An Alternative Method to RSK 175 using a Purge and Trap Concentrator and GC/FID

Application Note

Abstract

With the growing price of oil, many alternative energy sources are being explored. Natural gas prices are actually decreasing, in large part to the use of hydraulic fracturing in areas like the Marcellus Shale in Pennsylvania. Due to increased concern over the hydrofracturing process and the release of methane and other chemicals into the local drinking water, a need has developed for fast and accurate analysis of methane in water. This poster will evaluate a method developed for the determination of methane, ethane, ethene, and propane in water using a Purge and Trap concentrator, autosampler, and GC/FID. Comparisons to current headspace methods, RSK 175[1] and BOL6019[2], will be made.

Introduction

Hydraulic fracturing, also known as "fracking", is a drilling process currently used to recover natural gas from sources like coalbeds and shale formations. This involves injecting large amounts of water, mixed with sand and chemicals, at high pressures to break up the shale to release the gas. An outline of the hydraulic fracturing process can be found in Figure 1. Natural gas from these hard-to-extract sources is becoming increasingly popular and is projected to grow to nearly 45% of the nation's natural gas supplies by 2035[3].

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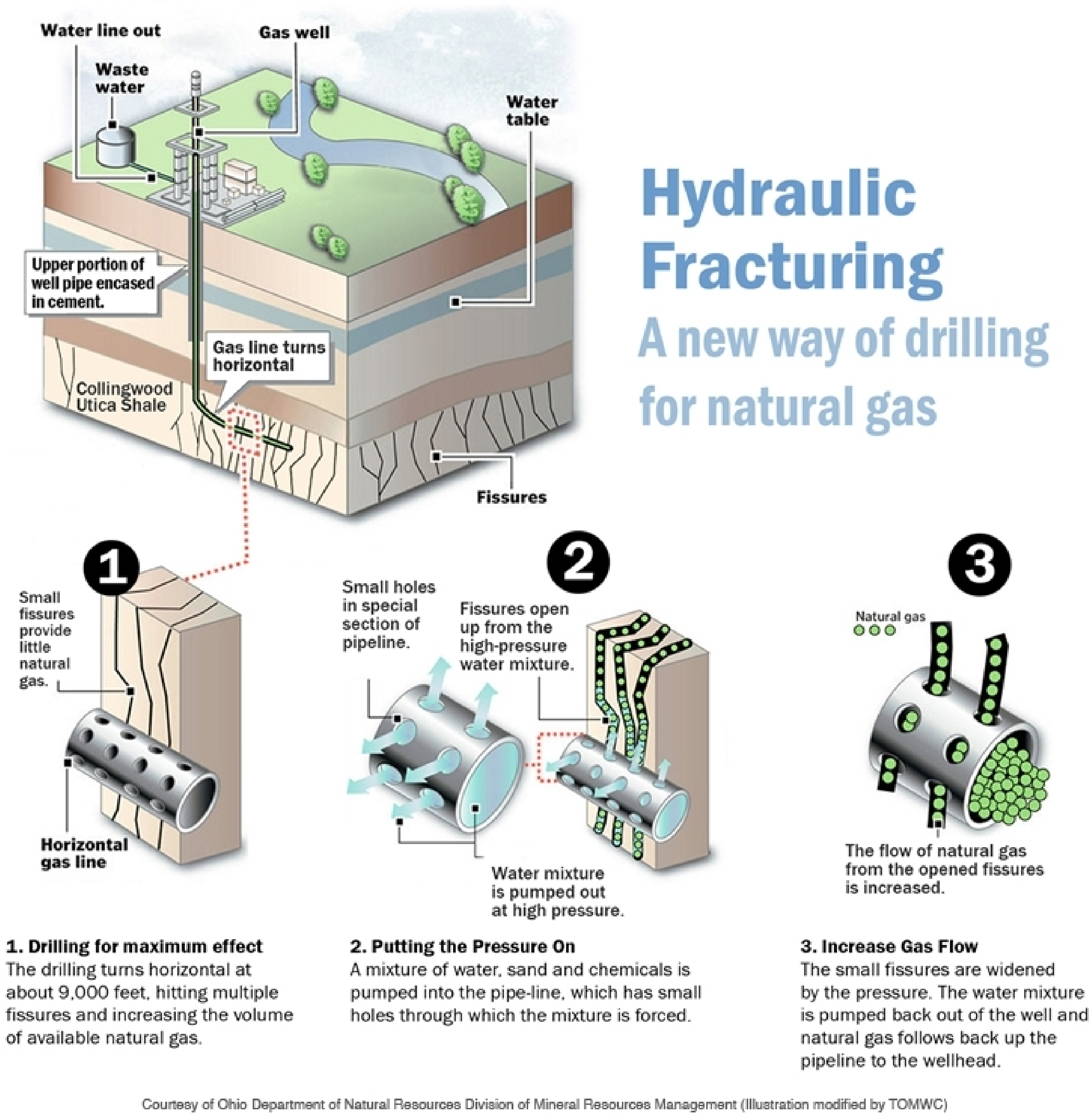

Figure 1: Process of Hydraulic Fracturing to Drill for Natural Gas[4]

Even though hydraulic fracturing is a relatively old practice, first employed over 60 years ago to drill for oil in Oklahoma[5], there has been little research into the impact of its increasing use as a drilling process for natural gas. With growing concern over the environmental effects of fracking on water quality, the United States EPA has begun studies to monitor the treatment methods and environmental impact with the goal of standardization by 2013/2014[6]. Figure 2 shows a map of shale gas formations in the North America indicating the potential widespread environmental impact the fracking process could have.

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The current method for determining natural gas constituents (methane, ethane, and ethene) in water is RSK 175[1]. This method is employed for the analysis of dissolved gases in drinking water using a headspace equilibration technique. Propane has been added to this list in modified methods such as BOL6019[2], developed by the Pennsylvania Department of Environmental Protection (PADEP). This analysis also requires more modern automated headspace analyzers. A flame ionization detector (FID) will be employed for this study, although RSK 175[1] also allows thermal conductivity (TCD) as well as electron capture detectors (ECD) to be used. Due to the lack of EPA methods requiring headspace analysis, these instruments are not normally found in environmental laboratories. This application demonstrates an alternative analysis using purge and trap concentration, which are typically available in many environmental labs.

Source: U.S. Energy Information Administration based on data from various published studies. Canada and Mexico plays from ARI.
Updated: May 9, 2011

Figure 2: Shale Gas Formations in North America[7]

For this study, a Stratum Purge and Trap Concentrator (PTC) was used in conjunction with an AQUATek 100 Autosampler. This set-up allows for complete automation of sample preparation for the analysis of liquid samples for purge and trap. A recirculating chiller bath was also utilized to maintain a sample temperature of less than 10°C. This technique also requires a 5mL purge volume.

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Utilizing a GC/FID, a linear calibration was performed and percent Relative Standard Deviation (%RSD) and Method Detection Limits (MDLs) were determined for the full list of compounds. Similarly to BOL6019[2], calibrations will be performed on aqueous standards rather than the gaseous standards used in RSK 175[1].

Experimental-Instrument Conditions

The Stratum PTC and AQUATek 100 Autosampler were coupled to a GC/FID for analysis. Teledyne Tekmar's new proprietary trap was also utilized. The GC was configured with a Restek Rt-U-BOND 15 m x 0.53 mm x 20 µm column. The GC/FID parameters are outlined in Tables 1 and 2. Table 3 outlines the P&T and autosampler conditions. A recirculating chiller bath was also employed to maintain sample temperatures below 10°C.

GC Parameters	
GC:	GC/FID
Column:	Restek Rt-U-Bond 15 m x 0.53 mm x 20 µm, 1.0 psi constant pressure
Oven Program:	35° C for 4 min, 20° C/min to 190° C hold for 2 min
Inlet:	190° C
Gas:	Helium
Split Ratio:	20:1

FID Parameters	
Temperature:	190°C
Hydrogen Flow:	35 mL/min
Air Flow:	300 mL/min
Mode:	Constant Makeup Flow
Makeup Flow:	30 mL/min
Makeup Gas:	Helium

Tables 1 & 2: GC and FID Parameters

Stratum PTC and AQUATek 100 Parameters			
Variable	Value	Variable	Value
Pressurize Time	0.35 min	Purge Time	1.5 min
Sample Transfer Time	0.35 min	Purge Temp	20°C
Rinse Loop Time	0.30 min	Purge Flow	10 mL/min
Sweep Needle Time	0.30 min	Dry Purge Time	0.0 min
Bake Rinse	On	Dry Purge Temp	20°C
Bake Rinse Cycles	1	Dry Purge Flow	100 mL/min
Bake Rinse Drain Time	0.35 min	GC Start	Start of Desorb
Presweep Time	0.25 min	Desorb Preheat Temp	95°C
Water Temp	90° C	Desorb Drain	On
Valve Oven Temp	80°C	Desorb Time	2.00 min
Transfer Line Temp	80°C	Desorb Temp	100°C
Sample Mount Temp	60°C	Desorb Flow	300 mL/min
Purge ready Temp	35°C	Bake Time	15.00 min
Condenser Ready Temp	40°C	Bake Temp	100°C
Condenser Purge Temp	20°C	Bake Flow	400 mL/min
Standby Flow	10 mL/min	Condenser Bake Temp	200°C
Pre-Purge Time	0.5 min		
Pre-Purge Flow	40.0 mL/min		

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Sample Heater	Off
Sample Preheat Time	1.00 min
Sample Temp	40°C

Table 3: Stratum PTC and AQUATek 100 Parameters (Stratum PTC Parameters are in Blue)

Calibration Data

To make the stock solutions, a 500 mL volumetric flask filled with de-ionized water was placed in an ice water bath and purged with a reference gas corresponding to each of the four analytes. Each gas was bubbled through chilled water for two hours to make individual concentrated standards. Unlike in RSK 175[1], calibrations in BOL6019[2] are performed using aqueous rather than gaseous standards. This study also employs an aqueous calibration, where standards are analyzed under the same conditions as samples.

Calibration standards were made from serial dilutions of these stock standards by calculating the concentration of saturated gas solutions in water at 0°C. For example, the saturation point of methane in 0°C water is 39.59 mg/L at atmospheric pressure. Calibration standards were made in 50 mL volumetric flasks filled to volume with chilled de-ionized water over a range of 7.92 ppb to 19.8 ppm. Samples were transferred to headspace free 40 mL vials for analysis. These standards were additionally made for the remaining compounds of interest.

The calibration data generated during this study was evaluated by linearity (r^2) and percent Relative Deviation (%RSD). Method detection limits were also established for all compounds by analyzing seven low level replicates. Calibration data and MDLs can be found in Table 4. In addition, an example of a chromatogram for a 40ppm methane standard can be found in Figure 3. A blank analyzed after the highest calibration standard was used to calculate the percent carryover which was less than 0.04% for all compounds.

Compound	Calibration Range	Relative Response Factor (RRF)	Linearity (r^2)	% Relative Deviation (%RSD)	Method Detection Limit (MDL)	% Carryover
Methane	**7.92 ppb to 19.8 ppm**	**166**	**1.000**	**2.0**	**0.4 ppb**	**0.04%**
Ethene	**56.2 ppb to 281 ppm**	**587**	**0.9995**	**4.5**	**31 ppb**	**0.03%**
Ethane	**26.4 ppb to 132 ppm**	**621**	**0.9998**	**13.9**	**21 ppb**	**0.04%**
Propane	**29.4 ppb to 147 ppm**	**803**	**0.9999**	**12.0**	**18 ppb**	**0.04%**

Table 4: Calibration and MDL Data for Methane, Ethane, Ethene, and Propane

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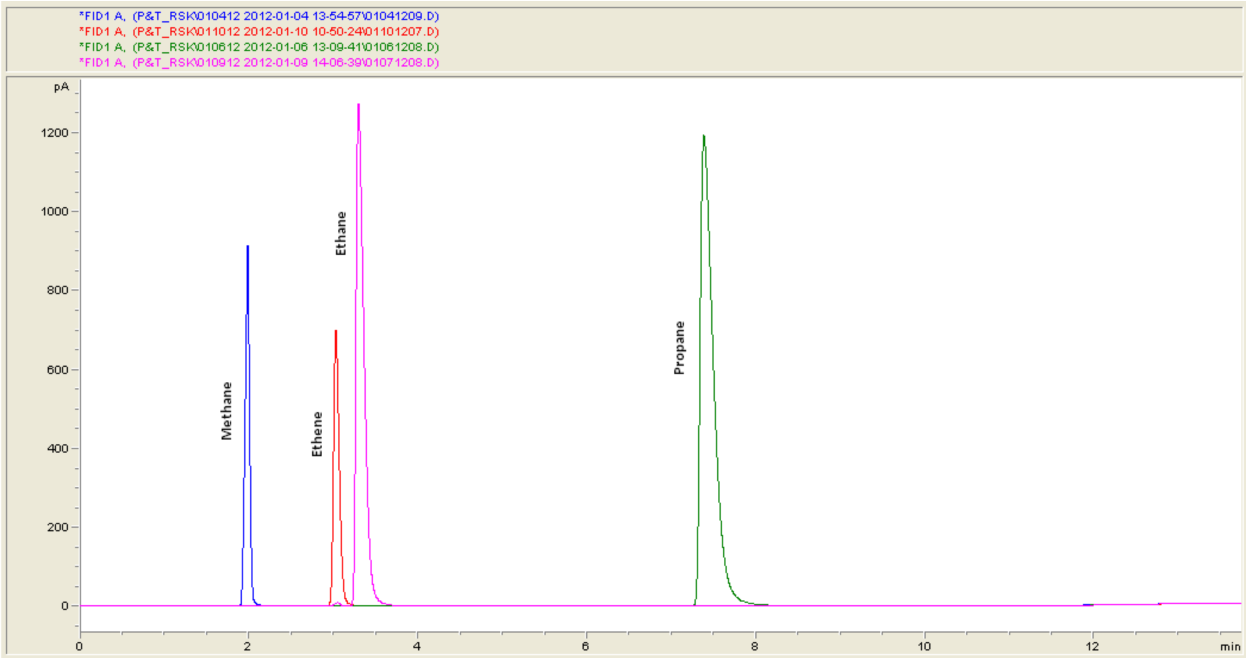

Figure 3: Overlay Chromatograms of Gas Standards

Conclusions

With increased interest in alternative energy sources, hydraulic fracturing has become a common practice in the extraction of natural gas from coalbeds and shale formations across the United States. Unfortunately, there has not been adequate time to measure the environmental impact of these procedures. Regulatory agencies are looking for easy and reliable testing methods to monitor these effects.

This study demonstrates a new method for analyzing these gases using the Teledyne Tekmar Stratum PTC and AQUATek 100 Autosampler coupled with a GC/FID system. This method met all performance criteria outlined in the current headspace methods, RSK 175[1] and BOL6019[2]. By completely automating the sample preparation in the purge and trap method, efficiency and throughput can be greatly increased while saving time and money. There is no need to manipulate the samples required by the headspace method which eliminates the potential for human error and employs instrumentation many environmental laboratories are already familiar with.

References

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