



Designation: D6159 – 17

# Standard Test Method for Determination of Hydrocarbon Impurities in Ethylene by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D6159; 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 methane, ethane, propane, propene, acetylene, *iso*-butane, propadiene, butane, trans-2-butene, butene-1, isobutene, cis-2-butene, methyl acetylene and 1,3-butadiene in high-purity ethylene. The purity of the ethylene can be calculated by subtracting the total percentage of all impurities from 100.00 %. Since this test method does not determine all possible impurities such as CO, CO<sub>2</sub>, H<sub>2</sub>O, alcohols, nitrogen oxides, and carbonyl sulfide, as well as hydrocarbons higher than decane, additional tests may be necessary to fully characterize the ethylene sample.

1.2 Data are reported in this test method as ppmV (parts per million by gaseous volume) and ppmMol (parts per million Mol). This test method was evaluated in an interlaboratory cooperative study in the concentration range of 4 ppmV to 340 ppmV (2 mg/kg to 204 mg/kg). The participants in the interlaboratory cooperative study reported the data in non-SI units. Wherever possible, SI units are included.

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.*

## 2. Referenced Documents

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

**D2504** Test Method for Noncondensable Gases in C<sub>2</sub> and Lighter Hydrocarbon Products by Gas Chromatography

**D2505** Test Method for Ethylene, Other Hydrocarbons, and Carbon Dioxide in High-Purity Ethylene by Gas Chromatography

**D5234** Guide for Analysis of Ethylene Product

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.D0.02 on Ethylene.

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<sup>2</sup> 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. Summary of Test Method

3.1 A gaseous ethylene sample is analyzed as received. The gaseous sample is injected into a capillary gas chromatograph. Sample may be introduced by direct valve injection or by split valve injection. The gas chromatograph is provided with a 6-port sampling valve and two wide bore capillary columns connected in series. These columns are a dimethyl polysiloxane column and a porous layer open tubular column (PLOT) Al<sub>2</sub>O<sub>3</sub>/KCl column. (See **Note 1**.) A flame ionization detector is used for detection. The integrated detector signal (peak areas) are corrected for detector response. The hydrocarbon impurities are determined and the total impurities are used to determine the ethylene content.

NOTE 1—This column is supplied by major column manufacturers.

## 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 certain hydrocarbon impurities can have deleterious effects. This test method is suitable for setting specifications, for use as an internal quality control tool, and for use in development or research work.

4.2 This test method does not detect such impurities as H<sub>2</sub>O, CO, CO<sub>2</sub>, and alcohols that may be present in the sample. Hydrocarbons higher than *n*-decane cannot be analyzed by this test method, if present in the sample. Test Method **D2504** addresses the analysis of noncondensable gases and Test Method **D2505** addresses the analysis of CO<sub>2</sub>. Guide **D5234** describes all potential impurities present in ethylene. These standards should be consulted when determining the total concentration of impurities in ethylene.

## 5. Apparatus

5.1 *Gas Chromatograph (GC)*, a gas chromatographic instrument provided with a temperature programmable column oven and a flame ionization detector (FID). Carrier gas is regulated by pressure control.

5.2 *Detector*—A flame ionization detector (FID) having a sensitivity of approximately 2.0 ppmV (1.2 mg/kg) or less for the compounds listed in 1.1. An FID was exclusively used in the interlaboratory cooperative study.

\*A Summary of Changes section appears at the end of this standard

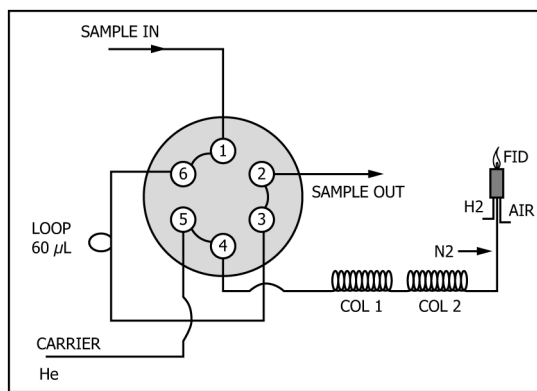


FIG. 1 Direct Valve Injection Sample Introduction: Valve Off—Sample Loading

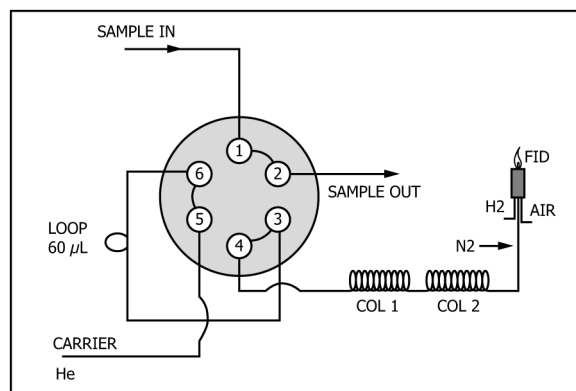


FIG. 2 Direct Valve Injection Sample Introduction: Valve On—Injection

5.3 *Column Temperature Programmer*—The chromatograph shall be capable of linear programmed temperature operation over a range sufficient for separation of the components of interest. Section 8 lists the recommended operating conditions. The programming rate shall be sufficiently reproducible to obtain retention repeatability of 0.05 min (3 s) throughout the scope of this analysis.

5.4 *Columns*—Couple the two columns in series with either a glass press tight connector or a mini-connector equipped with graphite ferrules.

5.4.1 *Column 1*, 50 m, 0.53 mm inside diameter (ID) KCl deactivated Al<sub>2</sub>O<sub>3</sub> PLOT column. Relative retention is dependent on the deactivation method of the column. Other deactivated Al<sub>2</sub>O<sub>3</sub> plot columns using sulfates as the deactivating agent were also used in the interlaboratory comparison.

5.4.2 *Column 2*, 30 m, 0.53 mm ID, 5 μm film thickness methyl polysiloxane. This column improves the separation of methyl acetylene, *iso*-pentane, and *n*-pentane.

5.5 *Sample Inlet System*—Two injection modes were used for the interlaboratory cooperative study.

5.5.1 A gas sampling valve placed in an unheated zone of the gas chromatograph injecting the sample directly into the column.

5.5.2 A gas sampling valve placed in an unheated zone of the gas chromatograph in conjunction with a splitter injector heated with a variable temperature control.

5.5.3 A gas sampling valve maintained at a constant temperature above ambient temperature may also be used, for example, by installation in a valve oven or equivalent.

### 5.6 Gas Sampling Valve and Injection System:

5.6.1 *Direct Valve Injection*—Use a 6-port valve provided with 1/16 in. fittings as the sample injection system. A typical valve arrangement is shown in Fig. 1 and Fig. 2. A 10 μL to 60 μL loop as shown in Fig. 1 has proven satisfactory to attain the detection limits described in this test method and not overload the column. Use good valve piping techniques to minimize dead volumes, cold spots, and long connections; as well as to ensure uniform heated zones. The preferred carrier gas control for sample introduction is pressure regulation. It is recommended that linearity for the impurity components be

verified either from multiple standards or careful dilution of the single calibration standard.

5.6.2 *Split Valve Injection*—Use a 6-port valve in conjunction with a splitter injector. A typical arrangement is shown in Fig. 3 and Fig. 4. Split ratios of 50:1 to 100:1 at split injector temperatures of 150 °C to 200 °C yield acceptable results. Loop sizes of 200 μL to 500 μL were used in the interlaboratory study. When using a splitter it is important to check linearity of the splitter. Inject the standard blend at 50:1, 75:1, and 100:1 split ratios. Check the response factors of the listed impurities as determined in 9.1, and the factors shall not vary more than 3 %. Linearity may be verified when the system is placed into service and when major maintenance is performed, such as installation of new GC columns.

5.7 *Data Acquisition System*—Use a computerized data acquisition system for peak area integration, as well as for recording the chromatographic trace.

## 6. Reagent Materials

6.1 *Standard Mixture*—Use a gravimetrically blended gas standard containing levels of 2 mg/kg to 204 mg/kg (4 ppmV to 340 ppmV as a gas) of each of the trace components listed in Table 1 to calibrate the detector's response. The standard gas mixture shall be prepared gravimetrically from known raw materials, and cross contaminants shall be taken into account. The mixtures should be certified analytically such that the gravimetric and analytically derived values agree to an acceptable tolerance; that is ± 1 % or ± 2 %. The concentration of the minor components in the calibration standard shall be within 20 % to 50 % above the concentration of the process stream or samples. Convert the gravimetric concentrations to ppmMol and its equivalent gaseous volumes ppmV as follows:

$$\text{Mol}_i = \text{g}/\text{MW}_i \quad (1)$$

where:

Mol<sub>i</sub> = the absolute mole from gravimetric standard of compound 'i' including ethylene,

g<sub>i</sub> = is the mass in grams of compound 'i' from the gravimetric standard, and

MW<sub>i</sub> = is the molecular weight of compound 'i'.

and the ppmMol and ppmV can then be calculated as follows:

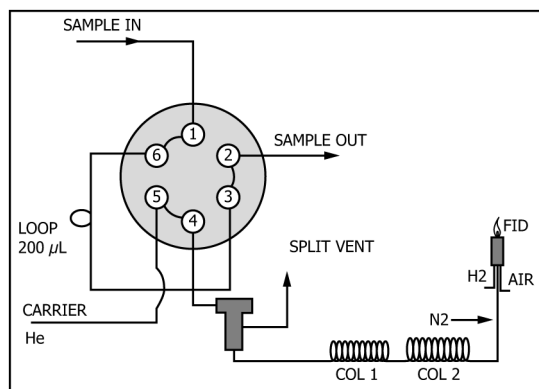


FIG. 3 Split Valve Injection Sample Introduction: Valve Off—Sample Loading

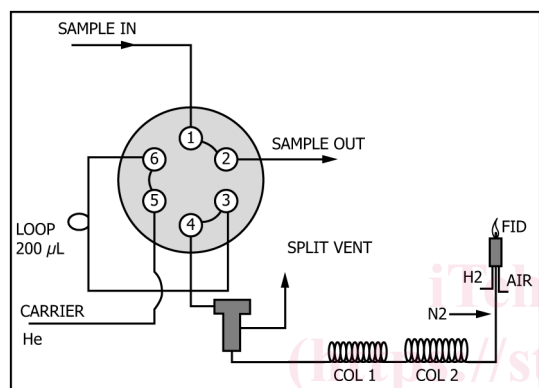


FIG. 4 Split Valve Injection Sample Introduction: Valve On—Injection

$Mol_{i \text{ to } n}$  = sum of moles of all components 'i' from 'i' to 'n' in the calibration standard and where 'n' is the number of distinct components, inclusive of ethylene.

Table 2 gives an example calculation.

6.2 Compressed Helium, gas having purity of 99.999 %, or better, with a total hydrocarbon level of <1 ppmV.

NOTE 2—Compressed helium is a gas under high pressure.

6.3 Compressed Hydrogen, gas used as fuel in the FID detector (less than 1.0 ppmV hydrocarbon impurities).

NOTE 3—Hydrogen is an extremely flammable gas under high pressure.

6.4 Compressed Air—Air having less than 1.0 ppmV of hydrocarbon impurities for the operation of the FID is recommended.

NOTE 4—Compressed air is a gas under high pressure and supports combustion.

6.5 Compressed Nitrogen—Nitrogen having less than 1.0 ppmV of hydrocarbon impurities is used as make up gas in order to increase the response of the FID.

NOTE 5—Compressed nitrogen is a gas under high pressure.

## 7. Sampling

7.1 Gas samples are collected in 1000 mL stainless steel cylinders equipped with a rupture disk capable of sustaining 5500 kPa to 6900 kPa (800 psi to 1000 psi) in order to protect against dangerous pressure build up. It is important to thoroughly flush the cylinder with the sample prior to sealing, thus excluding air and other contaminants that may be present in the cylinder. Ensure that sampling does not concentrate preferentially the higher boiling hydrocarbons during the purging step.

## 8. Preparation of Apparatus

8.1 Instrument Conditions—Adjust the instrumental parameters to the following conditions:

- Column Temperature
- Equilibration time: 2.0 min
- Initial: 35 °C
- Final: 190 °C (see Note 6)

NOTE 6—PLOT Al<sub>2</sub>O<sub>3</sub> columns should not be heated above 200 °C since above this temperature the column activity is changed.

- Rate: 4 °C/min
- Initial time: 2.0 min
- Final time: 15 min.
- Carrier Gas
- Helium at 6 mL/min to 8 mL/min
- Injection System with Splitter
- Sample valve loop volume = 200 µL to 500 µL
- Sample valve temperature = 35 °C to 45 °C
- Splitter temperature = 150 °C to 200 °C
- Split ratio = 50:1 to 100:1
- Flame Ionization Detector, 300 °C
- Air = 300mL/min (see Note 7)

TABLE 1 Typical Compounds and Retention Times for Common Hydrocarbon Impurities in Ethylene<sup>A</sup>

Components	Retention Time, min
Methane	7.02
Ethane	8.12
Ethene	9.00
Propane	12.41
Propene	16.93
Ethyne	19.52
Isobutane	19.76
Propadiene	20.48
Butane	20.78
t-2-Butene	24.99
Butene-1	25.23
Isobutylene	25.90
c-2-Butene	26.71
Propyne	29.14
1,3-Butadiene	30.37

<sup>A</sup> Conditions as specified in Section 8.

$$ppmMol_i = ppmV_i = 10E6 \times [Mol_i] / [\Sigma Mol_{i \text{ to } n}] \quad (2)$$

where:

- ppmMol<sub>i</sub> = final ppmMol of component 'i' in the calibration standard,
- ppmV<sub>i</sub> = final ppmV of component 'i' in the calibration standard, and