Application Note: 10043

Analysis of Natural Gas Including C1 through C8 Hydrocarbons and the Oxygen/Nitrogen Split

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Key Words

- TRACE GC Ultra
- BTU
- Oxygen Nitrogen Split
- Valved Configuration

Introduction

Recent fluctuations in the price of natural gas make it more important than ever to have good control over the heating value of the final product. Current methodology determines the value for natural gas by individually measuring the C1 through C5 hydrocarbons with a backflush of C6+ hydrocarbons as an aggregate peak. Air and Carbon Dioxide are also determined, but not generally Oxygen and Nitrogen. Unless Oxygen and Nitrogen are individually measured, only gross air contamination of a sample is detected. Small amounts of air contamination will negatively affect the gas heating value by adding to the air composite peak and reducing the hydrocarbon concentrations after normalization.

Separation of natural gas components through the C8 hydrocarbons is becoming more common as a technique between the traditional C6+ backflush method and extended analysis of natural gas. This technique gives more information about the C6 through C8 components for more precise calculation of heating value without the necessity to run the long extended analysis. Using a simple analysis approach, the values for Oxygen and Nitrogen can be determined along with the heating value of the hydrocarbons.

The Thermo Scientific TRACE GC Ultra with integral isothermal valve oven can be configured with heated valves and columns in the valve oven (Figure 1). This allows more flexibility in the analysis of natural gas using multi-column, multi-temperature techniques.

Description

The analysis of natural gas has evolved over the years as instrumentation improved. Early analyses used packed columns, but pricing by volume made peak errors insignificant. Since the pricing of natural gas has changed to composition based, accurate measurement has become more important. With packed columns, the heavier components produce increasingly broader peaks (Figure 2). Since the heavier components have higher heating values, accurate measurement of these later peaks affects the gas value significantly.

The current practice of backflushing the heavy hydrocarbons as a composite peak has increased accuracy somewhat. The average reference values used in the calculations for the composite peak must also be accurate. If a laboratory is only analyzing samples from a single source, an average value for the backflush composite peak is reasonably accurate. Most laboratories today analyze samples from many sources, so an average value is therefore inaccurate for most samples.

With capillary PLOT columns and a Pulsed Discharge Detector (PDD), it is possible to measure Oxygen, Nitrogen, Carbon Monoxide and Carbon Dioxide, and the hydrocarbons through C8, with a backflush of C9+ components (Figure 3).

Figure 1: TRACE GC Ultra with Valve Oven

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Results

This application increases measurement accuracy in two areas, C6 through C8 hydrocarbons, and determination of Oxygen and Nitrogen separately. Currently an extended analysis must be run in addition to the standard natural gas analysis to better measure the C6+ hydrocarbons. In laboratories that analyze only gas samples, instrumentation for extended analysis is not common. Samples must be sent to another laboratory for this analysis, so few samples are analyzed by this method.

Gas samples typically contain few hydrocarbons heavier than C9, so an analysis measuring hydrocarbons through C8 gives a significant improvement in accuracy. This application extends the accurate measurement of individual components through the C8 hydrocarbons, reducing the error caused by poor average values.

Likewise, the separate determination of Oxygen and Nitrogen is rarely done in most gas laboratories. A standard natural gas analysis reports only an air composite peak, so sample contamination must be high enough to noticeably change the air peak. Small amounts of air contamination in sampling will reduce the concentrations of the other components due to normalization of the data, lowering their values and giving erroneous data.

Advanced Reporting of Data

The Thermo Scientific ChromQuest™ data system can generate a custom report with flexibility in data reported and calculation of additional parameters using the chromatographic data. Calculations of heating value, compressibility, volume and weight %, GPM, or other calculations as desired are easily added to the advanced report (Table 1). The calculations are performed in a spreadsheet internal to the data system, eliminating the need to export data and risk corruption or errors.

Detector Repeatability

The PDD is an extremely stable detector, routinely yielding repeatability data with % RSD values less than 0.1 %. Even with the added variation of gas sample valve injection, the repeatability is less than 1.25 %, with most components less than 1 % (Table 2).

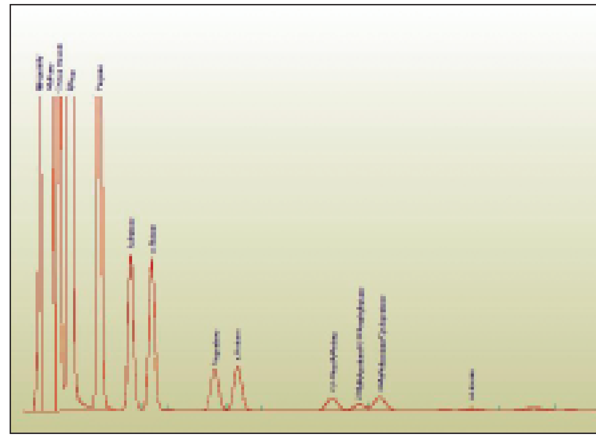

Figure 2: Packed column chromatogram with no backflush of heavy components

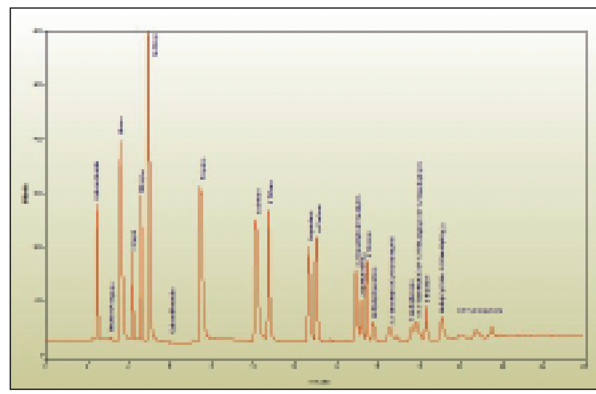

Figure 3: Chromatogram showing Oxygen/Nitrogen separation and Hydrocarbons through C8

Conclusion

The gas chromatograph configured as described here offers many of the benefits of an extended analysis for gas samples. Since many laboratories only analyze gas samples and do not have instrumentation for extended analysis, this application extends the advantages of extended analysis to routine gas analysis.

This configuration also allows the measurement of Oxygen during the natural gas analysis. The separate measurement of Oxygen and Nitrogen gives confirmation of sample integrity, since Oxygen should not be present in a properly obtained sample. The technique uses a single detector, simplifying post analysis calculations.

Acknowledgement

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COMPONENT	MOL %	GPM		GPM
Carbon Dioxide	0.964			
Ethylene/Acetylene	0.000	0.000		
Ethane	2.994	0.799	C2+	1.423
Hydrogen	0.000			
Oxygen	0.016			
Nitrogen	0.490			
Methane	93.547			
Carbon Monoxide	0.002			
Propane	0.987	0.271	C3+	0.624
Isobutane	0.301	0.098		
n-Butane	0.298	0.094		
Isopentane	0.100	0.036	i-C5+	0.255
n-Pentane	0.100	0.036		
2,3-dimethyl C4/2-methyl C5	0.036	0.015		
3-Methylpenthane	0.019	0.008		
n-Hexane	0.037	0.015		
Methylcyclopentane	0.009	0.003		
3,3-DimethylC5/CyC6/2-MethylC6	0.021	0.010		
3-Methylhexane	0.006	0.003		
c & t-1,3-DimethylCyC5/t-1,2-DimethylCtC5	0.006	0.003		
n-Heptane	0.010	0.005		
MethylCyC5/cis-1,2-DimethylCyC5	0.011	0.004		
C8 Hydrocarbons	0.046	0.023		
C9+ Hydrocarbons	0.000	0.000		
TOTALS	**100**	**1.423**		
Ideal Heating Value at:	14.696	**psia and 60 F**	**Saturated:**	1041.87
			Dry:	1060.32
Gas Specific Gravity (Air = 1):	0.6075			

Table 1: ChromQuest Advanced Report

Peak Area Repeatability

SAMPLE ID	CARBON DIOXIDE	ETHYLENE / ACETYLENE	ETHANE	NITROGEN	METHANE	PROPANE	ISOBUTANE
Nat Gas Std 01	9938705	96645	28308063	5041309	277698420	29809838	25072393
Nat Gas Std 02	9933464	96333	28070343	5032084	276731990	29604243	24927879
Nat Gas Std 03	9858105	95645	27968830	5001968	275747712	29401479	24821510
Nat Gas Std 04	9840767	96465	27893217	4993020	275680758	29289903	24740999
Nat Gas Std 05	9787873	96559	27711417	4973617	275218266	29092079	24636460
Nat Gas Std 06	9794090	95890	27531251	4977258	274780137	29014235	24561027
Nat Gas Std 07	9732875	96231	27511729	4956724	274880329	28896627	24506904
Nat Gas Std 08	9692652	96285	27397292	4939956	274648083	28786914	24434893
Average:	**9822316**	**96257**	**27799018**	**4989492**	**275673212**	**29236915**	**24712758**
Std Deviation:	**88088**	**338**	**314812**	**35044**	**1063162**	**354949**	**219307**
% RSD:	**0.897 %**	**0.352 %**	**1.132 %**	**0.702 %**	**0.386 %**	**1.214 %**	**0.887 %**

SAMPLE ID	N-BUTANE	ISOPENTANE	N-PENTANE	2,3-DIMETHYL C4 / 2-METHYLPENTANE	3-METHYLPENTANE	N-HEXANE	N-HEPTANE
Nat Gas Std 01	16682097	13946241	11045355	8423046	5042610	7965531	2620987
Nat Gas Std 02	16584184	13869658	10912590	8396383	5014127	7944905	2628236
Nat Gas Std 03	16509124	13832547	10952977	8379383	5016917	7945370	2631102
Nat Gas Std 04	16444011	13792337	10891856	8380368	5012863	7938232	2636928
Nat Gas Std 05	16356559	13755172	10829560	8355015	5007053	7909189	2644140
Nat Gas Std 06	16285753	13716961	10840020	8342465	5011447	7905776	2641954
Nat Gas Std 07	16228712	13673634	10759860	8336747	5001248	7895131	2648334
Nat Gas Std 08	16197299	13651507	10726714	8318629	4982871	7891467	2643431
Average:	**16410967**	**13779757**	**10869867**	**8366505**	**5011142**	**7924450**	**2636889**
Std Deviation:	**173926**	**100713**	**103594**	**34507**	**16688**	**27419**	**9360**
% RSD:	**1.060 %**	**0.731 %**	**0.953 %**	**0.412 %**	**0.333 %**	**0.346 %**	**0.355 %**

Table 2: Precision of the method

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