



# 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 D2504; 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.

## 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 SI units are to be regarded as the standard. The values given 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 the [Annex A1](#).

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

[D2505 Test Method for Ethylene, Other Hydrocarbons, and Carbon Dioxide in High-Purity Ethylene by Gas Chromatography](#)

[E260 Practice for Packed Column Gas Chromatography](#)

[F307 Practice for Sampling Pressurized Gas for Gas Analysis](#)

### 2.2 Other Standard:<sup>3</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

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Available from Compressed Gas Association (CGA), 4221 Walney Rd., 5th Floor, Chantilly, VA 20151-2923, <http://www.cganet.com>.

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 concentrations 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  $\pm 0.3$  % of full scale.

5.6 *Oven*—The oven used for activating molecular sieves must be maintained at 260 °C to 288 °C (500 °F 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 0.3 m (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.

## 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 mesh 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 mesh 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 mesh to 120 mesh 5A molecular sieve, a 3 m by 6.35 mm outside diameter column of 40 mesh 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 D2505. (**Warning**—Flammable gases. Hazardous pressure. See Annexes A1.1 – A1.5.) (**Warning**—Flammable. Poison. Harmful if inhaled. Dangerous when exposed to flame. See Annex A1.5.) (**Warning**—Hazardous pressure. See Annex A1.2.) Certified calibration blends are commercially available from numerous sources and can be used as the synthetic standard samples.

6.4 *Carrier Gases*—Argon or helium.

NOTE 3—Practice E260 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 F307 or similar methods.

## 8. Preparation of Apparatus

8.1 *Chromatographic Column Packing*—Crush in a porcelain mortar and sieve to 40 mesh 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  $274\text{ }^{\circ}\text{C} \pm 14\text{ }^{\circ}\text{C}$  ( $525\text{ }^{\circ}\text{F} \pm 25\text{ }^{\circ}\text{F}$ ) 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. Regen-

erate 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 4—Carrier gas rates of 36 mL/min to 60 mL/min and temperatures of  $50\text{ }^{\circ}\text{C}$  to  $60\text{ }^{\circ}\text{C}$  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 5—Synthetic standard samples should be prepared as described in Test Method D2505.

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

NOTE 6—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  $\frac{1}{2}$  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:

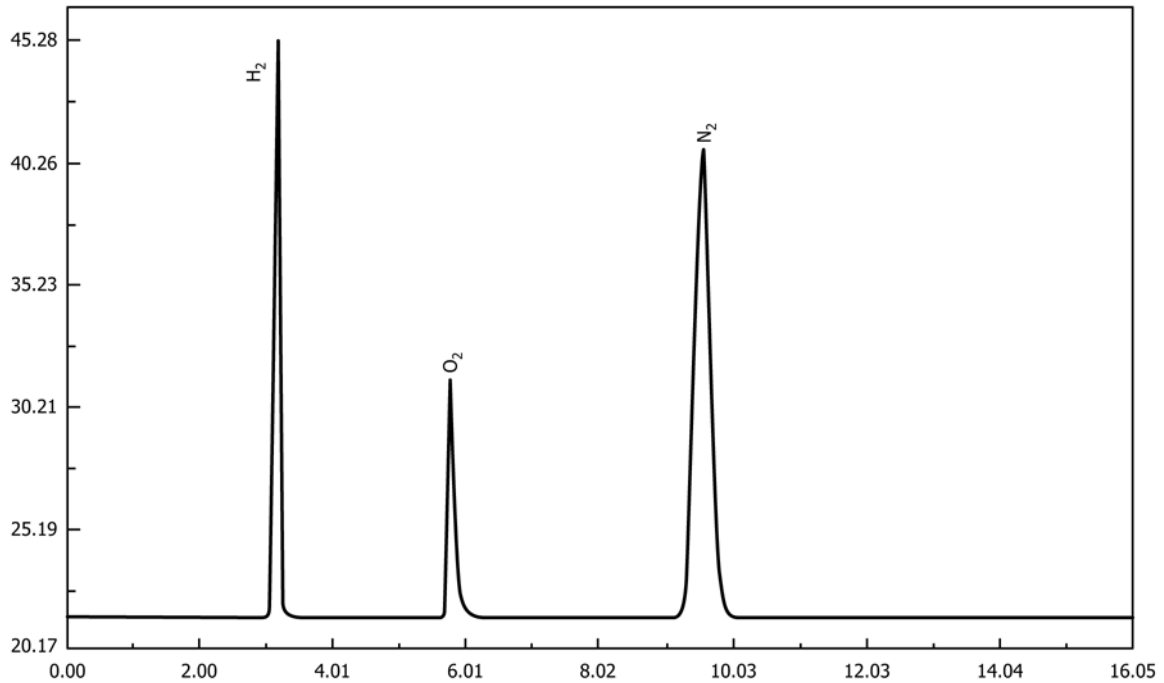


FIG. 1 Typical Chromatogram for Hydrogen, Oxygen and Nitrogen

| 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 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 | Reproducibility, ppmv |
|-----------------|-------------|-----------------------|
| Oxygen          | 10–150      | 155                   |
| Nitrogen        | 100–1000    | 875                   |
| Carbon Monoxide | 0–20        | 7                     |
| Hydrogen        | 0–15        | 8                     |

NOTE 7—The committee believes the methods for oxygen and nitrogen are better than the precision would indicate, and that the poor reproducibility is attributable to the difficulty of excluding air from these samples. Precise results are heavily dependent upon extreme care in sampling and handling. The use of continuous analyzers is preferred, and is recommended whenever circumstances permit.

12.2 *Bias*—The bias of the procedure in this test method has not yet been determined but it is now under consideration by the responsible committee.

### 13. Keywords

13.1 carbon dioxide; ethane; ethylene; gas chromatography; hydrocarbons; methane; nitrogen

## ANNEX

### (Mandatory Information)

#### A1. WARNING STATEMENTS

##### A1.1 Flammable Gas

- A1.1.1 Keep away from heat, sparks, and open flame.
- Use with adequate ventilation.
- Never drop cylinder. Make sure cylinder is supported at all times.
- Keep cylinder out of sun and away from heat.
- Always use a pressure regulator. Release regulator tension before opening cylinder.

- Do not transfer cylinder contents to another cylinder. Do not mix gases in cylinder.
- Keep cylinder valve closed when not in use.
- Do not inhale.
- Do not enter storage areas unless adequately ventilated.
- Stand away from cylinder outlet when opening cylinder valve.
- Keep cylinder from corrosive environment.

Do not use cylinder without label.  
Do not use dented or damaged cylinder.  
For technical use only. Do not inhale.

## A1.2 Compressed Gases

A1.2.1 Keep container closed.  
Use with adequate ventilation.  
Do not enter storage areas unless adequately ventilated.  
Always use a pressure regulator. Release regulator tension before opening cylinder.  
Do not transfer to cylinder other than one in which gas is received. Do not mix gases in cylinders.  
Do not drop cylinder. Make sure cylinder is supported at all times.  
Stand away from cylinder outlet when opening cylinder valve.  
Keep cylinder out of sun and away from heat.  
Keep cylinder from corrosive environment.  
Do not use cylinder without label.  
Do not use dented or damaged cylinder.  
For technical use only. Do not use for inhalation purposes.

## A1.3 Hydrogen

A1.3.1 **Warning**—Extremely flammable gas under pressure.  
Keep away from heat, spark, and open flame.  
Use with adequate ventilation.  
Never drop cylinder. Make sure cylinder is supported at all times.  
Keep cylinder out of sun and away from heat.  
Always use a pressure regulator. Release regulator tension before opening cylinder.  
Do not transfer cylinder contents to another cylinder. Do not mix gases in cylinder.  
Keep cylinder valve closed when not in use.  
Do not inhale.  
Do not enter storage areas unless adequately ventilated.  
Stand away from cylinder outlet when opening cylinder valve.  
Keep cylinder from corrosive environment.

## A1.4 Oxygen

A1.4.1 Keep oil and grease away. Do not use oil or grease on regulators, gauges or control equipment.  
Use only with equipment condition for oxygen service by carefully cleaning to remove oil, grease and other combustibles.  
Keep combustibles away from oxygen and eliminate ignition sources.  
Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.  
Always use a pressure regulator. Release regulator tension before opening cylinder valve.  
All equipment and containers used must be suitable and recommended for oxygen service.  
Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder.  
Do not mix gases in cylinders.  
Do not drop cylinder. Make sure cylinder is secured at all times.  
Keep cylinder valve closed when not in use.  
Stand away from outlet when opening cylinder valve.  
For technical use only. Do not use for inhalation purposes.  
Keep cylinder out of sun and away from heat.  
Keep cylinder from corrosive environment.  
Do not use cylinder without label.  
Do not use dented or damaged cylinders. See Compressed Gas Association booklets G-4 and G-4.1 for details of safe practice in the use of oxygen.

## A1.5 Carbon Monoxide

A1.5.1 Harmful or fatal if inhaled.  
Dangerous when exposed to flame.  
Keep away from heat, sparks, and open flame.  
Use with adequate ventilation.  
Use fume hood whenever possible.  
Avoid build-up of vapor and eliminate all sources of ignition, especially nonexplosion proof electrical apparatus and heaters.  
Avoid breathing.

## APPENDIX

### (Nonmandatory Information)

## X1. PREPARATION OF METHANATION REACTOR

### X1.1 Scope

X1.1.1 This method describes the preparation of a methanation reactor to convert carbon monoxide and carbon dioxide to methane, which can then be determined using a flame ionization detector at levels less than 1 ppm.

### X1.2 Significance and Use

X1.2.1 The use of a flame ionization detector to enhance the detection limits for carbon monoxide and carbon dioxide is made possible by conversion of these gases to methane.

### X1.3 Apparatus

X1.3.1 *Tubing*, 152.4 mm (6 in.) of 6.35 mm (¼ in.) stainless steel.  
X1.3.2 *Aluminum Block*—101.6 mm by 152.4 mm by 15.8 mm (4 in. by 6 in. by 5/8 in.) drilled to accept a ¼ in. tube snugly.  
X1.3.3 *Cartridge Heater*—175 W with variable autotransformer.  
X1.3.4 *Thermocouple Sensor*—Chromel alumel.

NOTE X1.1—Commercial instruments performing the determination in compliance with this procedure are available.

## **X1.4 Reagents and Materials**

### **X1.4.1 Insulation.**

X1.4.2 Harshaw methanation catalyst-Ni-104t, 100 mesh to 120 mesh, or catalyst prepared as in **X1.5**.

## **X1.5 Catalyst Preparation**

X1.5.1 Hydrogenation catalyst: Prepare by weighing 20 g  $\pm$  0.1 g of nickel nitrate hexahydrate into a 100 mL beaker. Add 40 mL of methanol. Weigh 20 g  $\pm$  0.1 g of Chromosorb “P” into an evaporating dish. After the nickel nitrate crystals have dissolved, slowly pour the solution over the Chromosorb. Warm the mixture to 65 °C on a hot plate and evaporate the methanol with constant stirring, until the mixture appears dry. The resultant catalyst is subsequently reduced in the hydrogenation tube during instrument preparation.

## **X1.6 Procedure**

X1.6.1 Using glass wool as a retainer, pack the 152.4 mm (6 in.) by 6.35 mm ( $\frac{1}{4}$  in.) stainless tube 38.1 mm (1.5 in.) from either end with catalyst. Allowing 38.1 mm (1.5 in.) of space at each end of the tube insures failure to produce a highly toxic compound, nickel-carbonyl.

X1.6.2 The aluminum block should have three holes drilled in it. One hole should be drilled through the block, lengthwise, in the center of the end, 6.35 mm ( $\frac{1}{4}$  in.) in diameter. Another hole should be drilled on either side of the center. Its dimensions should be 50.8 mm by 9.53 mm (2 in. by 0.375 in.) in diameter. This hole will accept the cartridge heater. The third hole should be 50.8 mm (2 in.) long and 3.18 mm ( $\frac{1}{8}$  in.) in diameter and on the opposite side of center as the cartridge heater. This will accept the thermocouple sensor.

X1.6.3 Place the packed tube through the block so that the ends extend equally from either end of the block. Place the cartridge heater in the block, wrap the system with insulation, and place the thermocouple in the 3.18 mm ( $\frac{1}{8}$  in.) hole. Use only stainless steel connectors and attach one end of the 6.35 mm ( $\frac{1}{4}$  in.) packed tube to detector inlet. Attach the discharge end of the chromatographic column to the other end of the reactor through a tee connector. The tee is provided in order to introduce 30 mL/min of hydrogen to the methanator.

X1.6.4 After setting the hydrogen flow, connect the heater to a variable autotransformer. The setting should be approximately 55. Allow the catalyst to condition for 24 h at 300 °C. Normal operating temperature for the methanator should be 325 °C  $\pm$  25 °C.

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