Agilent

Trusted Answers

Calculation of Natural Gas Calorific Value with the Agilent 990 PRO Micro GC System

Author

Jie Zhang
Agilent Technologies, Inc.

Abstract

This Application Note gives a functionality introduction of the Agilent 990 process (PRO) Micro GC on how to autonomously analyze and calculate the natural gas energy content.

IngenieríaAnalítica
Chromatography & Spectrometry

Introduction

Natural gas is an important energy resource. It is widely used in different industries to melt, dry, bake, and glaze a product. General households use it for cooking, heating, and lighting. It can also be used as fuel for vehicles. The chemical energy of natural gas is released by the reaction of the natural gas with oxygen. The trade of natural gas is mainly determined by its energy content. Usually, gas chromatography (GC) analysis of natural gas is used to estimate its energy content.

Several organizations, such as the Gas Processors Association (GPA), which collaborates with the American Petroleum Institute, ASTM international—formerly American Society of Testing and Materials—and the International Organization for Standardization (ISO) have developed different standards for calculation of natural gas energy based on the individual compound energy values and other physical constants.

The 990 process (PRO) Micro GC can work as an intelligent process GC to quickly analyze the composition of a natural gas stream, then automatically make onboard calculations of its energy content according to the above mentioned standards.

With the assistance of Agilent PROstation software, a user can load predefined energy calculation methods (following GPA/ATSM/ISO/GOST standards) to the 990 PRO Micro GC. With the completion of each chromatography analysis, the 990 PRO Micro GC generates the normalized mole concentration of each targeted component, then autonomously feeds them to an internal energy content calculation process. Finally, a report for the analyzed gas stream can be generated with information on energy content, including total superior/inferior calorific value (depending on water existing in either the liquid or gaseous state), density, relative density, and Wobbe index.

This Application Note demonstrates the composition analysis and calorific value calculation of natural gas by the 990 PRO Micro GC.

Experimental

Simulated natural gas was analyzed on a two-channel Agilent 990 PRO Micro GC. Channel 1 is a 10 m Agilent J&W CP-PoraPLOT U backflush channel for nitrogen, methane, carbon dioxide, and ethane analysis. Channel 2 is a 6 m Agilent J&W CP-Sil 5CB straight channel for propane, isobutane, butane, 2,2-dimethylpropane, isopentane, pentane, and hexane analysis.

The 990 Micro GC used has PRO and energy meter licenses. The PRO license enables the autonomous running of the instrument at prescheduled time and onboard data processing, including integration, identification, and quantitation based on the preloaded method. The energy meter license enables the automatic onboard calculation of fuel gas energy content based on the PRO GC quantitation result.

Table 1 lists the analytical methods used for natural gas composition analysis. The composition of the gas sample is tabulated in Table 2. The analytical parameters were prewritten into the 990 PRO Micro GC mainboard with assistance of Agilent PROstation software. The external standard calibration curve for each targeted component was developed using PROstation.

Table 1. Configuration and analytical conditions of the Agilent 990 PRO Micro GC.

The Agilent 990 PRO Micro GC Parameters		
Channel Type	10 m Agilent J&W CP-PoraPLOT U, backflush	6 m Agilent J&W CP-Sil 5 CB, straight
Sampling Time	30 seconds	30 seconds
Injector Temperature	110 °C	110 °C
Column Pressure	200 kPa	175 kPa
Column Temperature	80 °C	70 °C
Backflush Time	11.3 seconds	NA

Table 2. Composition of simulated natural gas.

Compound	Concentration (mol%)
Nitrogen	2.04%
Carbon Dioxide	3.12%
Ethane	0.575%
Propane	0.084%
Isobutane	0.011%
Butane	0.011%
2,2-Dimethylpropane	0.0106%
Isopentane	0.0097%
Pentane	0.011%
Hexane	0.0102%
Methane	Balance

The normalization method was defined and written into the mainboard together with the calibration and energy calculation methods prior to the real sample analysis. When the analysis was initiated, the PRO GC deploys these methods for onboard data collection and calculation to generate energy information about the sample. In this application, the calculation method was developed based on ISO standard 6976-2016 as shown in the method setting (Figure 1).

Figure 1. Settings of the calorific value calculation method based on ISO standard in Agilent PROstation software.

Results and discussion

Figures 2a and 2b show the chromatograms generated on channel 1 and channel 2 for simulated natural gas sample. The peaks were integrated onboard according to the integration parameters optimized for each analytical channel. The integration result was used to generate the quantitation result for each target component based on the prewritten ESTD curves. The concentration normalization was made over two analytical channels for all target components according to the setting in the normalization table (Figure 3). Then, the normalized concentrations were used for onboard calorific value calculation according to predefined energy calculation methods.

Figure 4 shows the quantitation and energy content calculation results for the simulated natural gas. The "energy" part shows the standard which is followed for calculation, and the key physical properties required to be calculated in the standard, such as compressibility, relative density/density, superior/inferior heating value in molar/weight/volume units, and Wobbe index. The types of properties shown in the report vary according to the standard requirement.

The quantitation results based on chromatography analysis are shown in the bottom of the report. Both the ESTD concentration and normalized concentration are reported. The report was generated in Agilent PROstation software as soon as each chromatography separation was finished. The analysis cycle under the applied conditions in this work is approximately 90 seconds from sampling to separation and report generated. If continuous flow mode is used, the analysis cycle time can be further reduced to 60s.
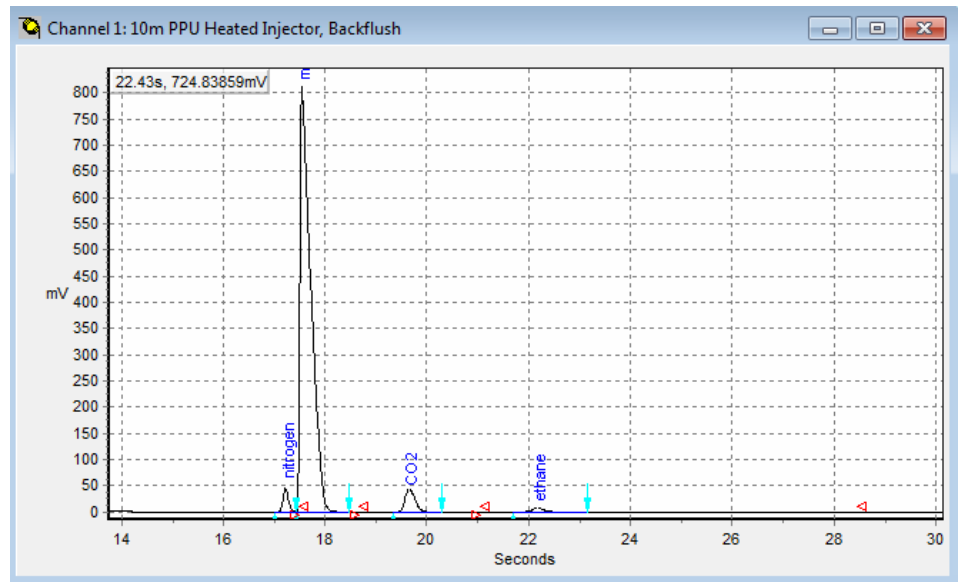

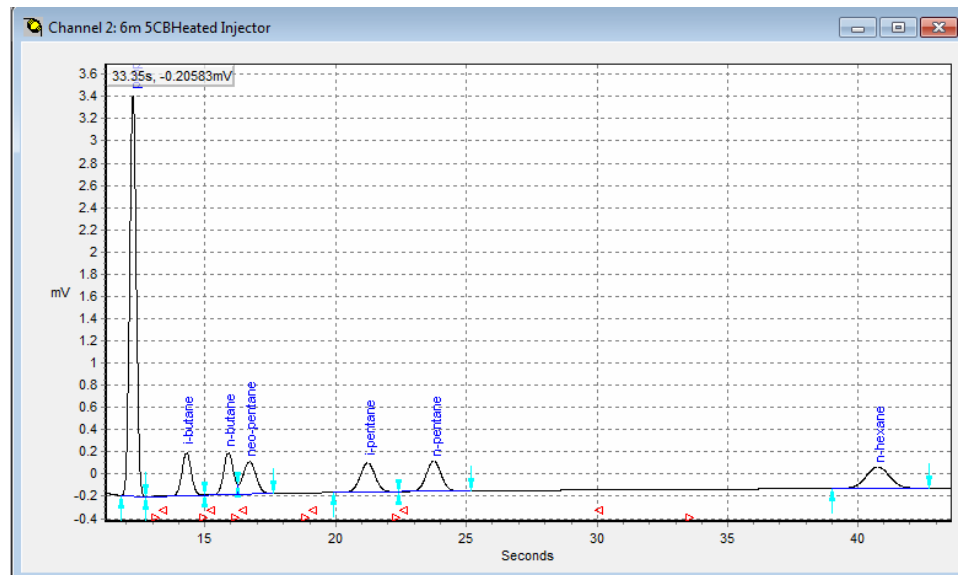**Figure 2a.** Chromatogram of N_2/methane/CO_2/ethane on 10 m Agilent J&W CP-PoraPLOT U backflush channel.

Figure 2b. Chromatogram of C3-C6 hydrocarbons on the 6 m Agilent J&W CP-Sil 5 CB channel.

Figure 3. Normalization table settings for natural gas analysis in this work.

Normalization Table

#	Active	Peak Name	Channel	Ignore	Bridge Comp #	Estimate	Estim.Conc	Test.Conc	RefConcPeak#	RefPeakConc%	Group#
1	✓	nitrogen	1		0. None		0	0	0	0	0
2	✓	methane	1		0. None		0	0	0	0	0
3	✓	CO2	1		0. None		0	0	0	0	0
4	✓	ethane	1		0. None		0	0	0	0	0
5	✓	propane	2		0. None		0	0	0	0	0
6	✓	i-butane	2		0. None		0	0	0	0	0
7	✓	n-butane	2		0. None		0	0	0	0	0
8	✓	neo-pentane	2		0. None		0	0	0	0	0
9	✓	i-pentane	2		0. None		0	0	0	0	0
10	✓	n-pentane	2		0. None		0	0	0	0	0
11	✓	n-hexane	2		0. None		0	0	0	0	0

SAMPLE

Sampling Time	08/10/2019 14:10:50
Run Number	3
Run Type	Analysis
Calibration Level	0
Stream #	1 (checked)
Sum ESTD	1.0238
Sum Estimates	0.0000
Sum Areas	1130262.3775
Total Peaks	11
Is Startup Run	False
Unknown Peaks	6
Current Stream #	0

☐ Hide non Appl.pks
☐ Hide Ignored Appl.pks

ENERGY

		Dry	Saturated
Calc.Method	ISO 6976-2016		
Water Mole.	[%]	--	2.31
Compressibility	[-]	0.9981	0.9975
Molar Mass	[kg/kmol]	17.2666	17.2839
Relative Density,Ideal	[-]	0.5961	0.5967
Relative Density,Real	[-]	0.5971	0.5980
Gas Density,Ideal	[kg/m3]	0.7178	0.7185
Gas Density,Real	[kg/m3]	0.7192	0.7203
Superior Heating Value (Volume Real)	[MJ/m3]	35.60	34.79
Inferior Heating Value (Volume Real)	[MJ/m3]	32.01	31.29
Superior Heating Value (Volume Idea)	[MJ/m3]	35.53	34.71
Inferior Heating Value (Volume Idea)	[MJ/m3]	31.95	31.21
Superior Heating Value(Mass)	[MJ/kg]	49.50	48.30
Inferior Heating Value(Mass)	[MJ/kg]	44.51	43.44
Superior Heating Value(Molar)	[kJ/mol]	854.62	834.88
Inferior Heating Value(Molar)	[kJ/mol]	768.57	750.82
Wobbe Index (Real)	[MJ/m3]	46.07	44.99
Wobbe Index inferior	[MJ/m3]	41.43	40.46

CONDITIONS

ENVIRONMENT

Cabinet Temperature	[°C]	34
Ambient Pressure	[kPa]	102.1

SITE INFO

Customer ID	
Instrument Name	990-PRO Micro GC
Serial Number	10001
Tag Number	
Cylinder 1 Tag	

#	Channel	Peakname	ESTD Conc.	Norm. Conc.	Retention [s]	Area	Height	Meth-Index	Group#	R.F.			Weight%	
1	1	nitrogen	0.019951	1.948797	17.38	24782.7169	13635198.2879	1	0	8.0504E-07			3.1617	
2	1	methane	0.965245	94.283973	17.60	746196.9431	132556588.1529	2	0	1.293553E-06			87.5998	
3	1	CO2	0.031328	3.060127	19.75	38813.4314	6589405.0554	3	0	8.071555E-07			7.7997	
4	1	ethane	0.005773	0.563867	22.33	7757.2239	1375294.4939	4	0	7.441665E-07			0.9820	
5	2	propane	0.000837	0.081791	12.24	1714.7951	352927.5260	5	0	4.883076E-07			0.2089	
6	2	i-butane	0.000107	0.010478	14.29	290.7882	39425.5766	6	0	3.688964E-07			0.0353	
7	2	n-butane	0.000106	0.010367	15.89	283.3521	38176.9311	7	0	3.745673E-07			0.0349	
8	2	neo-pentane	0.000106	0.010374	16.69	282.8061	29531.1083	8	0	3.755436E-07			0.0433	
9	2	i-pentane	0.000097	0.009514	21.22	290.1013	26104.6298	9	0	3.357591E-07			0.0398	
10	2	n-pentane	0.000110	0.010771	23.74	300.9403	27215.5715	10	0	3.664084E-07			0.0450	
11	2	n-hexane	0.000102	0.009941	40.74	332.8352	19101.1810	11	0	3.057677E-07			0.0496	

Figure 4. Energy content calculation report generated by the Agilent 990 PRO Micro GC.

The 990 PRO Micro GC works as a "detector" or "sensor" for natural gas stream analysis. PROstation software is used to

• Develop methods, including analytical, qualitative and quantitative method, and energy content calculation method

• Set the automation mode

• Define how to output the results

All these "commands" are written to the mainboard by PROstation. In the real analysis, the Pro Micro GC can run by itself without connection to the PROstation software. The quantitation result and energy content will not be displayed in the format shown here if PROstation software is not connected. Instead, the results can be displayed in a scrollable way on the touch screen of the 990 PRO Micro GC, as shown in Figure 5. Additionally, the result can be output through FTP in .txt file or using Modbus protocol to other terminals for monitoring and recording. Analog output

is another approach to produce analysis results in voltage or current signal through a connection to the extension analog board (Figure 6). The conversion of analog signal and the quantitation result or energy contents can be predefined and loaded on the PRO GC mainboard.
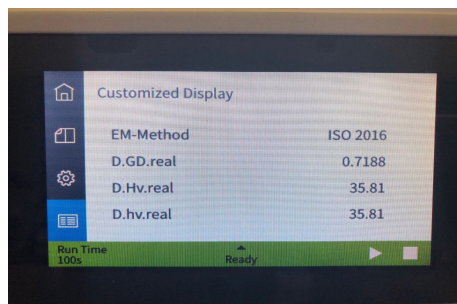

Figure 5. The calorific value calculation results displayed on the touch screen of the Agilent 990 PRO Micro GC.

Conclusion

This Application Note demonstrates natural gas composition analysis and energy content calculation by the Agilent 990 PRO Micro GC. The PRO license and energy content license are activated on the 990 PRO Micro GC to enable automated fuel gas composition analysis and energy content calculation. The analysis process from sampling, separation, quantitation to calorific value calculation and result output, are autonomously executed according to the prewritten method and automation mode on the PRO Micro GC mainboard. The energy calculation methods are developed with compliance to different international standards, including ASTM, ISO, GPA, and GOST standards. All methods are developed in PROstation and then downloaded to the 990 PRO Micro GC for its independent and automated operation. The energy content calculation results can be shown on a local touch screen or outputted through FTP, Modbus, and analog signal for monitoring and recording.
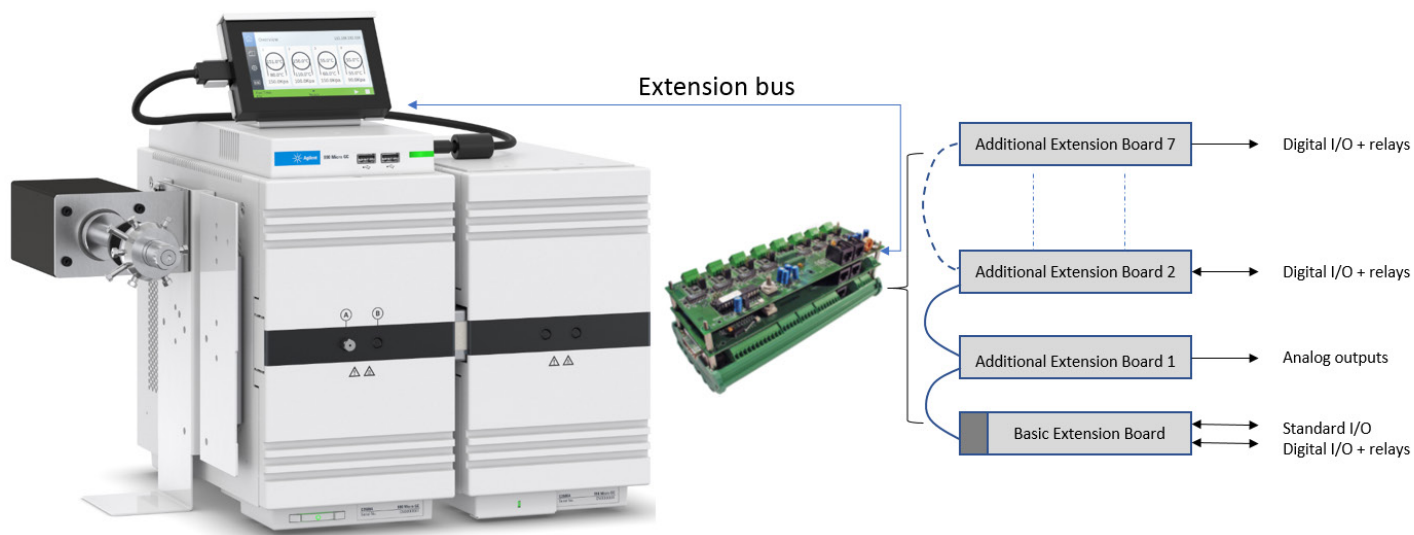

Figure 6. Agilent 990 PRO Micro GC connection with extension board for analog output of analysis results.

www.agilent.com/chem