Application Note 37920312

Purge-and-Trap GC Analysis of Methane in Water Samples Associated with Hydraulic Fracturing

Keywords

Eclipse 4660 Purge-and-Trap Sample Concentrator
Hydraulic Fracturing
Methane
Natural Gas
Underground Sources of Drinking Water (USDW)

Presented at the 2012 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Orlando, Florida, March 12–15, 2012

Introduction

Shale gas reservoirs, such as the Marcellus shale reserve in Pennsylvania and Barnett shale reserve in Texas are a growing source of natural gas in the United States. The U.S. Energy Information Administration (EIA) estimates that the total natural gas resource base of the United States to be 2,553 trillion cubic feet (Tcf).(1) Shale gas production represents greater than 20% of the current U.S. supply an increase from 1% in 2000.

Hydraulic fracturing or "fracking" involves pumping water, sand, and chemicals at extremely high pressure into deep underground wells to crack open hydrocarbon-rich shale formation and extract natural gas. Chemicals used for hydraulic fracturing include potentially toxic substances such as diesel fuel and disinfectants, which can contaminate underground sources of drinking water (USDW).

In some cases, methane has been detected in household drinking water from wells. A study conducted in the Marcellus and Utica shale formations found methane concentrations were 17-times higher on average (19.2 mg CH_4 L^{-1}) in wells from active drilling and extraction areas then in non-active areas (1.1 mg L^{-1} on average).(2) The average methane concentration found in shallow groundwater in areas of active drilling and hydraulic fracturing fell within the defined action level (10-28 mg L^{-1}) for hazard mitigation recommended by the U.S. Department of Interior.(2)

Methane is not a regulated contaminant under U.S. National Drinking Water Regulations. In fact, a provision in the Safe Drinking Water Act passed in 2005 exempts hydraulic fracturing from regulation under the USEPA'a Underground Injection Control Program (except in cases where diesel fuel is employed for fracking). Consequently, there are no USEPA-approved testing methods for measuring methane in drinking water and groundwater.

The application note describes the use of a purge-and-trap gas chromatography system to analyze methane, ethane, ethene, and propane hydrocarbons (C1-C3) in drinking water samples.

Experimental

Instrumentation used for this study was an OI Analytical Eclipse 4660 Purge-and-Trap sample concentrator (Figure 1) with a proprietary trap specifically designed to trap methane. The P&T was interfaced to an Agilent 7890 GC/FID with a split/splitless injector and a SUPEL-QPLOT column (30-meter x 0.32-mm I.D.).

A primary, saturated analytical standard was prepared by chilling 1 liter of

DI water to 0 °C in an ice bath, and bubbling UHP methane(3) through the cooled water for approximately one hour. Aliquots of the saturated solution (39.6 ppm methane in water) were diluted with ice water in volumetric flasks to create calibration standards at nine concentrations, ranging from 0.001 to 39.6 ppm. The standards were immediately transferred to 40-mL VOA vials, sealed with no headspace, stored at 4 °C, and analyzed within 48 hours.

Figure 1. OI Analytical Eclipse 4660 Purge-and-Trap Sample Concentrator and 4551A Water Autosampler (the chiller option is not shown)

The purge-and-trap operating parameters used in this study are summarized in Table 1.

Table 1. Operating Parameters for Purge-and-Trap GC Analysis of Methane and C1-C3 Hydrocarbons

Purge-and-Trap Operating Parameters	
Purge-and-Trap Sample Concentrator	Eclipse 4660
Autosampler	4551A Water Autosampler with chiller option
Trap	Proprietary Packing
Purge Flow Rate	20 mL/min Helium
Purge Time	3 minutes
Sample	5-mL sample at 40 °C
Desorb Temperature	240 °C
Desorb Time	1 minute
Water Management	110 °C during Purge 0 °C during Desorb 240 °C during Bake

Results & Discussion

Four unique sets of calibration standards (0.01 to 39.6 ppm methane in 0 °C water) were prepared as described above, and analyzed on the optimized system to generate individual calibration curves. Methane peak area counts were plotted as a function of concentration to generate an external calibration curve for each set of analyses. The four resulting curves are plotted together in Figure 2, along with their linear correlation coefficients (R2) and illustrate the overall reliability and stability of the analytical system.

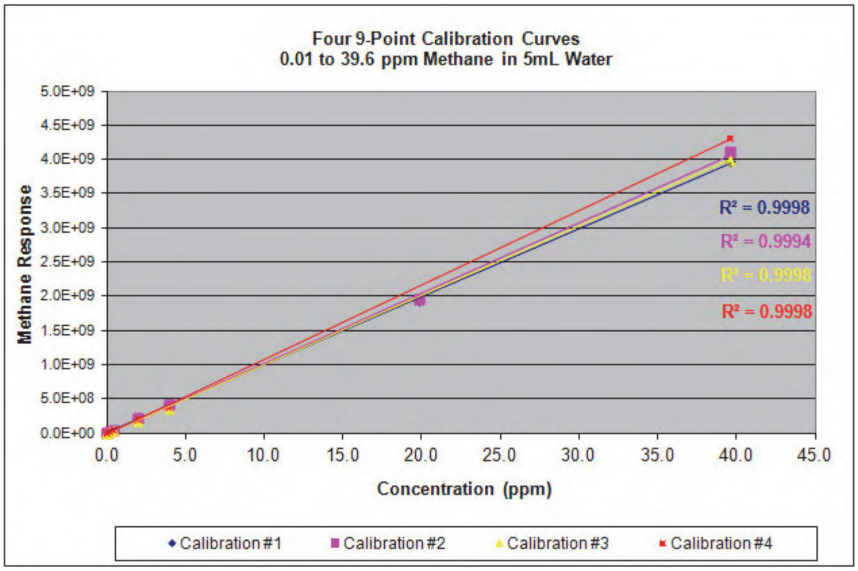

Figure 2. Four 9-Point Calibration Curves

Figure 3 is the FID chromatogram from analysis of a 5-mL water sample saturated with methane (~ 40 ppm) and containing single-digit ppm levels of ethane, ethene, and propane. Baseline resolution was obtained for all four peaks.

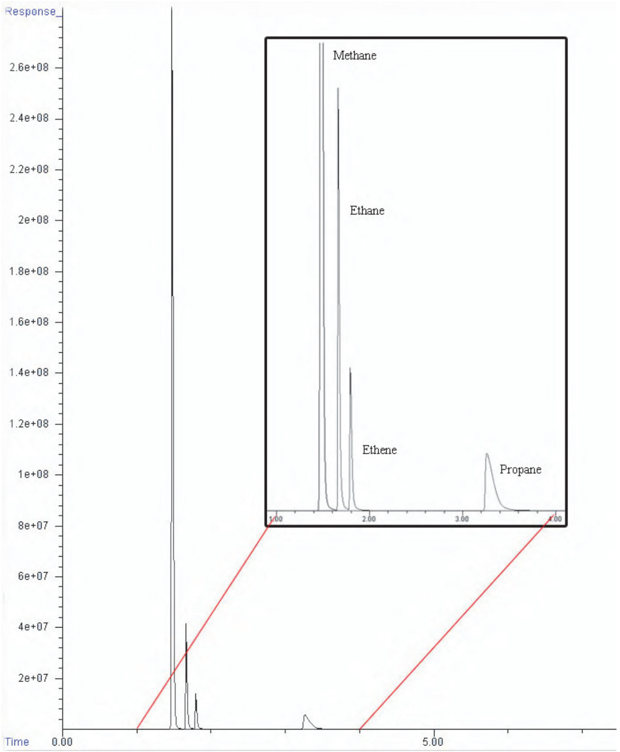

Figure 3. FID Chromatogram of Water Saturated with Methane (~ 40 ppm)

Summary & Conclusions

The results of this study demonstrate that purge-and-trap GC analysis can be used to measure methane contamination in water samples. The system yielded linear calibrations and complete baseline separation of methane, ethane, ethene, and propane.

References

1. The opportunities of abundance: How shale gas changes the energy landscape, Banaszak, S., Hydrocarbon Processing, January 2012, 41-42.
2. Osborn, S.G., Vengosh, A., Warner, N.R., Jackson, R.B. (2011). Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. Proceedings of the National Academy of Sciences, 109 (20), 8172-8176.
3. The Ultra High Purity (UHP) methane gas and a mixture of C1-C3 hydrocarbons, both in lecture bottles, were provided by DCG Partnership 1, Ltd (Pearland, TX).

Acknowledgement

The methane and hydrocarbon gases used to prepare the standards were provided by DCG Partnership 1, Ltd (Pearland, TX).

O·I·Analytical
a xylem brand

151 Graham Road
PO Box 9010
College Station, Texas
77842-9010

(979) 690-1711
(800) 653-1711 USA/Canada
FAX (979) 690-0440

www.oico.com
E-mail: oimail@oico.com

Publication 37920312