

Rapid Analysis of Dissolved Methane, Ethylene, Acetylene and Ethane using Partition Coefficients and Headspace-Gas Chromatography

Jasmine S. Lomond and Anthony Z. Tong*

Department of Chemistry, Acadia University, 6 University Avenue, Wolfville, Nova Scotia, Canada

Abstract

Analysis of dissolved methane, ethylene, acetylene, and ethane in water is crucial in evaluating anaerobic activity and investigating the sources of hydrocarbon contamination in aquatic environments. A rapid chromatographic method based on phase equilibrium between water and its headspace is developed for these analytes. The new method requires minimal sample preparation and no special apparatus except those associated with gas chromatography. Instead of Henry's Law used in similar previous studies, partition coefficients are used for the first time to calculate concentrations of dissolved hydrocarbon gases, which considerably simplifies the calculation involved. Partition coefficients are determined to be 128, 27.9, 1.28, and 96.3 at 30°C for methane, ethylene, acetylene, and ethane, respectively. It was discovered that the volume ratio of gas-to-liquid phase is critical to the accuracy of the measurements. The method performance can be readily improved by reducing the volume ratio of the two phases. Method validation shows less than 6% variation in accuracy and precision except at low levels of methane where interferences occur in ambient air. Method detection limits are determined to be in the low ng/L range for all analytes. The performance of the method is further tested using environmental samples collected from various sites in Nova Scotia.

Introduction

Methane is the primary product of anaerobic degradation of organic matter during the process of methanogenesis (1–3). Dissolved methane indicates anaerobic microbial activity in surface and ground water. It was also discovered that chlorinated hydrocarbons may be reduced and dechlorinated to methane, ethylene, or ethane in anoxic environments (4,5). In addition, significant amounts of C1-C2 hydrocarbons are present in vehicle emissions due to incomplete combustion of fossil fuels (6,7). Hydrocarbons in polluted air may deposit in surface water, which causes water pollution especially in urban areas. Other sources of light hydrocarbons in aquatic environments include accidental petroleum spills and leaks at gas stations due to over

pressurization of storage tanks (8). Monitoring dissolved C1-C2 hydrocarbon gases can help to trace sources of contamination and consequently protect aquatic ecosystems.

Current headspace chromatographic techniques (9) for dissolved gases can be divided into two groups: dynamic headspace (10,11) and static headspace (12–14). With the dynamic headspace technique, water samples are purged continuously with a high-purity inert gas, such as helium or nitrogen. The analytes are then trapped, thermally desorbed, and transferred to a gas chromatograph (GC) for analysis. With the static headspace technique, an aliquot of water is removed from a sealed sample bottle to create a defined headspace volume, and the two phases are left to equilibrate. A small fraction of the headspace is withdrawn using a syringe and injected into the GC for analysis. The dynamic headspace technique normally offers better sensitivity for analysis of volatile organic compounds (VOCs). However, C1-C2 hydrocarbons are difficult to trap using sorbents due to their ultra-high volatility at room temperature. Trapping to sorbents can be improved by using cryogenic devices with liquid nitrogen (15). The static headspace technique is much simpler and less expensive. Jalbert et al. developed a static headspace method for determining multiple dissolved gases in mineral insulating oils (16). Johnson et al. created headspace by inverting 50 mL serum bottles inserted with 5 mL pipet tips (12). This method is limited by the sizes of the pipet tip and the serum bottle, and the volume ratio of gas-to-liquid phase cannot be easily reduced to improve the method sensitivity. Furthermore, considerable experience is required from chemical analysts in order to avoid leaks. Kampbell et al. generated 6-mL inert headspaces in 50-mL glass bottles by displacing water with helium (13,14). This method can effectively eliminate the interference from ambient air. However, it requires the helium flow rate to be controlled accurately and its procedures are difficult to automate.

Beside chromatography, the use of spectroscopic techniques for measuring dissolved methane in water has been reported in the literature. Pironon et al. developed a quantitative method using Raman spectroscopy (17). In their experiments, methane was excited at 514.5 nm using an Argon-ion laser and monitored at 2,910 cm^{-1} (symmetric stretching band). Boulart et al. invented an optical sensor based on surface plasmon resonance (SPR) (18). A detection limit of 0.2 nM was reported for their prototype. Further miniaturization of the device could make it suit-

*Author to whom correspondence should be addressed: email anthony.tong@acadiau.ca.

able for in situ measurements. These spectroscopic techniques have advantages of simplicity and portability. However, they are susceptible to interferences, such as the broad absorption band of water and lack of the capability to distinguish between species of different hydrocarbons.

The purpose of this research was to develop a rapid chromatographic method for analyzing dissolved hydrocarbon gases, such as methane, ethylene, acetylene, and ethane in water. In this project, an improved static headspace method was developed. The new method provides better sensitivity and easier operation in comparison with previous published headspace methods. This research reports the first application that uses partition coefficients to determine dissolved hydrocarbon gases in water, although partition coefficients have been used in analysis of other VOCs (9).

Material and Methods

Chemicals

The gas calibration standard was purchased from Sigma-Aldrich (Oakville, Ontario, Canada). It was stored in a 48 L Scotty cylinder that contained a 1% mole fraction of each gas of interest. A second source of ultra-high purity (UHP) methane was supplied by PraxAir (Bridgewater, Nova Scotia). The carrier gas used was UHP helium (Praxair, Bridgewater, Nova Scotia). Other chromatographic gases including standard purity air, nitrogen, and hydrogen were also obtained from Praxair. Deionized water was supplied by a Millipore water purification system that was connected to a reverse osmosis system in the building.

Instrumentation and calibration

Experiments were conducted using a Hewlett Packard 5890 Series II gas chromatograph coupled with a flame ionization detector (GC-FID). The FID is simple and robust and has a wide linear range and excellent sensitivity, which makes it a better choice than the mass selective detector (MSD) for analysis of hydrocarbon gases. A Restek Rt-QPLOT column (30 m, 0.32 mm i.d.) was used to separate methane, ethylene, acetylene, and ethane. The QPLOT column is a fused silica column coated with porous polymer (100% poly-divinylbenzene). The column is insensitive to moisture, which makes it suitable for analyzing gas samples that contain water vapor. The QPLOT column was able to separate these compounds in a 4-min run using UHP Helium as the carrier gas. The chromatographic separation was run isothermally with an oven temperature of 30°C. The column was baked at 150°C once every week to eliminate contamination. The inlet pressure was set at 27 psi and a 2-mm glass liner was used. The temperature of the injector and FID were set to 200°C and 230°C, respectively. The pressures of FID gas supplies were 16 psi, 40 psi, and 12 psi for hydrogen, compressed air, and nitrogen (makeup gas).

Considering the goal of the project was to develop a fast analytical method and FID has a wide range of linearity, a 3-level calibration was used instead of the usual 5-level calibration. Most of experimental data were collected within the 3-level calibration range. To improve the validity of the 3-level calibration, fresh calibration curves were prepared daily, and their linearity and

response was proven to be consistent and adequate for this study. The 3-level calibration standards were prepared by diluting the initial standard into appropriate sizes of glass bottles. Ambient air was used to dilute standards, which is consistent with sample preparation.

Sample preparation

Water samples were prepared using 250 mL VOC vials (Fisher Scientific, Ottawa, Ontario). Using a pipetter, 5 mL of water was removed, and then caps with Teflon-faced septa were quickly put on to ensure the vials were airtight during the experiment. Control samples were spiked with an appropriate amount of gas standard. The water samples were shaken vigorously for 2 min. Sample vials were then immersed in a 30°C water bath, and the two phases, gas and liquid, were left to equilibrate until the sample temperature became the same as the water bath. For the determination of partition coefficients at different temperatures, samples were prepared at roughly 5°C increments from room temperature to 55°C. Vials were placed upside down in the water bath, which eliminated direct contact of the headspace with the septum and prevented gas from escaping through the septum. Using a gas tight syringe (Sigma-Aldrich, Oakville, Ontario), a volume of 100 µL was drawn from the 5 mL headspace and quickly injected into the GC-FID. The hydrocarbon concentrations in the headspace can be determined directly from the chromatographic data. The concentrations of dissolved gases in water are proportional to their concentrations in the headspace. Therefore, dissolved concentrations can be readily calculated with predetermined partition coefficients at a selected temperature (30°C in this study).

Analysis of most samples was repeated 3 times to statistically improve accuracy of measurements. Although manual injections were conducted during this study, the method could be automated with a headspace autosampler, which makes it well suited for industrial applications where large amounts of samples need to be processed.

Quality control

Calibration curves were prepared daily to ensure the quality of the GC-FID calibration. A second source, pure methane standard (PraxAir, Bridgewater, Nova Scotia, Canada), was used to verify the accuracy of the first source calibration standard (Sigma-Aldrich). For each sequence, an ambient air blank and a deionized water blank were included.

A sample containing only deionized water was immersed in the water bath, along with other samples. A digital thermometer was inserted into this sample, which was designed for monitoring the temperature in the sample vials. It was assumed that the other samples were heated up at the same rate as this deionized water sample. Thermal equilibrium was reached when the temperature in the sample was equal to the preset temperature of the water bath.

The 5 mL pipetter (Fisher Scientific, Ottawa, Ontario) was calibrated weekly using a gravimetric method to ensure the accuracy of the headspace volume. To address the variation of volumes of the 250 mL VOC vials, 8 vials were randomly chosen and the volumes were measured using a gravimetric method. The average volume of the VOC vials was determined to be 253.5

± 0.8 mL. Considering the vial volume uncertainty is statistically small, the average volume was assumed for all calculations rather than measuring the volume of every vial in use.

For method validation, two spike levels were used; the concentrations of spike were close to the medium and lower levels of the calibration. Eight replicates of each spike level were analyzed. The accuracy, precision and method detection limits (MDLs) were determined statistically from data generated from those analyses.

Environmental sample collection

Foreshore water samples were collected from various sites in the Annapolis Valley, Nova Scotia, Canada. The sites were chosen because of their close vicinity to possible sources of contamination, such as a gas station, municipal wastewater outflow, or petroleum storage facility. The 250 mL sampling vials were filled completely with water, slowly lifted out of the water, and capped immediately with Teflon-faced screw caps. The vials were inverted to ensure there was no air bubble present, creating a zero-volume headspace. Teflon tape was used to seal the vials around the caps to further prevent gas leaks. The vials were then labeled, placed in a cooler upside down, and transported to the laboratory for analysis. Two replicates were prepared for each site to ensure the repeatability of measurements. The laboratory analysis was carried out within 5 h of sample collection.

Theory and Calculation

Determination of partition coefficient

Henry's Law has been used for determining dissolved hydrocarbon gases in water in previous publications. Partition coefficients have been used for gases in this research. The constant in Henry's Law and the partition coefficient are closely related for a given substance. These two methods are theoretically equivalent. However, partition coefficients are much easier to use in practical applications, because concentrations are directly in mass-per-volume and calculations don't involve partial pressures. The partition coefficient between gas and liquid phases is defined as:

$$K_{gl} = \frac{C_g}{C_l} \quad \text{Eq. 1}$$

where C_g and C_l are the concentrations (m/V) of analyte in the gas phase (headspace) and the liquid phase (water) at equilibrium, respectively. The total mass of the analyte in the experimental vial, m_0 , is equal to:

$$m_0 = C_l V_l + C_g V_g \quad \text{Eq. 2}$$

where V_g and V_l are volumes of the gas phase and the liquid phase, respectively. By combining Equation 1 and Equation 2, K_{gl} can be solved as:

$$K_{gl} = \frac{C_g V_l}{m_0 - C_g V_g} \quad \text{Eq. 3}$$

Using Equation 3, K_{gl} can be calculated from C_g which is determined directly by the GC-FID method. If K_{gl} is regarded as a function of C_g , its derivative is given by:

$$\frac{dK_{gl}}{dC_g} = \frac{V_l + V_g K_{gl}}{m_0 - C_g V_g} = \left(1 + \frac{V_g}{V_l} K_{gl}\right) \frac{K_{gl}}{C_g} \quad \text{Eq. 4}$$

For measurable changes, Equation 4 may be rearranged to give:

$$\frac{\Delta K_{gl}}{K_{gl}} = \left(1 + \frac{V_g}{V_l} K_{gl}\right) \frac{\Delta C_g}{C_g} \quad \text{Eq. 5}$$

Equation 5 shows that the uncertainty of K_{gl} measurements depends on the uncertainty of C_g measurements, K_{gl} , and V_g/V_l . While $\Delta C_g/C_g$ reaches a limit after optimization of chromatographic parameters and K_{gl} is a property of the substance, the ratio of V_g/V_l is apparently a critical factor in determination of K_{gl} . This becomes very important especially for substances with large partition coefficients (more than 100). In this method, the headspace volume, V_g , was chosen to be 5 mL. For a headspace less than 5 mL, it would be difficult to obtain an appropriate sample volume for GC injection without interrupting the phase equilibrium in the headspace. Thus, large sampling vials or bottles should be used. In this method, 250 mL (253.5 mL by gravimetric measurements) VOC vials were chosen. The 250 mL VOC vials have a narrow neck near the top which make them ideal for holding a small headspace volume. Given the 5 mL headspace, a V_g/V_l ratio of 0.0201 was achieved. Since the largest K_{gl} in this study was around 100, the uncertainty of $\Delta K_{gl}/K_{gl}$ was approximately 1 to 3 times that of $\Delta C_g/C_g$. If desired, bottles larger than 250 mL can be used to further improve the analytical method.

Temperature dependence of partition coefficient

The solubility of gases in water changes with temperature variation. Therefore partition coefficient is dependent on temperature. Theoretically, the partition coefficient obeys a thermodynamic model (19) as given by the van't Hoff Equation:

$$\log K_{gl} = -\frac{\Delta H}{2.303RT} + C \quad \text{Eq. 6}$$

where ΔH , R , T , and C are the enthalpy of transfer, the gas constant, the temperature, and a constant, respectively. According to Equation 6, a plot of $\log K_{gl}$ versus $1/T$ gives a straight line. From the slope of the linear regression, the enthalpy of transfer can be calculated.

Determination of dissolved concentration

By rearranging Equation 3, one can obtain:

$$m_0 = C_g \left(\frac{V_l}{K_{gl}} + V_g \right) \quad \text{Eq. 7}$$

The initial concentration of the water sample, $C_{w,0}$, is the dissolved concentration before creation of the headspace. It is ultimately the concentration that the method needs to determine. An equation of $C_{w,0}$ can be derived by dividing both sides of Equation 7 by V_l :

$$C_{w,0} = \frac{m_0}{V_l} = \left(\frac{1}{K_{gl}} + \frac{V_g}{V_l} \right) C_g \quad \text{Eq. 8}$$

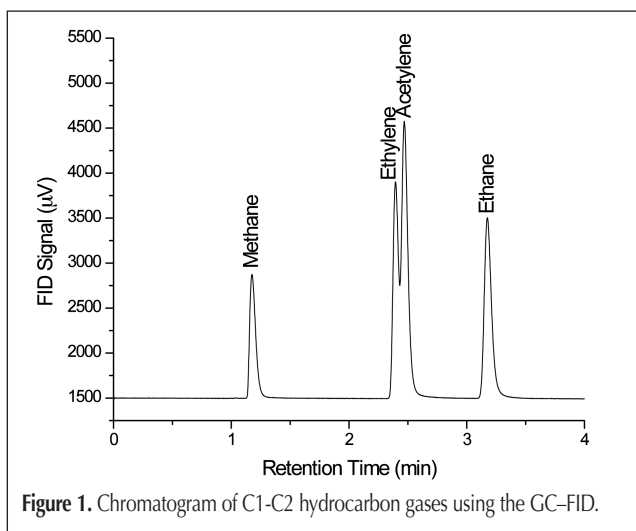
Since K_{gl} , V_g , and V_l are constants for given experimental conditions, $C_{w,0}$ can be readily determined by measuring the headspace concentration, C_g .

Results and Discussion

Chromatogram and calibration

The GC separation was completed in 4 min. The retention times for methane, ethylene, acetylene and ethane were 1.18, 2.40, 2.47, and 3.18 minutes, respectively. The retention times of these four compounds were short due to their low molecular masses. A typical chromatogram is shown in Figure 1. The chromatographic peaks of ethylene and acetylene were not completely resolved. The chromatographic resolution of these two peaks was calculated to be 0.82. Although the resolution was not ideal, it was adequate for integration. The chromatographic resolution could be improved by reducing the GC oven temperature using liquid nitrogen or dry ice. However, the cryogenic devices would make the system more complicated and contradict the objective of the method. Methane, ethylene, acetylene, and ethane are the first 4 light hydrocarbons. Other VOCs that have similar molecular weights and could cause interference are rare. Within the retention time range of the target hydrocarbons, interference from other VOCs was not noticed during the research. Considering the stability of the FID, an external calibration method was used rather than an internal calibration method. The calibration showed excellent linearity with R² values greater than 0.999 for all 4 hydrocarbons. Acetylene had a higher slope than the other 3 gases because of its highly unsaturated structure.

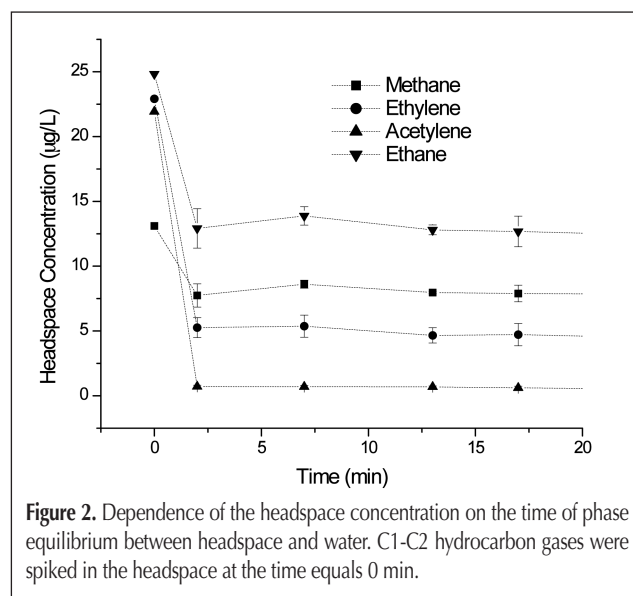
From the method blanks, it was confirmed that methane was present at a detectable level in ambient air. Therefore, the intercept of the linear regression of methane calibration was allowed to adjust, while the calibration curves of ethylene, acetylene and ethane were forced to fit through the origin. This allowed ambient interference to be subtracted directly from the calibration. A fresh calibration curve was prepared daily to address variation of methane's concentration in the atmosphere. By extrapolating the methane calibration curve (as in the standard addition method), the methane concentration in the laboratory's ambient air was determined to be about 1.85 µg/L. The methane concentration varied slightly day-to-day. This small variation was addressed by measuring an ambient blank and creating a fresh calibration curve every day during the experimental period.



A high-purity methane cylinder (Praxair, Bridgewater, Nova Scotia, Canada) was used as the second source gas standard to verify the accuracy of the methane calibration. Due to lack of availability, the other 3 gases were not verified. A methane sample using the second source was prepared at a concentration of 3.68 µg/mL. GC-FID analysis of this sample yielded a concentration of 3.93 µg/mL, which corresponded to a 6.7% difference with the target value. This difference between the two sources was acceptable considering manual injections were conducted. The elution order of ethylene, acetylene and ethane was determined from authors' previous studies using the same column. These C₂ hydrocarbons were also identified using their measured partition coefficients which depend on their molecular polarity.

Phase equilibrium time

The principle of this method is based on the equilibrium distribution between the gas and liquid phases. Therefore, it is critical to determine the time required to reach phase equilibrium. Deionized water samples with a 5 mL headspace were left in the water bath for an extended time to ensure that all samples were at the same temperature as the water bath. An appropriate amount of the C₁-C₂ mixture was spiked and the sample vials were shaken vigorously for 2 min. An aliquot (100 µL) of headspace was withdrawn and injected into GC for chromatographic analysis. The headspace sample was injected into the GC about every 4 minutes. Sampling of 100 µL from a 5-mL headspace corresponds a 2% change, which is acceptable for 4 injections. Multiple vials could be used to eliminate the 2% change caused by repeated analysis on the same vial; however the concentration difference between multiple vials introduced in sample preparation would give the similar level of alteration. In fact, single vial experiment is simple and easy to handle. Figure 2 depicts the experimental data of this experiment. The concentrations at time zero were the initial gas concentrations in the 5 mL headspace (before mixing), and calculated to be 13.1 µg/L, 22.9 µg/L, 21.9 µg/L, and 24.8 µg/L for methane, ethylene, acetylene, and ethane, respectively. These initial concentrations in



headspace are highest in the plots. As the system approaches phase equilibrium, gas starts to diffuse into the liquid phase and gas concentrations reduces gradually. Based on Figure 2, 2 min was sufficient for the mixture to achieve phase equilibrium. The slight decreasing trend of concentrations was due to repeated analysis where 100 μL was taken for each GC injection. It was assumed that phase equilibrium was reached as soon as thermal equilibrium was achieved. Therefore, the water samples could be tested in few minutes after being prepared.

Partition coefficient

As shown in Equation 6, partition coefficient is a function of temperature. The temperature dependence of partition coefficient from 25°C to 55°C was determined for C1-C2 light hydrocarbon gases. The experimental data is shown in Figure 3 and linear regression data ($\log K_{gl}$ versus $1/T$) for this study is listed in Table I. The negative sign of ΔH values indicates that the transfer of C1-C2 hydrocarbons from the water phase to the headspace is exothermic. For the range of temperature studied, partitioning to the gas phase is enhanced at low temperatures. It was decided that the most appropriate temperature for the method was 30°C. This temperature is only slightly above ambient temperature, making it easy to achieve and maintain. At 30°C, partition coefficients were determined to be 128, 27.9, 1.28, and 96.3 for methane, ethylene, acetylene, and ethane, respectively. Methane has the highest partition coefficient, which is consistent with its low molar mass and high volatility. The order of K_{gl} values of ethylene, acetylene and ethane agrees with the order of saturation in their structures; the hydrophilicity of the substance

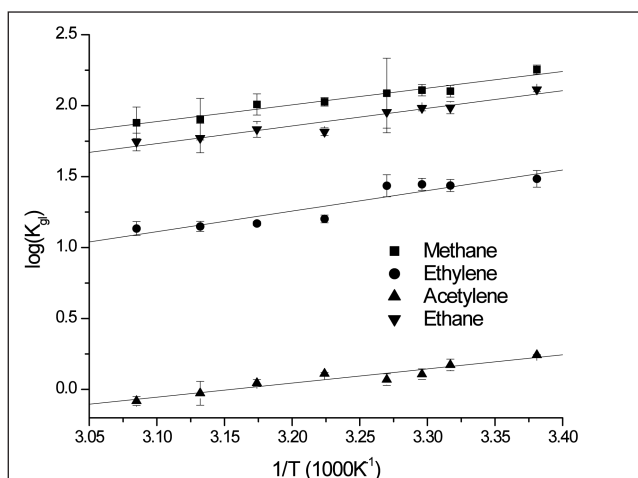


Figure 3. Van't Hoff plots of partition coefficients (K_{gl}) at different temperatures.

Table I. Regression Constants for van't Hoff Plots in Figure 3*

	ΔH (kJ \times mol $^{-1}$)	C	R^2	K_{gl} (30°C)
Methane	-22.5	-1.76	0.953	128.0
Ethylene	-27.7	-3.38	0.867	27.9
Acetylene	-19.1	-3.14	0.918	1.28
Ethane	-23.8	-2.12	0.934	96.3

*The table also lists the partition coefficients measured at 30°C.

increases with increasing numbers of π electrons in its structure. With a partition coefficient close to 1, acetylene is very soluble in water. Partition coefficients of dissolved hydrocarbon gases may vary as the ionic strength of the solution changes. All environmental samples studied in this research were collected from fresh water sources and no additional salt was added. The salinity in samples was so low that the effect of ionic strength was ignored.

Method precision, accuracy, and detection limits

Method validation was performed with two spike levels. The low level concentrations were close to the method detection limits, and the high level concentrations were near the middle of the calibration. These two spike levels were chosen to test the method performance at the low and medium ranges of the calibration. For each level, 8 replicates were analyzed. Precision was determined to be the relative standard deviation of multiple measurements in comparison with the average. Accuracy was calculated as the percent difference between the measured and the expected concentration. Using the low level spike data, method detection limits (MDLs) were calculated by taking the product of the student t and the standard deviation of multiple measurements. At a 99% confidence level (one-sided), the student t value is 2.896 for 8 replicates. The results of method precision, accuracy and detection limits are tabulated in Table II.

The precision and accuracy of measurements were all within 6% except the accuracy of methane, which demonstrated the excellent performance of this analytical method. The accuracy of methane measurements was large (57.0%) for the low level spike while it was small (5.0%) for the high level spike. This was due to interference from methane presence in the ambient air. The ambient methane concentration (1.85 $\mu\text{g/L}$) was much higher than the spike level (0.65 $\mu\text{g/L}$). This may limit the method from applications where the dissolved methane concentration is below

Table II. Method Precision, Accuracy, and Detection Limits

	Average	Precision	Target	Accuracy
<i>High spike level ($\mu\text{g/L}$)</i>				
Methane	15.1	4.6%	15.5	-3.0%
Ethylene	26.4	3.9%	27.1	-2.7%
Acetylene	25.9	4.2%	26.0	-0.4%
Ethane	28.9	4.7%	29.4	-1.6%
<i>Low spike level ($\mu\text{g/L}$)</i>				
Methane	0.28	5.0%	0.65	-57.0%
Ethylene	1.07	4.0%	1.13	-5.2%
Acetylene	1.04	3.3%	1.08	-3.7%
Ethane	1.21	5.1%	1.22	-0.9%
		In headspace	In water	
<i>Method detection limits (ng/L)</i>				
Methane	40.4		1.13	
Ethylene	125.0		7.01	
Acetylene	99.6		79.9	
Ethane	178.0		5.44	

that of the ambient level. In these applications, an inert headspace could be created using UHP nitrogen or helium to eliminate ambient methane interference; however, this would increase the complexity of the experimental setup.

MDLs in the headspace were determined directly from the GC method; MDLs in water were then calculated using Equation 8. All MDLs for measuring dissolved hydrocarbon gases in water were in the low ng/L range, which is remarkable considering the simplicity of the method. A MDL of 1.13 ng/L was achieved for dissolved methane using this method, which is lower than MDLs reported in other methods, such as Boulart et al.'s spectroscopic method (3.2 ng/L) (18) and Kampbell et al.'s chromatographic method (2 µg/L) (13). Relevant data for C2 hydrocarbons were not found in the literature. Therefore a direct comparison of the new method with other methods could not be conducted for C2 hydrocarbons.

A GC injection volume of 100 µL was used in analyzing all samples. The method detection limits could be readily improved by injecting a larger volume. However, this would decrease the chromatographic resolution of ethylene and acetylene. Furthermore, large injection volumes would significantly disturb the phase equilibrium and the headspace pressure considering the limited size (5 mL) of the headspace.

Environmental samples

Real-world environmental samples were collected at various locations of interest in Nova Scotia and tested to verify the performance of the analytical method. Experimental results are tabulated in Table III with each site's description and GPS coordinates. Table cells are left empty if compounds were not detected. Methane was detected in all sites with concentrations well above its MDL. Chromatographic peaks of ethane were identified in some sites but at levels less than its MDL; these results are in boldface in Table III and reported for qualitative reference only.

Site A is in a small brook in Middleton, Nova Scotia. With a methane concentration of 929 ng/L, Site A showed a moderate level of anaerobic activity, which was expected considering its low flow rate. Site B had a high methane concentration, which

indicated strong anaerobic activity that would occur in a small, calm pond. Ethylene and ethane were also detected in this pond; these contaminants might come from a gas station 100 m away. Water samples in Site E were collected from the municipal outflow of Kentville which lacks of sufficient wastewater treatment facility. The highest level of dissolved methane was found at this site, which is consistent with its high organic waste load and anaerobic digestion happens naturally in raw municipal wastewater. Site D is located upstream of the Site E along the Cornwallis River and the two sites are about 30 m apart. As expected, water samples collected from the Site D showed much lower methane content. The lowest level of methane was found at Site C, Gaspereau Lake, which occupies about 22 km². The organic waste is diluted in a large body of water. Its anaerobic activity was low, because the water was well aerated by waves near the shore. In summary, the results of these environmental samples were consistent with expectations according to sites' geological characteristics, and demonstrated the potential application of this analytical method.

Conclusions

A rapid gas chromatographic method has been developed for analysis of dissolved methane, ethylene, acetylene and ethane in water. In previously published headspace methods for analysis of dissolved hydrocarbon gases, concentrations in the liquid phase were calculated using Henry's Law and partial pressures in the gas phase. In this method, the calculation of dissolved concentrations is carried out by using partition coefficients of the two phases at equilibrium. The use of partition coefficients is much more straightforward for determining dissolved concentrations than Henry's Law where mole fractions and partial pressures are involved.

The method requires minimal sample preparation and standard laboratory apparatuses, yet offers low ng/L detection limits for dissolved C1-C2 light hydrocarbon gases. Using 250 mL standard VOC vials, 5 mL of liquid is directly removed from the opening, which creates a small gas-liquid volume ratio. Method validation demonstrated excellent accuracy, precision and method detection limits. The method was successfully applied to various environmental samples collected in Nova Scotia, Canada. This new method will find applications in studying water quality in aquatic environments.

Acknowledgements

The authors appreciate the financial support of Acadia University and the Natural Sciences and Engineering Research Council of Canada (NSERC). The authors thank Alex Fage, John Saunders, Dr. John Roscoe, and Dr. John Murimboh for their technical assistance. The authors are also grateful to Dr. David Magri, Jim Ghoshdastidar, and Emma Hebb for proof-reading the manuscript.

Table III. Experimental Results of Water Samples Collected at Various Sites in the Annapolis Valley, Nova Scotia, Canada*

Site	Location	GPS coordinates	Dissolved concentration (ng/L)			
			Methane	Ethylene	Acetylene	Ethane
A	Brook in Middleton	N44°56.411' W65°04.403'	929			
B	Pond in South Alton	N45°01.361' W64°32.482'	2,091	8.1		2.6
C	Gaspereau Lake	N44°58.859' W64°31.764'	249			3.7
D	Cornwallis River	N45°04.772' W64°30.218'	1,422			
E	Kentville municipal outflow	N45°04.783' W64°30.217'	2,498			2.8

* Boldface numbers of ethane indicate chromatographic peaks of these compounds were identified, but their concentrations were below its method detection limits and reported for qualitative reference only.

References

1. A.A. Bloom, P.I. Palmer, A. Fraser, D.S. Reay, and C. Frankenberg. Large-scale controls of methanogenesis inferred from methane and gravity spaceborne data. *Science* **327**: 322–325 (2010).
2. J. Lelieveld. Climate change: A nasty surprise in the greenhouse. *Nature* **443**: 405–406 (2006).
3. J. Murase, Y. Sakai, A. Sugimoto, K. Okubo, and M. Sakamoto. Sources of dissolved methane in lake biwa. *Limnology* **4**: 91–99 (2003).
4. L. Semprini, P.K. Kitanidis, D.H. Kampbell, and J.T. Wilson. Anaerobic transformation of chlorinated aliphatic hydrocarbons in a sand aquifer based on spatial chemical distributions. *Water Resour. Res.* **31**: 1051–1062 (1995).
5. T.M. Vogel, C.S. Criddle, and P.L. McCarty. Transformations of halogenated aliphatic-compounds. *Environ. Sci. Technol.* **21**: 722–736 (1987).
6. A.N. Rajkumar, J. Barnes, R. Ramesh, R. Purvaja, and R.C. Upstill-Goddard. Methane and nitrous oxide fluxes in the polluted adyar river and estuary, se india. *Mar. Pollut. Bull.* **56**: 2043–2051 (2008).
7. R. Zhu, Y. Liu, H. Xu, T. Huang, J. Sun, E. Ma, and L. Sun. Carbon dioxide and methane fluxes in the littoral zones of two lakes, east antarctica. *Atmos. Environ.* **44**: 304–311 (2010).
8. D.H. Kampbell, T.H. Wiedemeier, and J.E. Hansen. Intrinsic bioremediation of fuel contamination in ground water at a field site. *J. Hazard. Mater.* **49**: 197–204 (1996).
9. Z.E. Penton, *Comprehensive analytical chemistry: Sampling and sample preparation for field and laboratory*, 37, J. Pawliszyn (Ed.), Elsevier Science B.V., Amsterdam, the Netherlands, 2002, p. 279–296.
10. F.H. Chapelle, D.A. Vroblesky, J.C. Woodward, and D.R. Lovley. Practical considerations for measuring hydrogen concentrations in groundwater. *Environ. Sci. Technol.* **31**: 2873–2877 (1997).
11. K.P. Walsh and R.G. McLaughlan. Bubble extraction of dissolved gases from groundwater samples. *Water, Air, Soil Pollut.* **115**: 525–534 (1999).
12. K.M. Johnson, J.J.E. Hughes, P.L. Donaghay, and J.M. Sieburth. Bottle-calibration static head space method for the determination of methane dissolved in seawater. *Anal. Chem.* **62**: 2408–2412 (1990).
13. D.H. Kampbell, J.T. Wilson, and S.A. Vandegrift. Dissolved oxygen and methane in water by a gc headspace equilibration technique. *Int. J. Environ. Anal. Chem.* **36**: 249–257 (1989).
14. D.H. Kampbell, and S.A. Vandegrift. Analysis of dissolved methane, ethane, and ethylene in ground water by a standard gas chromatographic technique. *J. Chromatogr. Sci.* **36**: 253–256 (1998).
15. B.N. Popp, F.J. Sansone, T.M. Rust, and D.A. Merritt. Determination of concentration and carbon isotopic composition of dissolved methane in sediments and nearshore waters. *Anal. Chem.* **67**: 405–411 (1995).
16. J. Jalbert, R. Gilbert, and P. Tétrault. Simultaneous determination of dissolved gases and moisture in mineral insulating oils by static headspace gas chromatography with helium photoionization pulsed discharge detection. *Anal. Chem.* **73**: 3382–3391 (2001).
17. J. Pironon, J.O.W. Grimmer, S. Teinturier, D. Guillaume, and J. Dubessy. Dissolved methane in water: Temperature effect on raman quantification in fluid inclusions. *J. Geochem. Explor.* **78-79**: 111–115 (2003).
18. C. Boulart, M.C. Mowlem, D.P. Connelly, J.-P. Dutasta, and C.R. German. A novel, low-cost, high performance dissolved methane sensor for aqueous environments. *Opt. Express* **16**: 12607–12617 (2008).
19. N.P. Bahadur, W.-Y. Shiu, D.G.B. Boocock, and D. Mackay. Temperature dependence of octanol-water partition coefficient for selected chlorobenzenes. *J. Chem. Eng. Data* **42**: 685–688 (1997).

Manuscript received June 12, 2010
 revision received September 2, 2010.