White Paper

Extended Natural Gas Analysis Using Micro GC Fusion®

Summary

Procedure

A generalized procedure is described for the extended (grouping) analysis of natural gas derived from raw unprocessed gas streams using a 2-module Micro GC Fusion. This gas chromatographic (GC) protocol can be used as a guideline for determining composition of N_2, methane, CO_2, ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane, total hexanes (C6), total heptanes (C7), total octanes (C8) and the nonanes and heavier (C9+) components in the gas samples. This enhanced carbon number detail can act to provide additional component information for determining total BTU/heating values and other gas calculations.

Equipment, including typical method acquisition set points, peak integration parameters and calibration/validation techniques are presented and described. Example chromatograms are provided. The methodology can be used in the lab/stationary location for spot sampling from sample cylinders, or transported to the field where samples are obtained directly from the pipeline or well-head via heated sample lines. Principles discussed in this paper can also be applied to C6+ gas analysis with appropriate changes made only in the calibration procedure. The techniques described in this paper are based in part on industry protocols, GPA Midstream GC procedures[1] and guidelines in the new US rules regarding Bureau Land Management (BLM) Onshore orders for gas measurements[2].

Experimental

Micro Gas Chromatography

A 2-module Micro GC Fusion (Part Number F08900RR2R03) was used for this work[3]. Micro GC Fusion is configured with a 12 m x 0.25 mm x 8 µm Porous Polymer PLOT (Q-BOND) fused silica capillary column (module A) and a 10 m x 0.15 mm x 2 µm PDMS non-polar (Rxi-1ms) fused silica capillary column (module B)[4]. Each module is used to analyze a subset of components. The chromatographic columns, installed in each module are commercially available and bundled/temperature controlled by propriety techniques designed for Micro GC Fusion. Microelectromechanical (MEMS) based Fixed Volume (FV) injectors were used for sample injection as they are superior to traditional Micro GC Variable Volume (VV) injectors and act to minimize matrix effects, are less susceptible to changes in peak area vs. sample pressure, and overall more accurate and precise. Helium (99.999 %) is used as the carrier gas and set to deliver 60 psi using a dual stage regulator. Column temperature programming, unique for each column module is used to optimize the separation, to elute the high boiling components and to prevent ghost peaks. All detection was made using a MEMS-based micro thermal conductivity detector (TCD) also unique to each module. Low carrier gas consumption per channel (~1–4 cc/min) allows for typical helium supply tanks to last up to 1.5–2 years depending on tank capacity and in daily use 24/7.

A heated Integrated Sample Conditioner (ISC) Regulator, integrated into the Micro GC allowed for gas samples with higher pressures (<1000 psi) to be sampled directly into the inlet of the GC by reducing pressure (<12 psi) while maintaining temperature(100°C) well above HC due points. The ISC has a user replaceable 7 µm frit filter in the sample path to remove any solid particulates. Samples with pressures below 12 psi pass through the ISC without reduction. Calibration gas pressure is set to 15-20 psi and heated according to GPA guidelines[5]. Low pressure samples (1–2 psi) can also be analyzed with increased purge prior to analysis. The ISC purge time is controlled by the Micro GC Fusion software as part of a method parameter.

Chromatography Data Analysis

Method control, calibration and data analysis was performed using the Micro GC Fusion software. The software is embedded inside the system on a Solid State Drive (SSD) and accessed via the instruments IP address using any commercially available compliant web browser such as Google Chrome©, Microsoft Internet Explorer© or Mozilla Firefox©. Instruments that use this embedded software technique and accessed via a web browser are commonly referred to as “web-based” or “browser-based”. It is important to note that this does not mean that internet access is needed, but only a network connection must exist from the device using the browser to Micro GC Fusion. In this case, Micro GC Fusion can be accessed via its wired RJ45 network port or built-in wireless WIFI signal. All methods and the associated data files are stored on the SSD. Data files can be analytically reprocessed at any time. All files can be backed up to a local or networked drive by manual or automated routines available from the Micro GC Fusion software interface. A software API is available for custom user programming. Advantages of “browser-based” software include operating system independence and simplicity of operation.

Natural Gas Calculations

Software to perform and simplify GPA specific calculations[6], calibration and validation protocols was performed using Diablo Analytical EZReporter 4.0 software (Natural Gas Edition)[7]. EZReporter is configured to automatically monitor live or reprocessed runs on Micro GC Fusion. The software is capable of performing advanced quality control checks, export/csv file processing and other items specific to the needs of individual user requirements. This includes sample database imports and sample history comparisons.

Discussion

Micro GC Separations and Peak Identification

MEMS-based Micro GC analysis has been in use for many years and instrumentation available from several different companies. From the first commercialization of the technology, the application towards natural gas has developed and evolved over time[8]. The fast analysis, simple operation, small size, ease of transportability and accurate/precise analysis has enabled many users to apply this GC technology to natural gas; both in the lab and for “portable” applications where the Micro GC is installed in vehicles for on-site field gas measurement at wells or near pipelines gathering and or transporting gas. When enabled for “portable” use in rugged vehicles, the carrier gas and power are supplied to the Micro GC via in-vehicle helium tanks and DC/AC power invertors. In addition, it has been continuously demonstrated that when the Micro GC is subject to strict quality control and well-defined standard operating procedures, data obtained from Micro GC analysis is generally equivalent to that from a traditional full-featured laboratory GC or on-line GC systems. Having the ability to perform analysis in the field and connected directly to pipelines or well-heads, can reduce errors due to sample collection/handling, provides for faster and more efficient data flow and minimizes lost time in sample transporting. While speed of analysis is one important factor for any analysis, following defensible, well-developed calibration, validation and operating procedures leads to enhanced data quality.

The 2-module Micro GC Fusion can be viewed as two independent GC modules with a common sample inlet. The sample is first purged through the ISC. After this regulator purge, the sample exits the low pressure side of the ISC and splits to both modules simultaneously. During the injector purge (sampling time) a small pump, internal to Micro GC Fusion, is used to assist in pulling sample through the injectors in each module. Just before the injection, the pump stops and the exits of the sample injectors opened to atmosphere during a built-in “equilibration” phase, then the sample is injected. Both the ISC and sample injector purge times are user editable parameters in the method.

Module A (Q-Bond) is used for the “light” component analysis consisting of N_2, methane, CO_2, ethane, propane. In some cases, H_2S can be determined, generally at levels >0.005% for this specific Micro GC configuration. H_2S elutes after ethane. Other Micro GC Fusion configurations are available for lower ppm measurements. In addition, O_2 if present will co-elute with N_2 and can be analyzed using an alternate configuration[9]. Figures 1 and 6 below show example separations from two different Micro GC Fusion systems. All concentrations are in mole %. Module B (Rxi-1ms) is used for the “heavy” component analysis consisting of iso-butane, n-butane, iso-pentane, n-pentane, C6s, C7s, C8s, C9 plus. Neo-pentane will elute on the shoulder of n-butane (if present) and can be separated if desired. Figures 2 and 7 below show example separations from two different Micro GC Fusion systems. While the C3 “propane” peak is visible in this separation,

water contained in field samples and sometimes at significant concentrations levels, will co-elute and bias the measurement/peak integration. For that reason, propane is separated and analyzed via module A (Q-Bond). The table below lists the general acquisition parameters used for these chromatograms. These parameters can be used as a generic starting point and users can optimize column conditions for sample types encountered in everyday use.

Internal sample regulator	100°C, 7 s purge time, high flow
Inlet temperature	90°C
Sample pump time	25 s
Injector temperature	90°C
Inject time	35 ms (fixed volume)
Q-BOND temperature (module A)	60°C (40 s), hold until after CO_2 elutes, 1°C/s to 125°C (0 s), 1.5°C/s to 210°C (hold 30 s)
Q-BOND pressure	Helium 23 psi
Rxi-1ms temperature (module B)	70°C (40 s), hold until after n-butane elutes, 0.8°C/s to 200°C (hold 20 s)
Rxi-1ms pressure	Helium 23 psi
TCD data rate	100 Hz

Table 1: Typical operating conditions for a C9+ extended analysis. Adjust as necessary.

The 12 m Q-BOND separation (module A) is typically held isothermal at starting temperatures between 60-70°C for N_2, methane, CO_2 elution. In this example, the initial starting temperature of 60°C allows for baseline separation of N_2 from methane over a wide range of concentrations. Figure 2 shows the baseline separation of N_2 from methane. Other users have successfully used 65 or 70°C for starting temperatures, but with some reduced N_2/methane resolution. After CO_2 elutes, the column temperature is programmed at 1°C/second to sharpen ethane/propane peaks. After propane, the temperature ramped to 1.5°C/second to elute the C4+ hydrocarbons. This temperature ramp allows the columns to stay very clean between runs and avoid any ghost peaks while still maintaining simplicity of operation. Small amounts of C8+ elute during the column cool-down. To date, no carryover issues have been reported from users of this technique, a great improvement over past Micro GC models using isothermal temperatures that require longer cycle times or backflush columns that effect baseline stability and add cost/complexity. Even with a final column temperature of ~210°C, cool down only takes ~90 seconds. Note that if water is present in the gas, it will elute as a tailing peak between ethane and propane (and after H_2S). Quantitation of water is an active industry discussion, but GC presents many challenges due to calibration and absorption issues within sample pathways. Additionally, for some coal-seam gas or pipeline quality gases with no C5 and heavier hydrocarbons a single module Q-Bond can analyze all of the components thru C4[10].

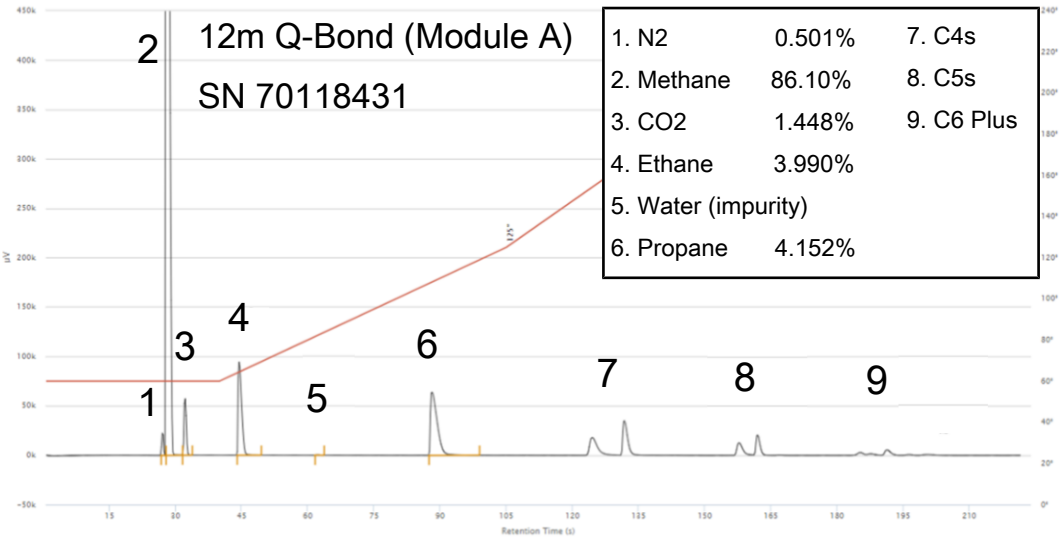


Fig. 1: Typical chromatogram of calibration gas using 12 m Q-BOND. Note that peaks 7-9 are not analyzed on this module.

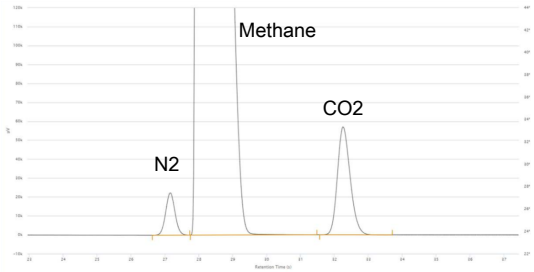


Fig. 2: Baseline separation of N2, methane and CO2 at initial column temperature 60°C. Column conditions set for baseline separation of a wide range of N2 and methane concentrations. Micro GC Fusion SN 70118431.

The 10 m PDMS Rxi-1ms separation (module B) is typically held isothermal at 70°C until n-butane elutes, then temperature programmed at a rate of 0.8°C/s to 200°C. Keeping the starting temperature at 70°C is user/sample type specific and allows for excellent separation of C4s from the large matrix peak. A linear temperature program is used to elute iso-pentane, n-pentane and hydrocarbons in the C6-C11 range. Figure 3 illustrates the example chromatogram from the Rxi-1ms Channel B. By adjusting starting temperature, temperature program rates, ending temperature and run times, C12 hydrocarbons can elute from the column. The challenge of analyzing C11-12 range is heating all sample lines and sample cylinders properly to transfer these components to the GC.

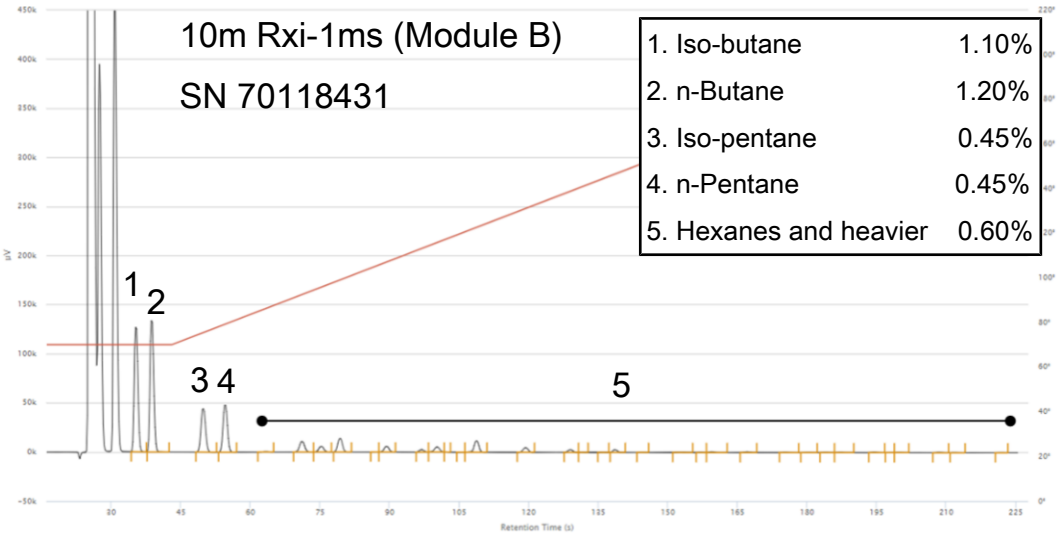


Fig. 3: Typical chromatogram of calibration gas using 10 m Rxi-1ms.The peak eluting at 30s and before iso-butane is propane. Water will co-elute with this component on the PDMS. See Figure 4 and Figure 5 for Hexanes+ breakdown. Micro GC Fusion SN 70118431.

Micro GC “extended” analysis specifically refers to “carbon number” grouping of the C6 and heavier hydrocarbons and not separation of the individual hydrocarbons. For individual separation of the isomers in the gas, GPA method 2286 is the recommended procedure and uses a high resolution non-polar PDMS capillary column and Flame Ionization Detector (FID)[11]. However, this GPA method requires a full-featured lab-style GC analysis and more intensive in data reduction with analysis times up to 40 minutes. For Micro GC “extended” analysis, the carbon number groups are bracketed by the n-hydrocarbon elution pattern and defined in the table below.

Group Name	Type	Start of Group	End of Group
Hexanes	C6	After n-C5 returns to baseline but do not include	After n-C6 (include)
Heptanes	C7	After n-C6 returns to baseline but do not include	After n-C7 (include)
Octanes	C8	After n-C7 returns to baseline but do not include	After n-C8 (include)
Nonanes Plus	C9	After n-C8 returns to baseline but do not include	End of run

Table 2: Micro GC extended groups definitions

This type of “extended” analysis is also referred to as “C9+” analysis. See Figure 4. At higher carbon numbers, the amount of isomers at each carbon number increase and this may lead to some species eluting in a lower/higher group area. For example, a small C7 peak can elute as a C8 depending on molecular structure. Regardless, the error in grouping is minor and the technique of using n-hydrocarbons to bracket groups is well accepted as an industry standard. The ability to group by carbon number allows for a better understanding of gas component concentrations and can lead to more accurate BTU/heating value calculations. However, for detailed separation of the isomers in the gas, GPA method 2286 can be utilized.

It is recommended that when performing “extended” Micro GC analysis, labs use a calibration gas that contains a “Hexanes Plus Isomer” mixture instead of the n-hydrocarbons for calibration of response factors. For example, the response factor determined using n-hexane to calibrate the total C6 response has been found to be significantly different than using a calibration mixture containing a series of C6 isomers, including n-hexane. This allows for a more realistic response factor and provides better accuracy, especially at higher C6+ concentrations. The ratio of the C6/C7/C8/C9+ isomers is also typically added at amounts similar to what is found in field samples. However, one practical use of having a calibration gas with only the n-hydrocarbons is to periodically aid in the proper verification of extended peak groups. It is recommended that users have both types of calibration gas available. Figures 5 is such an example and illustrates the proper groups. In practice, this type of overlay should be periodically performed. Since a calibration gas containing the “Hexanes Plus Isomer” mixture will also contain n-hydrocarbons, the user can use the chromatographic profile to set the peak groups once they get experience in system operation.

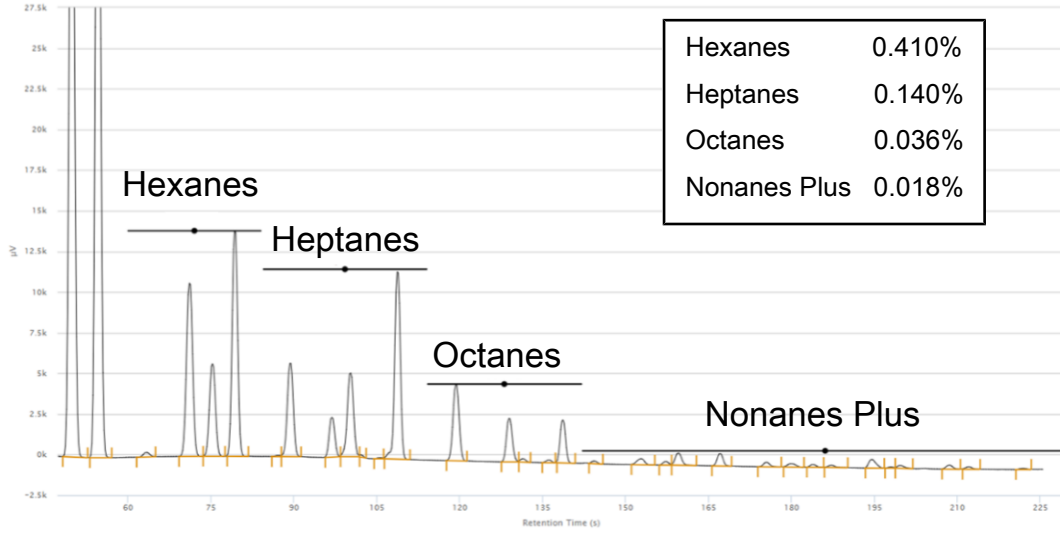


Fig. 4: Typical extended analysis chromatogram of calibration gas using 10 m Rxi-1ms (module B). Micro GC Fusion SN 70118431.

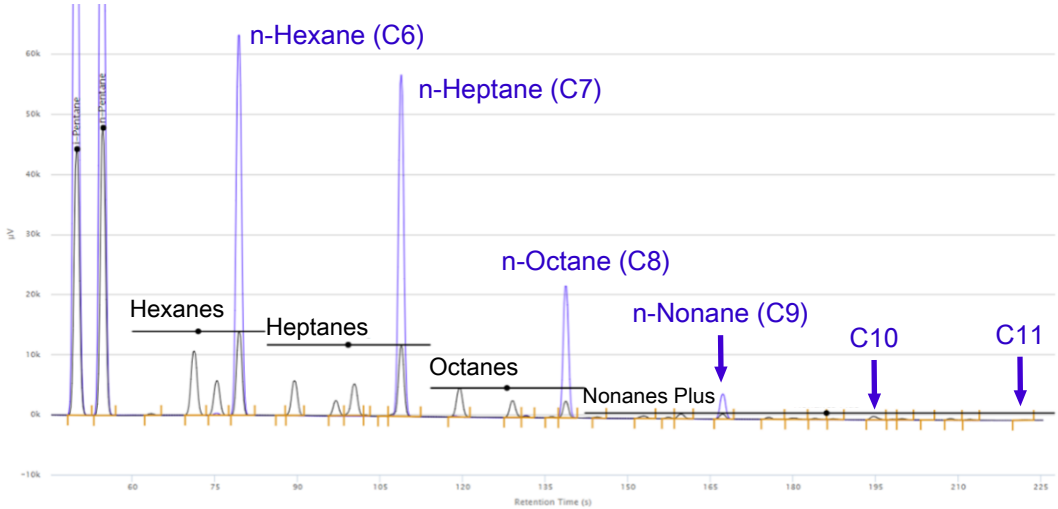


Fig. 5: Typical peak window range for the extended identification using 10m Rxi-1ms (module B). Calibration gas with “hexanes plus” mix overlaid with n-hydrocarbons. Micro GC Fusion SN 70118431.

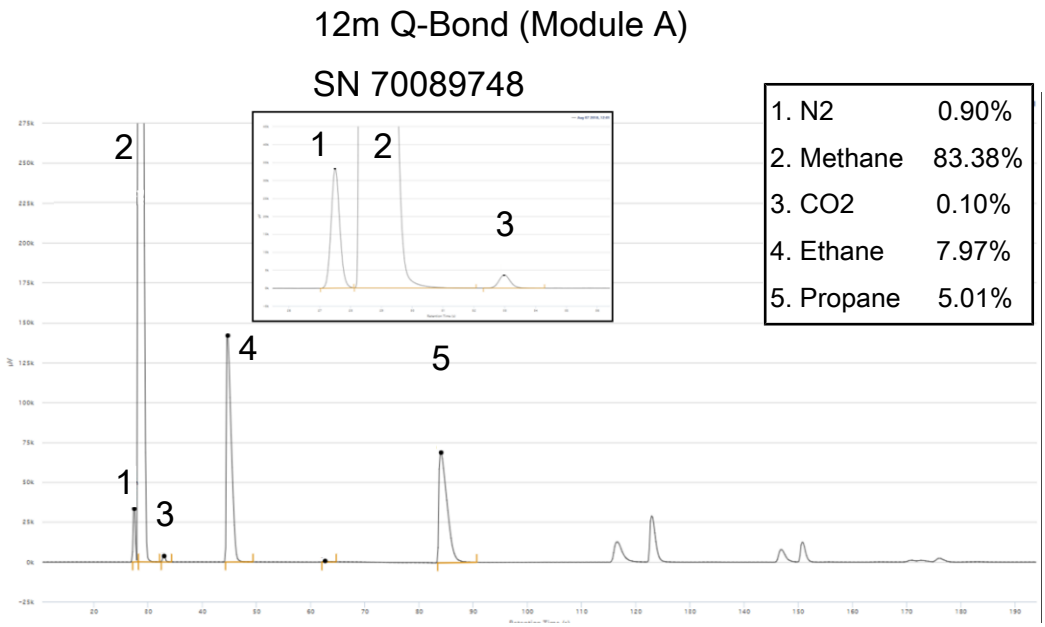


Fig. 6: Chromatogram of calibration gas using 12m PLOT Q-BOND (module A). Micro GC Fusion SN 70089748.

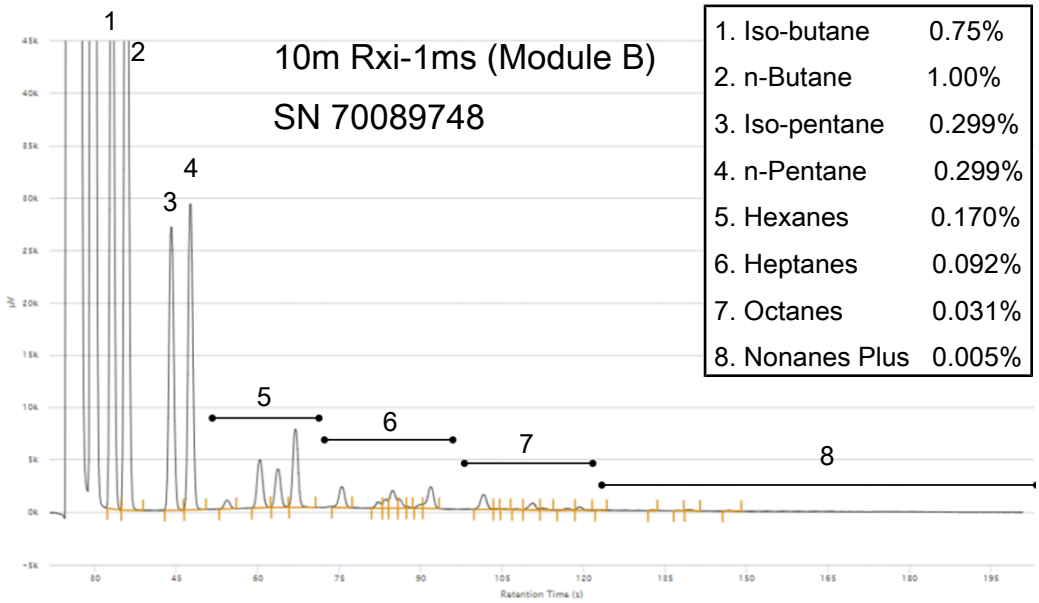


Fig. 7: Typical chromatogram of calibration gas using 10 m PDMS Rxi-1ms (module B). Micro GC Fusion SN 70089748.

Peak Integration Basic Setup

Proper peak integration is essential for accurate and precise analysis. Tables 3-4 illustrate a set of recommended Micro GC Fusion integration parameters for each channel and are summarized. These should be used as a starting point for any method and specifically correspond to entries in the Micro GC Fusion software calibration table, integration tab. Since the retention times vary slightly from system to system, even with similar set points, the user will need to use exact times appropriate for their systems. In addition, the peak integration values given are suggested starting points. Some small modifications will need to be made from system to system and based upon sample types.

In general, peak integration parameters should be kept to a minimum and initially be adjusted with the calibration gas but also optimized with actual field samples before completing the method development and calibration steps. Changes to peak integration in the field should also be kept at a minimum as it could affect determined area counts vs the calibration.

Parameter	Value	Start Time (s)	Stop Time (s)	Description
No peaks	On	0	22	Turn the integration on from time 0 until 5 seconds before the first peak.
Min. height threshold	150-250	0	225	Ignore any peak below 150 uV height for the entire run. This avoids the integration of noise peaks. The value is determined experimentally based upon samples.
No peaks	On	115	225	Turn the integration off at 115 seconds until the end of the run.
Baseline window	2	0	40	Apply the baseline window parameter from 0 seconds until 6 seconds before the retention time of ethane. This helps integrate N_2/CH_4.
Baseline window	6	225	40	Apply the baseline window parameter from just before ethane until the end of the run. This helps integrate the wider C2 and C3 peaks.

Table 3: Peak Integration module A (Q-Bond). These are suggested starting points. Times will vary from Micro GC to Micro GC. Times and values should be adjusted as necessary.

Parameter	Value	Start Time (s)	Stop Time (s)	Description
No peaks	On	0	22	Turn the integration on from time 0 until 3 seconds before iso-butane starts to elute.
Min. height threshold	25-100	0	230	Ignore any peak below 25 uV height for the entire run. This avoids the integration of noise peaks. The value is determined experimentally based upon samples.
Baseline window	6	60	230	Apply the baseline window parameter from 1-2 seconds after n-pentane elutes until the end of the run. This helps to integrate hexanes and the heavier peaks.
Peak sensitivity	10	60	230	Use the peak sensitivity values of 6-10 from 1-2 seconds after n-pentane elutes until the end of the run. This helps to integrate hexanes and the heavier peaks.
Group peaks	On	60	84	Group the hexanes (C6) peaks.
Group peaks	On	84.5	114	Group the heptanes (C7) peaks.
Group peaks	On	114.2	142	Group the octances (C8) peaks.
Group peaks	On	142.2	230	Group the nonanes plus (C9+) peaks.

Table 4: Peak Integration module B (Rxi-1ms). These are suggested starting points. Times will vary from Micro GC to Micro GC. Times and values should be adjusted as necessary.

Calibration and Validation

Users should follow industry guidelines in the calibration and validation of the Micro GC Fusion method, including the care of the blends used in these procedures. Calibration gases are typically kept heated to temperatures 30°F above the blend published due point. In almost all cases temperatures of 105-120°F are satisfactory. Sample lines used to connect these blends to Micro GC Fusion should also be heated and kept as short as possible. For both field and in-lab use, instruments should be calibrated on some routine schedule – typically weekly or bi-weekly if used within that period of time. Calibration can be performed at a single concentration level or multiple concentration levels. This is often dictated by the range of concentrations that intend to be analyzed by a given methodology. However, in most cases the Micro GC Fusion analysis provides a linear response over a given concentration range. Quality assurance and control (QA/QC) of the instrument is a multi-step process and should include the following steps at a minimum.

1. **Calibration** - The system should be calibrated at routine intervals using industry standard techniques with calibration gases that are not expired and have been heated according to industry guidelines previously referenced.

2. **Validation** - The system should go through a validation procedure after calibration (using the same calibration gas as an unknown), to prove that the analysis meets published specifications known as repeatability and reproducibility. GPA method 2261 provides both repeatability and reproducibility specifications. For this discussion and application, repeatability is defined as the difference between two sample measurements using the same instrument/operator/method while reproducibility is defined as the difference between two sample measurements using different instruments/operators but the same methodology.
3. **Audit Gas Test** - In addition, some users will also use another independent commercially prepared gas (often time called audit gas) at slightly different concentrations to check accuracy of the measurement, taking into account the published blend uncertainty values. This gas can also be checked for repeatability and reproducibility.
4. **Fidelity Plots** - Preparation of fidelity plots according to GPA 2198. An instrument fidelity plot can be used to monitor GC performance, the integrity of the calibration gas and overall instrument behavior. The fidelity plot should be generated using the primary calibration gas. Several types of fidelity plots can be generated to verify performance. Fidelity plots from Micro GC differ from “traditional” ones since the Micro GC uses two independent channels (TCD). The figure below is an example of a Fidelity Plot generated automatically from the Micro GC Fusion data using Diablo EZReporter software.

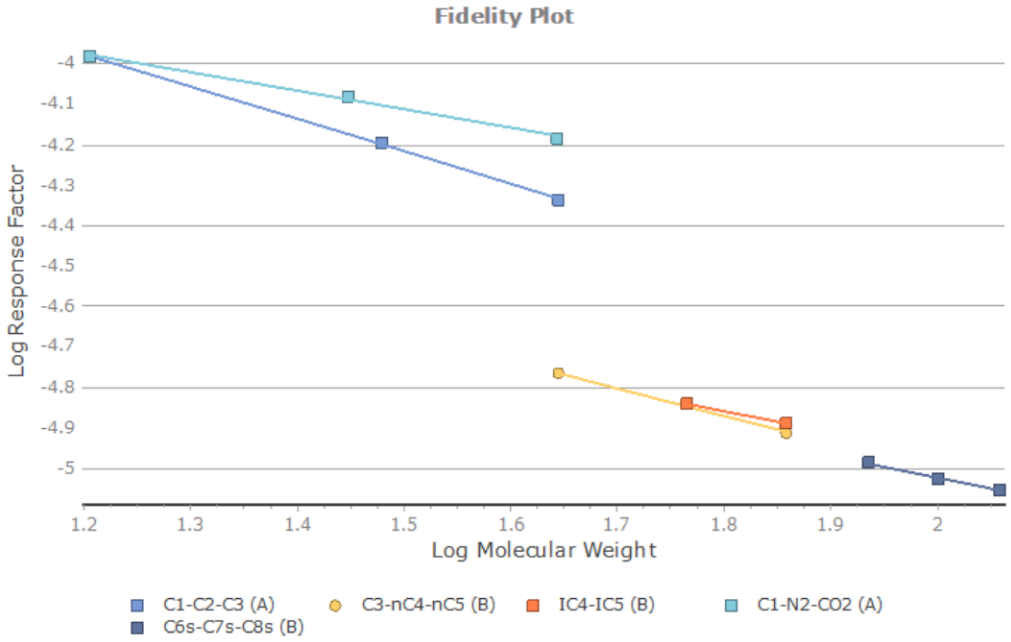


Fig. 8: Micro GC “Bernos” Fidelity Plot example. See Figures 6-7 for concentrations. For clarity purposes, the area counts of propane from Channel B was used to validate n-HC Channel B line. The C6s-C7s-C8s TCD response on Channel B represents the hexanes plus isomer group mixture containing n-HC, iso-HC, and cyclic-HC are often times skewed vs the other lines. Correlations values (r^2) for each line are > 0.99. Data generated from Micro GC Fusion SN 70089748. Consult with GPA 2198 for detailed information on Fidelity Plots.

5. **Control Charting** - Control charts can be used to track instrument performance by analysis of a given sample over time.
6. **Sample System Validation** - Any sampling system used to connect the sample/calibration source (regardless if used in the lab or in the field) should be periodically checked for contamination. Typically this is tested by running repeated helium blanks thru the complete sampling system.
7. **Documentation** - It is recommended that the user should keep ample documentation for each of the above QA/QC steps either in paper or electronic versions. Copies of Micro GC Fusion methods, EZReporter configuration files should be periodically archived on a networked folder, email system or portable storage device.

Results

Sampling procedures for live samples are not covered in this document, but should also follow industry guidelines[12]. Results shown were generated after calibration/validation of the method following industry protocol. For an example of day to day stability in a stationary setting, see the table containing results of the calibration gas over three days with the system turned off each night and calibration set on day 1. The Micro GC Fusion was then turned on and warmed up for 30-45 minutes at method conditions in the morning and then one sample was run before continuing sample analysis. This “throw-away” run (i.e. – data ignored) is used to exercise the system and purge columns out after initially turning on. This is a common practice for systems that are turned off each night in portable applications and subjected to ranges of ambient conditions. Data shown meets GPA repeatability limits except for a single data point of ethane. The C6-C9 results were summed in order to compare to C6+ repeatability. In each case the un-normalized totals were found to be 99.6-100.2%.

Date	N_2	CH_4	CO_2	C2	C3	i-C4	n-C4	i-C5	C6s	C7s	C8s	C9s
8/6/2018 12:06	0.9000	83.3878	0.1020	7.9570	5.0060	0.7490	1.0010	0.2990	0.2990	0.1693	0.0930	0.0316
8/6/2018 12:19	0.8975	83.3869	0.1008	7.9598	5.0137	0.7474	0.991	0.2988	0.2983	0.1688	0.0916	0.0318
8/6/2018 13:51	0.9046	83.3839	0.1032	7.9661	5.0062	0.7467	0.9977	0.2978	0.2980	0.1675	0.0915	0.0319
8/6/2018 15:25	0.9036	83.3775	0.1017	7.9681	5.0072	0.7478	0.9993	0.2985	0.2988	0.1677	0.0938	0.0311
8/7/2018 9:28	0.9161	83.3778	0.1020	7.9625	5.0066	0.7451	0.9950	0.2984	0.2984	0.1681	0.0915	0.0322
8/7/2018 10:12	0.9009	83.4107	0.01018	7.9679	5.0115	0.7444	0.9911	0.2945	0.2932	0.1627	0.0864	0.0295
8/7/2018 10:29	0.8981	83.3769	0.1015	7.9697	5.0145	0.7466	0.9964	0.2988	0.2993	0.1683	0.0928	0.0317
8/7/2018 11:30	0.9006	83.3742	0.1021	7.9744	5.0134	0.7461	0.9963	0.2981	0.2982	0.1670	0.0929	0.0316
8/7/2018 12:01	0.8965	83.3833	0.1008	7.9689	5.0106	0.7467	0.9971	0.2983	0.2990	0.1686	0.0919	0.0322
8/8/2018 9:35	0.9056	83.3806	0.1005	7.9708	5.0034	0.7469	0.9979	0.2982	0.2987	0.1687	0.0923	0.0313
8/8/2018 10:01	0.8999	83.3637	0.1009	7.9679	5.0272	0.7474	0.9987	0.2984	0.2988	0.1691	0.0913	0.0317
8/8/2018 11:46	0.9048	83.3689	0.1023	7.9736	5.0140	0.7466	0.9970	0.2984	0.2986	0.1684	0.0913	0.0319
8/8/2018 11:59	0.8977	83.3518	0.1024	7.9824*	5.0195	0.7488	0.9998	0.2988	0.2995	0.1682	0.0932	0.0322
%RSD	0.58	0.02	0.76	0.08	0.13	0.17	0.25	0.39	0,53	1.01	1.99	2.28

*Table 5: Data in mole% obtained over 3 days. Instrument turned off each night and then allowed to equilibrate for 45 minutes after turning on. One sample run discarded. Calibrated 8/6 12:06pm. All data meets GPA2261-13 repeatability specification except one ethane result (denoted with a *). C6-C9 summed to compare with total Hexanes Plus repeatability. All un-normalized totals between 99.6-101.2%. Micro GC Fusion SN 70089748.*

A second calibration gas was analyzed as an “unknown” and results are shown in the table below. This gas contained n-hydrocarbons as Hexanes Plus and was used to help set peak windows for the extended portion. It was also used as a check gas in this case. The results meet reproducibility with the exception of the C6+ which fell just outside the acceptable range. This is caused by the differences in C6+ response factors between the calibration containing isomers and “unknown” containing n-hydrocarbons. As previously noted, it is recommended to always have Hexanes isomers in the gas used for calibration.

Component (SN 70089748)	Known Value (Certified) (Mole %)	As Analyzed (Micro GC Fusion) (Mole %)
N_2	2.498	2.562
methane	89.64	89.53
CO_2	0.998	0.946
ethane	4.983	5.032
propane	0.996	1.014
iso-butane	0.299	0.299
n-butane	0.299	0.306
iso-pentane	0.100	0.102
n-pentane	0.100	0.100
total hexanes plus	0.090 (as n-HC)	0.112

Table 6: Results of secondary calibration “gas” used to verify peak window set points. All results pass GPA 2261 Reproducibility specifications. The % accuracy of the certified calibration gas was not taken into account. Differences on hexanes plus attributed to response factor difference between calibration gas which contained “isomers” and secondary “gas” which contained n-hydrocarbons. Micro GC Fusion SN 70089748.

Chromatograms of several actual field samples on both Micro GC Fusions are shown in the figures below. For “Sample A,” neo-pentane is present in the gas and separated out from the n-Butane using the Micro GC Fusion. The results of these samples are summarized in the tables below, including comparison with a traditional benchtop GC analysis using GPA 2261.

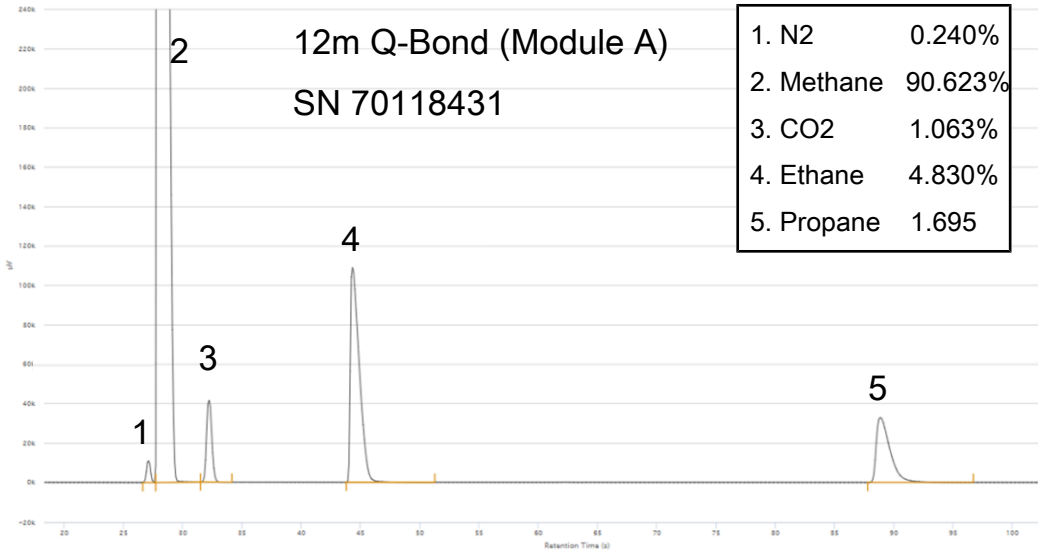


Fig. 9: Chromatogram of field sample module A. Peak results indicated on labels.

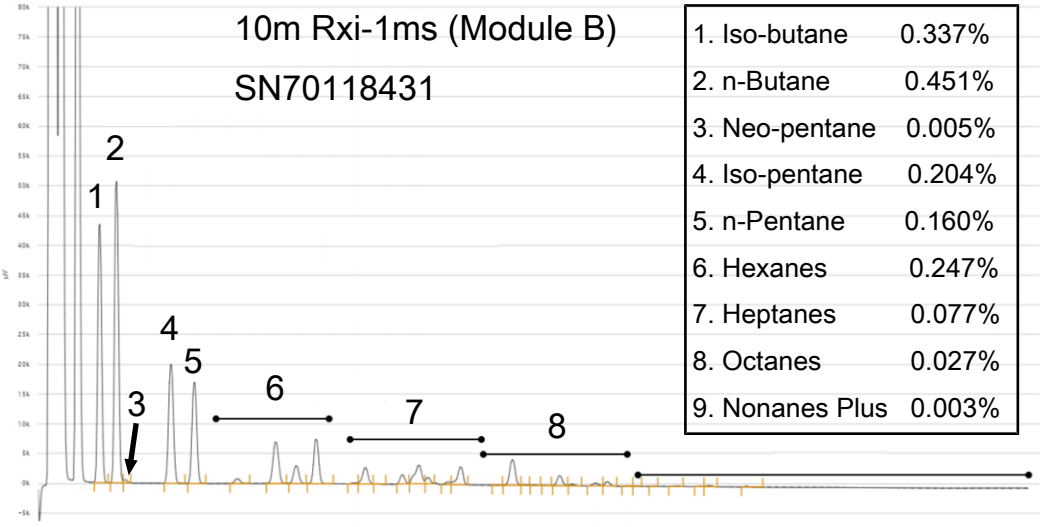


Fig. 10: Chromatogram of field sample module B. Peak results indicated on labels. Neo-pentane elutes on the tail of n-butane.

Component (SN 70118431)	Micro GC Fusion (mole %)	Lab GC (GPA2261) (mole%)
N_2	0.240	0.201
methane	90.62	90.72
CO_2	1.063	1.060
ethane	4.830	4.855
propane	1.695	1.678
iso-butane	0.377	0.363
n-butane	0.451	0.430
neo-pentane	0.005	(included with n-butane)
iso-pentane	0.230	0.196
n-pentane	0.160	0.171
hexanes	0.247	N/A
heptanes	0.077	N/A
octanes	0.027	N/A
nonanes plus	0.004	N/A
total hexanes plus	0.355	0.324

Table 7: Results of a field sample "A" analyzed on Micro GC Fusion and a traditional laboratory GC using GPA 2261. Sample contained in a large cylinder and used as a periodic "check gas." The lab results were generated at a much different time so sample integrity may be in question but shown here for comparison and informational purposes. See chromatograms Figures 9-10. Higher N2 typically indicates poor purge was done.

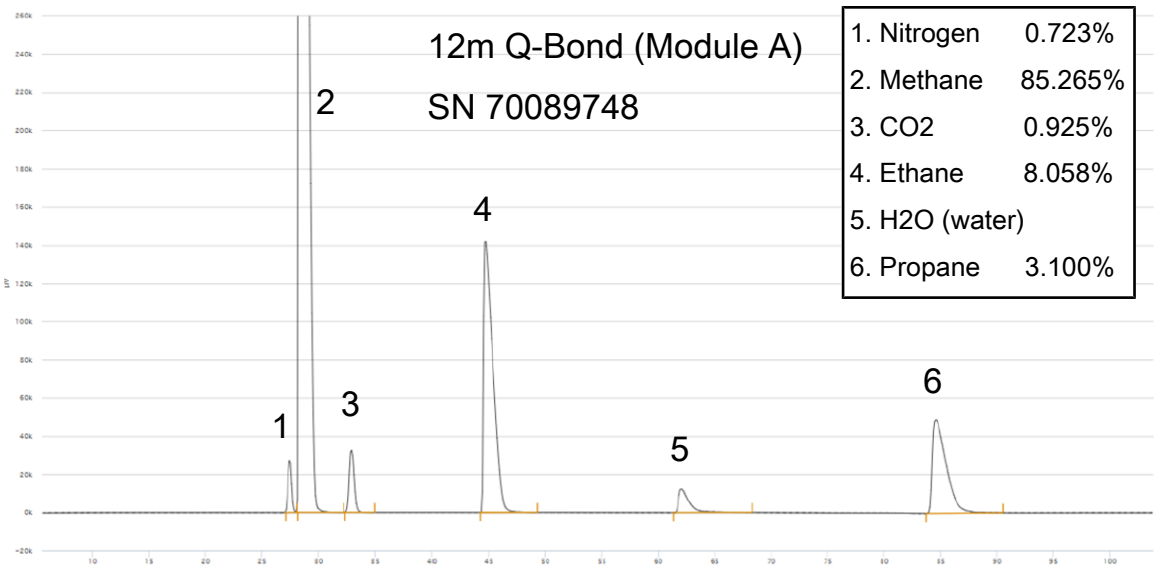


Fig. 11: Chromatogram of field sample module A. Peak results indicated on labels.

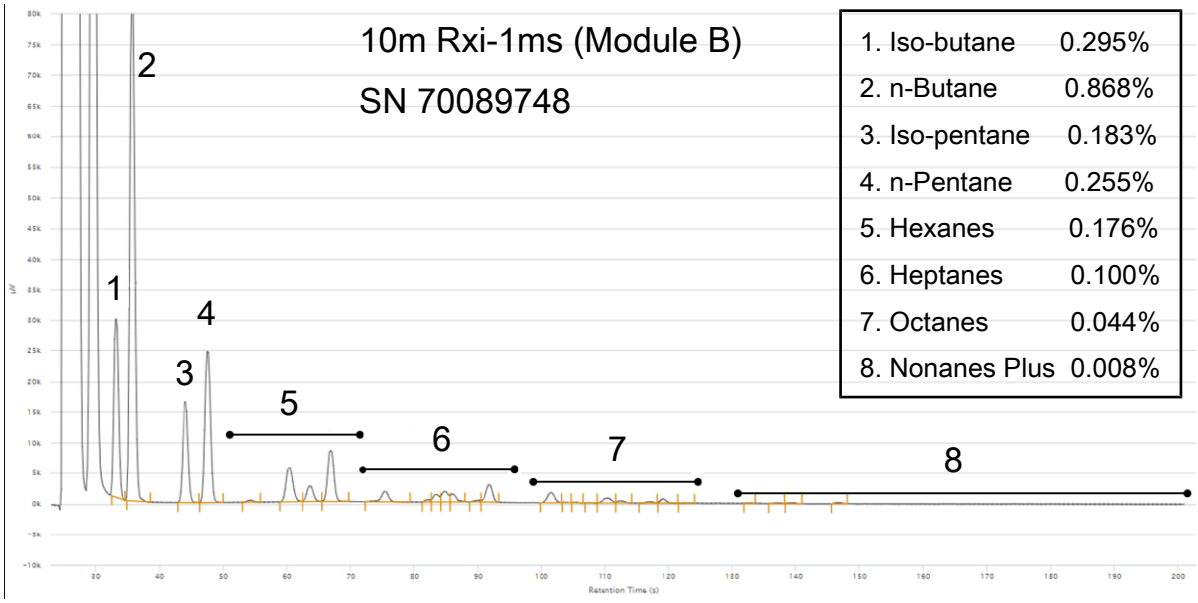


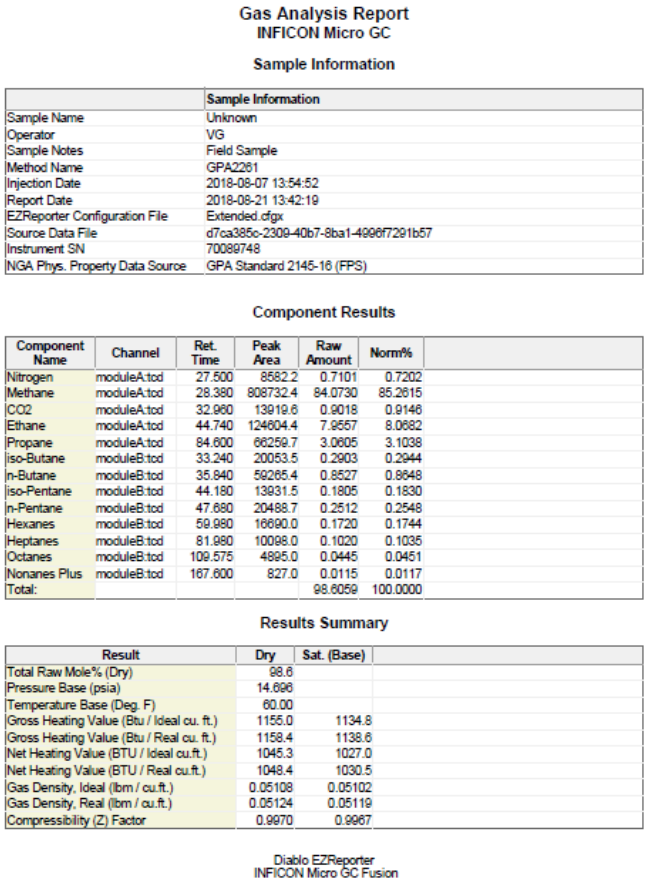
Fig. 12: Chromatogram of field sample Channel B. Peak results indicated on labels.

Component	Micro GC Fusion (mole %)	Lab GC (GPA2261) (mole%)
N_2	0.720	0.698
methane	85.26	85.44
CO_2	0.915	0.954
ethane	8.069	7.884
propane	3.104	3.057
iso-butane	0.294	0.303
n-butane	0.865	0.849
iso-pentane	0.183	0.185
n-pentane	0.255	0.255
hexanes	0.174	NA

Component	Micro GC Fusion (mole %)	Lab GC (GPA2261) (mole%)
heptanes	0.104	NA
octanes	0.045	NA
nonanes plus	0.011	NA
total hexanes plus	0.333	0.384

Table 8: Results of a field sample "B" analyzed on Micro GC Fusion and a traditional laboratory GC using GPA 2261. Sample contained in a small cylinder. See chromatograms Figures 11-12. Higher N2 indicates poor initial purge for that sample run.

A typical report from the Diablo EZReporter software is shown in the figure below. This report can be customized by the individual user to include other important information such as detailed sample information, component results and different gas calculations required.



Gas Analysis Report
INFICON Micro GC

Sample Information

	Sample Information
Sample Name	Unknown
Operator	VG
Sample Notes	Field Sample
Method Name	GPA2261
Injection Date	2018-08-07 13:54:52
Report Date	2018-08-21 13:42:19
EZReporter Configuration File	Extended.cfgx
Source Data File	d7ca385c-2309-40b7-8ba1-4996f7291b57
Instrument SN	70089748
NGA Phys. Property Data Source	GPA Standard 2145-16 (FPS)

Component Results

Component Name	Channel	Ret. Time	Peak Area	Raw Amount	Norm%
Nitrogen	moduleA:tcd	27.500	8582.2	0.7101	0.7202
Methane	moduleA:tcd	28.380	808732.4	84.0730	85.2615
CO2	moduleA:tcd	32.960	13919.6	0.9018	0.9146
Ethane	moduleA:tcd	44.740	124604.4	7.9557	8.0682
Propane	moduleA:tcd	84.600	66259.7	3.0605	3.1038
iso-Butane	moduleB:tcd	33.240	20053.5	0.2903	0.2944
n-Butane	moduleB:tcd	35.840	59265.4	0.8527	0.8648
iso-Pentane	moduleB:tcd	44.180	13931.5	0.1805	0.1830
n-Pentane	moduleB:tcd	47.680	20488.7	0.2512	0.2548
Hexanes	moduleB:tcd	59.980	16690.0	0.1720	0.1744
Heptanes	moduleB:tcd	81.980	10098.0	0.1020	0.1035
Octanes	moduleB:tcd	109.575	4895.0	0.0445	0.0451
Nonanes Plus	moduleB:tcd	167.600	827.0	0.0115	0.0117
Total:				98.6059	100.0000

Results Summary

Result	Dry	Sat. (Base)
Total Raw Mole% (Dry)	98.6	
Pressure Base (psia)	14.696	
Temperature Base (Deg. F)	60.00	
Gross Heating Value (Btu / Ideal cu. ft.)	1155.0	1134.8
Gross Heating Value (Btu / Real cu. ft.)	1158.4	1138.6
Net Heating Value (BTU / Ideal cu.ft.)	1045.3	1027.0
Net Heating Value (BTU / Real cu.ft.)	1048.4	1030.5
Gas Density, Ideal (lbm / cu.ft.)	0.05108	0.05102
Gas Density, Real (lbm / cu.ft.)	0.05124	0.05119
Compressibility (Z) Factor	0.9970	0.9967

Diablo EZReporter
INFICON Micro GC Fusion

Fig. 13: Example report from Micro GC Fusion – Diablo EZReporter. Report can be customized to meet individual analysis needs.

Conclusion

Micro GC Fusion offers an accurate and precise yet simple gas measurement solution for C9 plus extended analysis of natural gas. With its small size and fast analysis, Micro GC Fusion is ideal for remote office, lab or field transportable setup. Information described in this paper can be used as a starting point to building a successful method.

References

1. GPA 2261 Analysis of Natural Gas and Similar Gaseous Mixtures by Gas Chromatography, GPA Midstream Association Tulsa, OK USA www.gpamidstream.org
2. 43 US Code of Federal Regulations 3173-3175, Onshore Oil and Gas Operations; Federal and Indian Oil and Gas Leases; Measurement of Gas
3. INFICON, East Syracuse, NY USA www.inficon.com
4. Q-Bond PLOT and Rxi-1ms columns are commercially available from Restek Corp, Bellefonte, PA USA www.restek.com
5. GPA 2198 Selection, Preparation, validation, Care and Storage of Natural Gas and Natural Gas Liquids Reference Standard Blends, GPA Midstream Association Tulsa, OK USA
6. GPA 2172 Calculation of Gross Heating Value, Relative Density, Compressibility and Theoretical Hydrocarbon Liquid Content for Natural Gas Mixtures for Custody Transfer
7. Diablo Analytical, Antioch, CA USA www.diabloanalytical.com
8. Micro GC technology was first introduced by Microsensor Instruments (MTI) in 1979, Freemont, CA USA in the early 1980's with models M200/M400 and P200. MTI was acquired by Hewlett-Packard in March 1998.
9. Separation of O_2 from N_2 can be performed using a Molecular Sieve 5A PLOT column and requires an additional channel of operation for Micro GC Fusion.
10. Repeatability of C4/C5 is found to be better using the second non-polar column module approach and especially when the C4/C5's are at low concentration (<0.1%).
11. GPA 2286 Extended Analysis of Natural Gas and Similar Mixtures by Temperature Programmed Gas Chromatography, GPA Midstream Association Tulsa, OK USA www.gpamidstream.org
12. GPA 2166 Obtaining Natural Gas Samples for Analysis by Gas Chromatography, GPA Midstream Association Tulsa, OK USA www.gpamidstream.org

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