Designation: D 3362 – 05

Standard Test Method for
Purity of Acrylate Esters by Gas Chromatography[1]

1. Scope*

1.1 This test method covers the determination of the purity of acrylate, ethyl acrylate, *n*-butyl acrylate, and 2-ethylhexyl acrylate by gas chromatography and, in addition, provides a means for measuring certain impurities such as alcohols and other esters. Water and acidity are measured by other appropriate ASTM procedures and the results are used to normalize the chromatographic values.

1.2 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.

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

1.4 For hazard information and guidance, see the supplier's Material Safety Data Sheet.

1.5 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 1364 Test Method for Water in Volatile Solvents (Fischer Reagent Titration Method)

D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products

D 2593 Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography

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

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals

E 260 Practice for Packed Column Gas Chromatography

3. Summary of Method

3.1 A representative specimen is introduced into a gas chromatographic[3] column. The acrylate ester is separated from impurities such as alcohols, other esters, ethers, and several unidentified compounds as the components are transported through the column by an inert carrier gas. The separated components are measured in the effluent by a detector and recorded as a chromatogram. The chromatogram is interpreted by applying component attenuation and detector response factors to the peak areas and the relative concentrations are determined by relating the individual peak responses to the total peak response. Water and acidity are measured by the procedures listed in Test Methods D 1364 and D 1613 and the results are used to normalize the values obtained by gas chromatography.

4. Significance and Use

4.1 This test method provides a measurement of commonly found impurities in commercially available methyl acrylate, ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate. The measurement of these impurities and the results thereof can either individually or when totaled and subtracted from 100 (assay) be used for specification purposes.

5. Apparatus

5.1 *Chromatograph*—Any gas chromatograph having either a thermal conductivity or flame ionization detector, provided the system has sufficient sensitivity and stability to obtain for 0.01 weight % of impurity a recorder deflection of at least 2 mm at a signal-to-noise ratio of at least 5 to 1. The specimen size used in judging the sensitivity must be such that the column is not overloaded.

5.2 *Column*, 6 m (20 ft) of 6.4-mm (¼ in.).

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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.

[3] Messner, A. E., et al, *Analytical Chemistry*, ANCHA, Vol 31, 1959, pp. 230–233, Dietz, W. A., *Journal of Gas Chromatography*, JGCRA, Vol 5, No. 2, February 1967, pp. 68–71.

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

5.3 *Specimen Introduction System*—Any system capable of introducing a representative specimen into the column. Microlitre syringes have been used successfully.

5.4 *Recorder*—A recording potentiometer, or electronic meter with a full-scale deflection of 1 mV, full-scale response time of 2 s or less, and sufficient sensitivity and stability to meet the requirements of 5.1.

6. Reagents and Materials

6.1 *Carrier Gas*, appropriate to the type of detector used. Helium or hydrogen may be employed with thermal conductivity detectors, and nitrogen, helium, or argon with flame ionization detectors. The minimum purity of the carrier gas used should be 99.95 mol %.

6.1.1 **Warning**—If hydrogen is used, take special safety precautions to ensure that the system is free of leaks and that the effluent is vented properly.

6.2 *Column Materials*:

6.2.1 *Liquid Phase*— lubricant.[4]

6.2.2 *Solid Support*—synthetic polyester wax,[5] acid-washed, 45 to 60 mesh size. Only acid-washed material performs satisfactorily.

6.2.3 *Solvent*—Methylene chloride, reagent grade.

6.2.4 *Tubing Material*—Copper, stainless steel, and aluminum have been found satisfactory for column tubing. The tubing must be nonreactive with the substrate, sample, and carrier gas.

6.3 *Standards for Calibration and Identification*—Standard samples of all components present are needed for identification by retention time, and for calibration for quantitative measurements.

NOTE 1—Most of the compounds needed can be obtained from chemical supply houses. It may be necessary to contact the acrylate supplier for some of the minor components listed in Table 1.

7. Safety Precautions

7.1 Acrylate esters are skin and respiratory irritants. Prolonged exposure to the eyes may cause severe damage. Violent uncontrolled polymerization may occur under certain conditions. Methyl acrylate and ethyl acrylate are flammable liquids. Butyl acrylate and 2-ethyhexyl acrylate are combustible liquids. Consult supplier's Material Safety Data Sheet for specific hazard information.

8. Preparation of Apparatus

8.1 *Column Packing*—The amounts of liquid phase and solid support should be such that the final packing material contains 20 weight % liquid phase.

8.2 *Column Preparation*—The method used to pack the column is not critical, provided that the finished column produces the required separation of all of the components to be determined. The finished column may be obtained from most chromatography supply houses.

NOTE 2—Useful information on column preparation may be found in Test Method D 2593 and Practice E 260.

TABLE 1 Instrument Conditions and Relative Retention Times

	Methyl Acrylate	Ethyl Acrylate	*n*-Butyl Acrylate	2-Ethylhexyl Acrylate
Temperature, °C:				
Column, isothermal	110	100	140	195
Injection port	180	200	200	200
Detector block	240	260	260	300
Carrier gas:	helium	helium	helium	helium
Flow rate, mL/min^A	80	60	55	100
Typical retention time, min	9.6	17.7	19.4	20.1
Relative retention times (major component = 1.00)				
Methanol	0.61			
Methyl acetate	0.64			
Methyl propionate	0.95			
Methyl acrylate	1.00			
Ethyl acrylate	1.45			
Methyl methacrylate	1.65			
Ethanol		0.56		
Ethyl acetate		0.60		
Ethyl propionate		0.92		
Ethyl acrylate		1.00		
Isopropyl acrylate		1.13		
Isobutyl acetate and isobutanol			0.52	
Dibutyl ether			0.57	
n-Butyl acetate and *n*-butanol			0.63	
Isobutyl propionate			0.71	
Isobutyl acrylate			0.78	
n-Butyl propionate			0.91	
n-Butyl acrylate			1.00	
Unidentified			1.31	
Butyl 2-ethylhexyl ether				0.56
2-Ethylhexyl acetate				0.68
2-Ethylhexanol				0.73
2-Ethyl-4-methylpentyl acrylate				0.79
2-Ethylhexyl propionate and *n*-octanol				0.89
2-Ethylhexyl acrylate				1.00
Di(2-ethylhexyl)-ether				1.54

^{A} Adjust the carrier gas so that the major component will elute at approximately the time shown.

8.3 *Chromatograph*—Install the column in the chromatograph 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 recorder baseline.

9. Calibration and Standardization

9.1 Using the information in Table 1 as a guide, select the conditions of column temperature and carrier gas flow that will give the necessary resolution of the components. Determine the retention time of each component by injecting small amounts either separately or in known mixtures. Relative component retention times along with the typical retention times for methyl acrylate, ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate are given in Table 1.

9.2 *Standardization*—The area under each peak of the chromatogram is considered a quantitative measure of the corresponding compound. The relative area is proportional to concentration if the detector responds equally to all the sample components. When flame ionization detectors are used the response to different components is generally significantly different. Differences in detector response may be corrected by use of relative response factors obtained by injecting and

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[4] Liquid phase is now available from reputable chromatographic suppliers.

[5] Support packings are now available from reputable chromatographic suppliers.

measuring the response to pure (99 % weight minimum) compounds or known blends. When thermal conductivity detectors are used for the analysis of high purity acrylate esters, the difference between area percent and weight percent is within the precision of the method.

NOTE 3—Data on thermal conductivity and flame ionization detector responses may be found in the literature (see footnote 6).

10. Procedure

10.1 Introduce a representative specimen into the chromatograph, using sufficient specimen to ensure a minimum of 10 % recorder deflection for a 0.1 % concentration of impurity at the most sensitive setting of the instrument.

10.2 Using the same conditions as for component identification and standardization, record the peaks of all components at attenuation settings that provide maximum peak heights.

11. Calculation

11.1 Measure the area of all peaks (Note 4) and multiply each area by the appropriate attenuation factor to express the peak areas on a common basis. If a flame ionization detector was used, apply the appropriate detector response factors to correct for the difference in response to the components. Calculate the weight percent composition by dividing the individual corrected component areas by the total corrected area. Make corrections to account for water and acidity present, as determined by the ASTM procedures given in 2.1.

NOTE 4—Peak areas may be determined by any method that meets the precision limits given in Section 13. Electronic integration of peak areas was employed to obtain the results used to establish the precision of this method.

11.2 Calculate the weight percent of each component as follows:

$$\text{Weight } \% = (A/B) \times (100 - C)$$

where:

A = corrected peak response,
B = sum of corrected peak responses, and
C = sum of water and acidity.

12. Report

12.1 Report the weight percent purity of the acrylate being analyzed, and the weight percent levels of any impurities of interest to the nearest 0.01 % absolute. Duplicate runs that agree within 0.07 % absolute are acceptable for averaging (95 % confidence level).

13. Precision and Bias

13.1 The precision statements are based upon an interlaboratory study in which one operator in each of seven laboratories analyzed one sample each of commercial ethyl acrylate and 2-ethylhexyl acrylate in duplicate on two different days. The purity of the materials was 98.9 % for ethyl acrylate and 98.4 % for 2-ethylhexyl acrylate. The results were analyzed in accordance with Practice E 180. The within-laboratory and between-laboratories standard deviations were found to be as follows:

	Within-Laboratories	Between-Laboratories
Ethyl acrylate	0.025	0.051
2-Ethylhexyl acrylate	0.014	0.096
Degrees of freedom	7	6

Based upon these standard deviations which were pooled, the following criteria should be used for judging the acceptability of results at the 95 % confidence level for acrylate esters having a purity of 99 to 100 %:

13.1.1 *Repeatability*—Two results, each the mean of duplicates, obtained by the same operator on different days should be considered suspect if they differ by more than 0.06 % absolute.

13.1.2 *Reproducibility*—Two results, each the mean of duplicates, obtained by operators in different laboratories should be considered suspect if they differ by more than 0.27 % absolute.

13.2 *Bias*—The bias of this test method has not been determined.

14. Keywords

14.1 acrylate esters; acrylates; ethyl acrylate; gas chromatography analysis;*n*–butyl acrylate; methyl acrylate; purity;2–ethylhexyl acrylate

SUMMARY OF CHANGES

Committee D01.35 has identified the location of selected changes to this standard since the last issue (D 3362 – 93 (2000)) 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.
(3) Removed reference to calculation (1) in 11.2.

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