



Designation: D3545 – 22

Standard Test Method for Alcohol Content and Purity of Acetate Esters by Gas Chromatography¹

This standard is issued under the fixed designation D3545; 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.

This standard has been approved for use by agencies of the U.S. 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 For purposes of determining conformance of an observed or a calculated value using this test method to relevant specifications, test result(s) 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.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recom-*

mendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

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 (Withdrawn 2009)³

E260 Practice for Packed Column Gas Chromatography

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 D1364 and D1613, respectively, and the results are used to normalize the values obtained by gas chromatography.

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 The last approved version of this historical standard is referenced on www.astm.org.

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 μL with thermal conductivity and 1 to 2 μL with flame ionization detectors have been found acceptable.

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^{4,5,6} that has been coated with 9.05 % Dow Corning QF-1^{6,7} silicone and 0.45 % nonylphenoxypoly(ethyleneoxy)ethanol (CAS # 9016-45-9), HLB = 19.0 has been found suitable.⁸ 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. Microlitre 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^{6,7} silicone and nonylphenoxypoly(ethyleneoxy)ethanol (CAS # 9016-45-9), HLB = 19.⁸

6.2.2 *Solid Support*, Chromosorb G-HP,^{4,6,5} 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 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,^{4,6,5} 80 to 100 mesh, in a large evaporating dish. Dissolve 10 g of Dow Corning QF-1/FS 1265^{6,7} 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 = 19.0⁸ 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 **D2593** and Practice **E260**.

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

⁴ A registered trademark of Manville Products Corp., Lompoc, CA 93436.

⁵ The sole source of supply for this material known to the committee at this time is Manville Products Corp., Lompoc, CA 93436.

⁶ 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 committee¹ which you may attend.

⁷ The sole source of supply for Silicoups QF-1/FS 1265 (1000) known to the committee at this time is Dow-Corning Corp., Midland, MI 48640.

⁸ A registered trademark of GAF Corp., Dyestuff and Chemical Div., 140 W. 51st St., New York, NY 10020.

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 ⁴ | 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 |

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

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.⁹

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 D1364, D1613, D2593, and Practices E180 and E260.

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 Bias¹⁰

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 E180. Within-laboratory and between-laboratory standard deviations were found to be as follows:

| Ester Content | Ester Content | |
|--------------------------|------------------------|------------------------|
| | Within Laboratories | Between Laboratories |
| Ethyl acetate | 0.019 (8) ^A | 0.026 (7) ^A |
| <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) |

^A Degrees of freedom are shown in parentheses.

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

^A 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.

⁹ 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.

¹⁰ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1004. Contact ASTM Customer Service at service@astm.org.

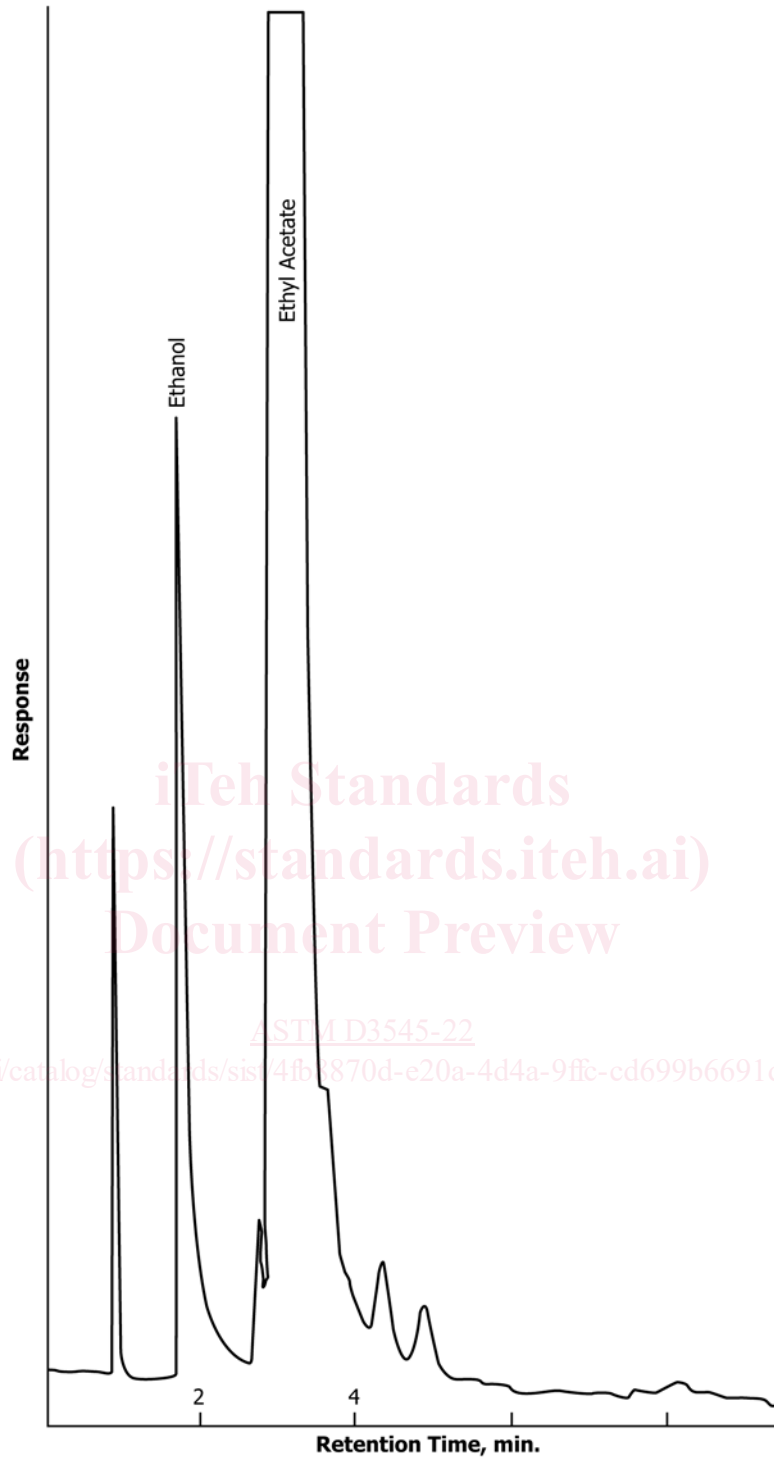


FIG. 1 Typical Chromatogram of Ethyl Acetate

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<https://standards.iteh.ai/catalog/standards/sis/4fb8870d-e20a-4d4a-9ffc-cd699b6691de/astm-d3545-22>

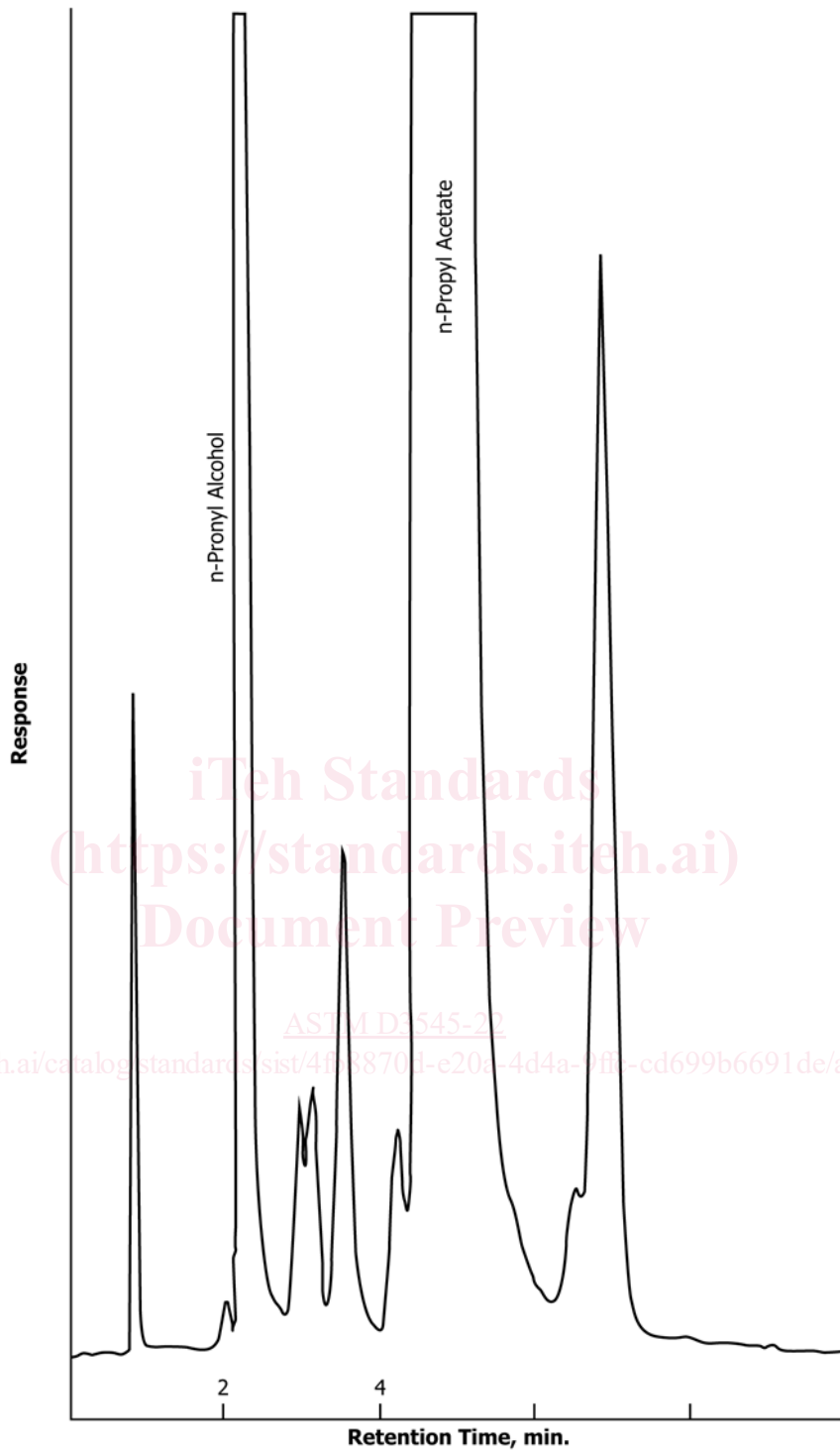


FIG. 2 Typical Chromatogram of *n*-Propyl Acetate

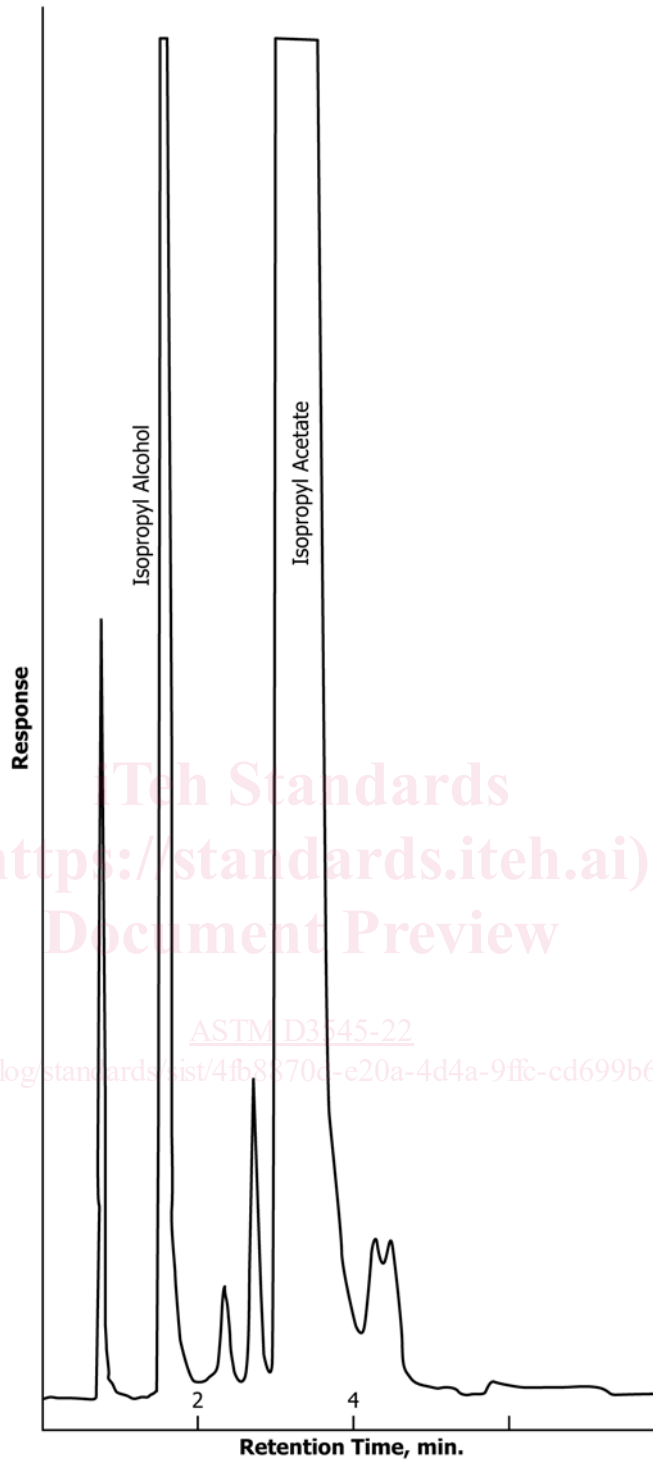


FIG. 3 Typical Chromatogram of Isopropyl Acetate

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