Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique

Don H. Kampbell*

U.S. Environmental Protection Agency, National Risk Management Research Laboratory, P.O. Box 1198, Ada, OK 74820

Steve A. Vandegrift

ManTech Environmental Research Services Corporation, National Risk Management Research Laboratory, P.O. Box 1198, Ada, OK 74820

Abstract

The measurement of dissolved gases such as methane, ethane, and ethylene in ground water is important in determining whether intrinsic bioremediation is occurring in a fuel- or solvent-contaminated aquifer. A simple procedure is described for the collection and subsequent analysis of ground water samples for these analytes. A helium headspace is generated above a water-filled bottle. Gases that are dissolved in the water partition between the gas and liquid phases and equilibrate rapidly. An aliquot of this headspace is analyzed by gas chromatography to determine the gases' concentration in this phase. The concentration of the gas dissolved in the water can then be calculated based on its partitioning properties, as indicated by its Henry's Law constant.

Introduction

Our involvement in ground water sampling and analyses at fuel and/or chlorinated solvent spill sites has required the determination of dissolved methane, ethane, and ethene. These constituents are frequently used to detect biodegradation processes in contaminated aquifers. Presence of the compounds is used to determine whether natural processes of contaminant attenuation and destruction are occurring at a spill site (1). Under anoxic conditions, the bioremediation processes for fuel hydrocarbons shift toward methanogenesis, which forms methane. Under similar conditions, chlorinated solvents such as trichloroethylene are subjected to reduction dechlorination: the final products are ethene and chloride (2).

Techniques for the analysis of dissolved gases in water have included direct aqueous injection into a GC equipped with a flame-ionization detector (FID) (3), membrane inlet mass spectrometry (4), and near-infrared Raman spectroscopy (5). Our need was for a simplified, rapid technique using readily available equipment to analyze ground water samples simultaneously for methane, ethane, and ethene. Previously, we reported on a gas chromatography (GC) headspace technique that emphasized dissolved oxygen (6). In recent years, the emphasis has been on methane and ethene analysis in water.

Experimental

Materials

Gas standards in helium were obtained from Scott Specialty Gases (Plumsteadville, PA). "Scotty II" cylinders of methane, ethane, and ethene at 10, 100, and 1000 ppm were used in addition to standards of methane at 1, 10, and 20%. High-purity helium was used as the GC carrier and as a source to prepare headspace in the sample bottles.

Instrumentation

Samples were analyzed using a Hewlett-Packard (Palo Alto, CA) 5890 GC equipped with a packed column (6-ft × 1/8-in. Porapak Q, 80/100) and an FID. The carrier gas was high-purity helium at 20 mL/min. The oven was programmed with an initial temperature of 55°C for 1 min, increased at 20°C/min to 140°C, then held for 5 min. The injector was set at 200°C, and the FID was set at 250°C. The FID hydrogen was set at 40 mL/min, and the air flow was set at 400 mL/min. The FID range and attenuation were both at 0. An HP 3396 Series II integrator was used for signal acquisition and peak integration.

Sample collection and preparation

Water samples from field monitoring wells were collected into 60-mL serum bottles (Wheaton, Millville, NJ). Water was gently added down the side of the bottle so as not to agitate or create bubbles, which could strip gases dissolved in the water. The

* Author to whom correspondence should be addressed.

bottle was completely filled, and several drops of 1:1 sulfuric acid were then added as a preservative. The bottle was capped and sealed using a 20-mm gray butyl rubber, Teflon-faced septum (Wheaton, Millville, NJ) and 20 mm aluminum crimp seal (Wheaton). The samples were kept cold in an ice chest in transit to the laboratory. Samples were kept at 4°C and analyzed within 14 days of collection.

GC analysis

The GC was calibrated by injecting 300 µL of each of the gas standards as listed in the *Materials* section. The Scotty II cylinders were sampled at atmospheric pressure. This was accomplished by attaching a short piece of $^1/_4$-in. stainless steel tubing with appropriate fittings to the cylinder outlet. At the cylinder outlet, a $^1/_4$-in. "tee" was fitted with a GC septum allowing for insertion of a gas-tight syringe needle into the gas stream. The exit end of the tubing was inserted into a 500-mL beaker of water. As gas "bubbled" through the water, 300 µL of the gas standard was removed and injected into the GC. The retention times for methane, ethene, and ethane were near 0.6, 1.9, and 2.5 min, respectively. Peak area counts generated for each sample were compared with a calibration standard curve.

Samples were allowed to reach room temperature prior to analysis. A headspace was prepared by replacing 10% of the bottled sample (in this case, 6 mL) with helium. To generate headspace in the sample bottle, the bottle was placed upside-down in a three-fingered clamp attached to a ring stand. Next, a 20-gauge needle attached to a 10-mL Luerlok glass syringe set for dead volume was inserted through the septum. Then an 8-cm 20-gauge needle attached to Teflon tubing and a needle valve was inserted through the septum up to the bottom of the bottle. The Teflon tubing was plumbed to a two-stage regulator on a cylinder of high-purity helium, and the helium was passed through the needle at 5 mL/min or less. The helium forced water out of the bottle and into the syringe. When the volume of water in the syringe reached 6 mL, the 8-cm needle was pulled out, followed by the syringe. The sample bottle was shaken on a rotary shaker at 1400 rpm for 5 min to allow the gases to equilibrate between the headspace and liquid phases.

A 500-µL gas-tight syringe with a sampling valve (Dynatech Precision Sampling, Baton Rouge, LA) and equipped with a side-port needle was used to withdraw 300 µL of headspace, which was subsequently injected into the GC. The temperature of the remaining sample was determined. The volume of the sample bottle was measured by filling the bottle with water and pouring the contents into a graduated cylinder.

For purposes of quality control, field trip blanks were included with samples, and 10% of samples were collected in duplicate and analyzed. Prior to analysis and at the end of the day, calibration of the GC was checked by analyzing at least one of the gas standards for each analyte. The GC was considered to be in calibration if the analyzed value was within 15% of that expected. Calibration standards for at least one of the gases were analyzed with a frequency of 10%. Control charts were maintained to monitor variability. In addition, a method blank consisting of a serum bottle of deionized, boiled water was analyzed on a daily basis. This was necessary to correct for background levels of methane. Quantitation limits for methane, ethane, and ethene were 0.001, 0.002, and 0.003 mg/L, respectively. Normally, two samples could be prepared and analyzed per hour.

Calculations

The concentrations of the gases dissolved in the water sample were calculated using the partial pressure of the gas, Henry's Law constant, the temperature of the sample, the volume of the sample bottle, and the molecular weight of the gas. Values for Henry's Law constant were obtained from Perry's *Chemical Engineer's Handbook* (7).

The linear regression equation of the standard curve was used to determine the partial pressure (p_g) of the gas. The concentrations of the gas standards should be converted to their decimal equivalent before generating the curve (i.e., 10 ppm is equivalent to 0.00001, as is 1% to .01). The sample's area count obtained from the chromatogram peak for the analyzed gas was "inserted" into the equation to determine its partial pressure. For methane, it was necessary to subtract the area count obtained from the analysis of a method blank. The following sequence of equations were used to determine the concentration of the dissolved gas.

For the equilibrium mole fraction of the dissolved gas:

$$x_g = p_g/H \qquad \text{Eq 1}$$

where H is Henry's Law constant for the gas. Let n_g represent the moles of gas and n_w the moles of water. Then:

$$x_g = n_g/(n_g + n_w) \text{ and } n_g = x_g(n_g + n_w) \qquad \text{Eq 2}$$

Because 1 L of water equals 55.5 g-moles:

$$n_g = x_g(n_g + 55.5) \qquad \text{Eq 3}$$

and because:

$$n_g x_g << n_g \qquad \text{Eq 4}$$

therefore:

$$n_g \approx x_g(55.5) \text{ or } n_g = 55.5(p_g/H) \qquad \text{Eq 5}$$

For the saturation concentration of the gas:

$$C = n_g(MW)(1000 \text{ mg/g}) \qquad \text{Eq 6}$$

where MW is the molecular weight of the gas. To correct gas density for temperature:

$$D = MW/(22.4 \text{ L/mole})(ST \text{ °K}/273\text{°K}) \qquad \text{Eq 7}$$

where ST is the sample temperature. Then:

$$A_h = (\text{mL of headspace})(p_g) = 6(p_g) \qquad \text{Eq 8}$$

where A_h is the milliliters of analyte in the headspace. Then:

$$A_l = (A_h/V)(D)(1000 \text{ mg/g})(1 \text{ L}/1000 \text{ mL}) \qquad \text{Eq 9}$$

where A_l is the analyte in liquid phase and V is the volume of water (bottle volume–headspace volume) in L; using a 60-mL serum bottle with 6 mL of headspace, V equals 0.054 L. Then:

$$TC = A_l + C \qquad \text{Eq 10}$$

where TC is the total concentration of analyte in the original sample, in milligrams of gas per liter of water.

Example calculation for methane

Methane will be used as an example of the calculations used for the analysis of dissolved gases. From the analysis of a sample, an area count was determined. This area count was used in the equation for the linear regression of the calibration curve to give its partial pressure (p_g). Parameters used for this example are as follows: the sample area count was 978264, the method blank area count was 2766, Henry's Law constant was 4.13E+4 (at 25°C), the sample temperature was 25°C (298°K), the bottle volume was 60 mL, and the headspace volume was 6 mL.

From the equation of a straight line ($y = mx + b$), the calibration standard responses generated the following curve:

$$p_g = (1.814E{-}9)x - 6.716E{-}6 \qquad \text{Eq 11}$$

Therefore, for this sample:

$$p_g = (1.814E{-}9[978264 - 2766]) - 6.716E{-}6 \qquad \text{Eq 12}$$

$$= 0.0018$$

Then, using the previous equations:

$x_g = 0.0018/4.13E{+}4 = 4.269E{-}8$ (from Eq 1)

$n_g = 55.5(4.269E{-}8) = 2.37E{-}6$ (from Eq 5)

$C = (2.37E{-}6)(16)(1000) = 0.038$ mg methane/L water (from Eq 6)

$D = (16\text{g/mole})/([22.4\text{ L/mole}][298/273]) = 0.654$ g methane/L (from Eq 7)

$A_h = 6(0.0018) = 0.0108$ mL methane (from Eq 8)

$A_l = (0.0108\text{ mL}/0.054\text{ L})(0.654\text{ g/L})(1\text{ L}/1000\text{ mL})(1000\text{ mg/g}) = 0.1308$ mg methane/L (from Eq 9)

$TC = 0.1308 + 0.038 = 0.169$ mg methane/L water (from Eq 10)

Results and Discussion

Water samples collected at field sites have been analyzed by the described procedure for over eight years. The method is relatively simple and reliable for the analyses of water samples. A typical chromatogram of a ground water sample from a contaminated site is shown in Figure 1. Table I lists the analytical data for several water samples. Calibration curves were generated using linear regression on a calculator or computer; area counts of the standards were plotted versus their concentrations.

Saturated solutions of methane and ethene in water were prepared with expected concentrations of 22.7 and 131 mg/L, respectively. They were analyzed to determine precision and accuracy. For methane, an average recovery of 87% was obtained for six replicates, the standard deviation was 0.64 mg/L, and the relative standard deviation (RSD) was 3.25%. For ethene, the

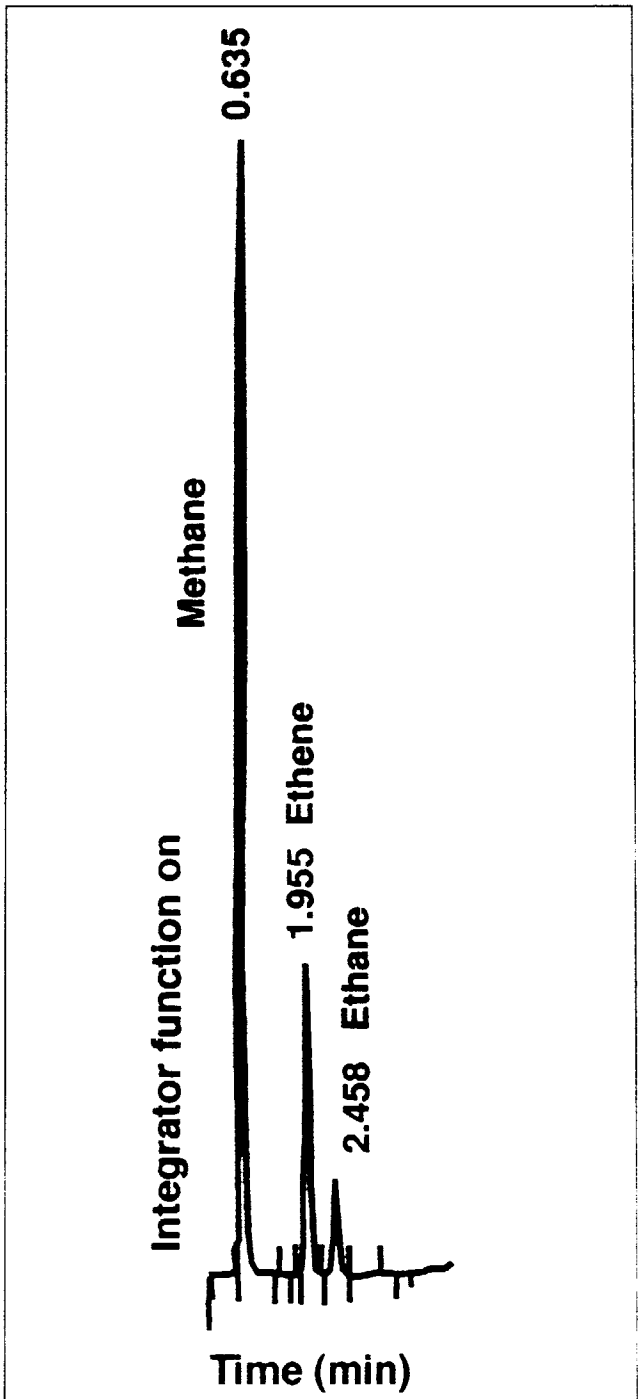

Figure 1. Typical chromatogram of a field sample. Retention times for methane, ethene, and ethane were 0.635, 1.955, and 2.458 min, respectively.

Table I. Analytical Data of Four Samples from a Field Site

Sample	Methane (mg/L)	Ethene (mg/L)	Ethane (mg/L)
RW-10	0.682	undetected	0.027
RW-11	4.753	undetected	0.219
RW-12	1.268	undetected	0.013
RW-12*	1.260	undetected	0.013
RW-13	3.074	0.268	0.112
RW-13†	3.143	0.258	0.107

* Lab duplicate (i.e., headspace of same sample analyzed twice).
† Field duplicate.

average recovery for three replicates was 90%, the standard deviation was 8.8 mg/L, and the RSD was 7.5%. Due to the unavailability of pure ethane in our lab, this exercise was not performed on ethane.

With appropriate GC detectors, this technique should be applicable to other volatile dissolved constituents in water such as carbon dioxide, nitrous oxide, nitrogen, and vinyl chloride. It should be noted that acid preservation should not be used for carbon dioxide analysis because inorganic carbon may be converted to carbon dioxide.

Conclusion

The sample preparation and analytical technique for dissolved methane, ethane, and ethene in ground water has been used successfully on a routine basis in our lab. We have analyzed thousands of ground water samples from numerous contaminated sites. The data from these analyses have been critical in determining the nature of the degradative processes in contaminated aquifers. This technique will continue to be used for routine analyses on water samples from both lab and field studies.

Acknowledgments

The authors are grateful to Bryan Newell and Jeff Hickerson of ManTech Environmental Research Services for their support as analysts. Pat Holt of National Risk Management Research Laboratory typed the manuscript. The research described has not been subjected to a review process by the United States Environmental Protection Agency. Therefore, the work does not necessarily reflect the views of the agency, and official endorsement should not be inferred.

References

1. D.H. Kampbell, T.H. Wiedemeier, and J.E. Hansen. Intrinsic bioremediation of fuel contamination in ground water at a field site. *J. Haz. Mat.* **49:** A7–204 (1996).
2. 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 Resources Research* **31(4):** 1051–62 (1995).
3. W.H. Schroeder, K.A. Brice, P. Fellin, and B. Kerman. Determination of dissolved argon and nitrogen in water by direct aqueous injection GC–HID. *Int. J. Environ. Anal. Chem.* **61:** 117–29 (1995).
4. T.M. Kana, C. Darkangelo, M.D. Hunt, J.B. Oldham, G.E. Bennett, and J.C. Cornwell. Membrane inlet mass spectrometer for rapid high-precision determination of N_2, O_2, and Ar in environmental water samples. *Anal. Chem.* **66:** 4166–70 (1994).
5. A.J. Berger, Y. Wang, D.M. Sammeth, I. Itzkan, K. Kneipp, and M.S. Feld. Aqueous dissolved gas measurements using near-infrared Raman spectroscopy. *Appl. Spectrosc.* **49:** 1164–69 (1995).
6. D.H. Kampbell, J.T. Wilson, and S.A. Vandegrift. Dissolved oxygen and methane in water by agc headspace equilibration technique. *Int. J. Environ. Anal. Chem.* **36:** 249–57 (1989).
7. *Chemical Engineer's Handbook.* 4th ed. J.H. Perry, Ed. McGraw-Hill, New York, NY, 1963, pp. 14-2–14-7.

Manuscript accepted December 11, 1997.