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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography[1]

This standard is issued under the fixed designation D 5501; 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.

ε[1] NOTE—Editorial corrections were made to Section 2 and 12.3 in April 1998.

1. Scope

1.1 This test method covers the determination of the ethanol content of denatured fuel ethanol by gas chromatography.

1.2 Ethanol is determined from 93 to 97 mass % and methanol is determined from 0.1 to 0.6 mass %. Equations used to convert these individual alcohols from mass % to volume % are provided.

1.3 This test method does identify and quantify methanol but does not purport to identify all individual components that make up the denaturant.

1.4 Water cannot be determined by this test method and shall be measured by a procedure such as Test Method D 1364 and the result used to correct the chromatographic values.

1.5 This test method is inappropriate for impurities that boil at temperatures higher than 225°C or for impurities that cause poor or no response in a flame ionization detector, such as water.

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

1.7 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method[2]

D 1364 Test Method for Water in Volatile Solvents (Fischer Reagent Titration Method)[3]

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[4]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[4]

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards[4]

D 4626 Practice for Calculation of Gas Chromatographic Response Factors[4]

D 4806 Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel[5]

E 355 Practice for Gas Chromatography Terms and Relationships[6]

E 594 Practice for Testing Flame Ionization Detectors Used in Gas Chromatography[6]

E 1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration[7]

3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions can be found in Practices E 355 and E 594.

4. Summary of Test Method

4.1 A representative aliquot of the fuel ethanol sample is introduced into a gas chromatograph equipped with a methyl silicone bonded phase fused silica capillary column. Helium carrier gas transports the vaporized aliquot through the column where the components are separated by the chromatographic process. Components are sensed by a flame ionization detector as they elute from the column. The detector signal is processed by an electronic data acquisition system. The ethanol and methanol components are identified by comparing their retention times to the ones identified by analyzing standards under identical conditions. The concentration of all components are determined in mass percent area by normalization of the peak areas.

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.D0.05 on C_5 Hydrocarbons and Oxygenated Hydrocarbons.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 06.04.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

[5] *Annual Book of ASTM Standards*, Vol 05.03.

[6] *Annual Book of ASTM Standards*, Vol 14.01.

[7] *Annual Book of ASTM Standards*, Vol 15.05.

5. Significance and Use

5.1 Fuel ethanol is required to be denatured with gasoline in accordance with Specification D 4806. State and federal laws specify the concentration of ethanol in gasoline blends. The determination of the amount of denaturant is important to ensure the blended fuel complies with federal and state laws. This test method provides a method of determining the percentage of ethanol (purity) of the fuel ethanol that is blended into gasoline.

6. Apparatus

6.1 *Gas Chromatograph*, capable of operating at the conditions listed in Table 1. A heated flash vaporizing injector injector designed to provide a linear sample split injection (for example, 200:1) is required for proper sample introduction. Carrier gas controls shall be of adequate precision to provide reproducible column flows and split ratios in order to maintain analytical integrity. Pressure control devices and gauges shall be designed to attain the linear velocity required in the column used. A hydrogen flame ionization detector with associated gas controls and electronics, designed for optimum response with open tabular columns, is required.

6.2 *Sample Introduction*—Manual or automatic liquid syringe sample injection to the splitting injector is employed. Devices capable of 0.1 to 0.5 µL injections are suitable. It should be noted that inadequate splitter design, poor injection technique, and overloading the column can result in poor resolution. Avoid overloading, particularly of the ethanol peak, and eliminate this condition during analysis.

6.3 *Column*—This test method utilizes a fused silica open tubular column with non-polar methyl silicone bonded (cross-linked) phase internal coating. Any column with equivalent or better chromatographic efficiency and selectivity to those described in 6.3.1 can be used.

6.3.1 Open tubular column with a non-polar methyl silicone bonded (cross-linked) phase internal coating, either 150 m by 0.25 mm with a 1.0 µm film thickness, or 100 m by 0.25 mm with a 0.5 film thickness is required.

TABLE 1 Typical Operating Conditions

Column Temperature Program		
Column length	100 m	150 m
Initial temperature	15°C	60°C
Initial hold time	12 min	15 min
Program rate	30°C/min	30°C/min
Final temperature	250°C	250°C
Final hold time	19 min	23 min
Injector		
Temperature	300°C	
Split ratio	200:1	
Sample size	0.1 to 0.5 µL	
Detector		
Type	Flame ionization	
Temperature	300°C	
Fuel gas	Hydrogen (≈30 mL/min)	
Oxidizing gas	Air (≈300 mL/min)	
Make-up gas	Nitrogen (≈30 mL/min)	
Carrier Gas		
Type	Helium	
Average linear velocity	21–24 cm/s	

6.4 *Electronic Data Acquisition System*—Any data acquisition and integration device used for quantification of these analyses must meet or exceed these minimum requirements:

6.4.1 Capacity for at least 80 peaks/analysis,

6.4.2 Normalized area percent calculation with response factors,

6.4.3 Identification of individual components based on retention time,

6.4.4 Noise and spike rejection capability,

6.4.5 Sampling rate for fast (<1 s) peaks,

6.4.6 Positive and negative sloping baseline correction,

6.4.7 Peak detection sensitivity compensation for narrow and broad peaks, and

6.4.8 Non-resolved peaks separated by perpendicular drop or tangential skimming as needed.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[8]

7.2 *Carrier Gas*, helium, with a minimum purity of 99.95 mol %. Oxygen removal systems and gas purifiers should be used.

NOTE 1—**Warning:** Helium, compressed gas under high pressure.

7.3 *Detector Gases*, hydrogen, air, and nitrogen. The minimum purity of the gases used should be 99.95 % for the hydrogen and nitrogen. The air should be hydrocarbon-free grade. Gas purifiers are recommended for the detector gases.

NOTE 2—**Warning:** Hydrogen, extremely flammable gas under high pressure.

NOTE 3—**Warning:** Air and nitrogen, compressed gases under high pressure.

7.4 *Standards for Calibration and Identification*—Standards of all components to be analyzed are required for establishing identification by retention time as well as calibration for quantitative measurements. These materials shall be of known purity and free of the other components to be analyzed.

7.4.1 *Ethanol* (**Warning**—See Note 4, Note 5).

NOTE 4—Two grades of ethanol are available. Only absolute ethanol 99.5 minimum percent meets the requirements of this test method.

7.4.2 *Methanol* (**Warning**—See Note 5).

7.4.3 *Heptane* (**Warning**—See Note 5).

NOTE 5—**Warning:** These materials are flammable and may be harmful or fatal, if ingested or inhaled.

8. Sampling

8.1 Denatured ethanol can be sampled into an open container since a vapor pressure of less than 21 kPa (3 psi) is

[8] *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.

expected. Refer to Practice D 4057 for instruction on manual sampling from bulk storage into open containers. Stopper container immediately after drawing the sample.

8.2 Transfer an aliquot of the sample into a septum vial and seal. Obtain the test sample for analysis directly from the sealed septum vial, for either manual or automatic syringe injection.

9. Preparation of Apparatus

9.1 Install and condition column in accordance with manufacturer's or supplier's instructions. After conditioning, attach column outlet to flame ionization detector inlet and check for leaks throughout the system. When leaks are found, tighten or replace fittings before proceeding.

9.2 Adjust the carrier gas flow rate so that the average linear gas velocity, at the initial temperature of the run, is between 21 and 24 cm/s, as determined by the following equation:

$$\bar{\mu} = \frac{L}{t_m} \tag{1}$$

where:
$\bar{\mu}$ = average linear gas velocity (cm/s),
L = column length (cm), and
t_m = retention time of methanes.

Flow rate adjustment is made by raising or lowering the carrier gas pressure (head pressure) to the injector.

9.3 Adjust the operating conditions of the gas chromatograph (Table 1) and allow the system to equilibrate.

9.4 *Linearity*—The linearity of the gas chromatograph system shall be established prior to the analysis of samples.

9.4.1 The split ratio used is dependent upon the split linearity characteristics of the particular injector and the sample capacity of the column. The capacity of a particular column for a sample component is proportional to the amount of liquid phase (loading or film thickness) and the ratio of the column temperature to the component boiling point (vapor pressure). Overloading of the column may cause loss of resolution for some components and, since overloaded peaks are skewed, variance in retention times. This can lead to erroneous component identification. During column evaluations and split linearity studies, be aware of any peaks that may appear *front skewed*, indicating column overload. Note the component size and avoid conditions leading to this problem during actual analysis.

9.4.2 Splitting injector linearity must be established to determine proper quantitative parameters and limits. Use a standard mixture of known mass percentages of ethanol, methanol, and 10 to 20 pure hydrocarbons, covering the boiling range of this test method. The determined mass percent for each component shall match the gravimetric known concentration within± 3 % relative.

9.4.3 The linearity of the flame ionization detector (FID) should be checked. A plot of the peak areas versus ethanol concentration for prepared standards in the concentration range of interest should be linear. If the plot is not linear, either the split ratio shall be increased or the detector range must be made less sensitive.

10. Calibration and Standardization

10.1 *Identification*—Determine the retention time of ethanol and methanol by injecting amounts of each, either separately or in known mixtures, in proportions expected in the final blend using *n*-heptane as the solvent.

10.2 *Calibration*—Typical mass relative response factors for the components of interest are found in Table 2. These response factors shall be determined by analyzing a standard that has been blended according to Practice D 4307. This standard is comprised of the proportions of ethanol and methanol expected in the sample using *n*-heptane in place of the denaturant. A typical standard blend would be ≅96 % ethanol, 0.1 % methanol and 3.9 % *n*-heptane. Calculate the mass relative response factor according to Practice D 4626.

11. Gas Chromatographic Analysis Procedure

11.1 Set the instrument operating variables to the values specified in Table 1.

11.2 Set instrumental sensitivity such that any component of at least 0.002 mass % can be detected and integrated.

11.3 Inject 0.1 to 0.5 µL of sample into the injection port and start the analysis. Obtain a chromatogram and peak integration report. A sample chromatogram is shown in Fig. 1.

11.4 The ethanol peak will require tangential skimming to be correctly integrated if components of the denaturant elute on the ethanol peaks tail.

12. Calculation

12.1 Multiply the area of each identified peak by the appropriate mass relative response factor. Use those factors determined for individual compounds and use a factor of 1.000 for unknowns.

12.2 Determine the relative mass percent of the individual alcohols by using the following equation:

$$RM_i = \frac{AR_i \times 100}{AR_t} \tag{2}$$

where:
RM_i = relative mass % of the individual alcohols,
AR_i = area of the individual alcohol peak corrected by the appropriate mass relative response factor (see 12.1), and
AR_t = total area of all detected peaks corrected by their appropriate mass relative response factors (12.1).

12.3 Obtain the mass % of water in the sample. Test Methods D 1364, E 1064, or equivalent, can be used.

12.4 Determine the mass % of the alcohols of interest by using the following equation:

$$M_i = \frac{RM_i \times (100 - \text{mass \% water in sample})}{100} \tag{3}$$

TABLE 2 Pertinent Physical Constants

	Typical Mass Relative Response Factors[A]	Relative Density at 15.56°C (60°F)
Methanol	3.20	0.796
Ethanol	2.06	0.794

[A] When *n*-heptane = 1.

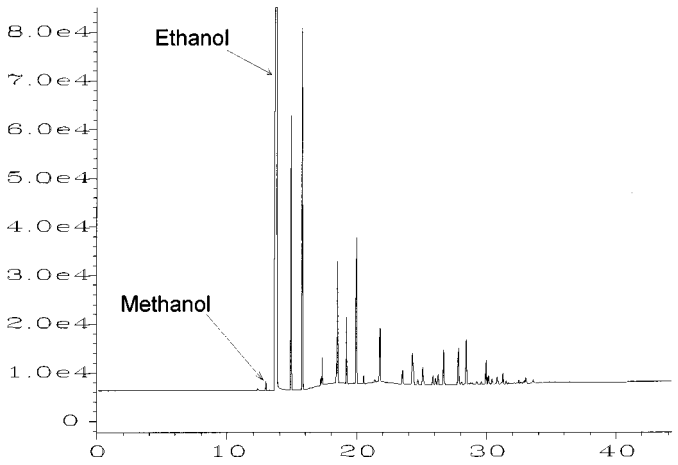

FIG. 1 Sample Chromatogram

where:

M_i = mass % of the individual alcohol being determined, and

RM_i = relative mass % of the individual alcohol from Eq 2.

12.5 For the volumetric concentration of the alcohol, calculate as follows:

$$V_i = \frac{M_i \times D_s}{D_i} \quad (4)$$

where:

V_i = volume % of component i,

M_i = mass % of component i from Eq 3,

D_i = relative density at 15.56°C (60°F) of component i as found in Table 2, and

D_s = sample under study as determined by Test Method D 1298 or D 4052.

13. Report

13.1 Report the purity of the individual alcohols to the nearest 0.01 mass % using Eq 3 or nearest 0.01 volume % using Eq 4.

14. Precision and Bias

14.1 *Precision*—The precision of this test method as determined by the statistical examination of the inter-laboratory gas chromatographic test results is as follows:

14.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty. See Table 1.

	Repeatability[A]	
Component	Range, Mass %	Repeatability, Mass %
Ethanol	93–97	0.21
Methanol	0.01–0.6	$0.01859 \times \sqrt{X}$

[A] Where X is the mass percent.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty:

	Repeatability[A]	
Component	Range, Mass %	Repeatability, Mass %
Ethanol	93–97	0.21
Methanol	0.01–0.6	$0.01172 \times \sqrt{X}$

[A] Where X is the mass percent.

14.1.3 *Bias*—No significant difference was found between the ethanol or methanol content obtained by this test method and the expected ethanol or methanol content (based on the concentrations of ethanol and methanol in the prepared samples) for the fuel ethanol samples analyzed in the round robin used to evaluate the precision of this test method. Supporting data have been filed at ASTM Headquarters. Request RR: D02-1266 and D02-1328.

15. Keywords

15.1 denatured; ethanol; fuel grade gas chromatography