Designation: D6159 – 23

Standard Test Method for
Determination of Hydrocarbon Impurities in Ethylene by Gas Chromatography[1]

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_2, H_2O, 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2504 Test Method for Noncondensable Gases in C_2 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
F307 Practice for Sampling Pressurized Gas for Gas Analysis

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_2O_3/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_2O, CO, CO_2, 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_2. Guide D5234 describes all potential impurities present in ethylene. These standards should be consulted when determining the total concentration of impurities in ethylene.

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

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.

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_2O_3 PLOT column. Relative retention is dependent on the deactivation method of the column. Other deactivated Al_2O_3 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 interlabora-
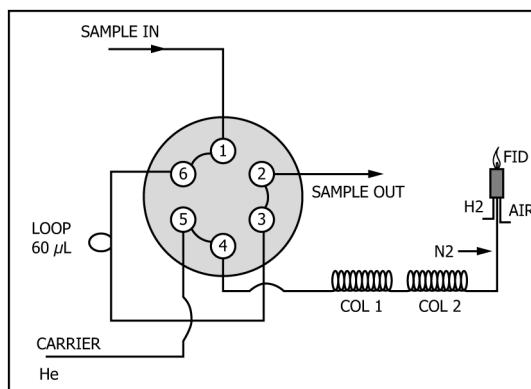

FIG. 1 Direct Valve Injection Sample Introduction: Valve Off—Sample Loading
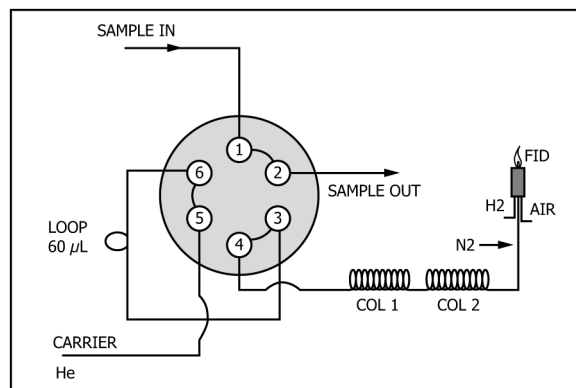

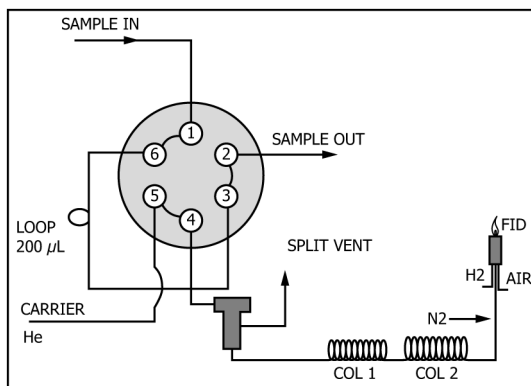FIG. 2 Direct Valve Injection Sample Introduction: Valve On—Injection

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

tory 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.