Designation: D3362 – 05

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

This standard is issued under the fixed designation D3362; 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 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 E29.

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]

D1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)

D1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products

D2593 Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals

E260 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 D1364 and D1613 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.).

[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.

Current edition approved May 15, 2005. Published July 2005. Originally approved in 1974. Last previous edition approved in 2000 as D3362 – 93 (2000). DOI: 10.1520/D3362-05.

[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 D2593 and Practice E260.

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

[4] Liquid phase is now available from reputable chromatographic suppliers.
[5] Support packings are now available from reputable chromatographic suppliers.