Rapid and Reliable Detection of Dissolved Gases in Water

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Key Words
Chromeleon CDS, Environmental, Fracking, Gas Chromatography, GC, Headspace, Hydraulic Fracturing, Methane, TRACE 1310, TriPlus 300, Water Quality

Goal

To describe a rapid and reliable gas chromatography method for identifying and quantifying methane, ethane, ethylene, and propane in waters affected by hydraulic fracturing operations.

Introduction

Hydraulic fracturing, or fracking, is a well stimulation technique in which water is typically mixed with sand and chemicals and injected at high pressure into a wellbore to create small (generally less than 1 mm) fractures to maximize fluid removal and well productivity. This technique enables the removal of large amounts of formerly inaccessible hydrocarbons. However, the gases liberated using this method may contaminate water reservoirs and have become a controversial environmental and health matter. Monitoring the gas content of affected waters is one way to assess the environmental impact of fracking on an area.

The U.S. Congress has instructed the U.S. Environmental Protection Agency not to regulate hydraulic fracturing, thus some individual states are developing their own regulations. Recently, several states finalized analysis requirements for baseline environmental monitoring of waters *prior* to hydraulic fracturing. This baseline monitoring aims to identify local water contaminants so that changes can be assessed post hydraulic fracturing to conclusively demonstrate that hydraulic fracturing alone (and not another process, such as mining) was responsible for detrimental impacts on the water.

Different approaches are available for measuring the gas content in water. The most common method is that outlined by the industry standard SOP RSK-175,[1] which tests for dissolved gases via static headspace gas chromatography and then calculates results according to Henry's Law, converting the concentration in the headspace into the partial pressure of the gas and using it to calculate the aqueous gas concentration.

Another possible approach, adopted in this application note, is to saturate water with a gas standard or a mix of gases and use that water to build a calibration curve via sequential dilution. This approach is currently being validated by the American Society for Test Methods (ASTM).

Sample and Standards Preparation

Water samples are collected directly into a 20 mL headspace vial without leaving any headspace. Cap vials immediately and remove 10 mL of water immediately before the analysis.

Prepare standards by bubbling gas standards into a 500 mL flask filled with deionized (DI) water in a temperature controlled bath at 21 °C. To achieve saturation of the water, use a flow of 12 mL/min for two hours. Completely fill a 20 mL headspace vial with saturated water and cap immediately without leaving headspace in the vial. This sample is referred to as the bulk sample. Take aliquots were from the saturated bulk sample using a valve syringe. These aliquots are used to build the calibration curve by spiking increasing volumes of the bulk sample into blank DI water samples.

Method Setup

A method was developed for the Thermo Scientific™ TriPlus™ 300 Headspace Autosampler and the TRACE™ 1310 Gas Chromatograph (Table 1).

Recommended Instrument Conditions

TriPlus 300 HS Autosampler	
Vial Equilibration Time:	15 min
Oven Temperature:	70 °C
Manifold Temperature:	80 °C
Transfer Line Temperature:	80 °C
Vial Pressurization:	Pressure mode, 1 bar, 0.2 min equilibration time
Loop Filling Mode:	Pressure mode, 0.5 bar, 0.2 min equilibration time
Injection:	Standard mode for 0.5 min
Purge Time:	0.5 min
Purge Flow:	50 mL/min
TRACE 1310 GC	
Injection Volume:	1 mL (standard Loop)
Liner:	Headspace liner (P/N 453A1335)
Column Type:	Thermo Scientific™ TracePLOT TG-Bond Q 25 m, 0.53 mm (P/N 26004-6120)
Column Oven:	Initial 45 °C, hold 1 min Ramp 16 °C/min to 200 °C, hold 1 min
Carrier Gas:	Helium
SSL Injector:	200 °C; split mode with a split ratio of 10:1
Column Flow:	Constant flow at 5 mL/min
Instant Connect Electron FID	
Temperature:	250 °C
Gas Conditions:	Standard

Methods

The TRACE 1310 GC system is equipped with one Instant Connect Split/Splitless (SSL) injector with a headspace liner (P/N 453A1335) and an Instant Connect Electron Flame Ionization Detector (FID). The column used is a TracePLOT TG-Bond Q 25 m, 0.53 mm (P/N 26004-6120). The gas standards used for calibration may be ordered from Air Liquide. The data are collected and processed using the Thermo Scientific™ Dionex™ Chromeleon™ 7.2 Chromatography Data System (CDS) software.

Results and Discussion

The saturation time was optimized by preparing the highest methane calibration standard at 30-minute intervals, while continuously flowing DI water (Figure 1). Other apparatuses and conditions may lead to different results in terms of saturation times.

The plot-type column used for this experiment is ideal for effectively retaining and separating compounds such as the gases analysed here. The FID guarantees excellent sensitivity and a wide range of linearity.

Chromatograms of the analyzed gas mixture are shown in Figures 2 and 3.

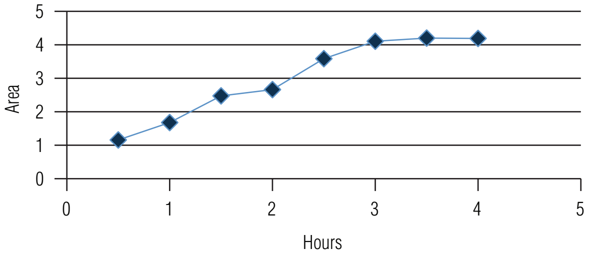

Figure 1. Optimization of saturation times.

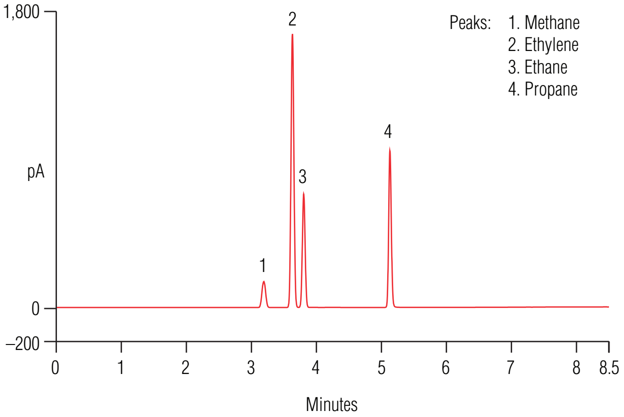

Figure 2. Chromatogram of the four gases analyzed (highest calibration point). In order from left to right, the peaks represent methane, ethylene, ethane, and propane.

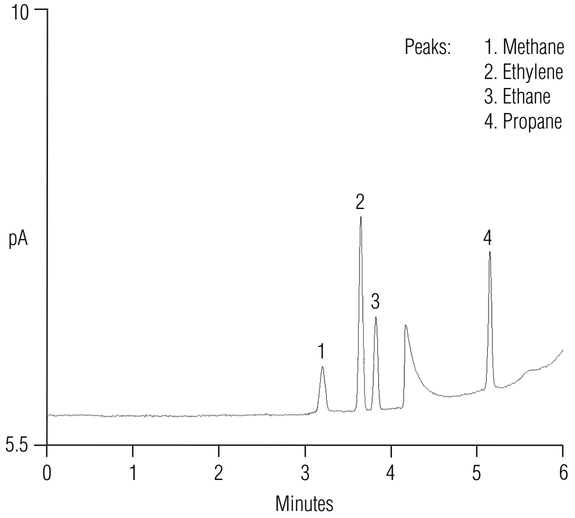

Figure 3. Chromatogram of the four gases analyzed (second calibration point, 10 µL added).

Two calibration curves were built. The calibration curve for low-level concentrations was suitable for detection of minimum traces of the analytes in the samples and assessing the sensitivity of the system. Another calibration curve was built for higher concentration intervals, including the saturation level most suitable for screening real samples. Calibration curves were built by adding aliquots of saturated water directly to 10 mL of DI water in 20 mL vials. For low level detection, aliquots of 5, 10, 25, 50, and 100 µL of saturated water were added. For the high level curve, aliquots of 25, 50, and 100 µL and 1, 5, and 10 mL of saturated water were used.

The gas content of each calibration point was calculated from the solubility of the gases at 21 °C, the temperature at which the standards are prepared. Solubility of the tested gases was:

Methane:	23 mg/L
Ethylene:	149 mg/L
Ethane:	62 mg/L
Propane:	77 mg/L

Tables 1 and 2 report the gas concentrations for each calibration point.

Table 1. Concentration at the calibration points for the low-level calibration curve.

	Level 1 (ppb)	Level 2 (ppb)	Level 3 (ppb)	Level 4 (ppb)	Level 5 (ppb)
Methane	12	23	57	115	230
Ethylene	75	149	370	745	1490
Ethane	30	62	155	310	620
Propane	38	77	192	385	770

Table 2. Concentration at the calibration points for the high-level calibration curve.

	Level 1 (ppb)	Level 2 (ppb)	Level 3 (ppb)	Level 4 (ppm)	Level 5 (ppm)	Level 6 (ppm)
Methane	57	115	230	2.3	11.5	23
Ethylene	370	745	1490	14.9	74.5	149
Ethane	155	310	620	6.2	31.0	62
Propane	192	385	770	7.7	38.5	77

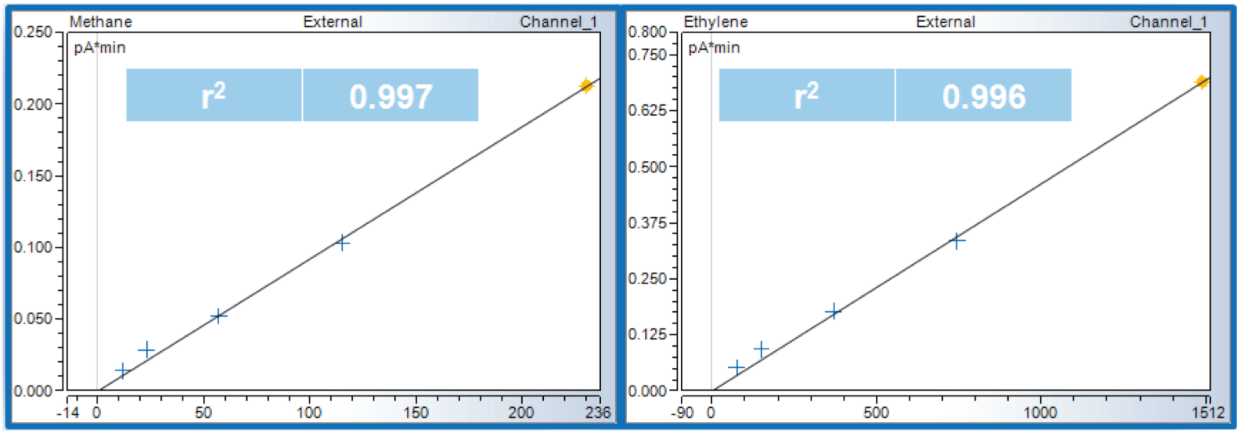

Figure 4. Low-level calibration curves for methane and ethylene.

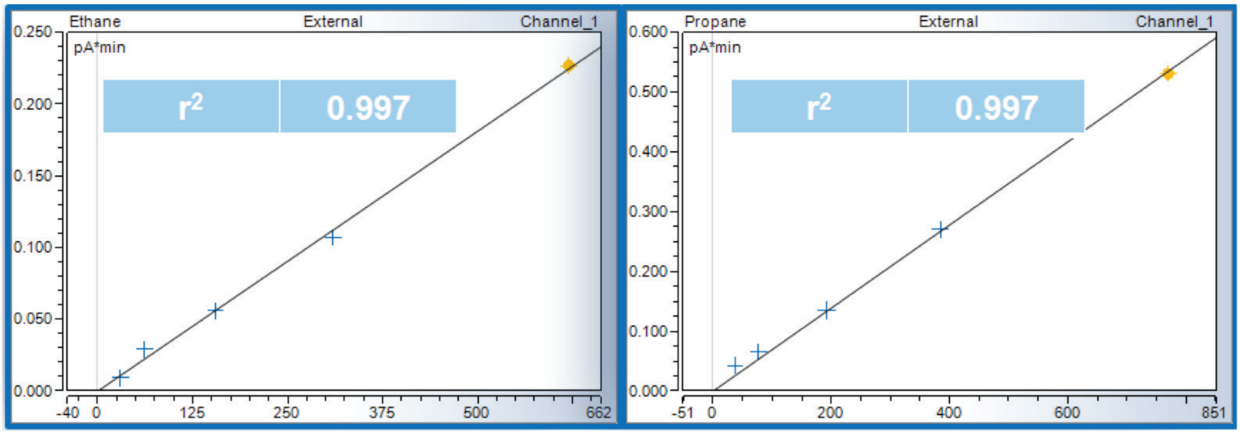

Figure 5. Low-level calibration curves for ethane and propane.

The results of the calibration show good performance in terms of linearity with a r^2 value above 0.99 for each one of the tested gases (Figures 4–6).

Table 3. High-level calibration results for the four gases.

Analyte	r^2
Methane	0.998
Ethylene	0.998
Ethane	0.998
Propane	0.995

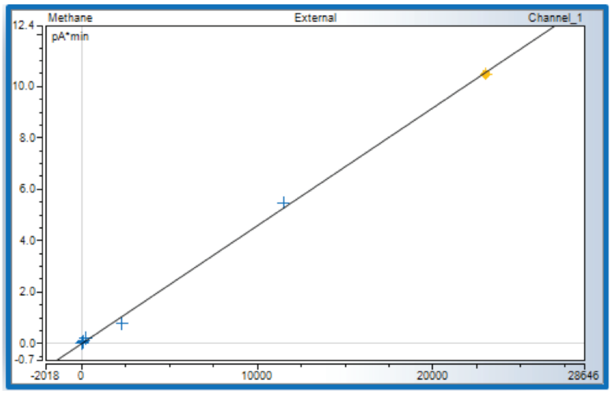

Figure 6. High-level calibration curve for methane.

Conclusion

This application is a viable solution for monitoring dissolved gases in water. The analytical procedure and sample preparation are simple and straightforward. Sample conservation and custody are the primary concerns. This method can be used to detect and quantitate both low and high levels of dissolved gases in water samples, making it an excellent option for testing possible impacts of hydraulic fracturing as well as gases in water from surface, non-well stimulated sources.

The 120-position tray of the TriPlus 300 HS autosampler coupled with the exclusive modularity concept of the TRACE 1310 GC offer high throughput capabilities with virtually no downtime for maintenance or switching to other analyses. Altogether, the system is a simple, robust and reliable option for performing this type of analysis in an unattended fashion.

References

1. Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using GC Headspace Equilibration Technique; U.S. Environmental Protection Agency, RSKSOP-175, Revision No. 2, May 2004.

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