Improved Performance From Packed GC Columns Used For the Analysis of Natural Gas and Natural Gas Liquids in Reference to GPA and ASTM Methods

R.B. George, L.M. Sidisky, M.V. Robillard, M.R. McCoy
Supelco/Sigma Aldrich

Abstract

Packed GC columns continue to be used in valved-GC configurations for the determination of BTU content in natural gas and natural gas liquids as described in Gas Processors Association (GPA) Methods 2261, 2177 and American Society for Testing and Materials (ASTM) Test Method 2597. Column manufacturing procedures have been optimized resulting in column sets that provide highly reproducible analyses. Tests using a commercially certified reference gas standard show individual component peak area variation from multiple injections not exceeding 0.2%.

Chromatograms demonstrating column performance, analysis times, and critical separations according to the GPA methods are shown. Column-set-to-column-set and run-to-run reproducibility is demonstrated by a statistical analysis of the variability in peak width, peak areas, and BTU values.

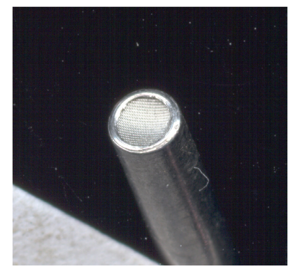
Introduction

The Gas Producers Association (GPA) has specified in their method that three columns be used in a multidimensional configuration with a backflush to detector or reverse column step design. The presence of air and carbon dioxide from introduced or natural sources can affect the final BTU calculation of the natural gas sample. For this reason, additional columns may be necessary to give a more accurate determination of the components of the sample.

The methods describe the use of a 1.5 ft column which is placed behind a 30 ft. column of the same packing during the run. The flow through the 1.5 ft. column is reversed 60 sec after sample injection to reverse the direction of the hexane and longer hydrocarbons on this column. These components elute together as a single peak before nitrogen at the detector.

A reduction in length of the 30 ft. column was achieved by utilizing improved packing techniques to reduce void space and by the installation of screen terminations. Installing integrated 316 stainless steel screens instead of glass wool plugs eliminated the void spaces at the column terminations. This elimination of void space improved the peak shape and the reproducibility of the measurement of each mole fraction of the gas components.

An example of a 10 micron 316 stainless steel screen installation.



With the reduction in void space from packing improvements and the installation of screen terminations, a reduction in column length from 30 feet to 24 feet was implemented with no loss of resolution of the components of natural gas.

Supelco Column Offerings

The Supelco columns offered for the two GPA methods are as follows:

GPA 2261: Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography

Columns for BTU Determination

1.5 ft. 316 SS 1/8 inch 30% DC-200/500 on Chromosorb P NAW, 80/100 mesh
24 ft. 316 SS 1/8 inch 30% DC-200/500 on Chromosorb P NAW, 80/100 mesh
20 in. 316 SS 1/8 inch 1.2% DC-200/500 on Chromosorb P NAW, 80/100 mesh

Additional Columns for Air and CO2 Separation

10 ft. 316 SS 1/8 inch Porapak Q, 80/100 mesh
10 ft. 316 SS 1/8 inch Molecular Sieve 13X, 45/60 mesh

GPA 2177: Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography

Columns for BTU Determination

1.25 ft. 316 SS 1/8 inch 30% DC-200/500 on Chromosorb P NAW, 80/100 mesh
24 ft. 316 SS 1/8 inch 30% DC-200/500 on Chromosorb P NAW, 80/100 mesh
30 in. 316 SS 1/8 inch 1.2% DC-200/500 on Chromosorb P NAW, 80/100 mesh

Measuring BTU Content

The BTU content is determined by multiplying the mole percent of each component of natural gas by its thermodynamic value of the heat of combustion. Many factors affect this determination of the BTU measurement of natural gas samples which go beyond the spectrum of this article. However, columns with packing voids, crushed packing beds, and poor coating of the diatomaceous support (Chromosorb P NAW) will produce analyses of mole fractions with poor reproducibility of each component's peak shape, area, and retention time.

Column-Set-to-Column-Set Reproducibility

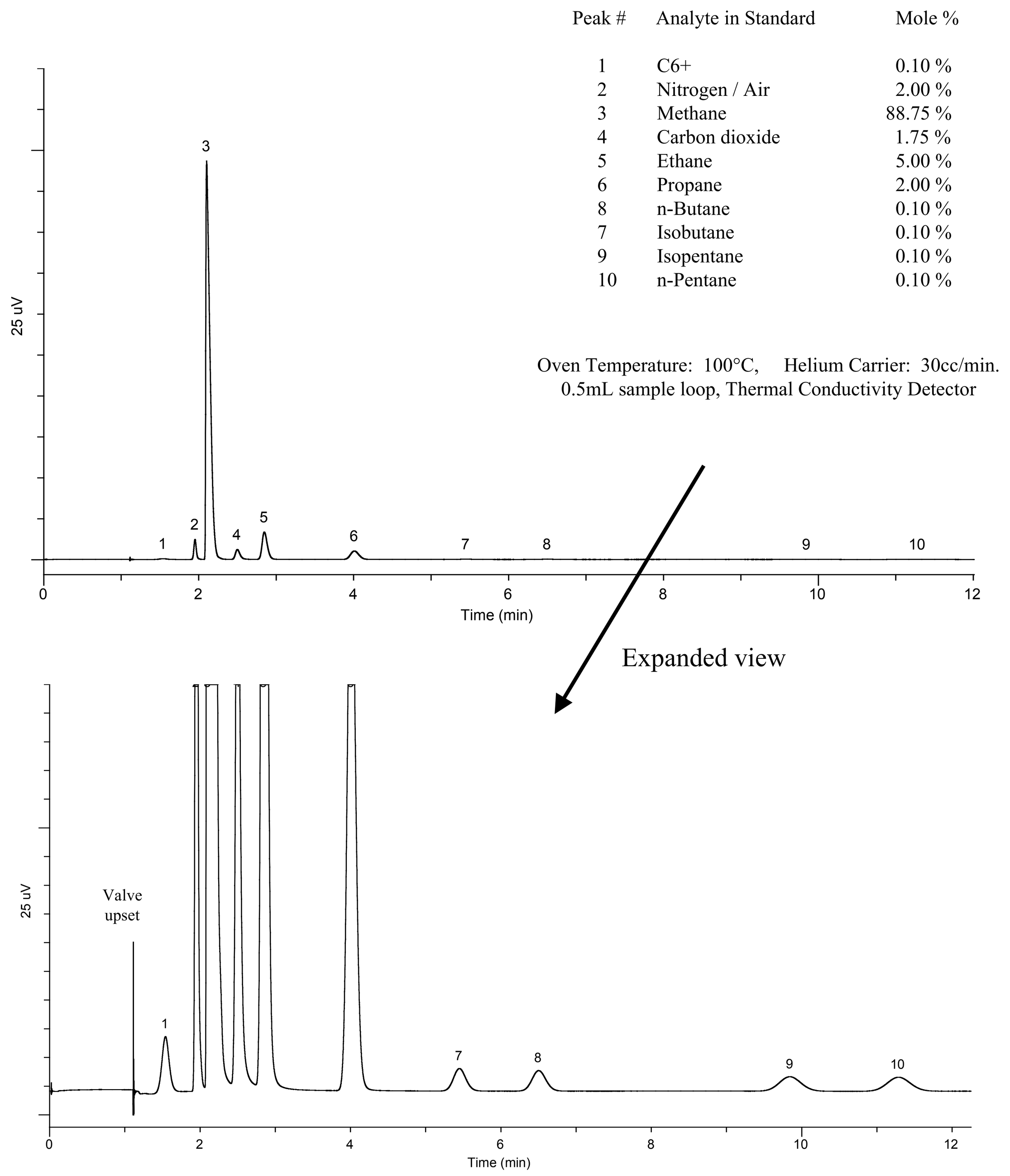
Two criteria may be used to judge the quality of the natural gas separation:

1. Reproducibility of the nitrogen peak width: demonstrates consistency of the separation
2. Nitrogen/methane separation: demonstrates the quality of the separation of the other sample components

Six sets of columns were prepared and tested. All six sets of columns separated the 2% v/v nitrogen peak from the adjacent 89% v/v methane peak. The average nitrogen peak width was 2.73 seconds. The standard deviation of the peak width values was 0.12 second.

The chromatogram below demonstrates the separation on one of the column sets evaluated.

Lean Gas BTU Calibration Standard from Air Liquid



Run-to-Run Reproducibility

Run-to-run reproducibility was demonstrated by calculating the variation in the summed peak areas of ten runs vs. a calibration standard. The table below demonstrates that the summed peak area % of each injection varied less than 0.2% from the calibrated value.

Area % for Natural Gas Components (10 Injections)

	1	2	3	4	5	6	7	8	9	10
C6+	0.30	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31
Nitrogen	2.48	2.48	2.48	2.48	2.48	2.48	2.48	2.49	2.49	2.48
Methane	83.06	83.05	83.07	83.04	83.05	83.05	83.05	83.04	83.05	83.05
Carbon dioxide	2.33	2.33	2.33	2.34	2.33	2.33	2.33	2.34	2.33	2.33
Ethane	7.30	7.30	7.29	7.31	7.30	7.31	7.30	7.31	7.30	7.30
Propane	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63
Isobutane	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Butane	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Isopentane	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.24
Pentane	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Area ±%	0.16%	0.18%	0.10%	0.10%	0.02%	-0.02%	-0.03%	-0.03%	-0.02%	0.09%
± BTU	0.08	0.10	0.01	0.09	0.06	0.03	0.03	0.00	-0.04	0.02

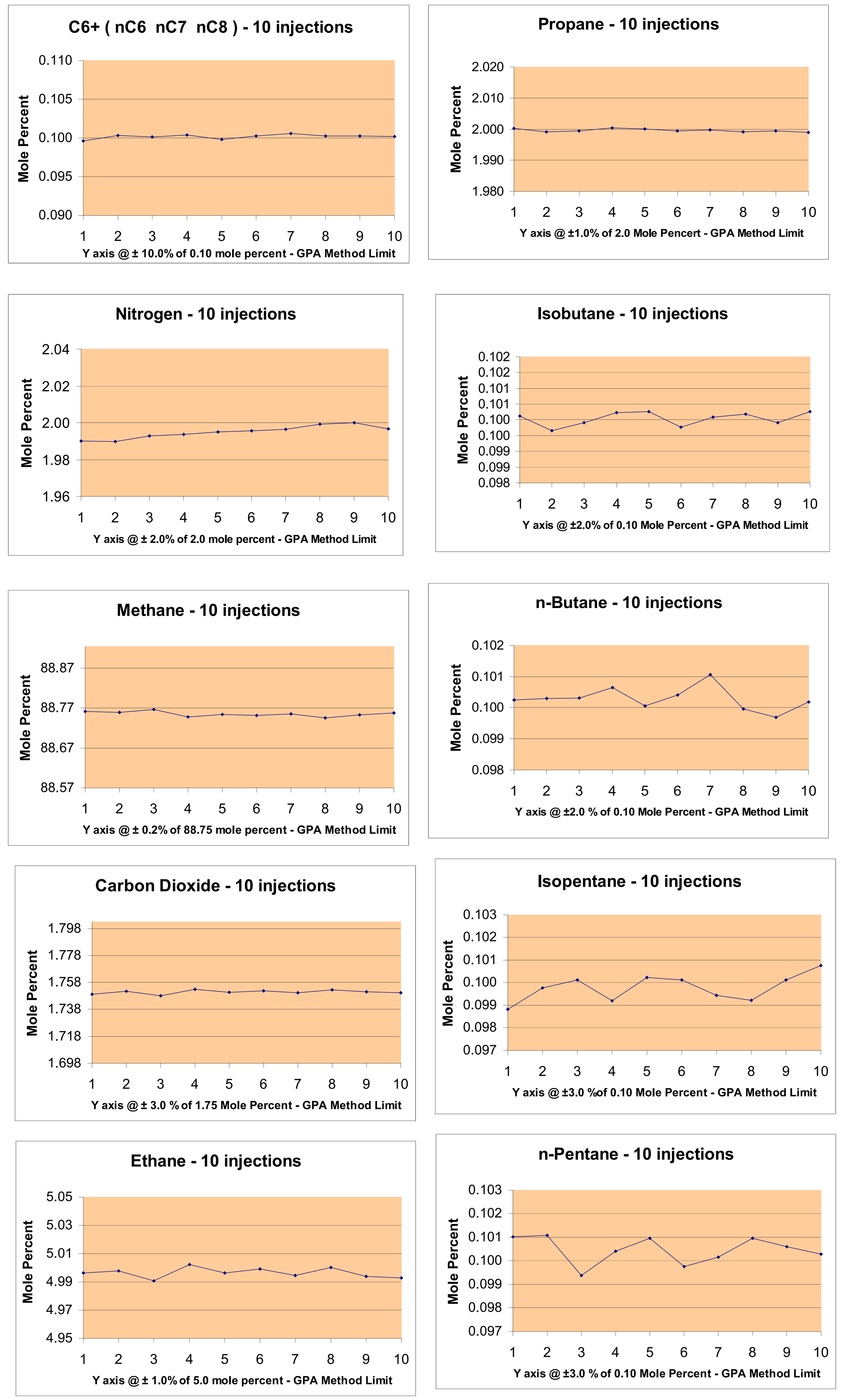
When the thermodynamic BTU values of each natural gas component were applied to the 10 GC injections the measured value of the BTU content varied by only **±0.10 BTU**.

Reproducibility of the Components of Natural Gas Calibration Standard

	Air Liquid Calibration Standard	Method Specification ± Mole %	Average of 10 Runs after Calibration	Standard Deviation n=10
C6+	0.10%	0.0100%	0.1002%	0.0003%
Nitrogen	2.0%	0.0400%	1.9949%	0.0034%
Methane	88.75%	0.2000%	88.7580%	0.0065%
Carbon dioxide	1.75%	0.0525%	1.7503%	0.0015%
Ethane	5.00%	0.0500%	4.9964%	0.0036%
Propane	2.00%	0.0200%	1.9996%	0.0005%
Isobutane	0.10%	0.0020%	0.1000%	0.0002%
n-Butane	0.10%	0.0020%	0.1003%	0.0004%
Isopentane	0.10%	0.0020%	0.0998%	0.0006%
n-Pentane	0.10%	0.0020%	0.1005%	0.0006%

Examining the data graphically, the run-to-run reproducibility of the columns becomes even more apparent. The mole percent for each component in the sample was plotted for each of the ten runs done after calibration.

In the graphs presented below, the Y-axis has been normalized to represent the acceptable range of mole percent variation as described in GPA Method 2261.



Summary

BTU value measurement errors can be expensive for either party in a pipeline custody transfer as well as a possible cause for costly litigation. Reproducibility of analysis and proper calibration ensure that both parties can be confident of the value of the transfer. Supelco supplies packed columns that exceed the performance criteria of the Gas Processors Association Methods. Customers can use these columns confidently, knowing their BTU measurements are being made accurately and reproducibly.