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

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, 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 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 dose 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 C_2 and Lighter Hydrocarbon Products by Gas Chromatography[2]
D 2505 Test Method for Ethylene, Other Hydrocarbons, and Carbon Dioxide in High-Purity Ethylene by Gas Chromatography[2]
D 5234 Guide for Analysis of Ethylene Product[3]

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) Al_2O_3/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 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 D 2504 addresses the analysis of noncondensable gases and Test Method D 2505 addresses the analysis of CO_2. 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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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.D0 on Hydrocarbons for Chemical and Special Uses.
Current edition approved Dec. 10, 2002. Published March 2003. Originally approved in 1997. Last previous edition approved in 1997 as D 6159 – 97.
[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 repro-ducible 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.[4] Relative retention is depen-dent on the deactivation method of the column. Other deacti-vated 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, 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 com-puterized data acquisition system for peak area integration, as well as for recording the chromatographic trace.
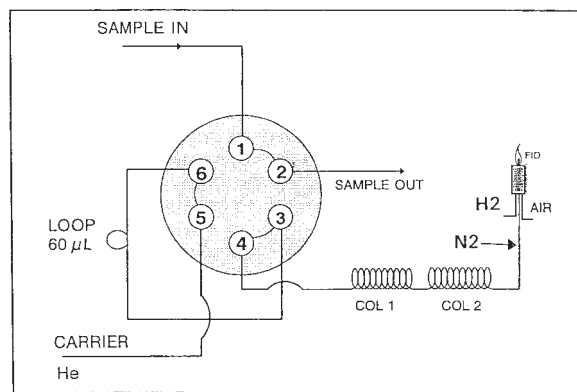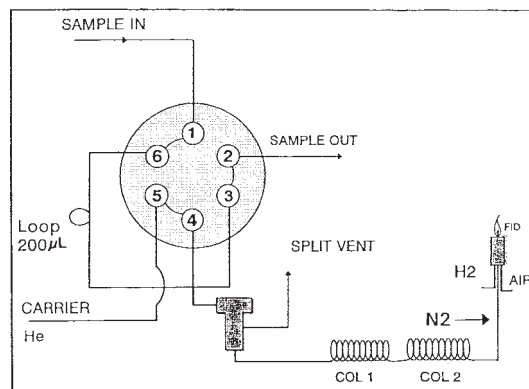

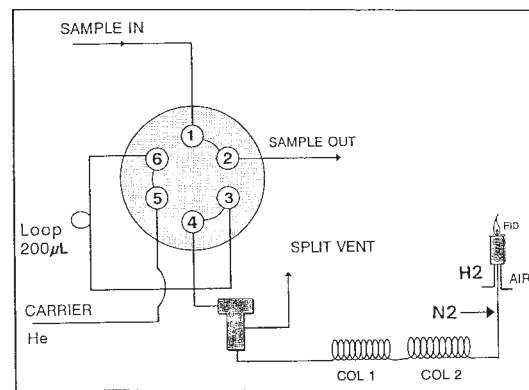**FIG. 2 Valve On – Injection**

FIG. 3 Valve Off – Sample Loading

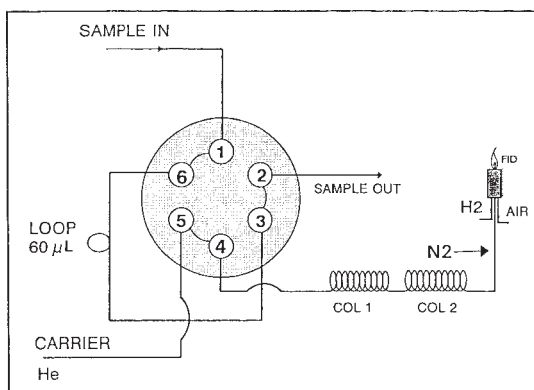
FIG. 4 Valve On – Injection

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 analyti-cally 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.

FIG. 1 Valve Off – Sample Loading

TABLE 1 Typical Compounds and Retention Times for Common Hydrocarbon Impurities in Ethylene[A]

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

[A] Conditions as specified in Section 8.

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

NOTE 1—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 2—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 3—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 4—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 to 6900 kPa (800 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.

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[5]
  Rate: 4°C/min
  Initial time: 2.0 min
  Final time: 15 min.
  Carrier Gas
  Helium at 6 to 8 mL/min

  Injection System with Splitter
  Sample valve loop volume = 200–500μl
  Sample valve temperature = 35° to 45°C
  Splitter temperature = 150° to 200°C
  Split ratio = 50:1 to 100:1
  Flame Ionization Detector, 300°C
  Air = 300mL/min[6]
  H_2= 30mL/min
  Makeup = N_2 at 20mL/min
  Range = suitable to obtain measurable counts for the impurities
  Injection System using a Valve Directly
  Sample valve loop volume = 10–60μl
  Sample valve temperature = 35 to 45°C

8.2 When the G.C. has achieved a ready status, proceed with analysis.

9. Calibration

9.1 Proceed to inject the standard mixture. Connect the gaseous sample to the sample port and flush the sample loop for a period of 30 s. Close the standard sample cylinder outlet and when the pressure drops to atmospheric pressure and no sample elutes, inject the standard sample and proceed with the analysis. At least three standard determinations should be made to obtain a relative standard deviation of the measurements.

9.2 *Determination of Calibration Factors*—For each impurity present in the standard, calculate the calibration factor as follows:

$$Cf = Ci/Ai \qquad (1)$$

where:
Cf = the calibration factor,
Ci = the concentration of the impurity i in the standard (usually expressed as ppmV), and
Ai = the area counts obtained for that impurity as integrated by the data acquisition system.

9.2.1 It is important that the system linearity is checked by injecting standard gas samples of varying impurity concentration over a range covering the impurity concentration range in the samples analyzed. Verify that the system responds linearly and that the response is of the type $y = mx + b$ with $b = 0$. Use a linear calibration forced through the origin.

10. Procedure

10.1 The sample shall be injected under the same temperature and pressure conditions as the standard mixture.

10.2 Connect the gas sample to the G.C. sample port. Flush the loop for a period of 30 s. Close the sample cylinder shut-off valve and inject the sample the moment the loop reaches atmospheric pressure. Integrate the areas of the impurities. Identify the impurities by comparing their retention time to that obtained with the standard mixture. A typical sample chromatogram is shown in Fig. 5.

11. Calculations

11.1 Calculate the concentration of each impurity to the nearest ppmV as follows:

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[5] PLOT Al_2O_3 columns should not be heated above 200°C since above this temperature the column activity is changed.

[6] Follow the values suggested by instrument manufacturer.

COMPONENT	mg/kg
1 METHANE	66
2 ETHANE	588
3 PROPANE	16.0
4 PROPYLENE	19.0
5 ACETYLENE	15.0
6 ISOBUTANE	30.0
7 PROPADIENE	16.0
8 N-BUTANE	39.0
9 t-2-BUTENE	16.0
10 BUTENE-1	32.0
11 ISOBUTYLENE	50.0
12 c-2-BUTENE	15.0
13 METHYL ACETYLENE	28.0
14 1,3, BUTADIENE	15.0
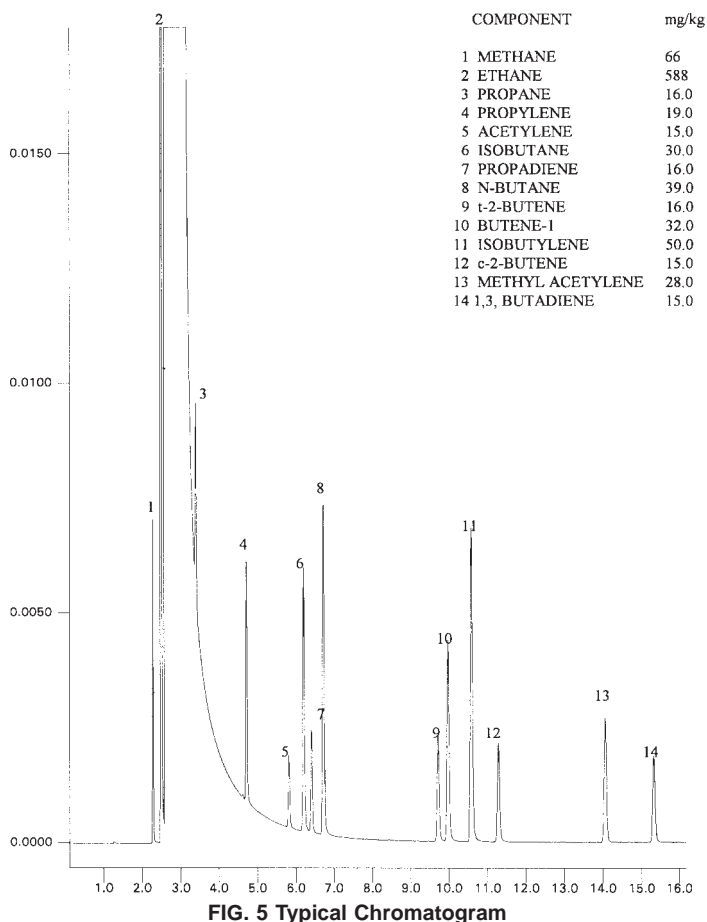
FIG. 5 Typical Chromatogram

$$Ci = (Cfi)(Ai) \qquad (2)$$

where

Ci = concentration of the impurity in the sample in ppmV,

Cfi = calibration factor previously calculated in Eq 1 (units are usually ppmV/counts), and

Ai = integrated area of the impurity from the data acquisition system.

11.2 Determine the total amount of hydrocarbon impurities by summing the concentrations of the individual impurities. Calculate the concentration of the ethylene by subtracting the total impurities concentration from 100.00 %. Since this test method cannot measure such impurities as CO, CO_2, O_2, N_2, H_2O and alcohols, it will be necessary to analyze the ethylene for these impurities as described in Test Methods D 2504 and D 2505. The sum total of all impurities analyzed should be used in reporting the ethylene concentration.

12. Precision and Bias [7]

12.1 *Precision*:

12.1.1 An interlaboratory cooperative study was adopted with 7 laboratories participating. Fourteen hydrocarbon impurities in ethylene were measured; the results obtained are shown in Table 2.

12.1.2 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, and in the normal and correct operation of the test method exceed the values only one case in twenty as shown in Table 2, where *r* is the repeatability and *X* is the concentration (ppmV) of the component.

12.1.3 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical material would, in the long run, exceed the values in only one case in twenty as shown in Table 2, where *R* is the reproducibility and *X* is the mean concentration (ppmV) of the component.

12.2 *Bias*—There is, at this time, no accepted reference material suitable for measuring bias for this test method.

13. Keywords

13.1 ethylene; gas chromatography; hydrocarbon impurities

TABLE 2 Repeatability and Reproducibility

Component	Range, ppmV	Repeatability, (r)	Reproducibility (R)
Methane	5.57 - 62.3	0.02277 X ^ 0.6	1.408 X ^ 0.6
Ethane	35.1 - 338	0.03811 X	0.3165 X
Propane	8.07 - 59.7	0.03273 (X + 21.23)	0.2277 (X + 4.558)
Propene	4.67 - 49.2	0.04780 X ^ 1.15	0.4849 X ^ 1.15
Ethyne	4.14 - 34.4	0.1189 X 0.8	5.471 X 0.8
*iso*butane	7.74 - 48.4	0.04370 X ^ 1.07	0.6728 X ^ 1.07
Propadiene	4.53 - 67.6	0.05091 (X + 0.7831)	0.7256 (X + 0.7831)
Butane	4.97 - 56.1	0.1156 X ^ 0.85	0.4399 X ^ 0.85
t-2-Butene	7.20 - 55.9	0.063960 X ^ 0.95	0.2196 X 0.95
Butene-1	6.18 - 56.9	0.03992 (X + 17.14)	0.1600 (X + 7.028)
*iso*butylene	4.13 - 55.6	0.1229 X ^ 0.85	0.3174 X ^ 0.85
C-2-Butene	8.16 - 56.6	0.08350 X ^ 0.93	0.3017 X ^ 0.93
Propyne	5.57 - 62.3	0.07518 ^ 0.9	1.136 X ^ 0.90
1,3 Butadiene	5.80 - 49.1	0.05205 X ^ 1.1	0.4613 X ^ 1.1