



Designation: D 3545 – 02

## Standard Test Method for Alcohol Content and Purity of Acetate Esters by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 3545; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope

1.1 This test method covers the determination by gas chromatography of the ester content and the corresponding alcohol content of acetate esters. This test method has been applied to ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and 2-ethoxyethyl acetates.

1.2 Water, and in some cases acetic acid, cannot be determined by this test method and must be measured by other appropriate ASTM procedures and the results used to normalize the chromatographic value.

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.*

1.4 For specific hazard information and guidance, see the supplier's Material Safety Data Sheet for material listed in this specification.

### 2. Referenced Documents

- 2.1 *ASTM Standards:*  
D 1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)<sup>2</sup>  
D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products<sup>2</sup>  
D 2593 Test Method for Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography<sup>3</sup>  
E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>4</sup>

<sup>1</sup> 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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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 06.04.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 15.05.

E 260 Practice for Packed Column Gas Chromatography<sup>5</sup>

### 3. Summary of Test Method

3.1 A representative specimen is introduced into a gas-liquid partition column. The acetate is separated from impurities such as alcohols, other esters, ethers, and several unidentified compounds while 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 Test Methods D 1364 and D 1613, respectively, and the results are used to normalize the values obtained by gas chromatography.

### 4. Significance and Use

4.1 This test method is useful for identifying and for determining the quantity of various impurities in acetate esters.

4.2 Total purity of the acetate esters must be determined by use of other appropriate ASTM procedures with this test method.

### 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 % of the parent alcohol a recorder deflection of at least 20 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, which would result in peak broadening, loss of resolution, shifting retention times and formation of leading peaks. Volumes of 5  $\mu$ L with thermal conductivity and 1 to 2  $\mu$ L with flame ionization detectors have been found acceptable.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 03.06.

5.1.1 The injection port of the chromatograph must have a volume of at least 1.2 mL to provide for proper vaporization of the material. The use of a smaller injection port or on-column injection has been found to cause peak broadening and tailing.

5.2 *Column*—A 3-m length of 6.4-mm outside diameter aluminum or stainless steel tubing packed with 80 to 100-mesh Chromosorb G-HP<sup>6,7</sup> that has been coated with 9.05 % Dow Corning QF-1<sup>8</sup> silicone and 0.45 % nonylphenoxypoly(ethyleneoxy)ethanol(CAS # 9016-45-9), HLB = 19.0 has been found suitable.<sup>9</sup> Any column, packed or capillary, or any packing material capable of resolving one acetate ester from any other esters and from any impurities that may be present and giving equivalent or superior performance may be used.

5.3 *Recorder*—A recording potentiometer with a full-scale deflection of 1 mV. Full-scale response time should be 2 s or less with sufficient sensitivity and stability to meet the requirements of 5.1.

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

## 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 If hydrogen is used special safety precautions must be taken 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*, Dow Corning QF-1/FS 1265<sup>10</sup> silicone and nonylphenoxypoly(ethyleneoxy)ethanol(CAS # 9016-45-9), HLB = 19.<sup>9</sup>

6.2.2 *Solid Support*, Chromosorb G-HP,<sup>7</sup> 80 to 100 mesh size.

6.2.3 *Solvents*—Methylene chloride and acetone, reagent grade.

6.2.4 *Tubing Material*—Stainless steel and aluminum have been found satisfactory for column tubing. The tubing must be nonreactive with the substrate, sample, and carrier gas and must be of uniform internal diameter.

6.3 *Standards for Calibration and Identification*—Standard samples of all components present are needed for identification

<sup>6</sup> A registered trademark of Manville Products Corp., Lompoc, CA 93436, has been found suitable for this purpose.

<sup>7</sup> The sole source of supply for this material known to the committee at this time is Manville Products Corp., Lompoc, CA 93436. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee which you may attend.

<sup>8</sup> Silicoups QF-1/FS 1265 (1000), a product of Dow-Corning Corp., Midland, MI 48640, has been found suitable for this purpose.

<sup>9</sup> A registered trademark of GAF Corp., Dyestuff and Chemical Div., 140 W. 51st St., New York, NY 10020 has been found suitable for this purpose.

<sup>10</sup> The sole source of supply for this material known to the committee at this time is Dow-Corning Corp., Midland, MI 48640. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee which you may attend.

by retention time and for calibration for quantitative measurements. Most can be obtained from chemical supply houses.

## 7. Preparation of Apparatus

7.1 *Column Packing Preparation*—Place 100 g of Chromosorb G-HP,<sup>6</sup> 80 to 100 mesh, in a large evaporating dish. Dissolve 10 g of Dow Corning QF-1/FS 1265<sup>8</sup> silicone in 50 mL of acetone and add to the solid support. Add sufficient acetone to wet and cover the solid support. Evaporate the acetone in a fume hood with gentle stirring and under a gentle stream of nitrogen. Dissolve 0.5 g of nonylphenoxypoly(ethyleneoxy)ethanol(CAS # 9016-45-9), HLB = 19.0<sup>9</sup> in 50 mL of methylene chloride and add it to the packing material. Add sufficient methylene chloride to wet and cover the packing. Evaporate the methylene chloride with gentle stirring under a gentle stream of nitrogen. Commercially available columns or packings, or both, are available from several chromatography supply sources.

7.2 *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. Commercially available columns or packings, or both, are available from several chromatography supply sources.

7.3 *Chromatograph*—Install the column in the chromatograph. Use the information in Table 1 as a guide to establish the conditions of column temperature and carrier gas flow that give the necessary resolution of the components in the product being analyzed. Allow sufficient time for the instrument to reach equilibrium as indicated by a stable recorder baseline. Control the detector temperature constant to within 1°C without thermostat cycling, which causes an uneven baseline. Adjust the carrier-gas flow rate to a constant value.

NOTE 1—Useful information on column preparation may be found in Test Method D 2593 and Practice E 260.

## 8. Calibration and Standardization

8.1 *Identification*—Determine the retention time of each component by injecting small amounts either separately or in known mixtures. The esters should elute close to the typical retention times given in Table 1 and the chromatograms should closely approximate those shown in Figs. 1-6.

8.2 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. The response to different components is generally significantly different for both flame ionization and thermal conductivity detectors and especially for flame ionization detectors. Difference in detector response may be corrected by use of relative response factors obtained by injecting and measuring the response to known blends. For precise and accurate determination of the parent alcohol, prepare and analyze a known blend of the acetate and alcohol in which the alcohol content approximates the maximum specification limit. Calculate the alcohol response factor relative to unity for the acetate. With thermal conductivity detectors, the response factor of all impurities other than the alcohol may be assumed to be one for

obtaining the purity value. With flame ionization detectors, use experimentally determined response factors.

NOTE 2—Data on thermal conductivity and flame ionization detector responses may be found in the literature.<sup>11</sup>

## 9. Procedure

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

9.2 Using the same conditions as for component identification and standardization, record the peaks of all components at attenuation settings that provide optimum peak heights. Measure the area of all peaks (Note 3) and multiplying each area by the appropriate attenuation factor to express the peak areas on a common basis.

NOTE 3—Peak areas may be determined by any method that meets the precision in Section 12. Electronic integration of peak areas was employed to obtain the results used to establish the precision of this test method.

## 10. Calculation

10.1 Apply the appropriate detector response factor to correct for the difference in response to the components. Make correction to account for water and acidity as determined by the ASTM procedures given in Test Methods D 1364, D 1613, D 2593, and Practices E 180 and E 260.

10.2 Calculate the weight percent of each component as follows:

$$\text{Weight \%} = (A/B) \times (100 - C) \quad (1)$$

where:

*A* = corrected peak response of a component,

*B* = sum of corrected peak responses, and

*C* = sum of water and acidity (as acetic acid), weight %.

10.3 Calculate the percent composition by dividing the individual corrected component areas by the total corrected area.

## 11. Report

11.1 Report the percent purity of the acetate being analyzed and the corresponding alcohol to the nearest 0.01 % absolute. Duplicate runs for ester content that agree within 0.06 % absolute are acceptable for averaging (95 % confidence level). Duplicate runs for the parent alcohol content that agree within 0.02 % absolute are acceptable for averaging.

## 12. Precision and Bias<sup>12</sup>

12.1 The precision statements are based upon an interlaboratory study in which one operator in each of nine laboratories analyzed in duplicate on two days one sample of each of the following esters:

Ester	Mean Purity	Mean Alcohol Content
Ethyl acetate	99.8	0.17
<i>n</i> -Propyl acetate	96.9	2.7
Isopropyl acetate	99.2	0.46
<i>n</i> -Butyl acetate	98.5	0.48
Isobutyl acetate	98.7	0.45
2-Ethoxyethyl acetate	99.1	0.51

The results were analyzed in accordance with Practice E 180. Within-laboratory and between-laboratory standard deviations were found to be as follows:

	Ester Content	
	Within Laboratories	Between Laboratories
Ethyl acetate	0.019 (8) <sup>A</sup>	0.026 (7) <sup>A</sup>
<i>n</i> -Propyl acetate	0.032 (8)	0.138 (7)
Isopropyl acetate	0.014 (7)	0.071 (6)
<i>n</i> -Butyl acetate	0.029 (6)	0.056 (5)
Isobutyl acetate	0.042 (8)	0.213 (7)
2-Ethoxyethyl acetate	0.014 (8)	0.142 (7)

<sup>A</sup> Degrees of freedom are shown in parentheses.

	Parent Alcohol Content	
	Within Laboratories	Between Laboratories
Ethyl acetate	0.004 (7) <sup>A</sup>	0.028 (6) <sup>A</sup>
<i>n</i> -Propyl acetate	0.015 (8)	0.062 (7)
Isopropyl acetate	0.003 (8)	0.009 (7)

	Parent Alcohol Content	
	Within Laboratories	Between Laboratories
<i>n</i> -Butyl acetate	0.004 (7)	0.011 (6)
Isobutyl acetate	0.014 (8)	0.017 (7)
2-Ethoxyethyl acetate	0.005 (8)	0.015 (7)

<sup>A</sup> Degrees of freedom are shown in parentheses.

Based upon these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

12.1.1 *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 the following:

	Ester content (% absolute)	Alcohol Content
Ethyl acetate	0.06	0.01
<i>n</i> -Propyl acetate	0.10	0.05
Isopropyl acetate	0.05	0.01
<i>n</i> -Butyl acetate	0.10	0.01
Isobutyl acetate	0.14	0.05
2-Ethoxyethyl acetate	0.04	0.02

12.1.2 *Reproducibility*—Two results, each the mean of duplicates, obtained by operators in different laboratories should be considered suspect if they differ by more than the following:

	Ester Content (% absolute)	Alcohol Content
Ethyl acetate	0.09	0.10
<i>n</i> -Propyl acetate	0.46	0.20
Isopropyl acetate	0.24	0.03
<i>n</i> -Butyl acetate	0.20	0.04
Isobutyl acetate	0.71	0.06
2-Ethoxyethyl acetate	0.47	0.05

<sup>11</sup> Messner, A. E., et al, *Analytical Chemistry*, Vol 31, 1959, pp. 230–233. Dietz, W. A., *Journal of Gas Chromatography*, Vol 5, No. 2, February 1967, pp. 68–71.

<sup>12</sup> Supporting data are available from ASTM International Headquarters. Request RR: D01-1004.

**TABLE 1 Instrument Conditions and Retention Times**

	Ethyl Acetate	<i>n</i> -Propyl Acetate	Isopropyl Acetate	<i>n</i> -Butyl Acetate	Isobutyl Acetate	2-Ethoxyethyl Acetate
<i>Temperatures, °C:</i>						
Column, isothermal	90	90	90	90	90	140
Injection port	180	180	180	180	180	180
Dectector block	280	280	280	280	280	280
Carrier gas:	helium	helium	helium	helium	helium	helium
Carrier flow rate, mL/min <sup>4</sup>	75	75	75	75	75	75
Typical retention time, min	3.1	4.8	3.5	8.1	6.8	3.9
<i>Relative retention times (major component = 1.00):</i>						
Air	0.33					
Ethanol	0.59					
Unidentified	0.96					
Ethyl acetate	1.00					
Unidentified	1.26					
Unidentified	1.48					
Unidentified	1.66					
Unidentified	2.74					
Air		0.19				
Unidentified		0.44				
<i>n</i> -Propanol		0.48				
Unidentified		0.62				
Unidentified		0.67				
Unidentified		0.73				
Unidentified		0.88				
<i>n</i> -Propyl acetate		1.00				
Unidentified		1.29				
Unidentified		1.38				
Air			0.25			
Isopropanol			0.51			
Unidentified			0.74			
Unidentified			0.86			
Isopropyl acetate			1.00			
Unidentified			1.31			
Unidentified			1.37			
Air				0.11		
<i>n</i> -Butanol				0.42		
Dibutyl ether				0.55		
Unidentified				0.60		
Unidentified				0.68		
Unidentified				0.70		
<i>n</i> -Butyl acetate				1.00		
Unidentified				1.05		
Unidentified				1.18		
Unidentified				1.33		
Unidentified				1.51		
Air					0.13	
Isobutanol					0.41	
Unidentified					0.51	
Unidentified					0.62	
Unidentified					0.68	
Isobutyl acetate					1.00	
Unidentified					1.12	
Unidentified					1.35	
Air						0.23
Unidentified						0.31
Unidentified						0.38
2-Ethoxyethanol						0.51
Unidentified						0.74
2-Ethoxyethyl acetate						1.00
Unidentified						1.18
Unidentified						1.36
Unidentified						1.64
Ethylene glycol diacetate						2.10
Unidentified						3.08

<sup>4</sup> Adjust the carrier gas flow so that the major component will elute at approximately the typical time shown.

12.2 *Bias*—Bias cannot be determined because there are no available materials having accepted reference values.

13. Keywords

13.1 acetate esters; alcohol content; purity

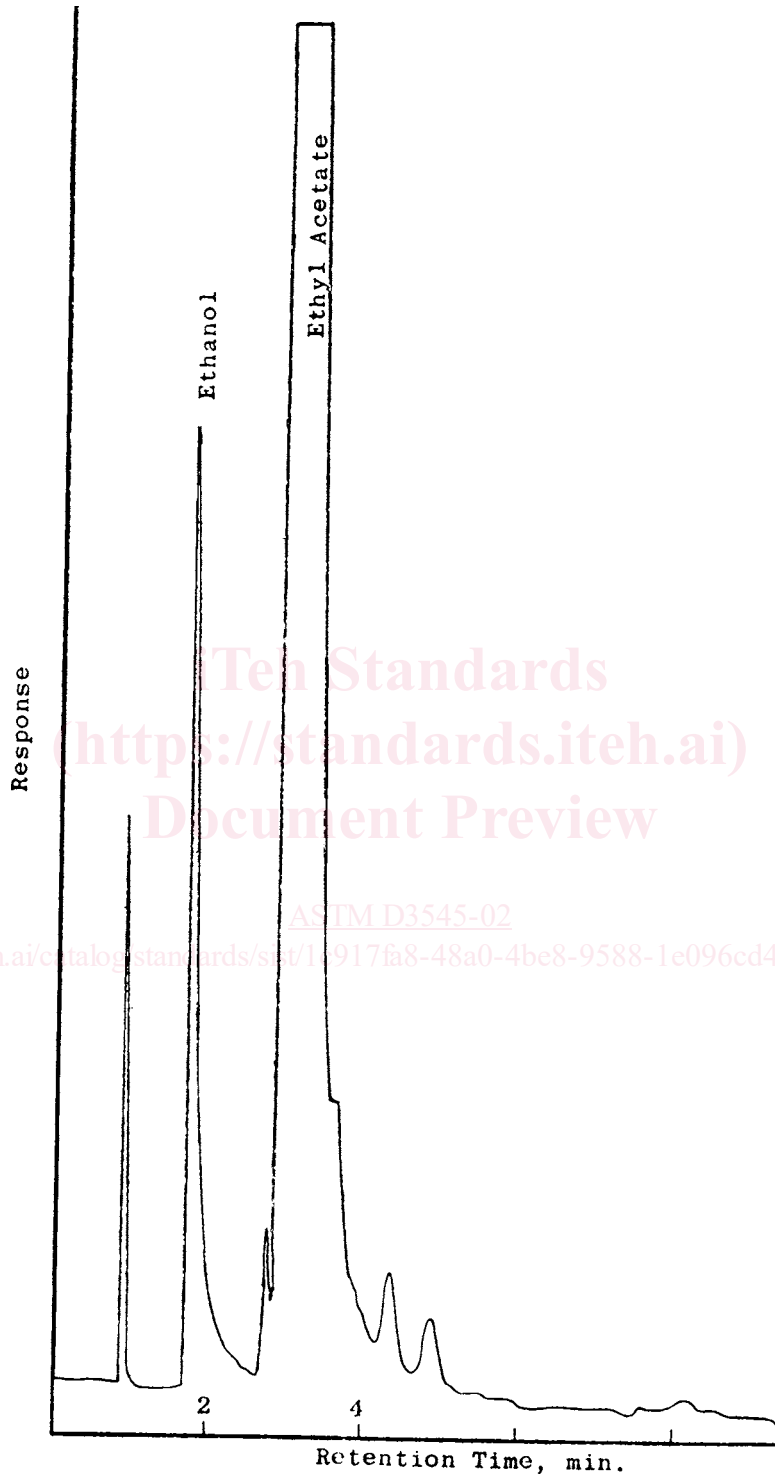


FIG. 1 Typical Chromatogram of Ethyl Acetate

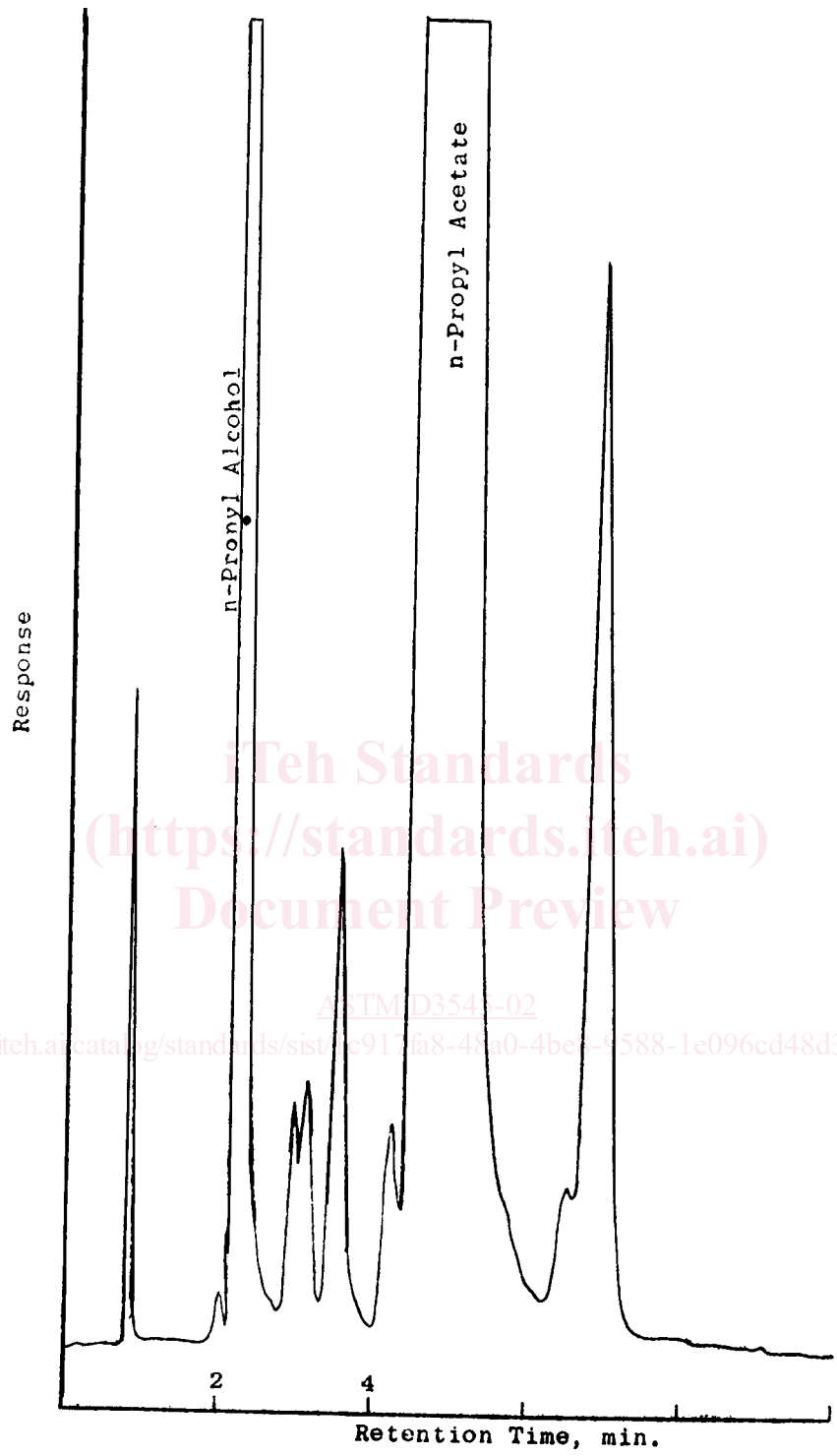


FIG. 2 Typical Chromatogram of *n*-Propyl Acetate