Analysis of Natural Gas Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography

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FOREWARD

GPA 2177 provides the gas processing industry a method for determining the compositional analysis of demethanized liquid hydrocarbon streams containing nitrogen, air and carbon dioxide. Purity products such as an ethane/propane mix and other products that meet the compositional ranges listed in the standard may also utilize this method.

The precision statements contained in this standard are based on the statistical analysis of round-robin laboratory data obtained by GPA Section B. The detail of how this data yielded the equations covered in the precisions statements can be found in GPA RR188.

This standard was developed by the cooperative efforts of many individuals from industry under the sponsorship of GPA Section B, Analysis and Test Methods.

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

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1. SCOPE

1.1 This method is intended for the analysis of demethanized liquid hydrocarbon streams containing nitrogen/air and carbon dioxide, and purity products such as an ethane/propane mix that fall within the compositional ranges listed in Table I. This method is limited to mixtures containing less than 5 mole percent of heptanes and heavier fractions (20 mole percent of hexanes and heavier fractions).

Table I Components and Recommended Compositional Ranges

Components	Concentration Range (mole %)
Nitrogen	0.01 – 5.0
Carbon Dioxide	0.01 – 5.0
Methane	0.01 – 5.0
Ethane	0.01 – 95.0
Propane	0.01 – 100.0
Iso-Butane	0.01 – 100.0
N-Butane and 2,2-Dimethylpropane	0.01 – 100.0
Iso-Pentane	0.01 – 15.0
N-Pentane	0.01 – 15.0
2,2-Dimethylbutane, 2,2-Dimethylbutane, and 2-Methylpentane, 3-Methylpentane, Cyclopentane, N-Hexane	0.01 – 15.0
Heptanes & Heavier	0.01 – 5.0

1.2 The heptanes and heavier fraction if present in the sample is analyzed by either (1) use of a pre-cut column to elute heptanes and heavier first as a single peak, or (2) reverse flow of carrier gas after n-hexane, and peak grouping of the heptanes plus fraction. For purity mixes without heptanes and heavier, no reverse of carrier flow is required.

NOTE 1 *– This method can be used for a hexanes plus analysis by adjusting the timing of the backflush event to occur following the elution of n-pentane.*

NOTE 2 *– CAUTION: In the case of unknown samples with a relatively large* C_6^+ *or* C_7^+ *fraction and where precise results are important, it is desirable to determine the molecular weight (or other pertinent physical properties) of these fractions. Since this method makes no provision for determining physical Properties, the physical properties needed must be determined by extended analysis or agreed to by the contracting parties. The extended analysis will be made according to GPA Publication 2186.*

NOTE 3 *– For samples containing more than 5 mole percent of heptanes and heavier fractions (20 mole percent of hexanes and heavier fractions), analysis will be made according to GPA Publication 2103.*

2. SUMMARY OF METHOD

2.1 Components to be determined in a demethanized hydrocarbon liquid mixture are physically separated by gas chromatography and compared to calibration data. A fixed volume of sample in the liquid phase is isolated in a suitable sample inlet system and flashed onto the chromatographic column.

NOTE 4 *– For lab chromatographs, the comparison to calibration data is performed under identical operating conditions. For on-line chromatographs, the sample may not necessarily be at the same conditions as the calibrations data so care should be taken to ensure that the pressure at the sample injection point is sufficiently above the vapor pressure of the product.*

2.2 A precut column is backflushed when n-hexane has eluted into the main analytical column, so that the heptanes+ are eluted as a single peak at the beginning of the chromatogram. Two advantages of this method are: (1) Better precision in measuring the C_7^+ portion of the sample, and (2) Reduction in analysis time over the single column approach by approximately 40%. See Figure 1.

2.2.1 As an alternate method, the components nitrogen/air through n-hexane are individually separated with the carrier flow in the forward direction. The numerous heavy end components are grouped into an irregular shaped peak by reversing direction of carrier gas through the column via a switching valve immediately following the elution of normal hexane. (See Figure 2.) Samples which contain no heptanes+ fraction are analyzed until the final component has eluted with no reverse of carrier flow.

2.3 The chromatogram is interpreted by comparing the areas of component peaks obtained from the unknown sample with corresponding areas obtained from a run of a selected reference standard. Any component in the unknown suspected to be outside the linearity range of the detector, with reference to the known amount of that component in the reference standard, must be determined by a response curve. (See Sections 5.1 & 5.1.1 for further explanation of instrument linearity check procedures.)

3. APPARATUS

3.1 Any gas chromatograph may be used which meet the criteria listed in Section 8, Precision. The following equipment specifications have been found useful in designing an instrument to meet those criteria.

3.1.1 *Environment* - The gas chromatograph shall be housed in a climate controlled environment to ensure stability.