



Standard Test Method for Determination of Hydrocarbon Impurities in Ethylene by Gas Chromatography¹

This standard is issued under the fixed designation D 6159; 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 is used for 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, CO₂, H₂O, 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 volume). This test method was evaluated in an interlaboratory cooperative study in the concentration range of 4 to 340 ppmV (2 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:

D 2504 Test Method for Noncondensable Gases in C₂ and Lighter Hydrocarbon Products by Gas Chromatography²

D 2505 Test Method for Ethylene, Other Hydrocarbons, and Carbon Dioxide in High-Purity Ethylene by Gas Chromatography²

D 5234 Guide for Analysis of Ethylene Product³

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.

A split-injector may or may not be used. 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 silicone column and a (porous layer open tubular column (PLOT) Al₂O₃/KCl column.⁴ 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.

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 H₂O, CO, CO₂, 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 D 2504 addresses the analysis of noncondensable gases and Test Method D 2505 addresses the analysis of CO₂. Guide D 5234 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). Regulate the carrier gas by pressure control.

5.2 *Detector*—Use 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

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

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

⁴ This column is supplied by major column manufacturers.

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 Al₂O₃ PLOT column.⁴ Relative retention is dependent on the deactivation method of the column. Other deactivated Al₂O₃ 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, 5µm film thickness methyl silicone. 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.

5.6 Gas Sampling Valve and Injection System—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. Use a 10–60µL loop as shown in Fig. 1. Use good valve maintenance techniques to avoid such problems as dead volumes, cold spots, long connections, and non-uniform heated zones. The preferred carrier gas arrangement for sample introduction is pressure regulation. Use a 6-port valve in conjunction with a splitter injector. A typical arrangement is shown in Fig. 3 and Fig. 4. Use split ratios of 50:1 to 100:1 at temperatures of 150°C to 200°C. Loop sizes of 200–500µL 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 as determined in 9.1, and the factors shall not vary more than 3 %.

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

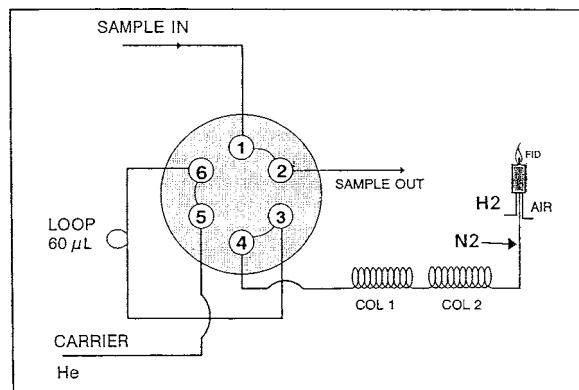


FIG. 2 Valve On – Injection

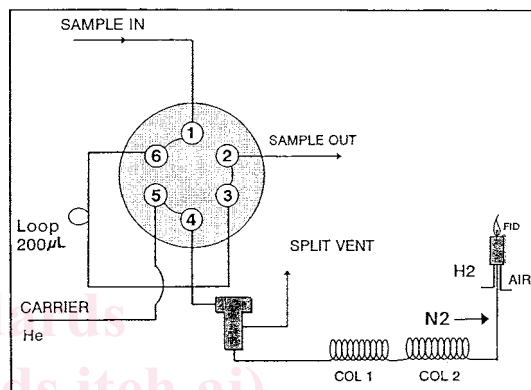


FIG. 3 Valve Off – Sample Loading

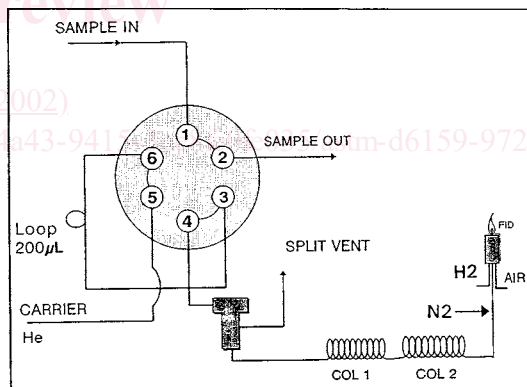


FIG. 4 Valve On – Injection

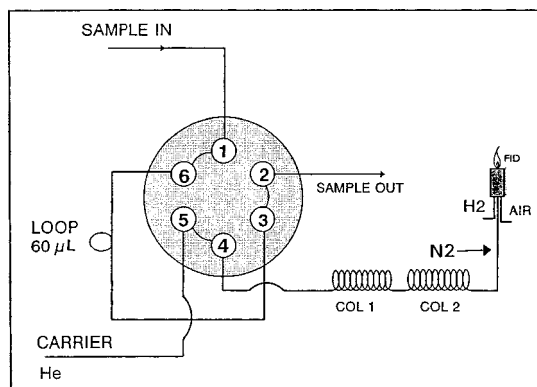


FIG. 1 Valve Off – Sample Loading

6. Reagent Materials

6.1 Standard Mixture—Use a gravimetrically blended gas standard containing levels of 2 to 204 mg/kg (4 to 340 ppmV) 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.