APPLICATION NOTE

Gas Chromatography

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Methane, Ethylene, and Ethane in Water by Headspace-Gas Chromatography (HS-GC) with Flame Ionization Detection (FID)

Introduction

The rapid development of natural gas from unconventional sources in North America has created an energy "gold rush" not seen in contemporary times. The advent of horizontal drilling technologies and hydraulic fracturing has made this production economical and presents an energy source of sufficient magnitude that could last 100 years.

The technology presents a number of environmental challenges as the wells are drilled vertically through aquifers on their way to the deep shale deposits thousands of feet under the surface, and then turned horizontally and drilled another several thousand feet through the shale deposit. Herein lies the challenge: in the process of drilling the wells and preparing them for production (including "fracking" to optimize production), opportunities arise for contamination of the clean drinking water aquifers with methane and other low molecular weight organics (e.g., propane and ethane). Correctly drilled and cemented well bores should not be an issue, but any errors in engineering could result in contamination.

It is also possible that methane already exists at a low concentration in the aquifer from diffusion of the gas occurring naturally. There is a need (by property owner and lease holder) to confirm the level of gas in the aquifer before and during drilling, and also after the well is placed into production.

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Traditionally, methane in water is determined using U.S. Environmental Protection Agency (EPA) method RSK 175 (RSKSOP175, 2004) or an alternative (Vandegrift, 1998). PerkinElmer's TurboMatrix™ HS and Clarus® 680 GC combination offers a simple, economical and reliable measurement technique to determine methane and other target gases in water. This application note summarizes the experimental approach and subsequent results to confirm the viability of the method.

Instrumentation

A PerkinElmer® TurboMatrix Headspace (HS) connected to a PerkinElmer Clarus 680 Gas Chromatograph (GC) with dual flame ionization detectors (FID) were used in these experiments.

Since detection is performed using an FID, the technique of column confirmation may be employed to confirm identity of components. An Elite-Q PLOT column with dimensions 30 m x 0.32 mm (PerkinElmer Part No. N9316359) was used for quantitation and the Elite-U PLOT column with dimensions 30 m x 0.32 mm was used for confirmation. These columns were directly connected to the deactivated fuse silica headspace transfer line via a "Y" connector.

Experimental Conditions

A stock standard was used for these experiments (Supelco® Part No. 23437). This stock standard contained methane, ethylene, acetylene and ethane in approximately one molar percent concentration in nitrogen for each component.

The headspace and GC operating conditions are displayed in Table 1.

To validate the method, the following experiments were performed:

1. **Background:** Blank air and water were investigated for interferences. Since methane may be present in ambient air, four (4) 22 mL Headspace Crimp Vials (PerkinElmer Part No. N9306079) containing 15 mL of the deionized (DI) water, used in preparing standards, were investigated to determine the concentration of the methane in the blank samples.
2. **Calibration:** A five-point calibration curve was created establishing method linearity and reporting limits. Five (5) headspace vials were prepared with 15 mL of DI water then capped using PTFE silicone septa. A 2 µL, 5 µL, 10 µL, 20 µL and 50 µL volume of the stock standard was inserted through the septum (PerkinElmer Part No. N9303992) into the water of five of the vials, respectively, attaining concentrations as described in Table 3.
3. **Accuracy:** Four (4) water samples were prepared as quality controls from 5 to 50 ppb to confirm method accuracy.
4. **Precision:** Five (5) 40 ppb standards were prepared from the stock standard, and analyzed for precision.

Table 1. **Headspace and GC Conditions.**

HS Conditions	
Sample Temperature:	90 °C
Equilibration Time:	10 min
Needle Temperature:	110 °C
Transfer Line Temperature:	120 °C
Inject Time:	0.06 min
Withdrawal Time:	0.4 min
Pressurization Time:	1.0 min
HS Mode:	Constant
HS Pressure:	20 psi
GC Conditions	
Oven Temperature	
Initial Temperature:	40 °C
Initial Hold:	4.5 min
Ramp:	40 °C/min
Final Temperature:	205 °C
Final Hold:	1 min
Detector (FID)	
Detector Temperature:	240 °C
Air Flow:	400 mL/min
Hydrogen Flow:	40 mL/min
Range:	1
Attenuation:	-6 (or 1)

Note: The columns are directly connected to the HS transfer line; therefore, inlet parameters are not applicable.

Results

Figure 1 demonstrates separation of the four gases in the stock standard on the Elite-Q PLOT column. The concentration of the standard represented in Figure 1 is 10 parts per billion (ppb). Since acetylene is not a target analyte of this application, and acetylene is not found in samples, it is recommended that a standard mix be used not containing this analyte to avoid integration challenges between ethylene and acetylene.

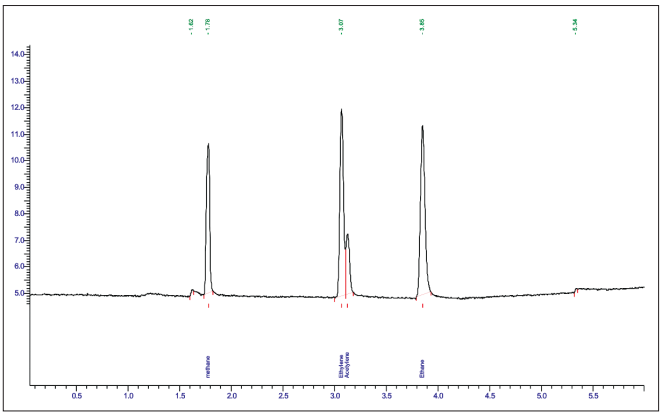


Figure 1. 10 ppb standard (Q PLOT).

Figure 2 is a chromatogram of a water blank (15 mL volume). To compensate for the methane present in ambient air, this point was incorporated on the calibration curve to subtract for the presence of methane in air. Since the headspace vials are sampled in air, this air is trapped in the vial. The concentration of methane in air is below the reporting limit. Table 2 tabulates the precision of methane in the blank.

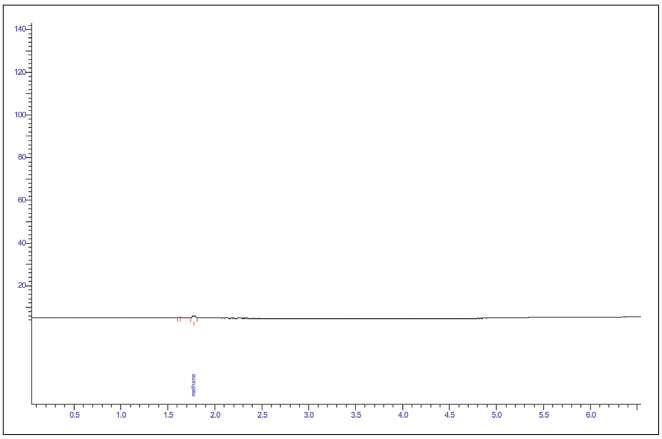
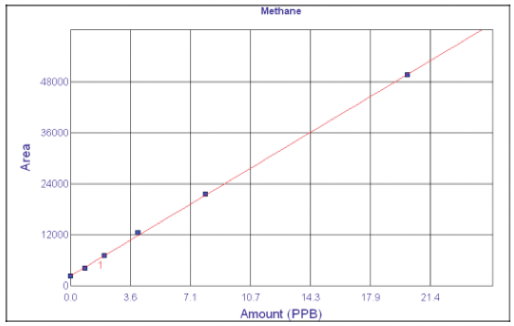


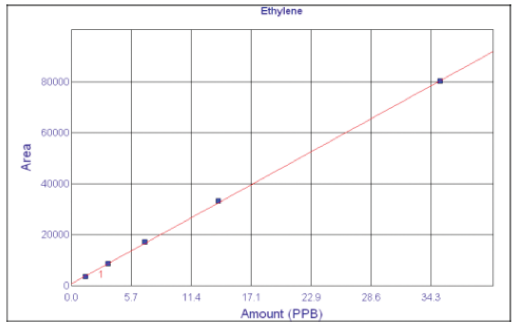
Figure 2. Chromatogram of blank (15 mL water).

Figure 3 graphically demonstrates the results of the external standard calibration curve of each component. The linearity achieved was excellent with a correlation coefficient (r^2) of 0.9996 and better. Table 3 contains the concentrations of the standards used to prepare these curves.

Methane: $r^2 = 0.9996$



Ethylene: $r^2 = 0.9998$



Ethane: $r^2 = 0.9999$

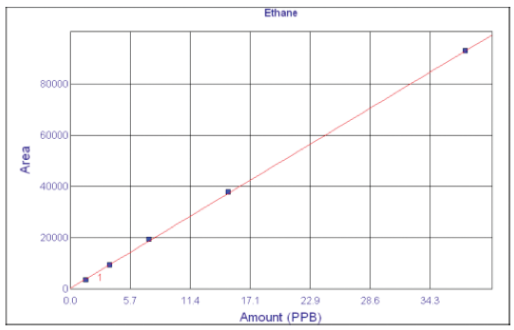


Figure 3. Calibration curves.

Table 2. **Repeatability of Four Blanks for Methane.**

Sample Name	Area (Methane)
15 mL Water Blank	2093.5
15 mL Water Blank	2163.7
15 mL Water Blank	2337.4
15 mL Water Blank	2124.3
Average	**2179.7**
%RSD	**5%**

Table 3. **Standard concentrations in Parts Per Billion (ppb) or µg/L.**

Level No.	Methane	Ethylene	Ethane
1	0.80	1.40	1.50
2	2.00	3.50	3.75
3	4.00	7.00	7.50
4	8.00	14.00	15.00
5	20.00	35.00	37.50

Table 4. **Repeatability of Peak Area Calculations Using Level 4 Concentration (Refer to Table 2).**

Methane			Ethylene			Ethane		
Actual Amt.	Calc. Amt.	%Dev	Actual Amt.	Calc. Amt.	%Dev	Actual Amt.	Calc. Amt.	%Dev
2.00	2.05	2.50	3.50	3.43	-2.00	3.75	3.59	-4.27
10.00	10.72	7.20	17.50	18.68	6.74	18.75	19.91	6.19
14.00	15.19	8.50	24.50	26.40	7.76	26.25	28.43	8.30
20.00	20.69	3.45	35.00	36.44	4.11	37.50	39.14	4.37

Table 5. **Repeatability of Peak Area Calculations Using Level 4 Concentration (Refer to Table 3).**

Conc. Level	Methane Area	Ethylene Area	Ethane Area
4	43180	70067	80441
4	44330	70199	81390
4	43421	67911	79164
4	44331	71017	82016
4	42184	66722	76234
Average	**43489**	**69183**	**79849**
% RSD	**2.1**	**2.6**	**2.9**

Table 4 tabulates the results of the quality control study. These controls were processed using the five-point calibration for each component.

Table 5 represents the results of the precision study at Level 4.

Discussion

In this experiment, the blank was used as a point on the calibration curve to correct for the presence of methane in ambient air (subtracting the blank), which improves accuracy for the low level methane amount and allows for very easy sample preparation essentially filling the vial with a known amount of water and capping it.

The reporting limit of 1 ppb methane in water was achieved. The lowest point of the curve prepared for this application for methane was 0.8 ppb, and 1st order is maintained through this point.

The recoveries obtained in this experiment from four (4) quality control samples are from 90% to 98%. This accuracy is excellent and incorporates errors due to method and operator. Since these gaseous standards and quality control samples are prepared manually with a gas-tight syringe human error is a contributory factor; therefore, the accuracy is exceptional.

Instrument and method repeatability (precision) is 2.1% for methane which is an acceptable repeatability for this application.

Conclusions

Examining the results of these experiments, the PerkinElmer TurboMatrix HS and PerkinElmer Clarus 680 GC provide a viable solution determining methane and other low molecular weight hydrocarbons in water delivering accuracy, precision and ease of use.

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