Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography

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FOREWARD

GPA 2261 provides the gas processing industry a method for determining the chemical composition of natural gas and similar gaseous mixtures using a Gas Chromatograph (GC).

The precision statements contained in this standard are based on the statistical analysis of round-robin laboratory data obtained by the GPA Midstream Analysis, Test Methods and Product Specifications Committee (Analysis Committee).

This standard was developed by the cooperative efforts of many individuals from industry under the sponsorship of GPA Midstream Analysis Committee.

Throughout this publication, the latest appropriate GPA Standards are referenced.

Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography

1. SCOPE

1.1 This standard covers the determination of the chemical composition of natural gas and similar gaseous mixtures within the ranges listed in Table 1, using a Gas Chromatograph (GC). The three columns represent the original Table 1, but separate the values to three distinct groups. The first group is concentrations lower than the data obtained from the round-robin project (RR-188). The second group is concentrations used in the round-robin project (RR-188). The equations listed in the precision statement in this standard cover the range listed in the middle column, after outliers were removed. The third group is concentrations higher than the data obtained from the round-robin project (RR-188).

The precision statement in this standard utilizes equations derived from a regression of the data in RR-188 and is detailed in GPA TP-31. The precision statement criterion applies only to values listed in Section 10, Table 6.

1.2 Components sometimes associated with natural gases, i.e., helium, hydrogen sulfide, water, carbon monoxide, hydrogen and other compounds are excluded from the main body of the method. These components may be determined and made a part of the complete compositional data. Refer to Appendix C.

Table 1 – Ranges of Natural Gas Components Covered

Component	Lower Region	Round Robin	Higher Region
Nitrogen	0.01 - 0.1	0.1 - 30	> 30
Methane	0.01 - 40	40 - 100	N/A
Carbon Dioxide	0.01 – 0.1	0.1 - 30	> 30
Ethane	0.01 - 0.1	0.1 - 10	> 10
Propane	0.01 - 0.1	0.1 - 10	> 10
Isobutane	0.01 - 0.25	0.25 - 4	> 4
n-Butane	0.01 - 0.25	0.25 - 4	> 4
Isopentane	0.01 - 0.12	0.12 - 1.5	> 1.5
n-Pentane	0.01 - 0.12	0.12 - 1.5	> 1.5
*Hexanes Plus	0.01 - 0.1	0.1 - 1.5	> 1.5
*Heptanes Plus	0.01 - 0.1	0.1 - 1.5	> 1.5

**Data from round –robin was only obtained for Hexanes Plus*

Table Note 1 - Uncertainty in the Lower region can easily be ten times greater and in the higher region two to three times greater than the center column.

NOTE 1 - Components not listed in Table 1 may be determined by procedures outlined in Appendix C or other applicable analytical procedures. Refer to Appendix C.

2. SUMMARY OF METHOD

2.1 Components to be determined in a gaseous sample are physically separated by gas chromatography and compared to calibration data obtained under identical operating conditions. A fixed volume of sample in the gaseous phase is isolated in a suitable inlet sample system and entered onto the column.

2.2 The full range analysis of a gaseous sample may require multiple runs to properly determine all components of interest. The primary run is on a partition column to determine air, methane, carbon dioxide, ethane and heavier hydrocarbons. When oxygen/argon content is critical in the unknown sample, or is suspected as a contaminant, a secondary run should be made to determine oxygen/argon and nitrogen in the air peak on the partition column. When carbon dioxide content in the unknown sample does not fall within the calibrated range on the partition column, a secondary run should be made to determine carbon dioxide content. When helium and/or hydrogen content are critical in the unknown sample, a secondary run should be made to determine helium and/or hydrogen.

2.2.1 These analyses are independent and may be made in any order, or may be made separately to obtain less than the full range analysis. The configuration can consist of a single or multiple GC's to accomplish this. Refer to Appendix C.

2.3 Response factors or response curves derived from calibration data are essential to accurately determine the composition of an unknown sample. The reference standard blend and the unknown samples must be run using identical GC operating conditions.

3. APPARATUS

3.1 *Chromatograph* - Any Gas Chromatograph may be used as long as the specifications for repeatability and reproducibility stated in *Section 10* within the round-robin test component ranges listed in *Table 1* are met or exceeded. The equipment described in this section has been proven to meet the above requirements; however other configurations including portable and online may be acceptable.

3.1.1 *Detector* - The Thermal Conductivity Detector (TCD) has proven to be a reliable and universal detector for this method.

3.1.2 *Sample Inlet System* - A gas sampling valve capable of introducing sample volumes of up to 0.500 ml may be used to introduce a fixed volume into the carrier gas stream at the head of the analyzing column. The sample volume should be repeatable such that successive runs meet the precision requirements of Section 10.

NOTE 2 -The sample size limitation of 0.500 ml or smaller is selected relative to linearity of detector response and efficiency of column separation. Larger samples may be used to determine low-quantity components in order to increase measurement accuracy.

3.1.3 *Chromatographic Columns*

3.1.3.1 *Partition Column* - This column must separate nitrogen (air), carbon dioxide, and the hydrocarbons methane through n-Pentane. (or n-Hexane when a C7 plus analysis is performed). Silicone DC 200/500, 30% by weight on 80/100 mesh Chromosorb P, acid washed, packed into 30' x 1/8" SS tubing has proven to be satisfactory for this purpose.

3.1.3.2 *Precut Column* – A backflush column similar to the partition column described in 3.1.3.1. This column must be of the same diameter and long enough to clearly separate the hexanes plus or heptanes plus fraction from the lighter components. *Figure 1A* shows an example chromatogram of a natural gas mixture using the precut column for grouping the hexanes and heavier (heptanes and heavier in *Figure 1B*).

3.1.3.3 *Pressure buffer Column* - A lightly loaded column placed between the detector inlet and the column switching/sampling valve (*Figure 2A*, Column 3) may help to position the hexanes and heavier peak to provide better resolution. This column is usually 1 wt% Silicone 200/500 between 12" and 40" long. (*Figures 2A* and *2B* show a typical column switching/sampling valve arrangement).

NOTE 3 -The arrangements of columns, detectors and valves depicted in Figure 2A and 2B have been determined to meet or exceed the performance criteria of this standard. (See Section 10, "Precision").

3.1.4 *Temperature Control* -The chromatographic columns and the detector should be maintained at temperatures consistent enough to provide repeatable peak retention times and compositional precision within the limits described in Section 10 during the reference standard and corresponding sample runs.

3.2 *Carrier Gas* - The contaminants in the carrier gas must be limited to levels that are known not to interfere with the analysis or cause maintenance problems with the GC. Refer to manufacturer for recommendations regarding carrier gas quality.

3.2.1 *Pressure and Flow Control Devices* - These devices should maintain flow rate consistent enough to provide repeatable peak retention times and compositional precision within the limits described in Section 10 during the reference standard and corresponding sample runs. Two Stage regulators with stainless steel diaphragms have been shown to be satisfactory for this purpose.