



# Standard Test Method for Noncondensable Gases in C<sub>2</sub> and Lighter Hydrocarbon Products by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 2504; 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 hydrogen, nitrogen, oxygen, and carbon monoxide in the parts per million volume (ppmv) range in C<sub>2</sub> and lighter hydrocarbon products. This test method should be applicable to light hydrocarbons other than ethylene, but the test program did not include them.

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

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.* For some specific hazard statements, see Note 3, Note 4, and Note 5.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 2505 Test Method for Ethylene, Other Hydrocarbons, and Carbon Dioxide In High-Purity Ethylene by Gas Chromatography<sup>2</sup>

E 260 Practice for Packed Column Gas Chromatography<sup>3</sup>

F 307 Practice for Sampling Pressurized Gas for Gas Analysis<sup>4</sup>

### 2.2 Other Standard:<sup>5</sup>

Compressed Gas Association Booklets G-4 and G-4.1 on the use of oxygen.

## 3. Summary of Test Method

3.1 The sample is separated in a gas-solid chromatographic system using molecular sieves as the solid adsorbent. The concentration of the gases to be determined is calculated from the recorded peak heights or peak areas. Argon can be used as a carrier gas for the determination of hydrogen in concentra-

tions below 100 ppmv. Argon, if present in the sample, interferes with oxygen determination.

## 4. Significance and Use

4.1 The presence of trace amounts of hydrogen, oxygen, and carbon monoxide can have deleterious effects in certain processes using hydrocarbon products as feed stock. This test 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 *Chromatograph*—Any chromatographic instrument having either a thermal conductivity or ionization detector with an overall sensitivity sufficient to detect 2 ppmv or less of the compounds listed in the scope, 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 monoxide with a flame ionization detector, a methanation reactor must be inserted between the column and the detector and hydrogen added as a reduction gas. Details on the preparation and use of the reactor are given in Appendix X1.

5.3 *Constant-Volume Gas Sampling Valve.*

5.4 *Column*—Any column or set of columns that is capable of resolving the components listed in the scope can be used. Copper, stainless steel, or aluminum tubing may be used. The columns chosen must afford a resolution such that the depth of the valleys ahead of the trace peak is no less than 50 % of the trace peak height.

5.5 *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.

5.6 *Oven*—The oven used for activating molecular sieves must be maintained at 260 to 288°C (500 to 550°F) and should be designed so that the gases may be displaced continuously by a stream of inert gas. The oven may be a thermostated piece of 1-in. pipe about 0.3m (1 ft.) in length. Electrical heating tapes or other means may be used for heating provided the heat is distributed uniformly.

NOTE 1—The use of copper tubing is not recommended with samples containing acetylene as this could lead to the formation of potentially explosive copper acetylide.

<sup>1</sup> 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.D0.02 on C<sub>3</sub> Test Methods.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 15.03.

<sup>5</sup> Available from Compressed Gas Association, 1253 Jefferson Davis Highway, Arlington, VA, 22202.

## 6. Reagents and Materials

6.1 *Molecular Sieves, 5A, 13A, or 13X*—Any mesh sizes can be used so long as sensitivity and resolution are maintained (see Note 2). If a 40 to 60-mesh sieve size is desired, but is not available, it may be prepared as described in 8.1.

6.2 *Coconut Charcoal*, 30 to 60-mesh sieve size (optional).

NOTE 2—Columns that have been found to give the desired separation include a 1-m by 3.175-mm outside diameter column of 100 to 120 mesh 5A molecular sieve, a 3-m by 6.35-mm outside diameter column of 40 to 60-mesh 5A sieve, and a 7.7-m by 6.35-mm outside diameter column with 13A or 13X sieve in the first 7.4 m and charcoal in the 0.3 m.

6.3 *Gases for Calibration*—Pure or research grade hydrogen, oxygen, nitrogen, and carbon monoxide will be needed to prepare synthetic standard samples as described in Test Method D 2505. (**Warning**—See Note 4 and Note 5.) Certified calibration blends are commercially available from numerous sources and can be used as the synthetic standard samples.

NOTE 3—**Warning:** Flammable gases. Hazardous pressure. See Annexes A1.1–A1.5.

NOTE 4—**Warning:** Flammable. Poison. Harmful if inhaled. Dangerous when exposed to flame. See Annex A1.5.

NOTE 5—**Warning:** Hazardous pressure. See Annex A1.2.

6.4 *Carrier Gases*—Argon or helium.

NOTE 6—Practice E 260 contains information that will be helpful to those using this test method.

## 7. Sampling

7.1 Samples shall 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 *Chromatographic Column Packing*—Crush in a porcelain mortar and sieve to 40 to 60-mesh size about 200 g of molecular sieves 5A in order to have enough for several columns. All work of preparing molecular sieves and packing columns with this material shall be done rapidly, preferably under a blanket of dry nitrogen in order to minimize moisture absorption. Heat the screened molecular sieves in an oven at  $274 \pm 14^\circ\text{C}$  ( $525 \pm 25^\circ\text{F}$ ) for 24 h purging with dry nitrogen at a rate of about 5 mL/min during this time. The nitrogen rate is not critical and can be measured by any convenient means such as an orifice meter, rotameter, manometer, etc. Do not use a wet test meter.

8.2 *Chromatographic Column*—Purge the metal tubing with dry nitrogen. Insert a small amount of glass wool in the end. Fill rapidly with the screened and activated molecular sieves, adding the latter in 1-g increments. Vibrate the column, adding additional sieves during this period, if necessary, to fill. Insert a small amount of glass wool in the top. Bend the column in the shape required to fit the chromatographic instrument. Regenerate the column in the oven in the same manner as described in 8.1 whenever the oxygen is not completely separated from the nitrogen peak.

## 9. Calibration

9.1 Bring the equipment and column to equilibrium and maintain a constant carrier gas rate and temperature.

NOTE 7—Carrier gas rates of 36 to 60 mL/min and temperatures of 50 to  $60^\circ\text{C}$  have been used successfully.

9.2 Prepare at least three synthetic standard samples containing the compounds to be determined over the range of concentration desired in the products to be analyzed, using the pure gases or the certified blend. For the preparation of the second, third, and following calibration samples it is always preferable not to dilute the first sample.

NOTE 8—Synthetic standard samples should be prepared as described in Test Method D 2505.

9.3 Inject a known volume of one of the standard samples, using a minimum of 1 mL for detecting 2 ppmv.

NOTE 9—Use of a reverse-flow arrangement will facilitate removal of heavier gases and decrease the elapsed time of analysis.

9.4 Record all of the desired peaks on each of the synthetic blends prepared.

9.5 Prepare a chart for each compound, plotting the peak height of the compound or peak area of the compound against the concentration of the compounds in ppmv. The peak area can be determined by any method that meets the precision requirements of Section 12. Methods found to be acceptable include planimetry, integration (electronic or mechanical or computer processing), and triangulation.

## 10. Procedure

10.1 Connect the sample cylinder containing a gaseous sample to the gas sample valve with a metal tube and allow the sample to flow from the sample tube for about 1/2 min. at a rate of 70 to 100 mL/min.

10.2 Inject into the instrument the same volume of sample as used for calibration, (pressure of sample and calibration gas must be the same in the sample loop) and record the peak areas or peak heights desired.

## 11. Calculation

11.1 From the peak height or area of the compound in the sample, determine the moles per million of the compound using the charts prepared in calibration. A typical characterization showing hydrogen, oxygen, and nitrogen in ethylene is presented in Fig. 1.

## 12. Precision and Bias

12.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

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

Component	Range, ppmv	Repeatability, ppmv
Oxygen	10–150	15
Nitrogen	100–700	72
Carbon Monoxide	0–20	3
Hydrogen	0–15	2

12.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in