



Designation: D8098 – 23

Standard Test Method for Permanent Gases in C₂ and C₃ Hydrocarbon Products by Gas Chromatography and Pulse Discharge Helium Ionization Detector¹

This standard is issued under the fixed designation D8098; 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 covers the determination of hydrogen, nitrogen, oxygen, methane, carbon monoxide, and carbon dioxide in the parts per billion mole (nmol/mol) to parts per million mole (μmol/mol) range in C₂ and C₃ hydrocarbons.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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.* For some specific hazard statements, see [Annex A1](#).

1.3.1 *The user is advised to obtain LPG safety training for the safe operation of this test method procedure and related activities.*

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

[D2505](#) Test Method for Ethylene, Other Hydrocarbons, and Carbon Dioxide in High-Purity Ethylene by Gas Chromatography

[D4175](#) Terminology Relating to Petroleum Products, Liquid

Fuels, and Lubricants

[D6300](#) Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants

[D7915](#) Practice for Application of Generalized Extreme Studentized Deviate (GESD) Technique to Simultaneously Identify Multiple Outliers in a Data Set

[E260](#) Practice for Packed Column Gas Chromatography

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

2.2 *Other Standards:*³

G-4 and G-4.1, Compressed Gas Association Booklet on the Use of Oxygen

3. Terminology

3.1 For definitions of terms used in this standard, see Terminology [D4175](#).

4. Summary of Test Method

4.1 The sample is separated in a gas chromatographic system using gas chromatography columns. Hydrogen, oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide (also known as the permanent gases) are detected on a pulse discharge detector. The concentration of the gases to be determined is calculated from the peak areas relative to an external standard. Helium is the required carrier gas for this detector. Ultra-high purity carrier gases and leak-free gas chromatography (GC) systems with getters are essential due to the extreme sensitivity of the detector. Argon, if present in the sample, may interfere with oxygen determination.

5. Significance and Use

5.1 The presence of trace amounts of hydrogen, oxygen, carbon monoxide, and carbon dioxide can have deleterious effects in certain processes using hydrocarbon products as feed stock. This test method is suitable for setting specifications, for use as an internal quality control tool, and for use in development and research work.

³ Available from Compressed Gas Association (CGA), 14501 George Carter Way, Suite 103, Chantilly, VA 20151, <http://www.cganet.com>.

¹ 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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² 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 this standard's Document Summary page on the ASTM website.

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

6. Apparatus

6.1 *Chromatograph*—Any gas chromatograph capable of maintaining the temperatures, pressures, and flows necessary for this analyses. The GC should also be capable of temperature programming of the oven to obtain optimum separation of the components. A typical configuration is shown in Fig. 1.

6.2 *Detectors*—(PDHID Pulse Discharge Detector Helium Ionization)—The PDHID detector is very sensitive to most organic or inorganic chemicals, thus requiring separation of the product gases from the permanent gas components.

6.2.1 *Alternative Detectors*—This test method is written for the pulsed discharge helium detector (PDHID), but other detectors can be used provided they have sufficient sensitivity, respond to all of the species in the scope, do not suffer from interferences, and satisfy quality assurance criteria. Regulatory agencies may require demonstration of equivalency of alternative detection systems to the PDHID.

6.3 *Gas Sample Valve*—Any valve that allows for column and/or sample inlet system selection. This valve may be purged with helium to minimize atmospheric air contamination into the valve rotor and column system.

6.4 *Helium Purifier*—Ultra-high purity carrier gas with an inline helium purifier installed to remove impurities is recommended. The purifier should be able produce gas with outlet impurities less than 10 nmol/mol of H₂O, H₂, O₂, N₂, NO, NH₃, CO, and CO₂, based on 100 μmol/mol total inlet impurities. A leak-free GC system is essential due to the high sensitivity of the detector.

6.5 *Constant-volume Gas Sampling Valve*—Any gas sampling valve capable of delivering a consistent volume of gas.

6.5.1 *Liquefied Petroleum Gas Samples*—Samples should be vaporized to allow introduction to the constant-volume gas sampling valve. The vaporization technique used must be

validated to ensure that sample discrimination is avoided. Pressure sampling devices may be used to inject a small amount of the liquid directly into the carrier gas.

6.6 *Materials of Construction*—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 analysis of oxygen and carbon monoxide may benefit from the use of treated metal surfaces.

6.7 *Column*—Any column may be used provided it will resolve the trace compound peaks present in concentrations of 20 ppmv or more so that the resolution ratio, A/B , will not be less than 0.4, where A is the depth of the valley on either side of peak B and B is the height above the baseline of the smaller of any two adjacent peaks (see Fig. 2). For compounds present in concentrations of less than 20 ppm, the ratio A/B may be less than 0.4. In the case where the small-component peak is adjacent to a large one, it may be necessary to construct the baseline of the small peak tangent to the curve as shown in Fig. 3.

6.7.1 Columns used to obtain the results in Fig. 4 using instrument conditions in Table 1:

6.7.1.1 *Column 1*, Porous divinylbenzene homopolymer, 30 m × 0.53 mm × 6 μm.

6.7.1.2 *Column 2*, Porous divinylbenzene homopolymer, 30 m × 0.53 mm × 6 μm.

6.7.1.3 *Column 3*, Molecular sieve, 30 m × 0.53 mm × 25 μm.

6.7.1.4 *Restrictor*, Fused silica open tube, 0.60 m × 5 m, restrictor should be sized as such to provide the same restriction as the molecular sieve column as to balance the flow across the six port bypass valve.

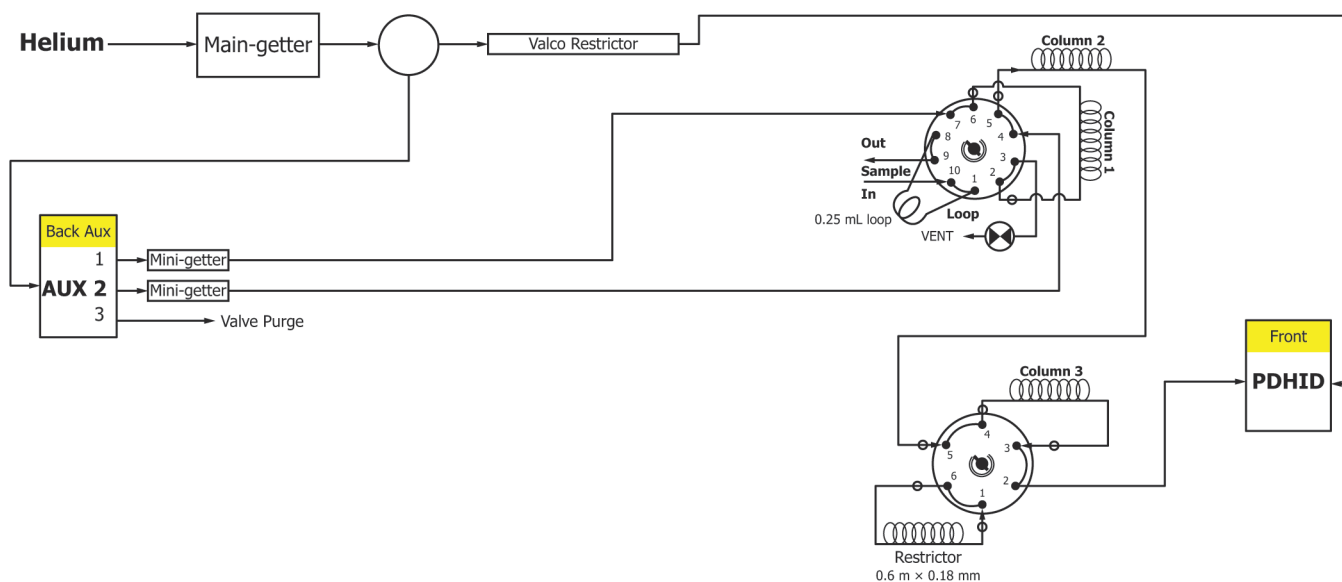


FIG. 1 Typical GC Configuration

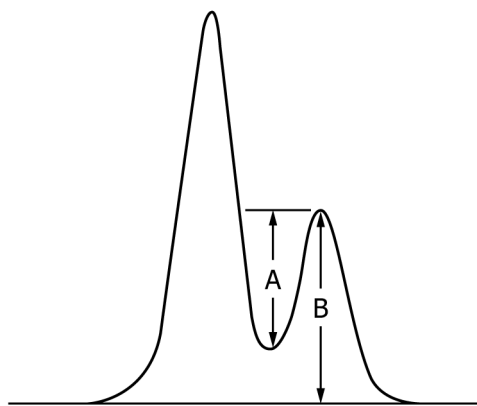


FIG. 2 Illustration of A/B Ratio

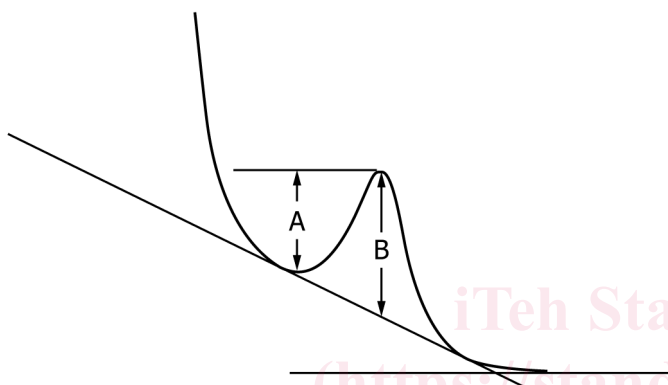


FIG. 3 Illustration of A/B Ratio for Small-component Peak

6.8 *Data System*—Any analytical data system that is capable of storing the retention time, integrating peak areas, and naming peaks is acceptable.

7. Reagents and Materials

7.1 *Gases for Calibration*—Pure or research-grade hydrogen, oxygen, nitrogen, carbon monoxide, and carbon dioxide will be needed to prepare synthetic standard samples as described in Test Method D2505. (**Warning**—Flammable gases. Hazardous pressure. See A1.1 through A1.5.) (**Warning**—Flammable. Poison. Harmful if inhaled. Dangerous when exposed to flame. See A1.5.) (**Warning**—Hazardous pressure. See A1.2.) Certified calibration blends are commercially available from numerous sources and can be used as the synthetic standard samples.

7.2 *Carrier Gases*—Helium, ultra-high purity (99.999 % pure, also known as 5.0 grade).

NOTE 1—Practice E260 contains information that will be helpful to those using this test method.

8. Sampling

8.1 Samples shall be supplied to the laboratory in high-pressure sample cylinders, obtained using the procedures described in Practice F307 or similar methods. All cylinders should meet all applicable safety requirements.

8.2 Sample system purging may require the use of an automated sampling system which provides for suitable sample system purge to eliminate atmospheric air contamination. Non-reproducible oxygen and nitrogen results relative to methane (refer to Table 1) indicate air contamination.

9. Calibration

9.1 Bring the equipment and columns to equilibrium and maintain a constant carrier gas rate and temperature.

9.2 Inject a known volume of the standard blends (prepared or purchased).

NOTE 2—The use of stripper columns, valves, and reverse-flow arrangement will facilitate removal of heavier gases and decrease the elapsed time of analysis.

9.3 Identify all of the desired peaks from the prepared synthetic blend. Multiple levels of blends can be used for generation of calibration tables.

9.4 The recommended method of measuring peak areas is electronic integration with capabilities of changing integration parameters. For each component present in the calibration standard, calculate the response factor according to Eq 1.

$$RF_i = C_i/A_i \quad (1)$$

where:

RF_i = the response factor for component i ,

C_i = the known concentration of i , and

A_i = the integrated area of peak i .

9.5 A data system may be used to automate these calculations and to plot peak areas versus concentrations of each compound in parts per million, by mole ($\mu\text{mol/mol}$).

10. Procedure

10.1 Connect the sample cylinder containing a gaseous sample to the gas sample valve inlet. Sample inlet system shall be purged thoroughly to eliminate ambient air. Either manual or automated purging may be used and shall be determined to be reliable when the lowest calibration standard containing oxygen and nitrogen are repeatable to less than 2 % relative standard deviation and the concentration is not decreasing from five successive injections.

10.2 Close the cylinder valve and allow the pressure of the sample in the tube to stabilize.

10.3 Inject the sample into the instrument using the gas sampling valve. The same valve should be used for calibration standard and sample (pressure of sample and calibration gas must be the same in the sample loop at injection time).

11. Calculation

11.1 The data system will automatically record the peak retention times and areas of the desired components. The detector response varies with the component being detected (do not assume equal response).

11.2 Using the area of the compound in the sample the data system will determine the concentration in $\mu\text{mol/mol}$ of the compound from the calibration table. A typical characterization

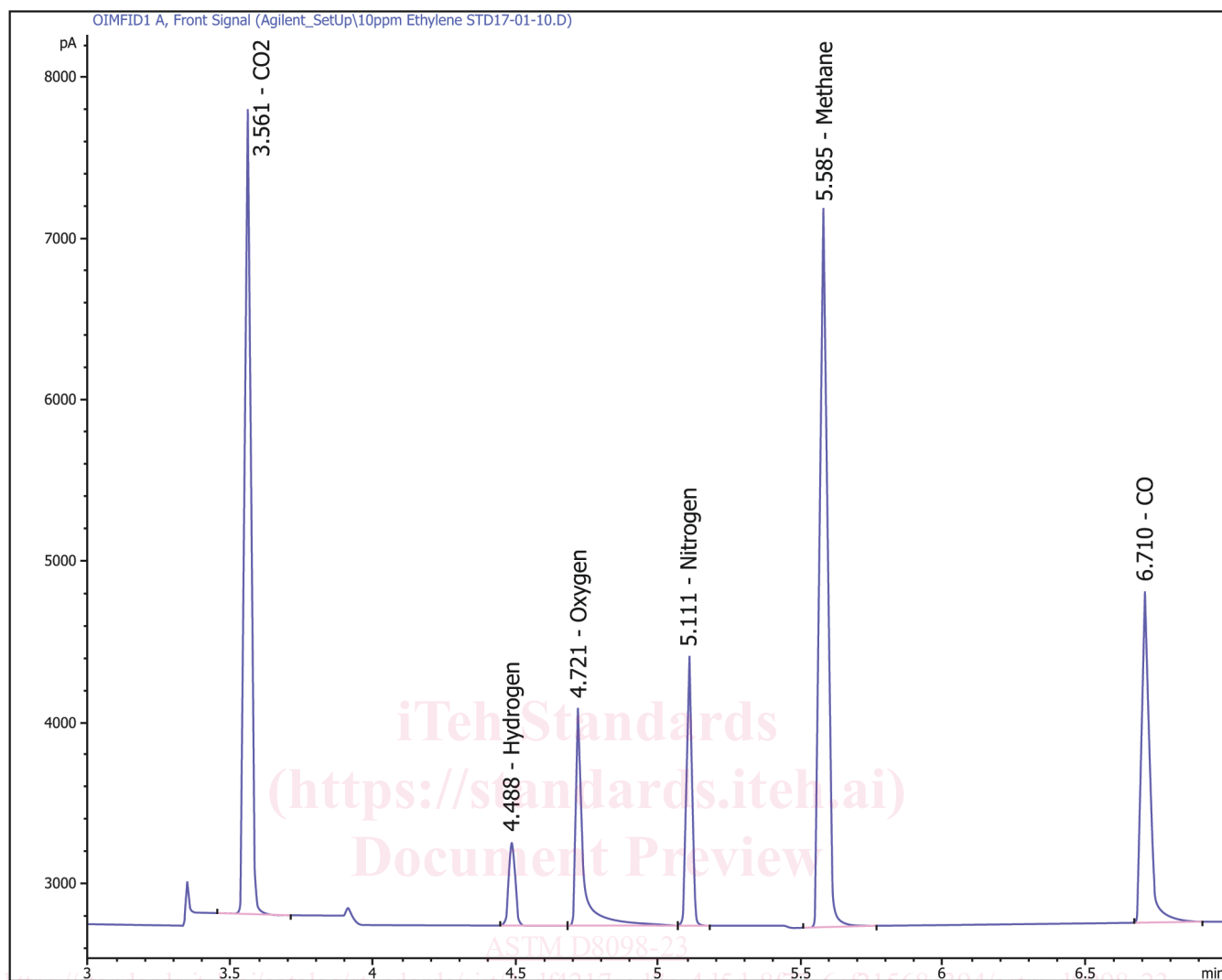


FIG. 4 Typical Chromatogram for Hydrogen, Oxygen, Nitrogen, Methane, Carbon Monoxide, and Carbon Dioxide

TABLE 1 Instrument Conditions

Temperatures	
Valve Box	100 °C
Column	50 °C (hold 5 min), ramp 20 °C/min to 85 °C (hold 1 min)
PDHID	200 °C
Flows	
Column 1, 2, 3	15 mL/min
Valve Timing	
Valve 1 (10 port)	On @ 0.01 min, Off @ 2.00 min
Valve 2 (6 port)	On @ 3.20 min, Off @ 3.80 min

showing hydrogen, oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide in ethylene is presented in Fig. 4.

12. Precision and Bias

12.1 The precision of this test method is based on an intralaboratory study of Test Method D8098, conducted in 2017. A single laboratory participated in this study, testing four concentration levels of two gas mixtures. Every “test result”

represents an individual determination. The laboratory reported 16 replicate test results for each compound analyzed. Practice D6300 was followed for the design and analysis of this interim repeatability study; the details are given in ASTM Research Report No. RR:D02-1866.⁴

12.1.1 *Repeatability (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying this same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would, in the long run, in the normal and correct operation of this test method, exceed the following values only in one case in 20.

12.1.1.1 Repeatability can be interpreted as maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of this test method.

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1866. Contact ASTM Customer Service at service@astm.org.

12.1.1.2 Repeatability limits are listed in [Table 2](#) and [Table 3](#). The data listed in [Table 2](#) and [Table 3](#) are based on 16 separate results for each compound.

12.1.2 It is not feasible to provide a complete precision statement covering repeatability and reproducibility for this test method at this time since test results from different laboratories and test samples meeting the required ASTM protocol are not available. This information is being determined and will be available on or before May 31, 2022.

TABLE 2 Concentration of Various Compounds in Ethylene (ppm)

Compound	Certified Concentration	Average \bar{X}	Variance v	Repeatability Standard Deviation S_r	Repeatability Limit r	RSD %	Average Recovery %	Number of Outliers Rejected per D7915
CO ₂	1	0.774	0.0007	0.0273	0.0764	3.53	77.4	0
	11.4	12.959	0.0029	0.0521	0.1459	0.40	113.7	0
	26.5	25.990	0.0011	0.0331	0.0927	0.13	98.1	0
	44	45.185	0.0319	0.1785	0.4998	0.40	102.7	0
H ₂	1.1	0.860	0.0004	0.0194	0.0543	2.26	78.2	0
	10.8	8.702	0.0056	0.0740	0.2072	0.85	80.6	0
	26.2	20.467	0.0092	0.0961	0.2691	0.47	78.1	0
	44	46.694	0.6109	0.7816	2.1885	1.67	106.1	0
O ₂	6	3.642	0.0058	0.0760	0.2128	2.09	60.7	0
	14.6	12.999	0.0188	0.1325	0.3710	1.02	89.0	0
	29.1	28.974	0.0306	0.1748	0.4894	0.60	99.6	0
	53.7	54.833	0.3519	0.5932	1.6610	1.08	102.1	0
N ₂	17.8	28.376	0.1482	0.3849	1.0777	1.36	159.4	0
	25.4	31.097	0.2781	0.5273	1.4764	1.70	122.4	0
	44.6	50.296	0.2781	0.5273	1.4764	1.05	112.8	0
	68.7	79.767	1.5678	1.2521	3.5059	1.57	116.1	0
CH ₄	1	0.982	0.0004	0.0192	0.0538	1.96	98.2	0
	11.1	10.575	0.0026	0.0503	0.1408	0.48	95.3	0
	26.5	24.136	0.0018	0.0429	0.1201	0.18	91.1	0
	44.4	42.704	0.0015	0.0384	0.1075	0.09	96.2	2
CO	1	0.857	0.0003	0.0046	0.0129	0.54	85.7	0
	10.5	8.811	0.0018	0.0418	0.1170	0.47	83.9	0
	25.7	22.307	0.0025	0.0502	0.1406	0.23	86.8	0
	43.2	43.627	0.0046	0.0675	0.1890	0.15	101.0	0