DETERMINING DISSOLVED HYDROGEN, METHANE, AND VINYL CHLORIDE CONCENTRATIONS IN AQUEOUS SOLUTION ON A NANOMOLAR SCALE WITH THE BUBBLE STRIP METHOD

D.H. Kampbell[1], J.T. Wilson[1], and D.M. McInnes[2]

[1]U.S. EPA, National Risk Management Research Laboratory, Subsurface Protection and Remediation Division, P.O. Box 1198, Ada, OK 74820; [2]ManTech Environmental Research Services Corp., East Central University, Ada, OK 74820

ABSTRACT

The Bubble Strip Method is a viable method for determining concentrations of hydrogen, methane, and vinyl chloride in aqueous solution. Information regarding the concentrations of these gases in groundwater is useful in monitoring bioremediation and predicting the fate of contaminants at a given site. Concentrations of dissolved gases on the nanomolar scale are measurable with this technique.

Employing the method involves filling a gas sample bulb with the solution being analyzed, charging the bulb with a 20 mL headspace, and then pumping the solution through the bulb over a length of time sufficient for equilibrium between phases to be attained. Subsequent gas chromatographic analysis of the sample bulb headspace enables concentration of dissolved gas in solution to be calculated using Henry's law.

The results of this study indicate that a solution flow rate of 400 mL/minute through the sample bulb is optimum. A flow time of twenty minutes is sufficient for equilibrium between phases to be established with aqueous solutions of hydrogen gas. With aqueous solutions of methane and vinyl chloride, equilibrium is attained within 10 minutes. A slightly longer time to equilibrium (about thirty minutes) was observed with solutions of hydrogen gas at 4^0C.

Key words: *hydrogen, methane, vinyl chloride, Bubble Strip Method, bioremediation*

INTRODUCTION

Intrinsic bioremediation of common groundwater contaminants

Fuels such as jet fuel, diesel fuel, and gasoline are a common source of groundwater contamination. At sites where spills have occurred, the slightly soluble organic fuel components are partitioned into the groundwater over potentially lengthy periods of time. The four contaminants which are of most concern are benzene, toluene, ethylbenzene, and xylenes (collectively known as BTEX). These compounds, while a relatively small percentage of the fuels by mass, account for most of the organic contaminants in fuel-tainted groundwater due to their high solubilities relative to other fuel components. BTEX compounds pose a health risk and, therefore, are the primary focus of many cleanup efforts (Wiedemeier et al., 1996).

A degreasing solvent, trichloroethylene (TCE), and the products of its degradation are also a common source of contamination in groundwater. TCE can degrade to methane, ethane, and ethylene with the hazardous compounds dichloroethylene and vinyl chloride as intermediates.

In some cases, natural processes are relied upon to aid in the remediation of groundwater contaminants. This strategy, known as intrinsic remediation, involves allowing natural attenuation

processes to bring about a depletion of contaminant concentration over time. For an example of a site where intrinsic bioremediation was found to be a viable option for restoration see Kampbell et al. Natural attenuation of contaminants occurs through a variety of physical, chemical, and biological processes. The processes of advection, dispersion, dilution from recharge, sorption, and volatilization do not change the identity of a contaminant, but serve to limit its potential as a biohazard by diluting it or transporting it to another location. A natural attenuation process which does change the identity of a contaminant, thereby rendering it harmless, is biodegradation. The process by which contaminants are biodegraded by microorganisms is referred to as intrinsic bioremediation.

[H2] as an indication of the predominant pathway of biodegradation

Intrinsic bioremediation occurs via mechanisms known as terminal electron accepting processes (TEAPs). TEAPs are microorganism mediated redox processes, the net result of which is the transfer of electrons from organic matter to a terminal electron acceptor. Terminal electron acceptors include O2 in aerobic conditions (i.e., [O2] > 0.5 mg/L), and CO2, $NO3^-$, $SO4^{2-}$, Fe^{3+}, and chlorinated hydrocarbons in anaerobic conditions.

Molecular hydrogen is an intermediate in terminal electron accepting processes (Lovley, Chapelle, and Woodward, 1994). In an aquifer where bioremediation of organic matter is occurring, fermentative microorganisms produce hydrogen as they metabolize the organic matter. Simultaneously, hydrogen is consumed by resperative microorganisms, which use a terminal electron acceptor as an electron sink. The concurrent processes of hydrogen production and hydrogen consumption produce a steady state concentration of dissolved hydrogen, the magnitude of which depends on the efficiency of the predominant terminal electron acceptor in the process. The more efficient the terminal electron acceptor in promoting hydrogen consumption, the lower the steady state hydrogen concentration. Therefore, hydrogen concentration in a given aquifer (when considered in conjunction with other information such as depletion of terminal electron acceptors and accumulation of reduced products) is a reliable indicator of which TEAP predominates (Lovley, and Goodwin, 1988; Chapelle et al., 1996). Table 1 indicates the relationship between measured hydrogen concentration and the predominant TEAP in anaerobic conditions (Chapelle et al., 1995).

Once a site is characterized in regards to the terminal electron-accepting processes taking place, decisions can be made as to what treatments are appropriate and models can be devised to predict the fate of contaminants at that site (Wiedemeier et al., 1996; Vroblesky and Chapelle, 1994).

Use of the Bubble Strip Method for determining gaseous concentrations in well water

The Bubble Strip Method is a chemical testing method developed for the purpose of determining dissolved hydrogen concentrations in well water (Chapelle et al., 1997). The method is based on the principle that gases will undergo a partitioning between a vapor phase and a liquid phase that

are in contact with each other. At equilibrium, the partitioning of a gas between a vapor and liquid phase can be quantified by applying Henry's Law. Different gases have characteristic, temperature-dependant Henry's law constants in a given solvent.

The stripping procedure involves filling a gas sample bulb with the aqueous solution being analyzed and then charging it with 20 mL of air to produce a headspace (Figure 1). The bulb is positioned at a 45^0 angle to horizontal, and a peristaltic pump upstream of the bulb is used to pump the solution through the bulb such that a stream of water flows through the headspace and produces agitation in the aqueous phase. During the flowing process, a partitioning of dissolved gases between the two phases occurs, and equilibrium is eventually attained. Gas chromatographic analysis of the headspace and subsequent application of Henry's Law enables the determination of gaseous concentration in the aqueous solution.

In this study, we employ a specially designed system to determine the optimum flow rate at which water should be pumped through the gas sample bulb. We also determine the minimum flow time required for equilibrium to be established in the process of stripping aqueous solutions of each of the three gases being investigated. The effect of varying temperature on time to equilibrium in the stripping of hydrogen is also investigated.

METHODS AND MATERIALS

Pressure and temperature measurements

A digital manometer (Dwyer Series 475 Mark III) was used to measure differential pressure between the gas sample bulb headspace and the atmosphere during the stripping process.

A digital barometer (Fisherbrand) was used to measure barometric pressure. Pressure was not corrected for altitude. Temperature was also displayed on this device.

Instrumentation

Analysis of hydrogen was accomplished using a Trace Analytical RGA3 Reduction Gas Analyzer. Injection volume was 2 mL; the column temperature was set at 100^0C; and the detector temperature was set at 265^0C. The retention time of H2 was 0.50 minutes with a carrier gas (High Purity Nitrogen) flow rate of 22 mL/min.

Methane was analyzed using a Finnigan 9001 Gas Chromatograph equipped with a 1/8-inch, 6-foot, stainless steel, packed-column (Porapak N), and FID detector. Injection volume was 200 µL. The injector temperature was set at 175^0C; the column temperature was set at 80^0C; and the detector temperature was set at 200^0C. The retention time of methane was 0.490 minutes with a carrier gas (High Purity Helium) flow rate of 25 mL/min.

Vinyl chloride was analyzed using a Finnigan 9001 Gas Chromatograph equipped with a 1/8-inch, 6-foot, stainless steel, packed-column (Porapak N), and FID detector. Injection volume was 200 µL. The injector temperature was set at 175^0C; the column temperature was set at 120^0C;

and the detector temperature was set at 200^{0}C. The retention time of vinyl chloride was 2.85 minutes with a carrier gas (High Purity Helium) flow rate of 25 mL/min. For very low concentrations of vinyl chloride, an ECD or HECD detector may be preferred over an FID detector.

All injections were made with appropriately sized Pressure-Lok gas tight syringes (Precision Sampling Corporation).

Gas standards

Hydrogen, methane, and vinyl chloride standards were prepared using gases and gaseous mixtures purchased from Scott Specialty Gases.

Preparation of calibration curves

Hydrogen

Standard samples were prepared by diluting a hydrogen mixture (100 ppm in nitrogen) into sealed serum bottles (Wheaton) containing nitrogen. Serum bottles were prepared by placing them in a container filled with water purified by reverse osmosis. The bottles were completely filled with water and inverted such that nitrogen gas could be bubbled into them. After the bottles were filled with nitrogen, they were sealed with a rubber septum (Wheaton, 13 mm x 20 mm Gray butyl Teflon-faced, straight Plug Style). The sealed bottles were removed from the water and tear away aluminum seals (Supelco) were applied to secure the septa. Standards were then prepared by withdrawing from the bottles an amount of nitrogen equal to the amount of 100 ppm hydrogen mixture to be added (Table 2). The appropriate amount of 100 ppm hydrogen was then injected and the bottles were allowed to sit for 1 hour before gas chromatographic analysis was attempted. Gas tight syringes were used throughout the procedure.

Methane

Three standards were used to prepare a calibration curve for methane: 100 ppm, 50 ppm, and 10 ppm methane in nitrogen. The 100 ppm standard was withdrawn directly from a gas cylinder. The 50 ppm and 10 ppm standards were prepared by diluting 100 ppm methane using the same technique as described above for the hydrogen standards.

Vinyl chloride

Five standards were used to prepare a calibration curve for vinyl chloride: 10 ppm, 100 ppm, 255 ppm, 510 ppm, and 1020 ppm vinyl chloride in nitrogen. The 10 ppm, 100 ppm, and 1020 ppm standards were withdraw directly from gas cylinders. The 510 ppm and 255 ppm standards were prepared by diluting the 1020 ppm vinyl chloride using the same technique as described above for the hydrogen standards.

Equilibration studies apparatus

A gas sample bulb, 250 mL (Supelco, Inc.), with thermogreen LB-1 cylindrical, half-hole type septa (Supelco, Inc.) was positioned down field of a peristaltic pump (Masterflex, Model 7518-

12), such that water could be pumped from a reservoir (Pyrex, 13.45 L), through the gas sample bulb, and back to the reservoir. Another peristaltic pump was used to circulate reservoir headspace through the aqueous solution in order to maintain a constant concentration of gas in the solution during the stripping process. Masterflex tubing (6424-15) was employed in assembling the system along with assorted other tubes of various makes and sizes (Figure 2).

Preparing solutions for stripping

The following summarizes the procedures used to prepare solutions for stripping. Separate experiments were done for each of the three gases.

To produce a headspace concentration of approximately 10 ppm H2 in the reservoir, reverse osmosis water was pumped into the reservoir until the reservoir had a headspace of 4.5 L. The sample bulb was also completely filled with water in the process. Hydrogen gas (500 mL, 100 ppm in nitrogen) was injected into the chamber, after which 500 mL of water was released. The headspace was then sparged through the water in the reservoir for 24 hours. Simultaneously, water was circulated through the bulb and reservoir in order to achieve mixing in solution.

To produce a reservoir headspace concentration of approximately 100 ppm methane, the reservoir was filled with reverse osmosis water as described above so that there was a 5 L headspace. Methane gas (0.5 mL) was then injected into the chamber headspace, followed by sparging and water circulation for 24 hours.

To produce a reservoir headspace of approximately 900 ppm vinyl chloride, the reservoir was filled with reverse osmosis water as described above so that there was a 5 L headspace. Vinyl chloride gas (4.5 mL) was then injected into the chamber headspace, followed by sparging and water circulation for 24 hours.

The headspace concentrations above were significantly lower after equilibrium was established between water and headspace due to the solubility of the gases in water.

Determining time to equilibrium

Studies were conducted to determine how much stripping time is required for equilibrium to be established between the aqueous and gas phases in the gas sample bulb. The procedure involved subjecting the water from the reservoir to the stripping process over several different time periods (5 min., 10 min., 20 min., etc.). For each time period, the gas sample bulb was charged with a new volume of nitrogen gas. On completion of the stripping process over a given time interval, the reservoir and sample bulb headspaces were analyzed by gas chromatography, after which the sample bulb headspace was discharged into the reservoir. Upon injection of a new volume of nitrogen into the gas sample bulb, stripping started over again from time zero. This procedure was repeated until data from all relevant time periods were collected. For use in calculations, differential pressure between the sample bulb headspace and the atmosphere was measured with a digital

manometer by way of the septum in the sample bulb during pumping. Additionally, atmospheric pressure (uncorrected for altitude) was recorded during the equilibration studies.

Concentrations of the gas in chamber headspace and sample bulb headspace were plotted against flow time. All concentrations were corrected to 1 atm as described in the calculations section. Equilibrium was considered attained when the gaseous concentrations in the chamber and sample bulb headspaces were within 10% of each other.

CALCULATIONS

Correcting calibration curve data

Areas reported by GC were corrected to standard atmospheric pressure by applying equation 1:

$$\text{Area (corrected)} = \text{Area (uncorrected)} * (29.92 \text{ in Hg}/P_{atm}) \quad (1)$$

where 29.92 in Hg = standard atmospheric pressure, and Patm = the atmospheric pressure (uncorrected for altitude).

Corrected areas were plotted against concentrations and a line estimation was performed to yield a slope, m, such that gaseous concentration could be calculated directly from peak area (equation 2).

$$[\text{gas}] \text{ (ppm)} = m * \text{area (corrected)} \quad (2)$$

where [gas] = the concentration of gas being analyzed, and area (corrected) = the area of the corresponding peak as reported by GC (corrected to standard atmospheric pressure).

Correcting sample bulb headspace concentrations

When the stripping process was complete, the headspace concentrations were calculated using equation 2, and a correction was made for differential pressure in the sample bulb headspace using equation 3:

$$[\text{gas}]_{\text{headspace}} \text{ (ppm)} = [\text{gas}] \text{ (ppm)} * (1 \text{ bar} + \Delta P \text{ (bar)}/1 \text{ bar}) \quad (3)$$

where ΔP is the difference in pressure between the headspace in the sample bulb and the ambient atmosphere during the pumping process. Standard atmospheric pressure is approximated as 1 bar.

Concentration of dissolved gas in solution

Concentration of dissolved gas in solution is calculated using equations 4 and 5 (Maron and Prutton, 1965):

$$X(\text{gas})_{\text{solution}} \text{ (mol } H_2/\text{mol } H_2O) = [\text{gas}]_{\text{headspace}} \text{ (ppm) x } 10^{-6} \text{ atm} * [K' \text{ (atm}^{-1})] \quad (4)$$

and

$$[\text{gas}]_{\text{solution}} \text{ (mol/L)} = X(\text{gas})_{\text{solution}} \text{ (mol } H_2/\text{mol } H_2O) * 55.345 \text{ mol } H_2O/L \quad (5)$$

Where $X(gas)_{solution}$ is the mole fraction of dissolved gas in solution (mole H_2O » mol gas); $[gas]_{headspace}$ is the concentration of gas in the headspace in ppm as determined by GC analysis and corrected to 1 atmosphere; K' is the Henry's law constant, which differs for different gases and is dependant on temperature; $[gas]_{solution}$ is the concentration of dissolved gas in the aqueous solution in moles/liter.

Henry's constants are recorded for methane at 25^0C (Manahan, 1994), for hydrogen at various temperatures (Maron and Prutton, 1965), and for vinyl chloride (Lide, 1996).

Sample calculation

For a corrected headspace concentration of 0.50 ppm hydrogen at 4^0C:

$X(gas)_{solution}$ (mol H_2/mol H_2O) = 0.50 x 10^{-6} atm * 1.72 x 10^{-5} atm^{-1}

= 8.6 x 10^{-12} mol H_2/mol H_2O

and

$[gas]_{solution}$ (mol/L) =8.6 x 10^{-12} mol H_2/mol H_2O * 55.345 mol H_2O/L

= 4.8 x 10^{-10} mol H_2/L H_2O = 0.48 nM

A hydrogen concentration of 0.50 ppm in the sample bulb headspace translates into a concentration of 0.48 nM in solution.

RESULTS

Experiments were done to determine how much stripping time was necessary in order for equilibrium to be achieved between the aqueous and gas phases in the gas sample bulb. Flow rates of 300 mL/minute and 400 mL/minute were employed at room temperature for aqueous solutions of hydrogen (figures 3,4), vinyl chloride (figures 5,6), and methane (figures 7,8). For hydrogen solutions, experiments were also done at 4^0C (figures 9,10).

The results show that at room temperature, equilibrium is achieved within 20 minutes when hydrogen is stripped from water at a rate of 400 mL/minute. This is evidenced by the hydrogen concentration in the sample bulb headspace reaching 90% of that in the reservoir headspace. Concentration of hydrogen in solution (as calculated using reservoir headspace data) was approximately 3 nM. At the same flow rate and temperature, equilibrium is achieved within ten minutes for methane and within five minutes for vinyl chloride, with solution concentrations of 240 nM and 10 mM, respectively. At 4^0C, equilibrium is attained within 30 minutes for an aqueous solution of hydrogen.

The slower flow rate of 300 mL/minute resulted in longer times to equilibrium. Flow times of less than 300 mL/minute did not produce the agitation necessary for equilibrium to be attained in a reasonable amount of time. Flow rates of greater than 400 mL/minute resulted in the rapid loss of

sample bulb headspace as a result of a large pressure differential which existed between the bulb headspace and the reservoir headspace during pumping.

CONCLUSION

It is demonstrated in this paper that the Bubble Strip Method is a viable technique for the collection of hydrogen, vinyl chloride and methane from aqueous solution. We show that after the stripping process is complete, nanomolar concentrations of these gases in aqueous solution can be determined by gas chromatographic analysis of sample bulb headspace, followed by application of Henry's law. Stripping time required for equilibrium to be attained between solution and headspace was determined to be on the order of 20 minutes for aqueous solutions of hydrogen at room temperature. A longer time to equilibrium (30 minutes) was required at 4^0C. Aqueous solutions of vinyl chloride and methane reached equilibrium with a headspace after five and ten minutes of stripping, respectively, at room temperature. The optimum flow rate for the stripping process was determined to be 400 mL/min. Lower flow rates resulted in longer times to equilibrium, while higher flow rates resulted in significant loss of bubble volume with time due to a large differential pressure between the sample bulb headspace and the reservoir headspace.

Based on this study, the Bubble Strip Method is potentially useful at field sites for quickly obtaining reliable data regarding the concentrations of various gases in well water.

ACKNOWLEDGMENTS

The authors would like to acknowledge funding support from the Air Force Center for Environmental Excellence at Brooks AFB, Texas (IAG-RW57938459). Although this research was conducted at an U.S. EPA facility, the report has not been subjected to U.S. EPA review. It does not necessarily reflect the views of the agancy and an official endorsement should not be inferred.

REFERENCES

Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford, and D.A. Vroblesky, 1995. Deducing the Distribution of Terminal Electron-Accepting Processes in Hydrologically Diverse Groundwater Systems, Water Resources Research, 31 (2), pp. 359-371.

Chapelle, F.H., S.K. Haack, P. Adriaens, M.A. Henry, and P.M. Bradley, 1996. Comparison of Eh and H2 Measurements for Delineating Redox Processes in a Contaminated Aquifer, Environ. Sci. Technol., 30 (12), pp. 3565-3569.

Chapelle, F.H., D.A. Vroblesky, J.C. Woodward, and D.R. Lovley, 1997. Practical Considerations for Measuring Hydrogen Concentrations in Groundwater, Environ. Sci. Technol., 31 (10), pp. 2873-2877.

Kampbell, D.H., T.H. Wiedemeier, and J.E. Hansen, 1996. Intrinsic Bioremediation of Fuel Contamination in Groundwater at a Field Site, Journal of Hazardous Materials, 49, 197-204.

Kampbell, D.H., and S.A. Vandergrift, 1998. Analysis of Dissolved Methane, Ethane, and Ethylene in Groundwater by a Standard Gas Chromatographic Technique, Journal of Chromatographic Science, 36, pp. 253-256.

Lide, D.R., (Ed.), 1996. CRC Handbook of Chemistry and Physics, 77th Edition, CRC Press, Inc., Boca Raton, p. 16-23.

Lovley, D.R., and S. Goodwin, 1988. Hydrogen Concentrations as an Indicator of the Predominant Terminal Electron-Accepting Reactions in Aquatic Sediments, Geochim. Cosmochim. Acta, 52, pp. 2993-3003.

Lovley, D.R., F.H. Chapelle, and J.C. Woodward, 1994. Use of Dissolved H2 Concentrations to Determine Distribution of Microbially Catalyzed Redox Reactions in Anoxic Groundwater, Environ. Sci. Technol., 28 (7), pp. 1205-1210.

Manahan, S.E., 1994. Environmental Chemistry, 6th ed., CRC Press, Inc., Boca Raton, p. 117.

Maron, S.H. and C.F. Prutton, 1965. Principles of Physical Chemistry, The MacMillan Company, London, 4th ed., p. 298.

Vroblesky, D.A., and F.H. Chapelle, 1994. Temporal and Spacial Changes of Terminal Electron-Accepting Processes in a Petroleum Hydrocarbon-Contaminated Aquifer and the Significance for Biodegradation, Water Resources Research, 30 (5), pp. 1561-1570.

Wiedemeier, T.H., M.A. Swanson, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen, 1996. Approximation of Biodegradation Rate Constants for Monoaromatic Hydrocarbons (BTEX) in Groundwater, Groundwater Monitoring & Remediation, 16 (3), pp. 186-194.

Table 1. Hydrogen concentration versus predominant TEAP in anaerobic conditions.

$[H_2]$	**Predominant TEAP**
<0.1 nM	NO_3^- reduction
0.2-0.6 nM	Fe^{3+} reduction
1-4 nM	SO_4^{2-} reduction
> 5 nM	CO_2 reduction
> 1.0 nM	reductive dechlorination

Table 2. Preparation of hydrogen standards.

160 mL serum bottle

$[H_2]$	**volume (mL) of 100 ppm hydrogen mixture**
0.0 ppm	0.0 mL
0.5 ppm	0.8 mL
1.25 ppm	2.0 mL
2.50 ppm	4.0 mL
5 ppm	8.0 mL

40 mL serum bottle

$[H_2]$	**volume (mL) of 100 ppm hydrogen mixture**
10.0 ppm	4.0 mL
20.0 ppm	8.0 mL

Figure 1. A solution-filled gas sample bulb is charged with 20 mL of headspace in preparation for stripping.

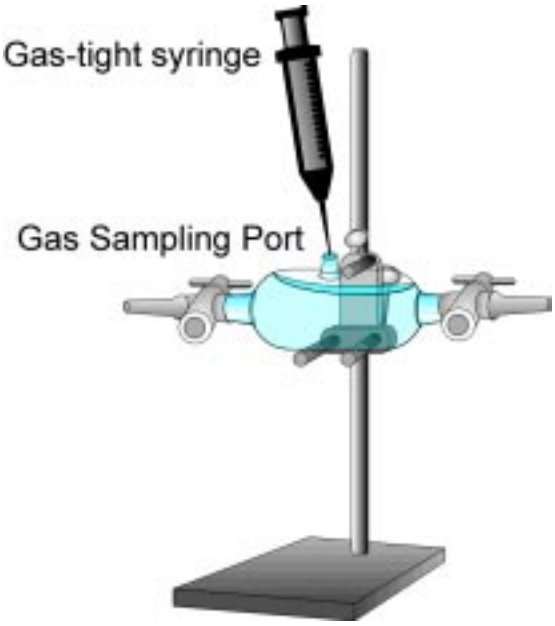

Figure 2. Equilibration studies are performed by stripping a solution whose concentration is kept constant.

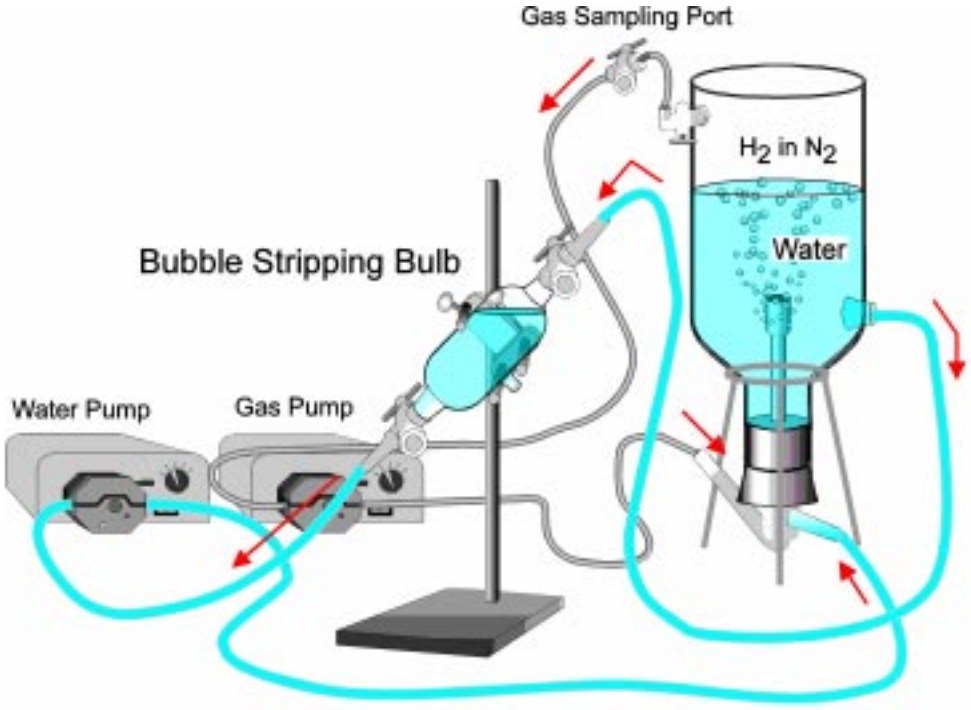

Figure 3. A comparison of reservoir and sample bulb headspace concentrations of hydrogen as a function of stripping time.

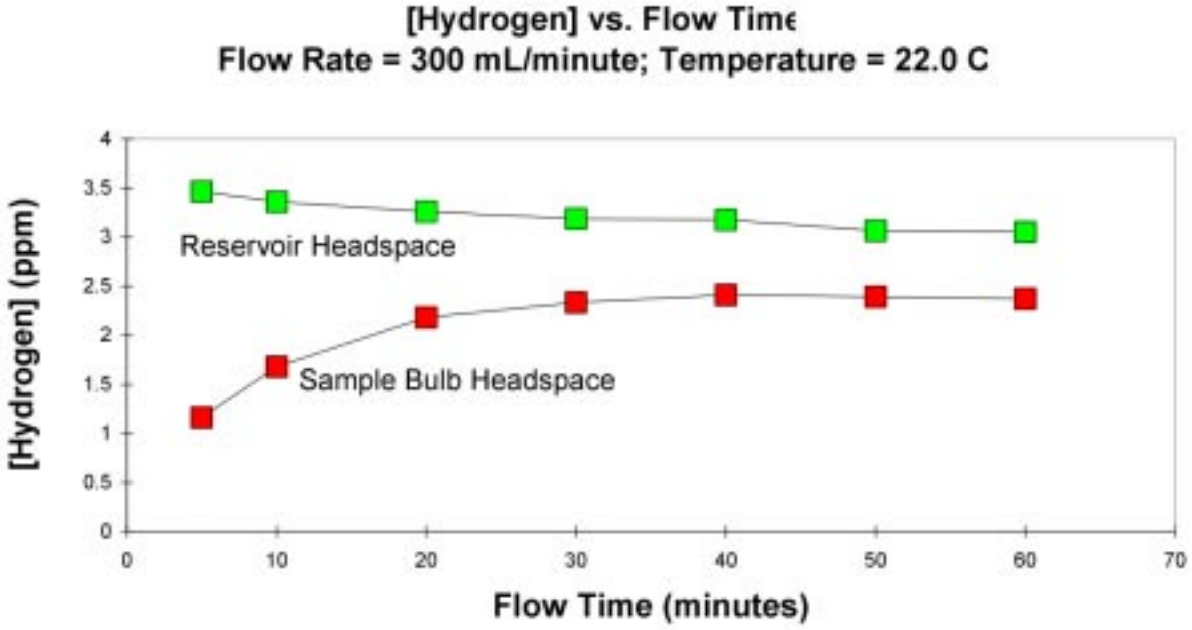

Figure 4. A comparison of reservoir and sample bulb headspace concentrations of hydrogen as a function of stripping time.

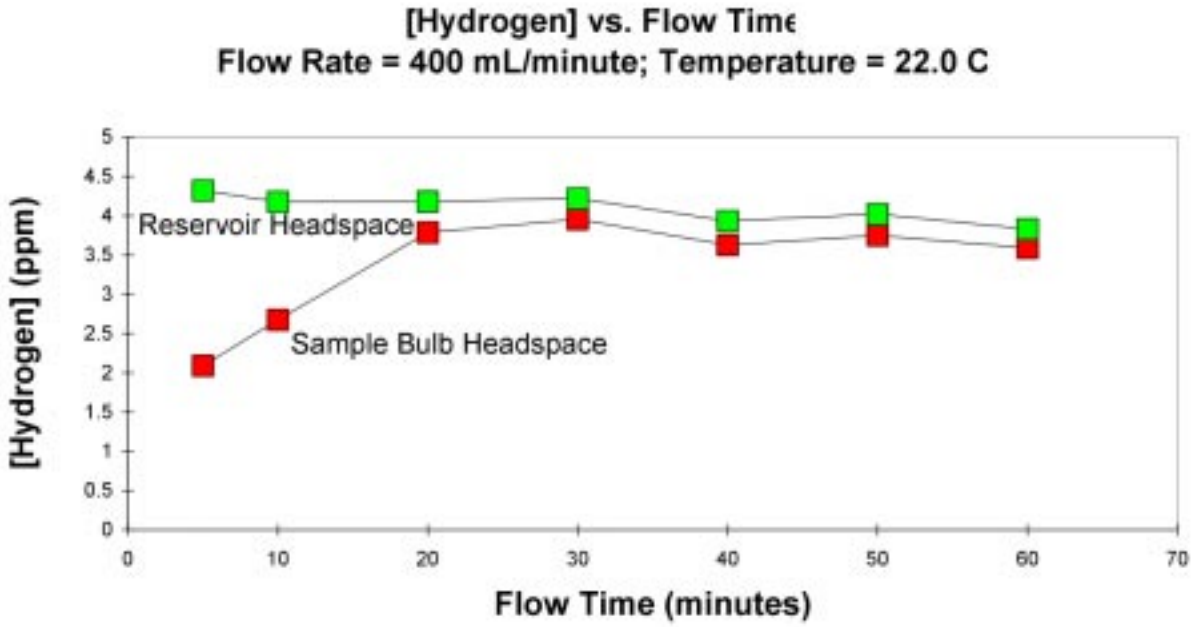

Figure 5. A comparison of reservoir and sample bulb headspace concentrations of vinyl chloride as a function of stripping time.

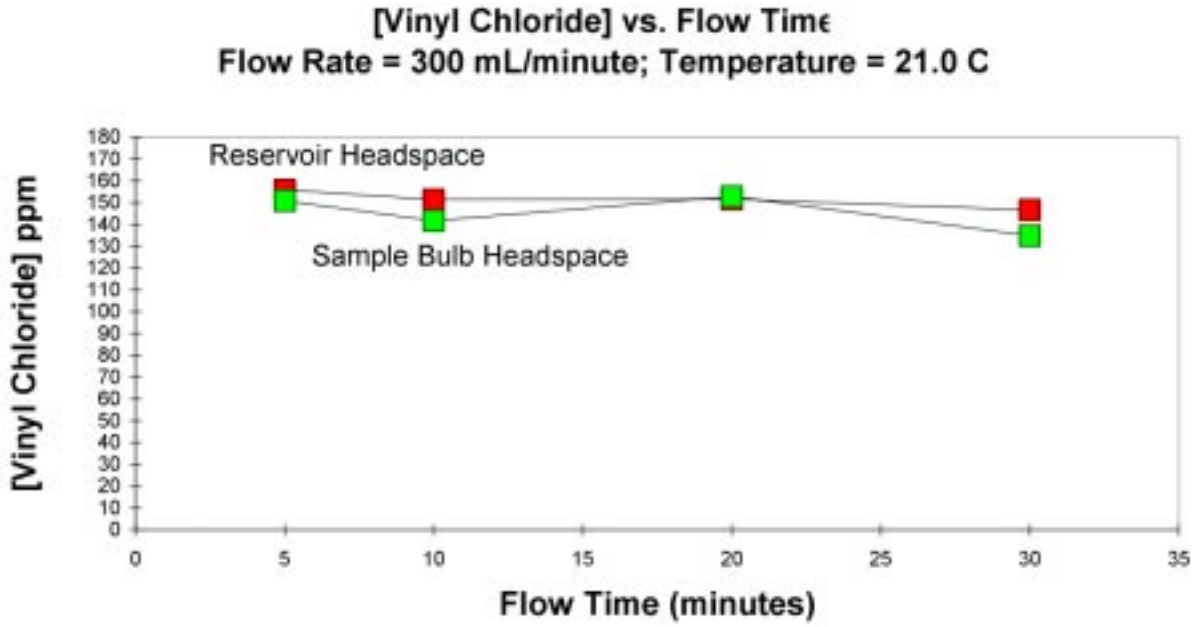

Figure 6. A comparison of reservoir and sample bulb headspace concentrations of vinyl chloride as a function of stripping time.

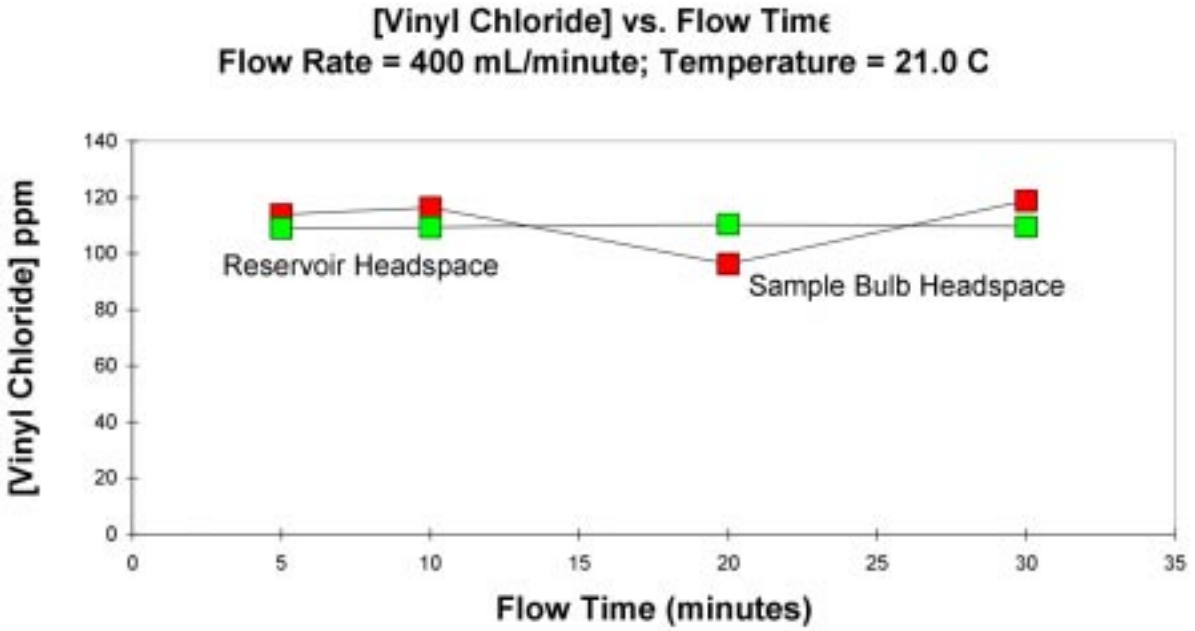

Figure 7. A comparison of reservoir and sample bulb headspace concentrations of methane as a function of stripping time.

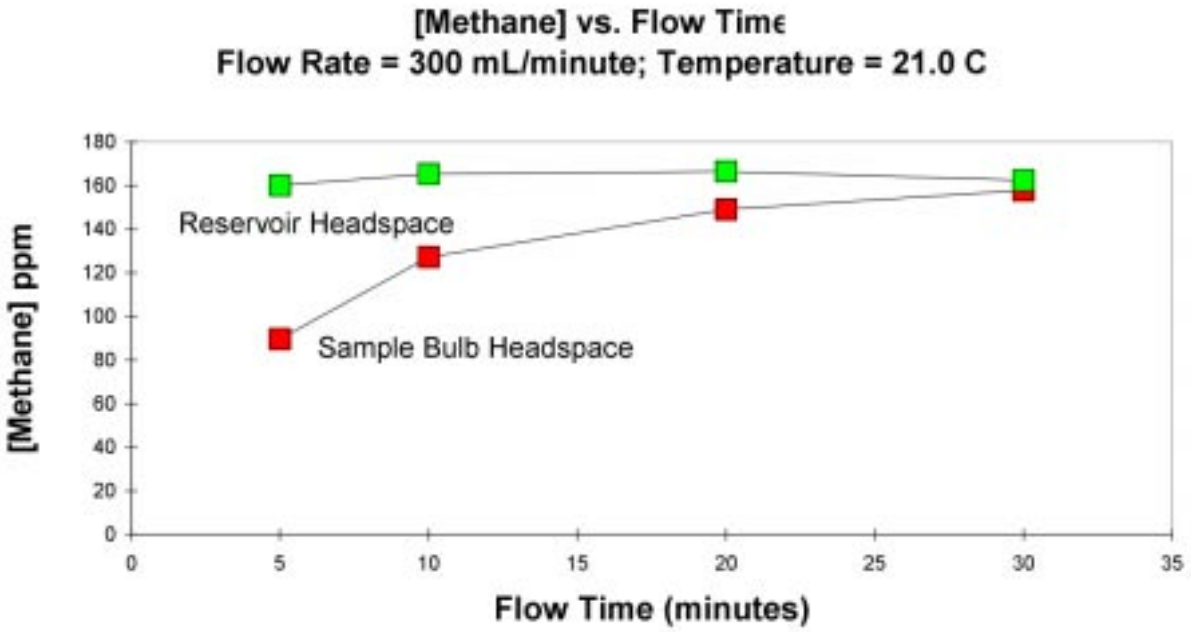

Figure 8. A comparison of reservoir and sample bulb headspace concentrations of methane as a function of stripping time.

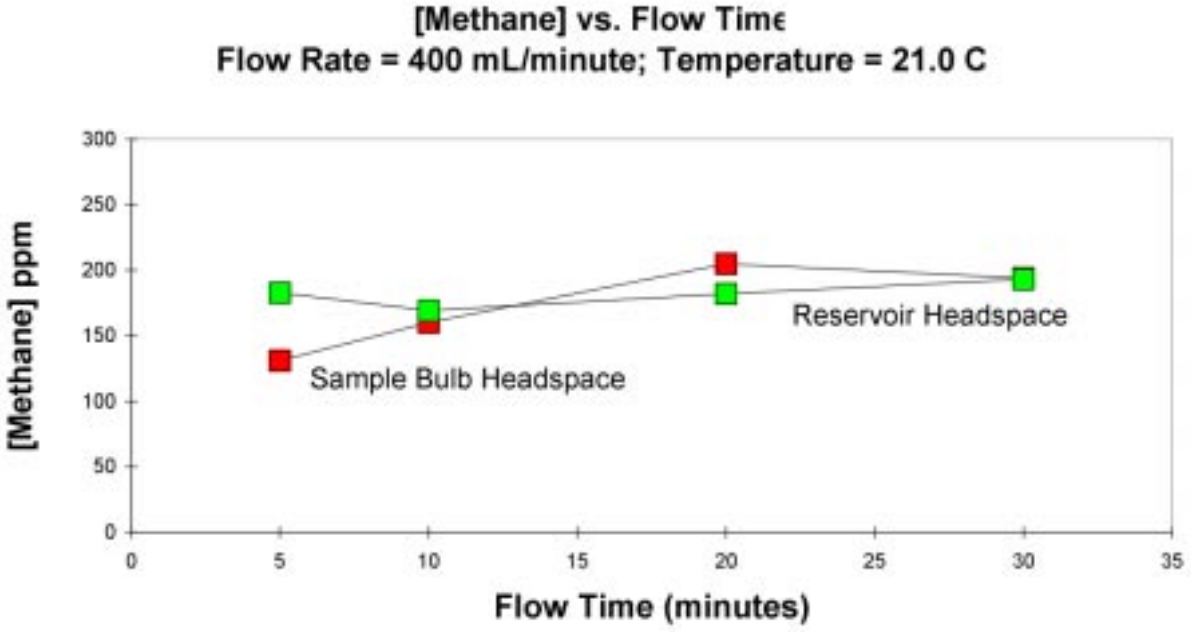

Figure 9. A comparison of reservoir and sample bulb headspace concentrations of hydrogen as a function of stripping time.

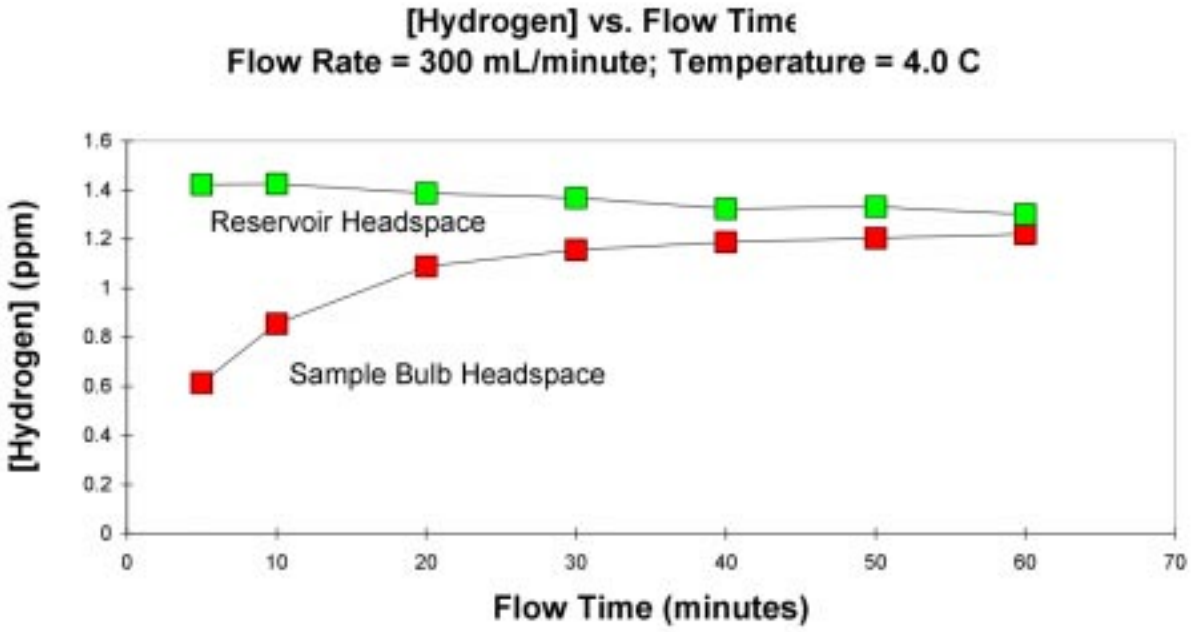

Figure 10. A comparison of reservoir and sample bulb headspace concentrations of hydrogen as a function of stripping time.