *Column*—A 30 to 50-m long by 0.32-mm inside diameter fused silica capillary column with a 0.2 to 0.3-μm film of a bonded, esterified polyethylene glycol phase. Any other column, capable of providing the necessary separation and precision, may be used.

6.2.3 *Sample Introduction System*—Any system capable of introducing a representative specimen into the column. Microlitre syringes and autosampler systems have been used successfully.

6.2.4 *Recorder*—A recording potentiometer with a full-scale deflection of 1 mV, full scale response time of 1 s or less, and sufficient sensitivity and stability to meet the requirements of 6.2.1. A recording integrator or computerized data station may also be used.

6.2.5 *Gas Purifiers*—The use of a gas purifier, to remove moisture and other contaminants from the carrier gas, and an oxygen trap or oxygen removal system is strongly recommended to prolong column life.

6.2.6 *Volumetric Flasks*, 100-mL capacity.

7. Reagents and Materials

7.1 *Test Method A*:

7.1.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

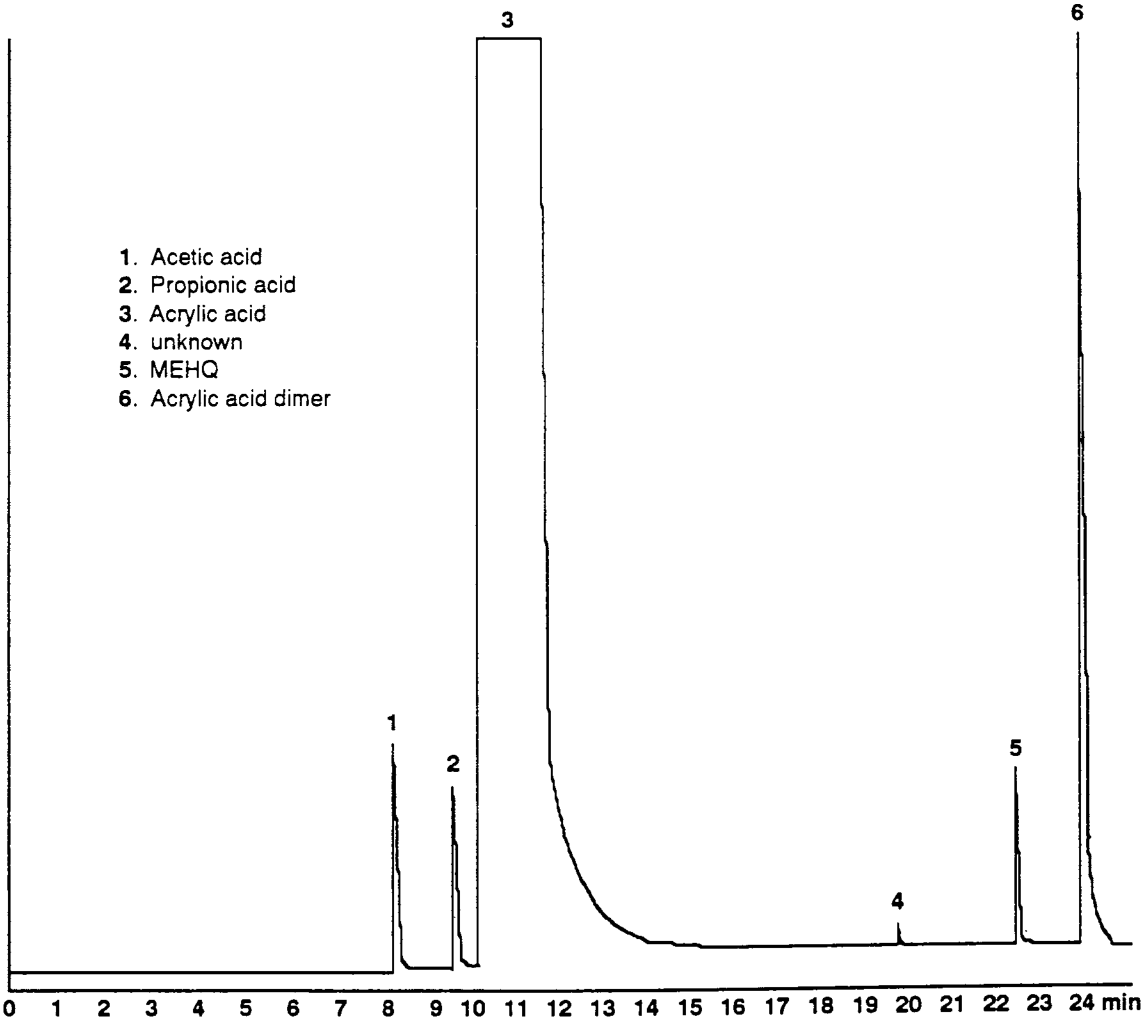

FIG. 1 Typical Chromatogram of Acrylic Acid

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.

7.1.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type IV of Specification D 1193.

7.1.3 *Methanol* (99 %).

7.1.4 *Phenolphthalein Indicator (10-g/L solution)*—Dissolve 1 g of phenolphthalein in methanol and dilute to 100 mL. Titrate this solution with 0.1 N sodium hydroxide (NaOH) solution to a faint pink coloration.

7.1.5 *Sodium Hydroxide, Standard Solution* (0.5 *N*)—Prepare and standardize in accordance with Practice E 200.

7.1.6 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Prepare in accordance with Practice E 200 and standardize to four significant figures.

7.1.7 *Sulfuric Acid* (H_2SO_2)*, Standard Solution* (0.1 *N*)—Prepare in accordance with Practice E 200 and standardize to four significant figures.

7.2 *Test Method B*:

7.2.1 *n-Dodecane* (99 %).

7.2.2 *Carrier Gas*—Helium, 99.99 % pure.

7.2.3 *Flame Gas*—Hydrogen, 99.99 % pure.

7.2.4 *Flame Support Gas*—Air, hydrocarbon-free, sometimes know as “zero” grade is required.

8. Hazards

8.1 Acrylic acid is a corrosive liquid and will polymerize easily, especially on heating or in bright light. Take samples in brown bottles and store in the dark or subdued light. It has an acrid, repulsive odor and may act as a strong irritant. Avoid eye and skin contact and inhalation of vapors. For further information, see supplier’s Material Safety Data Sheet.

8.2 Glacial acrylic acid freezes at 12.3°C (54°F) and dispersion of the inhibitor in frozen acid is poor. Take care to thaw slowly. Frequent mixing with complete thawing should be accomplished before removing any of the contents.

9. Preparation of Apparatus

9.1 *Test Method B*:

9.1.1 *Column Conditioning*—If column has not been previously conditioned, connect column to the injection port of the gas chromatograph but do not connect to the detector. Set up the conditions shown in Table 1, except for the column temperature. This should be held at ambient for about 15 min and then programmed to 220°C and held there for 16 to 24 h. Do not operate the detector, nor have any gas flowing to the detector during this operation.

TABLE 1 Instrument Conditions Found Satisfactory for Measuring Dimer and Other Impurities in Acrylic Acid (see Fig. 1)

Column	30 m by 0.32 mm ID fused silica capillary
Stationary phase	Bonded, esterified polyethylene glycol[9]
Column oven	100°C, held for 5 min, then programmed to 220°C at 5°C/min and held until analysis is complete
Injection port	Split injector; split ratio range 15:1 to 60:1; 250°C
Detector	FID; 25 mL/min helium makeup gas; 300°C
Carrier gas	Helium; flow rate 3.5 to 4.3 mL/min (72 to 90 cm/s)
Specimen size	1 µL

9.1.2 Connect column to the detector and establish the conditions shown in Table 1.

10. Procedure

10.1 *Test Method A*:

10.1.1 Analyze all samples and blanks in duplicate using the heat-resistant pressure bottles.

10.1.2 Into each pressure bottle, introduce 100 mL of ice.

10.1.3 Into each of the two bottles, introduce 2 mL of the acid being analyzed and weigh to 0.1 mg.

10.1.4 Add 6 to 8 drops of the phenolphthalein indicator solution to the bottles and titrate to a pink end point with 0.5 *N* NaOH solution.

10.1.5 To the bottles in the procedure in 10.1.4, carefully introduce 40 mL of 0.1 *N* NaOH solution by means of a 50-mL calibrated buret. Stopper the bottles and flasks after the addition of the reagent.

10.1.6 To the bottles reserved as blanks, melt the ice, add 6 to 8 drops of the phenolphthalein indicator solution to the bottles and titrate to a pink end point. Then carefully introduce 40 mL of 0.1 *N* NaOH solution by means of a 50-mL calibrated buret. Stopper the bottles and flasks after the addition of the reagent.

10.1.7 Enclose each bottle securely in a suitable safety device to restrain fragments of glass should the pressure bottle rupture. Place the specimens and blanks as close together as possible in a boiling water bath maintained at at least 98°C for 30 min. Maintain sufficient water in the bath to just cover the liquid in the bottles. Remove the bottles from the bath and allow to cool to room temperature. When the bottles have cooled, remove them from the safety devices. Uncap them carefully and wash the caps with several millilitres of water, catching the washings in the bottles.

10.1.8 Add 6 to 8 drops of the phenolphthalein indicator to each bottle and titrate with 0.1 *N* H_2SO_4 just to the disappearance of the pink color.

10.2 *Test Method B*:

10.2.1 *Specific Gravity*—Determine the apparent specific gravity by any convenient method that is accurate to the third decimal place, the temperature of both specimen and water being 20°C. See Guide D 268 or Test Method D 4052.

10.2.2 Analyze all samples in duplicate.

10.2.3 Weigh 200 mg of internal standard, *n*-dodecane, to 0.1 mg into a 100-mL volumetric flask.

10.2.4 Dilute to mark with acrylic acid specimen, stopper and mix well. Make sure that solution is clear.

10.2.5 Inject 1 µL of sample into gas chromatograph injection port and start temperature program.

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[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.

11. Calculation

11.1 *Test Method A*:

11.1.1 Calculate the weight percent of acrylic acid dimer, D, as follows:

$$D = \frac{(B - V)(N \times F)}{S} \times 100 \quad (1)$$

where:

B = 0.1 N H_2SO_4 required for titration of the blanks (10.1.8), mL,

V = 0.1 N H_2SO_4 required for titration of the specimens, mL,

N = normality of the H_2SO_4 solution,

F = factor (0.144) for acrylic acid dimer. If the method is used to analyze for dimer in other acids, for example, methacrylic acid, use the proper factor, the milliequivalent weight of the acid times 2, and

S = specimen weight (10.1.3), g.

11.2 *Test Method B*:

11.2.1 Calculate the weight percent of acrylic acid dimer, D, as follows:

$$D = \frac{A_D \times R_{FD} \times C_{IS}}{A_{IS} \times \text{sp gr}} \quad (2)$$

where:

A_D = peak area for dimer,

R_{FD} = response factor for dimer relative to the internal standard (see Appendix X1),

A_{IS} = peak area for internal standard,

C_{IS} = concentration of internal standard (% by weight), and

sp gr = apparent specific gravity of the specimen at 20°C.

12. Precision and Bias

12.1 *Test Method A*:

12.1.1 The precision statements are based upon an interlaboratory study in which two analysts in each of eight different laboratories analyzed one sample of acrylic acid dimer, 3.0 to 4.0 % and one sample of acrylic acid dimer, 0.1 to 1.5 % in duplicate on two different days. The following criteria should be used for judging the acceptability of the results:

12.1.2 *Repeatability*—The standard deviation of the results (each the mean of duplicates), obtained by the same analyst on different days has been estimated to be 0.094 at 16 df for the 3.0 to 4.0 % dimer, and 0.052 at 14 df for the 0.1 to 1.5 % dimer. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.283 for the 3.0 to 4.0 % dimer and 0.157 for the 0.1 to 1.5 % dimer.

12.1.3 *Reproducibility (Multilaboratory)*— Not attainable due to instability of the product that is affected by time and temperature.

12.1.4 *Checking Limits for Duplicates*— Duplicate results that agree within 0.18 for the 3.0 to 4.0 % dimer and 0.13 for the 0.1 to 1.5 % dimer are acceptable for averaging.

12.2 *Test Method B*:

12.2.1 Precision and bias have not been determined for this test method. This will be the subject of a round robin testing in the near future.

13. Keywords

13.1 acrylic acid; dimer; gas chromatograph; titrametric

APPENDIX

(Nonmandatory Information)

X1. RESPONSE FACTORS

X1.1 Determination of Response Factors

X1.1.1 Response factors are normally determined as a calibration step by comparing the area of the component of interest to the area of the internal standard using a sample with known concentrations of each. In the case of acrylic acid dimer, pure standards are not available to make the comparison. In this case, the use of published response factors for a similar compound, octanoic acid ($R_F = 1.54$), may be used.

X1.2 Published Response Factors

X1.2.1 Table X1.1 shows a list of response factors calculated from published relative responses for other compounds possibly present as impurities in acrylic acid and may be used to estimate the concentrations of these compounds. The response factor is the reciprocal of the relative response.

TABLE X1.1 Response Factors[A]

Compound	Relative Response	Response Factor
Acetic acid	0.24	4.17
Propionic acid	0.42	2.50
Octanoic acid	0.65	1.54
n-dodecane	1.00	1.00

[A] Dietz, W. A., *Journal of Gas Chromatography*, Vol 5, No. 68, 1967.

SUMMARY OF CHANGES

Committee D01.35 has identified the location of selected changes to this standard since the last issue (D 4415 – 91 (2000)$^{\epsilon 1}$) that may impact the use of this standard.

(1) Added reference to Practice E 29 in Scope section.

(2) Added Practice E 29 to list of Referenced Documents.

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