



# Standard Test Method for Determination of Hydrocarbons and Non-Hydrocarbon Gases in Gaseous Mixtures by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D7833; 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 is intended to quantitatively determine the non-condensed hydrocarbon gases with carbon numbers from  $C_1$  to  $C_{5+}$  and non-hydrocarbon gases, such as  $H_2$ ,  $CO_2$ ,  $O_2$ ,  $N_2$ , and  $CO$ , in gaseous samples. This test method is a companion standard test method to Test Method [D1945](#) and Practice [D1946](#) differing in that it incorporates use of capillary columns instead of packed columns and allows other technological differences.

1.2 Hydrogen sulfide can be detected but may not be accurately determined by this procedure due to loss in sample containers or sample lines and possible reactions unless special precautions are taken.

1.3 Non-hydrocarbon gases have a lower detection limit in the concentration range of 0.03 to 100 mole percent using a thermal conductivity detector (TCD) and  $C_1$  to  $C_6$  hydrocarbons have a lower detection limit in the range of 0.005 to 100 mole percent using a flame ionization detector (FID); using a TCD may increase the lower detection limit to approximately 0.03 mole percent.

1.3.1 Hydrocarbon detection limits can be reduced with the use of pre-concentration techniques and/or cryogenic trapping.

1.4 This test method does not fully determine individual hydrocarbons heavier than benzene, which are grouped together as  $C_{7+}$ . When detailed analysis is not required the compounds with carbon number greater than  $C_5$  may be grouped as either  $C_{6+}$ , or  $C_{7+}$ . Accurate analysis of  $C_{5+}$  components depends on proper vaporization of these compounds during sampling at process unit sources as well as in the sample introduction into the analyzer in the laboratory.

1.5 Water vapor may interfere with the  $C_{6+}$  analysis if a TCD detector is used.

1.6 Helium and argon may interfere with the determination of hydrogen and oxygen respectively. Depending on the

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee [D03](#) on Gaseous Fuels and is the direct responsibility of Subcommittee [D03.07](#) on Analysis of Chemical Composition of Gaseous Fuels.

Current edition approved Nov. 1, 2012. Published December 2012. DOI: 10.1520/D7833-12.

analyzer used, pentenes, if present, may either be separated or grouped with the  $C_{6+}$  components.

1.7 The values stated in SI units are to be regarded as standard.

1.8 *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>

[D1945 Test Method for Analysis of Natural Gas by Gas Chromatography](#)

[D1946 Practice for Analysis of Reformed Gas by Gas Chromatography](#)

[D3588 Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels](#)

[E355 Practice for Gas Chromatography Terms and Relationships](#)

[E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs](#)

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

### 2.2 ASTM Publication:

[ASTM DS 4B, 1991 Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds](#)

## 3. Terminology

3.1 Terminology related to the practice of gas chromatography can be found in Practice [E355](#).

### 3.2 Definitions:

3.2.1 *sample set*—a collection of samples taken from the same source or at similar component composition and concentrations.

<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.

#### 4. Summary of Test Method

4.1 Components in a representative sample are physically separated by gas chromatography (GC) and compared to calibration data obtained under identical operating conditions from a reference standard mixture of known composition. The numerous heavy-end components of a sample can be grouped into irregular peaks by reversing the direction of the carrier gas through the column at such time as to group the heavy ends either as C<sub>5</sub> and heavier, C<sub>6</sub> and heavier, or C<sub>7</sub> and heavier or alternatively elute them in the non-backflushed mode and summed accordingly. The composition of the sample is calculated by comparing the peak areas with the corresponding values obtained with the reference standard.

#### 5. Significance and Use

5.1 The hydrocarbon component distribution of gaseous mixtures is often required for end-use sale of this material. Applications such as chemical feedstock or fuel require precise compositional data to ensure uniform quality. Trace amounts of some hydrocarbon impurities in these materials can have adverse effects on their use and processing. Certain regulations may require use of such method.

5.2 The component distribution data of gaseous mixtures can be used to calculate physical properties such as relative density, vapor pressure, and heating value calculations found in Practice D3588. Precision and accuracy of compositional data is extremely important when this data is used to calculate various properties of petroleum products.

#### 6. Apparatus

6.1 *Gas Chromatograph (GC)*—This method allows the use of most gas chromatographic analyzers designed for gas analysis. Generally, any gas chromatographic instrument with a linear temperature programmable column oven or adequate temperature control to provide the required separation of gaseous compounds being analyzed may be used. The temperature control must be capable of obtaining retention time repeatability within 5% of the retention time for each component throughout the scope of this analysis for hydrocarbon and non-hydrocarbon gas analyses.

6.1.1 *Detector*—The type and number of detectors employed is dependent on gas analyzer model and vendor used. Detectors that can be used include, but are not limited to FID, TCD, AED (Atomic Emission Detector), HID (Helium Ionization Detector), and MS (Mass Spectrometer). Many systems use a 3 detector system:

(1) One FID (Flame Ionization Detector) for the determination of the hydrocarbon gases for the compounds listed in Table 1,

(2) One TCD (Thermal Conductivity Detector) dedicated to the determination of hydrogen utilizing nitrogen or argon as a carrier gas, and

(3) One TCD for the determination of all other required non-hydrocarbon gases using helium as the carrier gas.

6.1.2 A TCD may also be used for the analysis of the hydrocarbon gases (replacing the FID) when high sensitivity (< 0.03 mole percent) for trace analysis is not required.

**TABLE 1 List of Components Typically Analyzed (Hydrocarbons)**

Component	FID	TCD
C <sub>5</sub> olefin / C <sub>6</sub> + composite	X	X
oxygen/argon composite		X
hydrogen		X
carbon dioxide		X
hydrogen sulfide		X
nitrogen		X
carbon monoxide		X
methane	X	X
ethane	X	X
ethylene	X	X
propane	X	X
propylene	X	X
acetylene	X	X
isobutane	X	X
propadiene	X	X
n-butane	X	X
trans-2-butene	X	X
1-butene	X	X
isobutylene	X	X
cis-2-butene	X	X
neopentane	X	X
cyclopentane	X	X
isopentane	X	X
methyl acetylene	X	X
n-pentane	X	X
1,3-butadiene	X	X

6.1.3 Other detectors or combination of detectors may be used provided that they have sufficient response, linearity, and sensitivity to measure the components of interest at the concentration levels required for this application and meeting all of the quality controls specified in this method. Some analyzers, such as micro-analyzers, may contain up to 4-channels and separation systems to accomplish the analysis described in this method.

6.2 *Data Acquisition*—Any commercial computerized data acquisition system may be used for display of the chromatographic detector signal and peak area integration from all of the detectors used in the analysis. The device should be capable of generating and storing a calibration and reporting the final corrected response factor results.

6.3 *Sample Introduction and System Configurations*—Sample introduction is typically performed with automated valves containing sampling ‘loops’ of appropriate sizes. Fig. 1 gives a suggested configuration, although systems may vary slightly among gas analyzers. The combination of valve injection size and/or splitting inlet ratio must be selected such that the required sensitivity for the application is achieved and also that no component concentration in a sample is greater than the detector upper linearity limit. The sample inlet system shall be constructed of materials that are inert and non-adsorptive with respect to the components in the sample. The preferred material of construction is stainless steel. Copper, brass, and other copper-bearing alloys are unacceptable. The sample size limitation of 0.5 mL or smaller is selected relative to the linearity of the detector response, and efficiency of column separation. Larger samples may be used to determine low-quantity components to increase measurement accuracy. Sample sizes may be determined by experimentation or as recommended by analyzer vendors.

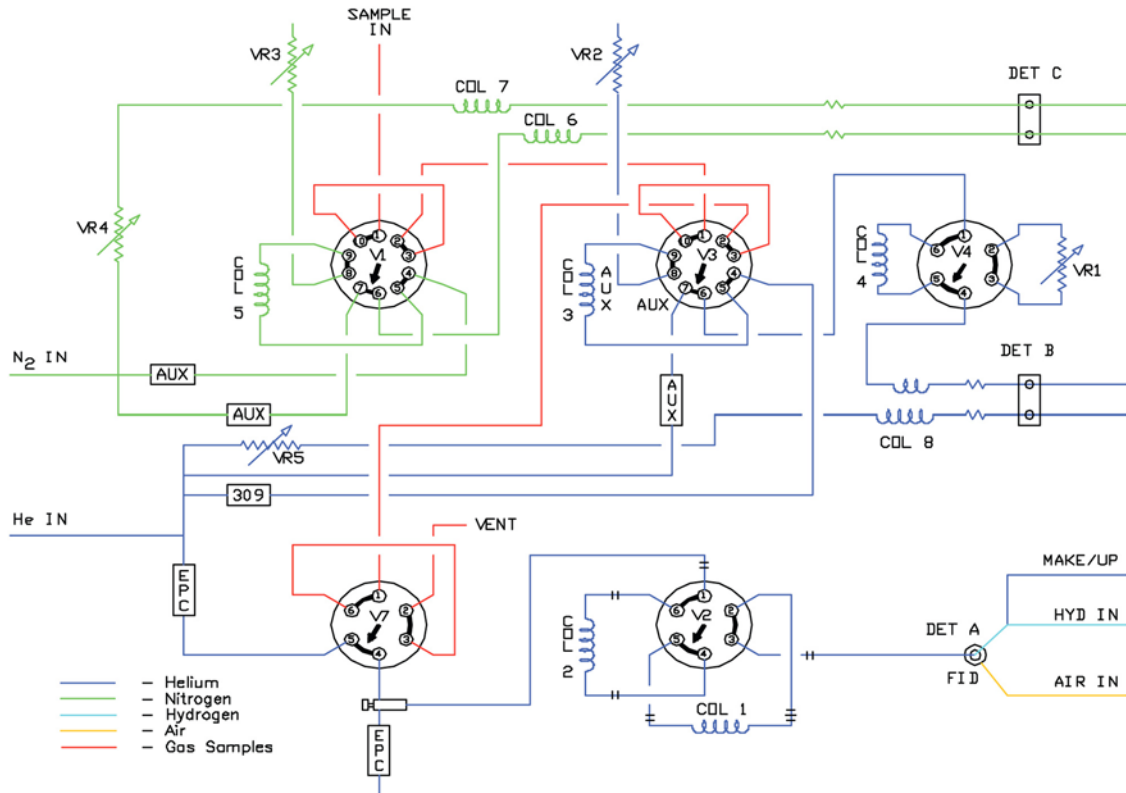


FIG. 1 Example of a Three Detector System for Analysis of Hydrocarbons and Non-Hydrocarbon Gases

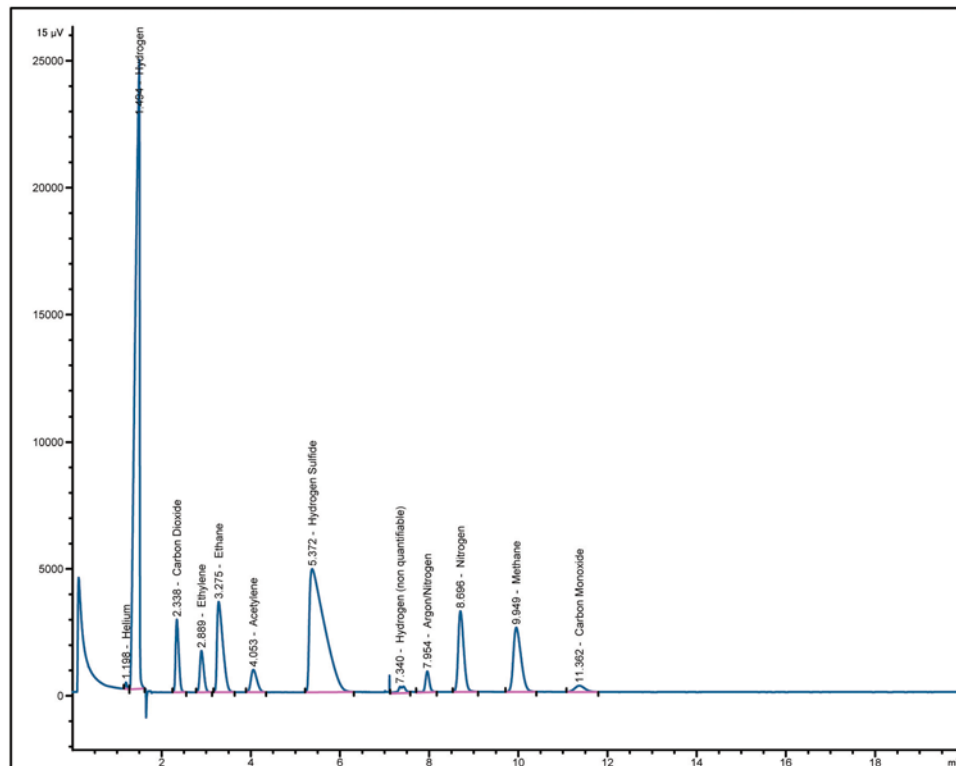


FIG. 2 Example Chromatogram of Non-Hydrocarbon and Light Hydrocarbon Gases from System Configuration in Fig. 1

6.3.1 Hydrogen Sulfide and Other Reactive Gases— Samples containing hydrogen sulfide and trace reactive gases

may benefit from use of surface treated metal surfaces, such as