

ATTACHMENT 6



Standard Practice for Analysis of Reformed Gas by Gas Chromatography¹

This standard is issued under the fixed designation D 1946; 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 practice covers the determination of the chemical composition of reformed gases and similar gaseous mixtures containing the following components: hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene.

1.2 *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:

E 260 Practice for Packed Column Gas Chromatography²

3. Summary of Practice

3.1 Components in a sample of reformed gas are physically separated by gas chromatography and compared to corresponding components of a reference standard separated under identical operating conditions, using a reference standard mixture of known composition. The composition of the reformed gas is calculated by comparison of either the peak height or area response of each component with the corresponding value of that component in the reference standard.

4. Significance and Use

4.1 The information about the chemical composition can be used to calculate physical properties of the gas, such as heating (calorific) value and relative density. Combustion characteristics, products of combustion, toxicity, and interchangeability with other fuel gases may also be inferred from the chemical composition.

5. Apparatus

5.1 *Detector*—The detector shall be a thermal conductivity type or its equivalent in stability and sensitivity. The thermal conductivity detector must be sufficiently sensitive to produce

a signal of at least 0.5 mV for 1 mol % methane in a 0.5-mL sample.

5.2 *Recording Instruments*—Either strip chart recorders or electronic integrators, or both, are used to display the separated components. Although a strip chart recorder is not required when using electronic integration, it is highly desirable for evaluation of instrument performance.

5.2.1 The recorder, when used, shall be a strip chart recorder with a full-range scale of 5 mV or less (1 mV preferred). The width of the chart shall be not less than 150 mm. A maximum pen response time of 2 s (1 s preferred) and a minimum chart speed of 10 mm/min shall be required. Faster speeds up to 100 mm/min are desirable if the chromatogram is to be interpreted using manual methods to obtain areas.

5.2.2 *Electronic or Computing Integrators*—Proof of separation and response equivalent to that for the recorder is required for displays other than by chart recorder.

5.3 *Attenuator*—If manual methods are used to interpret the chromatogram, an attenuator must be used with the detector output signal to keep the peak maxima within the range of the recorder chart. The attenuator must be accurate to within 0.5 % between the attenuator range steps.

5.4 Sample Inlet System:

5.4.1 The sample inlet system must be constructed of materials that are inert and nonadsorptive with respect to the components in the sample. The preferred material of construction is stainless steel. Copper and copper-bearing alloys are unacceptable.

5.4.2 Provision must be made to introduce into the carrier gas ahead of the analyzing column a gas-phase sample that has been entrapped in either a fixed volume loop or tubular section. The injected volume must be reproducible such that successive runs of the same sample agree within the limits of repeatability for the concentration range as specified in 11.1.1.

5.4.3 If the instrument is calibrated with pure components, the inlet system shall be equipped to introduce a sample at less than atmospheric pressure. The pressure-sensing device must be accurate to 0.1 kPa (1 mm Hg).

5.5 Column Temperature Control:

5.5.1 *Isothermal*—When isothermal operation is used, the analytical columns shall be maintained at a temperature constant to 0.3°C during the course of the sample run and the corresponding reference run.

¹ This practice is under the jurisdiction of ASTM Committee D-3 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.07 on Analysis of Chemical Composition of Gaseous Fuels.

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² *Annual Book of ASTM Standards*, Vol 14.02.

5.5.2 *Temperature Programming*—Temperature programming may be used, as feasible. The oven temperature shall not exceed the recommended temperature limit for the materials in the column.

5.6 *Detector Temperature Control*—The detector temperature shall be maintained at a temperature constant to 0.3°C during the course of the sample run and the corresponding reference run. The detector temperature shall be equal to, or greater than, the maximum column temperature.

5.7 *Carrier Gas*—The instrument shall be equipped with suitable facilities to provide flow of carrier gas through the analyzer and detector at a flow rate that is constant to 1% throughout the analysis of the sample and the reference standard. The purity of the carrier gas may be improved by flowing the carrier gas through selective filters before its entry into the chromatograph.

5.8 Columns:

5.8.1 The columns shall be constructed of materials that are inert and nonadsorptive with respect to the components in the sample. The preferred material of construction is stainless steel. Copper and copper-bearing alloys are unacceptable.

5.8.2 Either an adsorption-type column or a partition-type column, or both, may be used to make the analysis.

NOTE 1—See Practice E 260 for general gas chromatography procedures.

5.8.2.1 *Adsorption Column*—This column must completely separate hydrogen, oxygen, nitrogen, methane, and carbon monoxide. If a recorder is used, the recorder pen must return to the baseline between each successive peak. Equivalent proof of separation is required for displays other than by chart recorder. Fig. 1 is an example chromatogram obtained with an adsorp-

tion column.

(1) Because of similarities in thermal conductivities, helium should not be used as the carrier gas for hydrogen when hydrogen is less than 1% of the sample. Either argon or nitrogen carrier gas is suitable for both percent and parts per million quantities of hydrogen.

(2) The use of a carrier gas mixture of 8.5% hydrogen and 91.5% helium will avoid the problem of reversing polarities of hydrogen responses as the concentration of hydrogen in the sample is increased.

(3) The precision of measurement of hydrogen can be increased by using a separate injection for hydrogen, using either argon or nitrogen for the carrier gas.

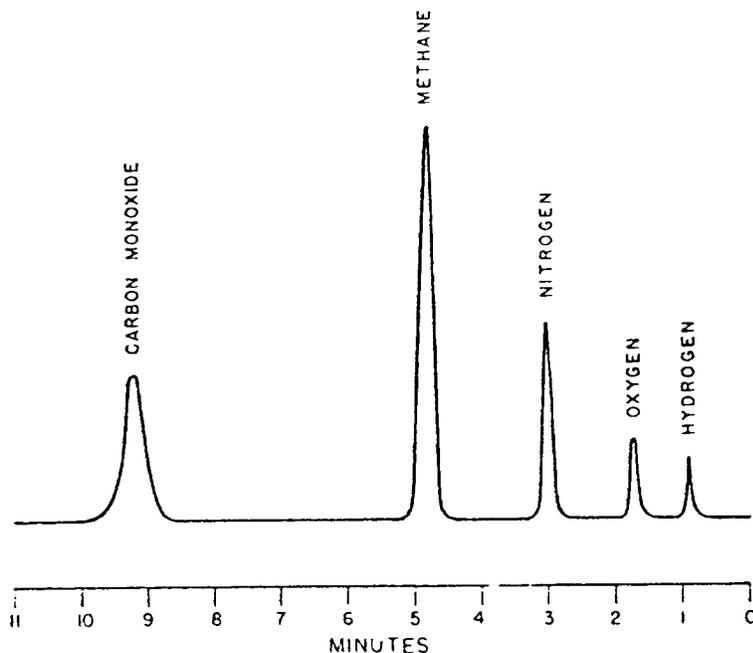
(4) Another technique for isolating the hydrogen in a sample is to use a palladium transfer tube at the end of the adsorption column; this will permit only hydrogen to be transferred to a stream of argon or nitrogen carrier gas for analysis in a second thermal conductivity detector.

5.8.2.2 *Partition Column*—This column must separate ethane, carbon dioxide, and ethylene. If a recorder is used, the recorder pen must return to the baseline between each successive peak. Equivalent proof of separation is required for displays other than by chart recorder. Fig. 2 is an example chromatogram obtained with a partition column.

5.8.3 *General*—Those column materials, operated either isothermally or with temperature programming, or both, may be used if they provide satisfactory separation of components.

6. Reference Standards

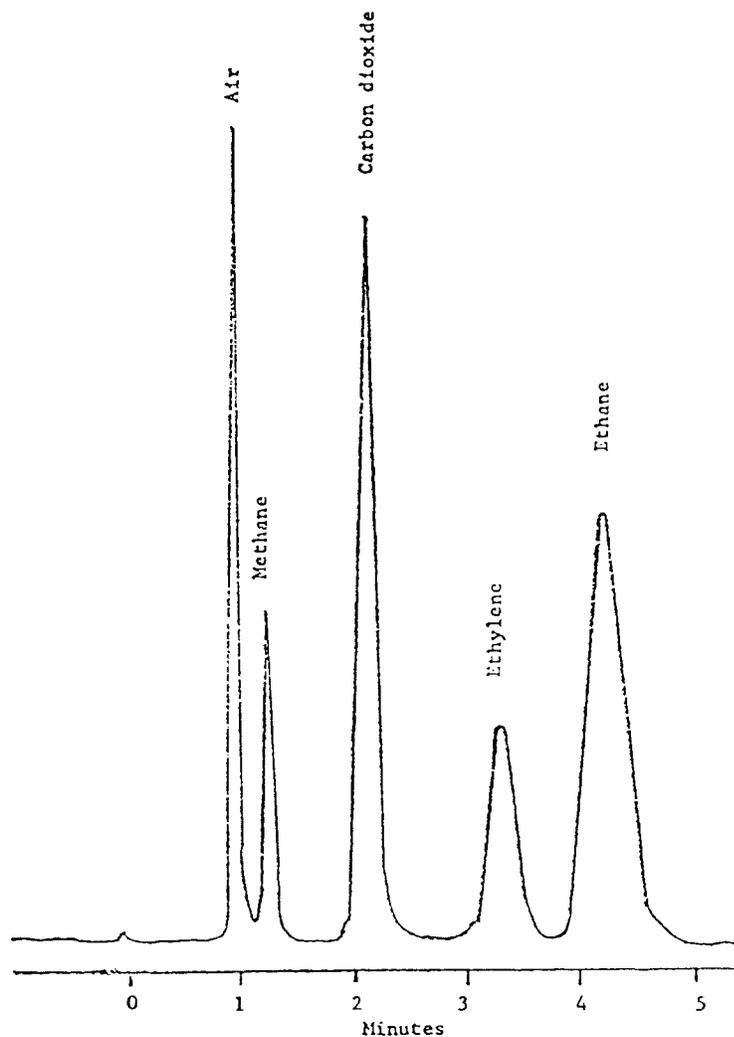
6.1 Moisture-free mixtures of known composition are required for comparison with the test sample. They must contain known percentages of the components, except oxygen (Note



Column: 2-m by 6-mm inside diameter Type 13X
molecular sieves, 14 to 30 mesh
Temperature: 35°C

Flow rate: 60-mL helium/min
Sample size: 0.5 mL

FIG. 1 Chromatogram of Reformed Gas on Molecular Sieve Column



Column: 1.2 m by 6.35 mm
 Porapak Q, 50 to 80 mesh
 Current setting: 225 mA

Temperature: 40°C
 Flow rate: 50-mL helium/min
 Sample size: 0.5 mL

FIG. 2 Chromatogram of Reformed Gas on Porapak Q Column

2), that are to be determined in the unknown sample. All components in the reference standard must be homogeneous in the vapor state at the time of use. The fraction of a component in the reference standard should not be less than one half of, nor differ by more than 10 mol % from, the fraction of the corresponding component in the unknown. The composition of the reference standard must be known to within 0.01 mol % for any component.

NOTE 2—Unless the reference standard is stored in a container that has been tested and proved for inertness to oxygen, it is preferable to calibrate for oxygen by an alternative method.

6.2 Preparation—A reference standard may be prepared by blending pure components. Diluted dry air is a suitable standard for oxygen and nitrogen.

NOTE 3—A mixture containing approximately 1 % of oxygen can be prepared by pressurizing a container of dry air at atmospheric pressure to 20 atm (2.03 MPa) with pure helium. This pressure need not be measured

precisely, as the fraction of nitrogen in the mixture such prepared must be determined by comparison to nitrogen in the reference standard. The fraction of nitrogen is multiplied by 0.280 to obtain the fraction of oxygen plus argon. Argon elutes with oxygen in the molecular sieves column. Do not rely on oxygen standards that have been prepared for more than a few days. It is permissible to use a response factor for oxygen that is relative to a stable component.

7. Preparation of Apparatus

7.1 Column Preparation—Pack a 2- to 3-m column (6-mm inside diameter stainless steel tubing) with Type 13× molecular sieves, 14 to 30 mesh, that have been dried 12 h or more at 300 to 350°C. Pack a second column (1 m by 6 mm) with Porapak Q,³ 50 to 80 mesh, that has been dried 12 h or more at about 150°C. Shape the columns to fit the configuration of the oven in the chromatograph.

³ Available from Waters Associates, Inc., Framingham, MA 01701.

NOTE 4—Variations in column material, dimensions, and mesh sizes of packing are permissible if the columns produce separations equivalent to those shown in Fig. 1 and Fig. 2. Better performance may be obtained by using a 2.1-mm stainless steel tubing with corresponding smaller mesh packing materials and substituting Haysep Q for Porapak Q.

7.2 *Chromatograph*—Place the proper column and sample volume in operation for the desired run in accordance with 8.1 and 8.2. For isothermal operation, the column should be maintained at a temperature between 30 and 45°C. When appropriate, column temperatures may be increased. Adjust the operating conditions and allow the instrument to stabilize. Check the stability by making repeat runs on the reference standard to obtain reproducible peak heights as described in 5.4.2 for corresponding components.

8. Procedure

8.1 *Sample Volume*—The sample introduced into the chromatographic column should have a volume between 0.2 and 0.5 mL. Sufficient accuracy can be obtained for the determination of all but the very minor components with this sample size. When increased sensitivity is required for the determination of components present in low concentrations, a sample size of up to 5 mL is permissible. However, components whose concentrations are in excess of 5 % should not be analyzed by using sample volumes greater than 0.5 mL.

8.2 *Chromatograms*:

8.2.1 *Adsorption Column* (Fig. 1)—Obtain a steady baseline on the recorder with a constant carrier gas flowrate appropriate to the column diameter. Introduce a sample of the unknown mixture at atmospheric pressure into the chromatograph and obtain a response similar to that of Fig. 1 of the components hydrogen, oxygen, nitrogen, methane, and carbon monoxide, which elute in that order. Repeat with a sample of the reference standard. If oxygen is present in the mixture, run a sample of air, either at an accurately measured reduced pressure, or air freshly diluted with helium, so that the partial pressure of oxygen is approximately equal to that of the oxygen in the mixture being analyzed.

NOTE 5—The peak for carbon monoxide can appear between those of nitrogen and methane if the molecular sieves have become contaminated. If this occurs, replace or regenerate the column packing by heating in accordance with 7.1.

8.2.2 *Partition Column* (Fig. 2)—Establish a steady baseline with the helium carrier gas flowing through the Porapak Q column. Introduce a sample of the reference standard and then a sample of the unknown mixture. Obtain responses similar to that shown in Fig. 2 for carbon dioxide, ethane, and ethylene.

8.2.3 All chromatograms for manual measurement should be run at a sensitivity setting that permits maximum peak height to be recorded for each component.

8.2.4 Column isolation valves may be used to make the entire analysis with a single injection if the separations specified in 5.8.2.1 and 5.8.2.2 are produced.

9. Calculation

9.1 The number of significant digits retained for the quantitative value of each component shall be such that accuracy is neither sacrificed nor exaggerated. The expressed numerical

value of any component in the sample should not be presumed to be more accurate than the corresponding certified value of that component in the calibration standard.

9.2 *Manual Measurement*—Measure the response of each component, convert to the same sensitivity for corresponding components in the sample and reference standard, and calculate the mole percent of each component in the sample as follows:

$$C = (A/B)(S) \quad (1)$$

where:

C = mole percent of the component in the sample,
 A = response of the component in the sample,
 B = response of the component in the standard at the same sensitivity as with A , and
 S = mole percent of the component in the reference standard.

9.3 If a helium-diluted air mixture was run for oxygen calibration, calculate the fraction of oxygen in the mixture from the fraction of the nitrogen and the composition of the diluted air. Calculate the fraction of nitrogen in the mixture in accordance with 9.1, using the nitrogen response of the reference standard for comparison. Air composition values of 78.1 % nitrogen and 21.9 % oxygen should be used, as argon (0.9 % in air) elutes with oxygen on the molecular sieves column.

9.4 If air has been analyzed at reduced pressure to calibrate for oxygen, correct the equation for pressure as follows:

$$C = (A/B)(S)(P_a/P_b) \quad (2)$$

where:

P_a = absolute pressure at which air was analyzed and
 P_b = barometric pressure when sample was analyzed, with both pressures being expressed in the same units.

9.5 Normalize the mole percent values by multiplying each value by 100 and dividing by the sum of the original values. The sum of the original values should not differ from 100.0 % by more than 1.0 %.

10. Analysis of the Reference Standard

10.1 If the composition of the reference standard is not known to a sufficient degree of accuracy, analyze it by the use of pure components for calibration. Obtain chromatograms of the standard as described in 8.2, except measure the pressure of each sample introduced to 0.133 kPa (1 mm Hg). When each chromatogram is obtained, calibrate each component by introducing a sample of the pure component at a pressure that closely approximates its partial pressure in the blend (for example, a component whose concentration in the standard is 50 % is analyzed at 50 % of the pressure at which the standard was analyzed). Use a minimum pressure of 0.665 kPa (5 mm Hg) for minor components. Repeat the analysis with the reference standard. Corresponding peak heights should agree within 1 mm or 1 % (whichever is larger) when recorded on a sensitivity setting that allows maximum response on the recorder chart.

10.2 Calculate the composition of the reference standard by the adjustment of responses of like components to the same sensitivity and calculate the concentration of each component as follows:

$$C = \frac{(100)(R)(P_p)}{(P)(P_r)} \quad (3)$$

where:

- C = component concentration, mole percent;
- R = response of the component in the reference standard;
- P = response of the pure component;
- P_p = pressure at which the pure component was analyzed; and
- P_r = pressure at which the reference standard was analyzed, with both pressures being expressed in the same absolute units.

10.2.1 Normalize all values as described in 9.4.

11. Precision

11.1 The following data should be used to judge the acceptability of the results:

11.1.1 *Repeatability*—Duplicate results by the same operator should not be considered suspect unless they differ by more

than the following amounts:

Component, mol %	Repeatability
0 to 1	0.05
1 to 5	0.1
5 to 25	0.3
Over 25	0.5

11.1.2 *Reproducibility*—Results submitted by different laboratories should not differ by more than the amounts given in 11.1.1 when the same reference standard is used for calibration and the same composition is used for calculations. If calibration is made with pure components or with different reference standards, results submitted by each of two laboratories should not be considered suspect unless the results differ by more than the following amounts:

Component, mol %	Reproducibility
0 to 1	0.1
1 to 5	0.2
5 to 25	0.5
Over 25	1.0

12. Keywords

12.1 gaseous fuels

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