



Standard Test Method for Ethylene, Other Hydrocarbons, and Carbon Dioxide in High-Purity Ethylene by Gas Chromatography¹

This standard is issued under the fixed designation D 2505; 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 carbon dioxide, methane, ethane, acetylene, and other hydrocarbons in high-purity ethylene. Hydrogen, nitrogen, oxygen, and carbon monoxide are determined in accordance with Test Method D 2504. The percent ethylene is obtained by subtracting the sum of the percentages of the hydrocarbon and nonhydrocarbon impurities from 100. The method is applicable over the range of impurities from 1 to 500 parts per million volume (ppmV).

1.2 *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.* For some specific hazard statements, see Notes 8 and 9.

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

2. Referenced Documents

2.1 ASTM Standards:

- D 2504 Test Method for Noncondensable Gases in C₂ and Lighter Hydrocarbon Products by Gas Chromatography²
- D 4051 Practice for Preparation of Low-Pressure Gas Blends³
- E 260 Practice for Packed Column Gas Chromatography⁴
- F 307 Practice for Sampling Pressurized Gas for Gas Analysis⁵

3. Summary of Test Method

3.1 The sample is separated in a gas chromatograph system utilizing four different packed chromatographic columns with

helium as the carrier gas. Methane and ethane are determined by using a silica gel column. Propylene and heavier hydrocarbons are determined using a hexamethylphosphoramide (HMPA) column. Acetylene is determined by using, in series, a hexadecane column and a squalane column. Carbon dioxide is determined using a column packed with activated charcoal impregnated with a solution of silver nitrate in β, β' -oxydipropionitrile. Columns other than those mentioned above may be satisfactory. (see 5.3.) Calibration data are obtained using standard samples containing the impurities, carbon dioxide, methane, and ethane in the range expected to be encountered. Calibration data for acetylene are obtained assuming that acetylene has the same peak area response on a weight basis as methane. The acetylene content in a sample is calculated on the basis of the ratio of peak area of the acetylene peak to the peak area of a known amount of methane. Calculations for carbon dioxide, methane, and ethane are carried out by the peak-height measurement method.

4. Significance and Use

4.1 High-purity ethylene is required as a feedstock for some manufacturing processes, and the presence of trace amounts of carbon dioxide and some hydrocarbons can have deleterious effects. This method is suitable for setting specifications, for use as an internal quality control tool and for use in development or research work.

5. Apparatus

5.1 Any chromatographic instrument with an overall sensitivity sufficient to detect 2 ppmV or less of the compounds listed with a peak height of at least 2 mm without loss of resolution.

5.2 *Detectors—Thermal Conductivity*—If a methanation reactor is used, a flame ionization detector is also required. To determine carbon dioxide with a flame ionization detector, a methanation reactor must be inserted between the column and the detector and hydrogen added as a reduction gas (see Test Method D 2504, Appendix X1).

5.3 *Column*—Any column or set of columns can be used that separates carbon dioxide, methane, acetylene and C₃ and heavier compounds. There may be tailing of the ethylene peak but do not use any condition such that the depth of the valleys

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

³ *Annual Book of ASTM Standards*, Vol 05.02.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ *Annual Book of ASTM Standards*, Vol 15.03.

ahead of the trace peak is less than 50 % of the trace peak height. (See Fig. 1 for example.)

5.4 *Recorder*—A recorder with a full-scale response of 2 s or less and a maximum rate of noise of ± 0.3 % of full scale.

5.5 *Gas-Blending Apparatus*—A typical gas-blending apparatus is shown in Fig. 2. A high-pressure manifold equipped with a gage capable of accurately measuring ethylene pressures up to 3.4 MN/m² gage (500 psig) is required. Other types of gas-blending equipment, such as described in Practice D 4051, can be used.

NOTE 1—Practice E 260, contains information that will be helpful to those using this method.

6. Reagents and Materials

6.1 *Copper or Aluminum, or Stainless Steel Tubing*, 6.4-mm (1/4-in.) outside diameter, and nylon tubing, 3.2-mm (1/8-in.) outside diameter.

6.2 *Solid Supports*—Crushed firebrick or calcined diatomaceous earth, such as Chromosorb P,⁶ 35 to 80-mesh and 80 to 100-mesh. Other supporting materials or mesh sieves can be satisfactory.

6.3 *Active Solids*—Activated carbon, 30 to 40-mesh,⁷ silica gel, 100 to 200-mesh.⁸ Other sizes may be satisfactory.

6.4 *Liquid Phases*—Hexamethylphosphoramide (HMPA⁹), hexadecane,⁹ squalene,⁹ silver nitrate, and β,β' -oxydipropionitrile.¹⁰ Other liquid phases may be satisfactory.

NOTE 2—**Warning:** Combustible solvents. See A1.7.

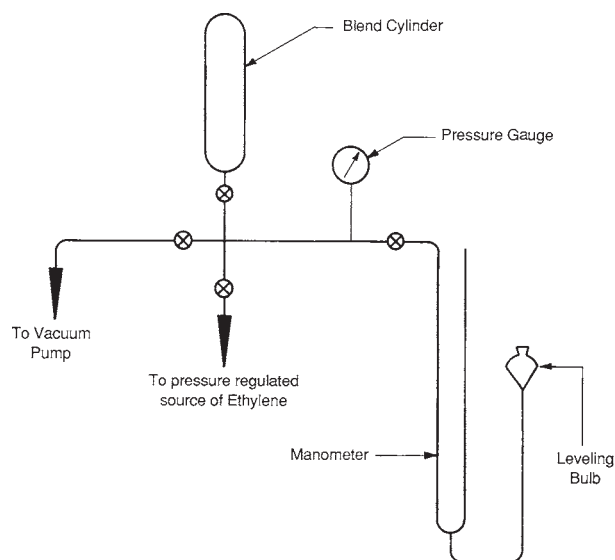


FIG. 2 Gas-Blending Manifold

NOTE 3—**Warning:** HMPA may be harmful if inhaled. Causes irritation. A potential carcinogen (lungs). See A1.5.

6.5 *Helium*.

NOTE 4—**Warning:** Compressed Gas, Hazardous Pressure. See A1.2.

6.6 *Hydrogen*.

NOTE 5—**Warning:** Flammable Gas, Hazardous Pressure. See A1.6.

6.7 *Acetone*.

NOTE 6—Extremely Flammable. See A1.1.

6.8 *Gases for Calibration*—Pure or research grade carbon dioxide, methane, ethane, acetylene, ethylene, propane, and propylene. Certified calibration blends are commercially available from numerous sources and may be used.

NOTE 7—**Warning:** Flammable Gases, Hazardous Pressure. See A1.2 and A1.3.

6.9 *Methanol*.

NOTE 8—**Warning:** Flammable. Vapor Harmful. See A1.4.

NOTE 9—The use of copper tubing is not recommended with samples containing acetylene as this could lead to the formation of potentially explosive copper acetylide.

7. Sampling

7.1 Samples should be supplied to the laboratory in high pressure sample cylinders, obtained using the procedures described in Practice F 307, or similar methods.

8. Preparation of Apparatus

8.1 *Silica Gel Column*—Dry the silica gel in an oven at 204°C (400°F) for 3 h, cool in a desiccator, and store in screw-cap bottles. Pour the activated silica gel into a 0.9-m (3-ft) length of 6.4-mm (1/4-in.) outside diameter copper or aluminum tubing plugged with glass wool at one end. Tap or vibrate the tube while adding the silica gel to ensure uniform packing and plug the top end with glass wool. Shape the column to fit into the chromatograph.

8.2 *Silver Nitrate*— β,β' -Oxydipropionitrile—Activated Carbon Column—Weigh 10 g of β,β' -oxydipropionitrile into a

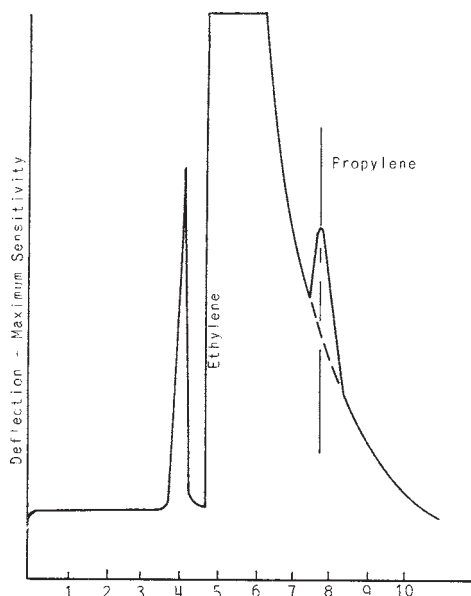


FIG. 1 Typical Chromatogram for Propylene

⁶ Available from the Celite Division, Johns Mansville Co., New York, NY.

⁷ A fraction sieved in the laboratory to 30 to 40 mesh from medium activity charcoal, 20 to 60 mesh, sold by Central Scientific Co., 1700 Irving Park Road, Chicago, IL 60613, has been found satisfactory for this purpose.

⁸ Silica gel Code 923 available from the Davison Chemical Co., Baltimore, Md. 21203, has been found satisfactory for this purpose.

⁹ Available from the Fisher Scientific Co., St. Louis, MO.

¹⁰ β,β' -oxydipropionitrile, sold by Distillation Products Industries, Division of Eastman Kodak Co., Rochester, NY, has been found to be satisfactory.

brown 125-mL (4-oz) bottle. Add 5 g of silver nitrate (AgNO_3) crystals. With occasional shaking, dissolve as much AgNO_3 as possible, and allow the bottle to stand overnight to ensure saturation. Prepare this solution fresh, as required. Without disturbing the crystals at the bottom of the bottle, weigh 2.5 g of supernatant AgNO_3 solution into a 250-mL beaker and add 50 mL of methanol. While stirring this mixture, slowly add 22.5 g of activated carbon. Place the beaker on a steam bath to evaporate the methanol. When the impregnated activated carbon appears to be dry, remove the beaker from the steam bath and finish drying in an oven at 100 to 110°C for 2 h. Plug one end of a 4-ft (1.2-m) length of 6.4-mm (1/4-in.) outside diameter aluminum or stainless steel tubing with glass wool. Hold the tubing vertically with the plugged end down and pour freshly dried column packing into it, vibrating the column during filling to ensure uniform packing. Plug the top end with glass wool and shape the tubing so that it may be mounted conveniently in the chromatograph.

8.3 Hexamethylphosphoramide Column (HMPA)—Dry the 35 to 80-mesh inert support at 204°C (400°F). Weigh 75 g into a wide-mouth 500-mL (16-oz) bottle. Add 15 g of HMPA to the inert support and shake and roll the mixture until the support appears to be uniformly wet with the HMPA. Pour the packing into a 6-m (20-ft) length of 6.4-mm (1/4-in.) outside diameter copper or aluminum tubing plugged at one end with glass wool. Vibrate the tubing while filling to ensure more uniform packing. Plug the top end of the column with glass wool and shape the column to fit into the chromatograph.

8.4 Hexadecane-Squalane Column—Dissolve 30 g of hexadecane into approximately 100 mL of acetone. Add 70 g of 80 to 100-mesh inert support. Mix thoroughly and pour the mixture into an open pan for drying. The slurry should be stirred during drying to ensure uniform distribution. When the acetone has evaporated, add a portion of the packing to a 7-m (25-ft) length of 3.2-mm (1/8-in.) outside diameter nylon tubing which has been plugged at one end with glass wool. Vibrate the column while filling to ensure more uniform packing. Fill the column with packing to only 4 m (15 ft) of the length of the column. Fill the remainder of the column with squalane packing prepared in the same manner as the hexadecane packing. Plug the open end of the tubing with glass wool and shape the column to fit into the chromatograph with the hexadecane portion of the column at the front end of the column. The column shall be purged under test conditions (no sample added) until a constant baseline is obtained.

NOTE 10—Columns made with liquid phases listed above were used satisfactorily in cooperative work. Other columns may be used (see 5.3).

9. Calibration

9.1 Preparation of Standard Mixtures:

9.1.1 Preparation of Concentrate—Prepare a concentrate of the impurities expected to be encountered. A certified calibration blend containing the expected impurities can be obtained and used as the concentrate. An example of a satisfactory concentrate is given in Table 1. The concentrate can be prepared using the gas blending manifold as shown in Fig. 2 or

TABLE 1 Suggested Composition of a Concentrate of Impurities Used in Preparing Standard Mixtures for Calibration Purposes

Component	Percent
Carbon dioxide	10
Methane	45
Ethane	25
Propylene	20

using a similar apparatus as follows: Evacuate the apparatus and add the components in the order of increasing vapor pressure; that is, propylene, carbon dioxide, ethane and methane. Record the increase in pressure on the manometer as each component is added. Close the reservoir and evacuate the manometer after each addition.

9.1.2 Dilution of Concentrate—Dilute the concentrate with high-purity ethylene in a ratio of approximately 1:4000. This can be done by adding the calculated amount of the concentrate and high purity ethylene to an evacuated cylinder using the gas-blending apparatus (Fig. 2). Use a source of high-pressure, high-purity ethylene equipped with a needle valve and a pressure gage capable of accurately measuring the pressure of the blend as the ethylene is added to the cylinder containing the concentrate. Add the calculated amount of ethylene; warm one end of the cylinder to ensure mixing of the blend. Allow the temperature to reach equilibrium before recording the final pressure on the cylinder. Prepare at least three calibration samples containing the compounds to be determined over the range of concentration desired in the products to be analyzed.

NOTE 11—**Precaution:** As a safety precaution, use a manifold and fittings such as valves and gages that will withstand the pressure encountered.

9.2 Calculation of Composition of Standard Mixtures—Calculate the exact ratio of the concentrate dilution with ethylene by correcting the pressure of the ethylene added for the compressibility of ethylene (Table 2). Multiply the dilution ratio or factor by the percentage of each component present in the original concentrate (Table 1). These calculations give the amount of each component that has been added to the high-purity ethylene blend stock. The actual composition of the final blend must be ascertained by making corrections for the impurities present in the high-purity ethylene used for the blend stock. The amount of correction is determined by making chromatograph runs on the high-purity ethylene and measuring the peak heights of the impurities. These peak heights will be used in adjusting the calibration factors described in 9.3. Since peak height is very sensitive to changes in conditions, it is extremely important in correlating peak heights obtained in making calibrations, calibration adjustments, and final impurity determinations that these values be obtained under the same GLC column operating conditions in all cases.

9.3 Determination of Calibration Factors—Chromatograph the standard blend and the high-purity ethylene blend stock by each of the procedures given in Section 10.

9.3.1 Calculate calibration factors for carbon dioxide, methane, ethane, propylene, and heavier hydrocarbons as follows:

$$F = C/(S - B) \quad (1)$$