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»» **A COMPREHENSIVE LITERATURE REVIEW ON THE APPLICABILITY OF FREE AND DISSOLVED GAS SAMPLING FOR BASELINE WATER WELL TESTING**

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A COMPREHENSIVE LITERATURE REVIEW ON THE APPLICABILITY OF FREE AND DISSOLVED GAS SAMPLING FOR BASELINE WATER WELL TESTING

FINAL REPORT

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SUMMARY

Collecting accurate baseline data on the chemical and isotopic composition of gases in shallow aquifers is an important first step in addressing concerns related to the potential for aquifer contamination with fluids or gases from coalbed methane (CBM) operations. Sampling and analysis of free gas obtained from selected well water samples has been mandatory in Alberta since May 1, 2006, consistent with the requirements of the “Standard for Baseline Water Well Testing for Coalbed Methane Operations” (AENV, 2006). This report summarizes and evaluates currently available methods for free gas and dissolved gas sampling from water wells and discusses their applicability to groundwater testing near CBM operations in Alberta. The ultimate goal is to assess advantages and disadvantages of the currently available techniques for determining the chemical and isotopic compositions of free and dissolved gases in groundwater obtained from water wells. Another objective was to evaluate whether suitable techniques exist to reliably analyze the chemical and isotopic composition of dissolved gas in groundwater, and if so, whether this would add important new information.

Sampling techniques and requirements for obtaining free gas or dissolved gas for the Alberta Environment well-water testing program must be comparatively simple while ensuring reliable and accurate results. Because of the liability issues related to removing pump assemblies or other well installations, sampling is in most cases restricted to above-ground access points, essentially eliminating down-hole sampling devices. For sampling of free gas for chemical and isotopic analyses, the inverted bottle technique (3.1.1) and flow-through cells (3.1.3) are two suitable methods. To determine the chemical and isotopic composition of dissolved gases in groundwater, the inverted bottle method (3.2.3) followed by a headspace equilibrium technique (3.3.1) constitutes a simple and effective analytical method.

Transport and storage containers for free and dissolved gases must prevent gas leakage, chemical conversions of the compounds of interest, and degradation of the sample due to microbial processes. For free gas samples, electro-polished stainless steel air sampling canisters ensure the longest holding times, while FlexFoil grab bags and Tedlar bags constitute cheaper alternatives for gas storage in the order of several days rather than months (4.1). For preservation of groundwater samples for dissolved gas analysis, the addition of a bactericide is highly recommended (4.2). Analytical techniques to determine concentrations (5.1) and isotope ratios (5.2) of free and dissolved gases are highly sensitive and capable of generating very accurate and reproducible results on comparatively small samples, provided that the samples have been properly obtained, transported and stored. It appears that the highest potential for introducing large uncertainties on concentration data for free and dissolved methane in groundwater is in all likelihood associated with the sampling procedures in the field (3.4). Future research should evaluate the influence of sampling procedures and sampler design on the obtained concentration and isotope data for free and dissolved gas (8). It is also recommended that the natural variability of concentrations and isotope ratios of free and dissolved methane be assessed in groundwater obtained from selected wells completed in a variety of hydrogeological settings in the province of Alberta (6, 7).

Current sampling procedures using predominantly flow-through cells are not designed to accurately determine concentration and isotope ratios for groundwater in which methane occurs

only in dissolved form. However, sampling (3.2.3) and analytical procedures (3.3.1) exist to accurately determine concentrations and isotope compositions of dissolved methane at levels of less than 2 mg/L. Hence, it is possible to obtain reliable concentration and isotope data for dissolved methane in groundwater at concentrations levels that are more than one order of magnitude lower than what is currently accessible with sampling techniques designed for free gas.

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1.0 INTRODUCTION

The extraction of natural gas from coal seams (NGC), often also referred to as coalbed methane (CBM), is a rapidly growing industry in Alberta. However, there is some concern, for instance among rural residents, regarding the potential impact of the CBM industry on shallow aquifers. These concerns center around two main issues: (1) potential drawdown of the water table; and (2) potential contamination of shallow groundwater by gases, especially methane, and fluids produced by CBM operations (e.g. Chafin et al., 1996). Effective May 1, 2006, the Alberta Government released the Standard for Baseline Water Well Testing for Coalbed Methane Operations in response to these concerns (see also EUB, Directive 035). This document requires, among others, baseline testing of well water including common water quality parameters, bacteriological analysis, compositional analysis and carbon isotope ratio determinations on free gas prior to CBM development occurring within 600-800 m of a water well (AENV, 2006). The instructions for gas testing are currently restricted to free gas sampled via a flow-through cell or an equivalent method. Currently there is no requirement to sample and analyze gases dissolved in groundwater.

Free gas is defined as gas that readily comes out of solution at atmospheric pressure (Coleman et al., 1988). Under environmental conditions, gases only exsolve from a stagnant solution if their concentrations exceed their saturation points (Coleman et al., 1988). The saturation point of methane at atmospheric pressure and environmental temperatures ranges between 22 mg/L and 28 mg/L (Walsh and McLaughlin, 1999; Eltschlager et al., 2001; Yager and Fountain, 2001). Therefore, free gas sampling may not extract any methane at concentrations below 22 mg/L, i.e. in situations where this gas occurs only in dissolved form. Hence, the analysis of dissolved gas aims at obtaining information on the chemical and isotopic compositions of gases at comparatively low concentrations. Analysis of dissolved gases may yield information in situations where no free gas phase is present.

Temperature and pressure affect gas solubility and, therefore, the boundary between free gas and dissolved gas in a particular water sample. The solubility of methane decreases with increasing temperature (Figure 1). Other short-chain hydrocarbon gases that may be associated with methane such as ethane, propane, and butane, are more soluble than methane, but have the same general trend of decreasing solubility with increasing temperature (Yalowsky and He, 2003). Gas solubility in water also increases with increasing pressure. For example, the hydrostatic pressure exerted by a 360 m water column would allow 863 mg of methane to dissolve into a liter of water at 25°C (Yager and Fountain, 2001). The effect of pressure is important because it results in the tendency of water samples to degas as they are brought from elevated pressure conditions at depth to atmospheric pressure at surface. In free gas samplers, this gas is captured as it leaves solution in and on its way to the flow through cell. However, if the gas contents in a water sample are low (e.g., below the saturation point) and the pressure differences are small, then all the gas may remain dissolved, and free gas samplers may not be able to collect a gas sample.

In practice, agitation from the pumping process and the process of the water flowing through internal structures in a free gas sampling cell can lead to undersaturated methane being detected in free gas samplers, making a clear distinction between free gas and dissolved gas somewhat difficult (Browne, 2004). For the purposes of this report free gas sampling techniques will be defined as those that rely on pumping induced pressure changes, possibly combined with internal structures in a flow-through cell, to remove and capture gas at or near atmospheric pressure. Dissolved gas sampling methods will be defined as methods where gas is extracted from the water sample by any means other than pumping induced pressure changes.

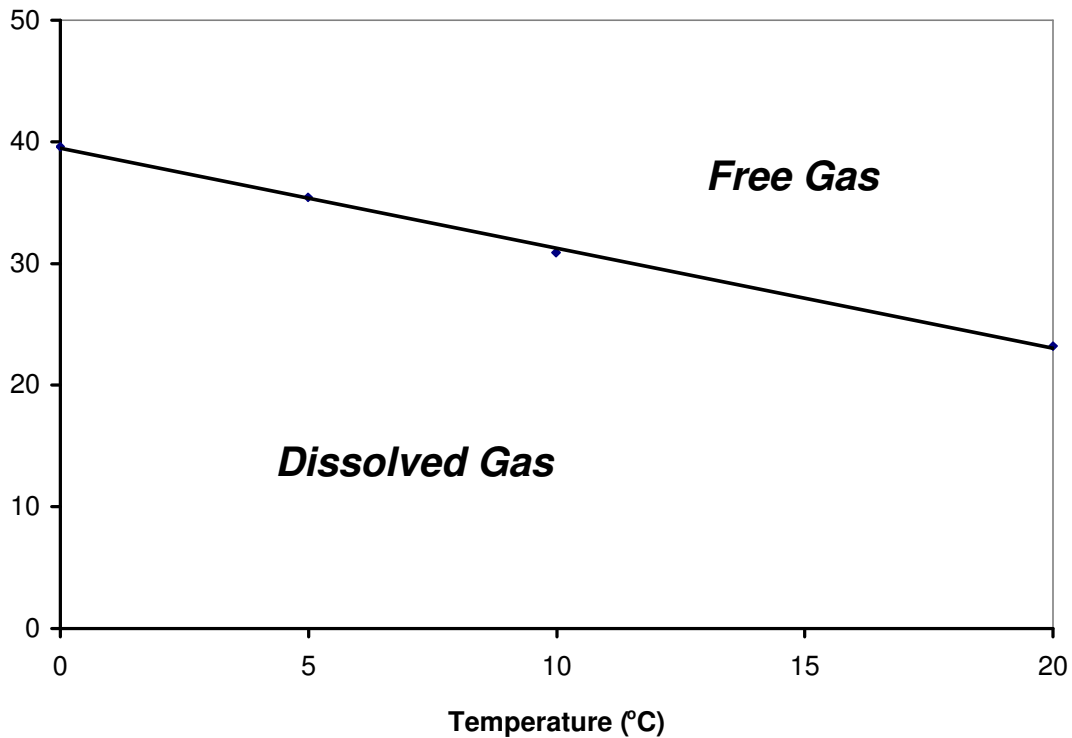


Figure 1: Schematic diagram showing the dissolved gas stability field for methane at different temperatures. At a given temperature, methane present at concentrations above the line occurs as free gas at atmospheric pressure, whereas methane present at concentrations below the line occurs as dissolved gas (data from Yalowsky and He, 2003).

It is important to note that the task of collecting representative baseline data for the chemical and isotopic composition of gases in water wells is not only dependent on choosing an appropriate and reliable sampling technique. While selecting a suitable sampling method is an essential first step, it is also important to properly store and handle the samples once they have been obtained, and to perform proper analytical procedures in a timely fashion. Once chemical and isotopic data have been obtained, they must be interpreted in light of the natural variability of gas concentrations and isotope ratios within the aquifer. In addition potentially occurring biogeochemical transformation

processes, such as methane oxidation, must be considered while interpreting the obtained data.

Collecting accurate baseline data on the chemical and isotopic composition of gases in shallow aquifers is an important first step in addressing concerns related to the potential for aquifer contamination with fluids or gases from CBM operations. Sampling and analysis of free gas obtained from selected well water samples is mandatory in Alberta since May 1, 2006, consistent with the requirements of the “Standard for Baseline Water Well Testing for Coalbed Methane Operations” (AENV, 2006). The question arises whether suitable techniques exist to also reliably analyze the chemical and isotopic composition of dissolved gas in groundwater, and if so, whether this would add important new information.

2.0 OBJECTIVES

The purpose of this report is to summarize and evaluate the currently available methods for free gas and dissolved gas sampling from water wells and to discuss their applicability to groundwater testing near CBM operations in Alberta. This will be accomplished by a thorough review of the peer-reviewed scientific literature, supplemented by a survey of the practical experiences of scientists and practitioners in academia, industry, and consulting companies. In addition to reviewing appropriate and practical sampling techniques, issues related to sample storage and analytical challenges will be discussed. The ultimate goal is to assess advantages and disadvantages of the currently available techniques for determining the chemical and isotopic compositions of free and dissolved gases from water wells.

3.0 SAMPLING METHODS

For more than 30 years, scientists have made a variety of different attempts to analyze the chemical and isotopic composition of dissolved and free gases in groundwater. This section provides a review of free gas (section 3.1) and dissolved gas (section 3.2) sampling methods for groundwater as reported in peer-reviewed scientific literature and elsewhere. Note that many of the described techniques were developed for sampling gases other than methane. For each method, the reproducibility of the obtained results and the detection limits for the analyzed gases are reported, provided that such information was reported in the literature. Furthermore, the suitability of the described technique for isotope analysis on methane, ethane, propane, butane and CO₂, and the ease of use of the sampler under field conditions are discussed.

3.1 Free Gas Samplers

Free gas sampling techniques capture gas that has been exsolved from groundwater, either as it is pumped out of the well (e.g. Aravena and Wassenaar, 1993), or as it travels through a flow-through cell (Browne, 2004; Maxxam Analytics, 2006). Flow-through cells often contain internal structures that cause the water to degas by reducing the hydrostatic pressure acting on the gases, rather than simply relying on degassing induced by pressure changes.

3.1.1 *Inverted Bottle Method for Free Gas*

The simplest, and historically the most commonly used, method for free gas sampling is the inverted bottle method. This method has been widely used for sampling methane from drinking water wells (e.g. Keech and Gaber, 1982; Coleman et al., 1988; Drimmie et al., 1991; Aravena and Wassenaar, 1993; Aravena et al., 1995). The sampling apparatus is quite simple, consisting of an inverted bottle that is submerged in a pail filled with sample water. A standpipe attached to a hose that leads to the well (Figure 2) is inserted into the inverted bottle in the water-filled pail. The bottle is purged with a minimum of two bottle volumes and subsequently, filled with groundwater, which degasses near atmospheric pressure when free gas is present. The gas displaces water in the inverted sample bottle, accumulating in the bottle's headspace. Once a sufficient volume of gas is collected the standpipe is slowly removed from the inverted bottle and the bottle is closed with a septum or screw cap while it remains submerged in the bucket (Clark and Fritz, 1997). The amount of water that flowed through the inverted bottle is estimated by multiplying the pumping rate (measured prior to sampling) by the length of time required to obtain the gas sample. This information is subsequently used to estimate the concentration of free methane in the water sample once compositional analysis has been conducted on the obtained gas sample. The sample is transported upside down to the laboratory for analysis in the sealed bottle. This method is simple, and does not require expensive equipment. A similar technique can also be used to sample dissolved gases for chemical and isotopic analyses (see section 3.2.3).

Inverted bottle method summary:

Gases tested: CH₄, N₂, Ar, O₂, CO₂

Type of results: compositional data (mole fraction and μmol/L), isotopic composition of methane and higher alkanes

Accuracy of the technique: Not stated

Reproducibility of the technique: Not stated

Detection limit: Only reported for methane: 0.165 mg/L

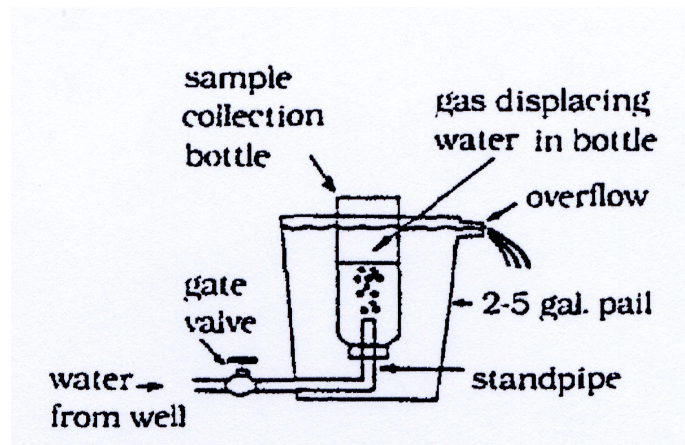


Figure 2: Schematic diagram displaying a setup for sampling free gas using the inverted bottle technique (from: Keech and Gaber, 1982).

3.1.2 Pumping Induced Ebullition Method

Browne (2004) designed a more complex free gas sampling technique that he termed Pumping Induced Ebullition (PIE). In this method, water is pumped through a narrow (2mm) diameter tube called a restrictor before it is released into the collection reservoir (Figure 3). The friction caused in the restrictor leads to a loss of hydrostatic pressure acting on the sample to the point where the total gas pressure exceeds the hydrostatic pressure in the tube. This allows free gas as well as some dissolved gas to exsolve from the solution and accumulate in the headspace of the collection area. Once enough gas has accumulated, it is removed via a gas tight syringe (Figure 3) for chemical and isotopic analyses.

Though data were not provided for methane, Browne (2004) claimed that the PIE technique is able to detect lower concentrations than would be possible using static headspace methods (section 3.3.1). Some potential advantages of this method are that it gathers gas samples reasonably quickly (about 1 mL/minute) and that the free gas sample can be easily removed by a syringe for transport and storage in a suitable container (see section 4) separated from the water sample. A potential complication is that less soluble gases will tend to exsolve more rapidly than highly soluble gases. Since this may skew the obtained results slightly, a correction factor may be required (Browne, 2004).

Pumping induced ebullition method summary (Browne 2004):

Gases tested: CH₄, N₂, Ar, O₂, CO₂, N₂O, CFCs, SF₆

Type of results: Compositional analysis (mole fractions), isotopic analysis not performed;

Accuracy of the technique expressed as correlation factor against established methods:

R² values: O₂ – 0.99, CFCs and SF₆ – 0.97, N₂ – 0.99;

Reproducibility of the technique: Coefficients of variation: N₂ = 0.95%, Ar = 2.51%, O₂ = 1.83%, CO₂ = 7.42%, N₂O = 5.56%, H₂ = 6.81%, SF₆ = 2.97%, CFC11 = 5.67%, CFC12 = 4.58%, CFC113 = 4.60%

Detection limit: On the order of 0.016 mg/L for CH₄, 0.032 mg/L for O₂, 54 mg/L for N₂O, and 1 mg/L for N₂

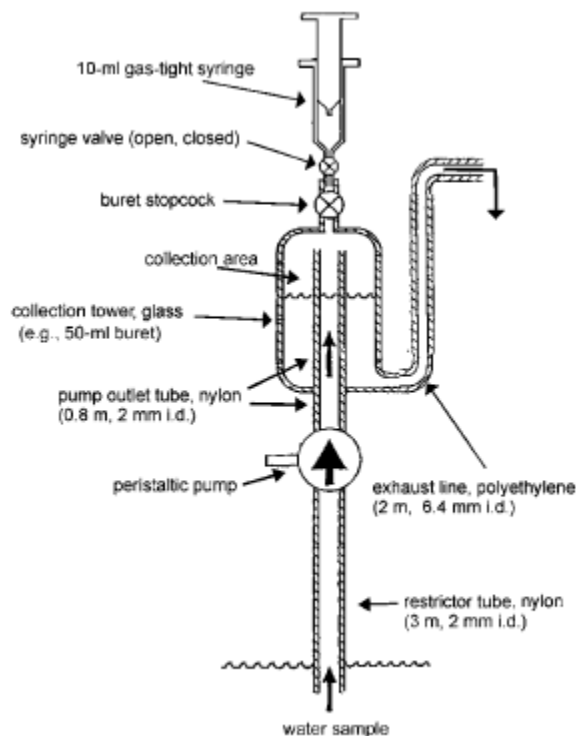


Figure 3: The pumping induced ebullition (PIE) sampling apparatus from Browne (2004)

3.1.3 Flow-Through Samplers

Several models of flow-through cells are currently being used by environmental consulting companies to obtain free gas samples from shallow groundwater for baseline water well testing in Alberta (Magdich, personal communication, 2006; Kennedy personal communication, 2006). Both Oak Environmental Ltd. (Oak, Calgary, Alberta) and Maxxam Analytics Inc. (Maxxam, Mississauga, Ontario) manufacture flow-through cells that are being sold to environmental consultants throughout Alberta. The samplers basically consist of a plastic or glass cylinder with a cane-shaped curved metal tube that enters at the bottom of the cell and opens in the middle of the cylinder (Figure 4). The

water sample flows through the cane-shaped metal tube and cascades out of its open end. The cell contains three valves: one where the water enters, one where the water exits, and one for the extraction of the gas sample (Figure 4). The first step in collecting a free gas sample is to close the water exit valve and open the gas exit valve to completely fill the cell with the sample water. Subsequently, the water exit valve is opened, the water inlet valve is closed slightly so that no more water is escaping through the gas outlet valve, and the gas outlet valve is closed. When no water flows out of the gas outlet valve, it indicates that the water inflow is equal to the outflow in the cell, and therefore there is no pressure accumulating in the cylinder. As the water exits from the cane-shaped metal tube, gases that are supersaturated at atmospheric pressure will be released, and they will accumulate at the top of the cell. As gas is progressively released during the sampling period, it forms a headspace bubble that displaces water in the sampler. Once a sufficient volume of gas has been collected, a gas sampling container (see section 4) is attached to the gas exit valve, the valve is opened, and the gas sample is obtained.

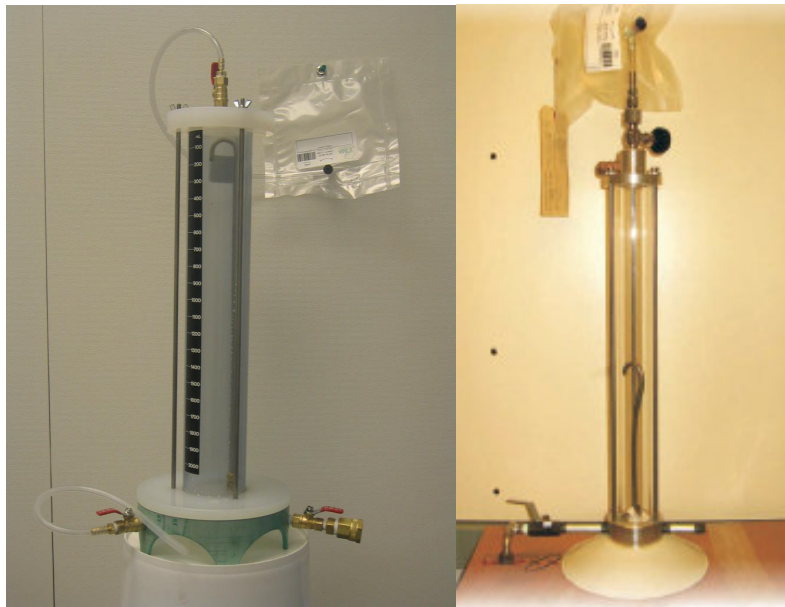


Figure 4: The Oak (left) and Maxxam (right) flow-through sample cells. Note that the cane-shaped tube is much closer to the top of the Oak cell (left) than in the Maxxam cell (right).

Several methods are used to determine how much water has been pumped through the flow-through cell. Some consultants estimate the water flow by multiplying the maximum flow rate through the cell by the amount of time that the sampler is operational. Others place a bucket of known volume underneath the water exit valve and measure how many times it fills during the sampling interval. Alternate approaches include measuring the pumping rate prior to sampling and assuming it remains constant throughout the sampling period, or placing a flow meter in line between the wellhead and the sampling cell. Relating the obtained gas volume to the amount of water that was pumped through the cell provides an estimate of the gas content in the groundwater.

Although the Maxxam and Oak samplers appear rather similar in their design, they do have some important differences. The Oak sampler has 100 mL graduations on its sides, which can be used to approximate the volume of gas in the sampler, whereas the Maxxam sampler uses a syringe to measure the amount of gas removed once sampling is complete (Magdich, 2006; Kennedy, 2006, personal communications). Moreover, the cane-shaped tube in the Oak sampler is significantly longer than that in the Maxxam sampler (Figure 4). As water is pumped through the sampler and the headspace gradually fills with exsolved gas, the end of the cane-shaped tube in the Oak sampler will be exposed to free gas earlier than is the case with the Maxxam sampler with its shorter cane-shaped tube. Once the end of the tube is exposed to gas, the water will cascade through gas rather than water, causing significantly more turbulence in the water sample, which may help drive dissolved gases out of solution. Consequently, the Oak sampler may collect slightly more gas than the Maxxam sampler under identical conditions.

There are also several modified versions of the Oak and Maxxam samplers currently being used for sampling free gases for baseline water well testing in Alberta. Some practitioners have modified the Oak sampler by placing a plate directly under the end of the cane, thereby spreading the water out and making it more likely to degas (Magdich, personal communication, 2006). Some consulting companies design and manufacture their own flow-through cells that work on similar principals, but have different shapes and dimensions (Magdich, personal communication, 2006).

Maxxam and Oak flow-through cells method summary:

Gases tested: CH₄, N₂, Ar, O₂, CO₂

Type of results: compositional analyses, isotopic analyses

Accuracy of the technique: Not stated

Reproducibility of the technique: Not stated

Detection limit: Maxxam suggests 10 ppm (roughly 10 mg/L) for all gases

3.2 Dissolved Gas Samplers

3.2.1 Downhole Diffusion Samplers

Diffusion samplers generally contain a membrane that is permeable to gas, but not to water, where the inside of the membrane is filled with gas-free distilled water, or a gas other than the target of the analysis (e.g., Hesslein, 1976; Barber and Briegel, 1987; Chapelle et al., 1997). To collect the gas sample, the membrane is left in direct contact with the target water while dissolved gases diffuse to the area of lower concentration inside of the sampler (e.g., Hesslein, 1976; Sanford et al., 1996; Jacinthe and Groffman, 2001). Once equilibrium is reached between the dissolved gases outside of the sampler and the gases inside such that no further diffusion will occur, the dissolved gas concentration in the water can be calculated from the concentration of the target gas in the sampler using Henry's Law (Sanford et al., 1996; Jacinthe and Groffman, 2001):

$$C_g = C_w H_{cc}$$

where:

C_g = the concentration of the target gas in the free phase (on the inside of the sampler),

C_w = the concentration of the target gas dissolved in groundwater,

H_{cc} = a dimensionless temperature-dependent coefficient describing the partitioning of the gas between the dissolved phase and the free phase inside the sampler.

This type of diffusion sampler was originally developed to sample dissolved methane in pore water of lake sediments (Hesslein, 1976). The initial design used a type of clear acrylic plastic as the gas permeable membrane. Barber and Briegel (1987) later modified the sampler to obtain methane dissolved in groundwater from piezometers. Their sampler consisted of a gas permeable TFE Teflon tube with 0.4mm thick walls wrapped around a PVC pipe (Figure 5). The Teflon tube connects to a methane-impermeable Nylon II tube that runs through the PVC tube back to the surface where the gas is sampled. Peristaltic pumps were used to pump gas through the tubing and back to the surface. This apparatus required only 2 to 2.5 hours to equilibrate with the dissolved gas in the groundwater and air was used to purge the gas sampling line. Some disadvantages of this method include the complexity of the sampling apparatus, the relatively low precision of the obtained results, and the need to use a peristaltic pump. Also, some Teflon membranes have been shown to cause inaccurate results because gas can become trapped in the membrane itself (Chapelle et al., 1997). An advantage of the sampler is that the required time to equilibrate is comparatively short relative to most other downhole diffusion samplers.

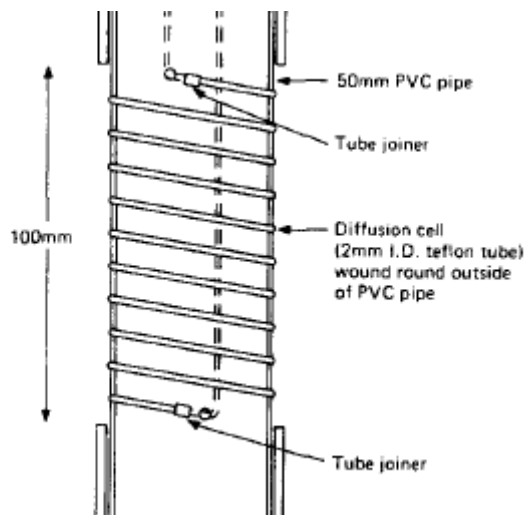


Figure 5: The design of Barber and Briegel's downhole diffusion methane gas sampler (slightly modified from Barber and Briegel, 1987).

Method summary: Barber and Briegel's downhole diffusion sampler

Gases tested: CH₄

Type of results: Compositional analysis (ppmv), not tested for isotopic analysis

Accuracy of the technique: Not stated
Reproducibility of the technique: $2\sigma = \pm 10\%$
Detection limit: 1.6 ppmv

A similar method for obtaining dissolved gases from groundwater described by Takahata et al. (1997) uses a gas-permeable polypropylene membrane attached by tygon tubing to a quadrupole mass spectrometer. To obtain a gas sample, vacuum is slowly applied to draw gas through the membrane to the mass spectrometer where the chemical and isotopic composition of the gas is measured. Unfortunately, the membrane causes some isotopic fractionation because light and heavy isotopes diffuse through the membrane at different rates, resulting in inaccurate isotope ratios. This method, however, eliminates errors associated with sample storage and transport since the analysis is performed directly in the field, and therefore provides chemical data rapidly. Major disadvantages are the complexity of the system of pumps and valves required to obtain the sample and the high cost of purchasing a quadrupole mass spectrometer.

Method summary: Diffusion sampler by Takahata et al. (1997)
Gases tested: CH₄, He, CO₂, O₂
Type of results: Gas composition (%), isotope ratios (biased)
Accuracy of the technique: Not stated
Reproducibility of the technique: Not stated
Detection Limit: Not stated

More recent research has focused on designing a diffusion sampler that is simpler to operate for obtaining reliable data on dissolved gases in groundwater. Jacinthe and Groffman's (2001) sampler consists of a PVC tube with an inflow and outflow valve, and a hollow gas-permeable silicone tube that is housed in the sampler (Figure 6). To collect a sample, water in the sampled well is allowed to flow into the sampler, where equilibrium is eventually reached between the gas inside the sampler and the dissolved gas in the groundwater over a period of several hours. Once equilibrium is achieved, the sampler is brought to the surface, and a gas sample is removed using a syringe introduced through a rubber septum at the top of the silicone tube. The gas sample is then transferred into a suitable container (see section 4) for transport to the laboratory. The sampler was found to perform well for methane concentration analysis (Jacinthe, personal communication). Jacinthe and Groffman (2001) also demonstrated that the silicone membrane does not compromise the accuracy of the results by trapping gas. This apparatus is simpler to use than the sampler designed by Barber and Briegel (1987), but care must be taken to avoid gas leaks when the sample is transferred from the silicone tube to an appropriate transport container.

Method summary: Diffusion sampler by Jacinthe and Groffman (2001)
Gases tested: CH₄, CO₂, N₂O
Type of results: Composition (µg/L), no isotope data
Accuracy of the technique: Tested by comparing to headspace analysis: $r^2 = 0.996$ for N₂O, $r^2 = 0.756$ for CO₂

Reproducibility of the technique: Not stated
Detection limit: 0.1 $\mu\text{g/L}$ for N_2O and CO_2

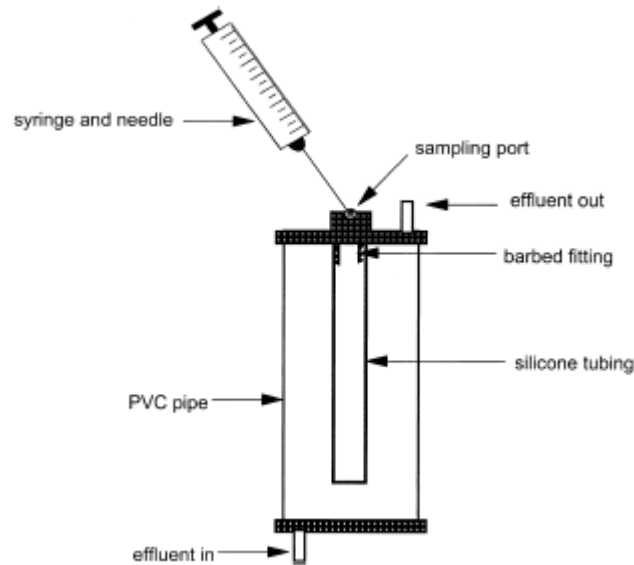


Figure 6: The Jacinthe and Groffman diffusion sample cell (Jacinthe and Groffman, 2001).

De Gregorio et al. (2005) recently developed a diffusion sampler to determine the chemical and isotopic composition of volcanic gases in Italy. Their sampler consists of a long tube of polytetrafluoroethylene (PTFE) gas-permeable plastic that is sealed at one end and attached to a glass sample-holder with stopcocks at the other end (Figure 7). To sample well water, the sample-holder is evacuated with a syringe and subsequently the stopcock between the sample-holder and the syringe is closed. Immediately before the sampler is lowered into the groundwater, the stopcock between the PTFE tube and the evacuated sample-holder is opened. After equilibrium is achieved between the gas in the sample-holder and the dissolved gas in the groundwater, the sampler is removed from the well and the stopcock between the sample-holder and the PTFE tube is closed to trap the gas sample. Laboratory tests involving the sampling of helium confirmed that this method accurately determines the isotopic composition of the sampled gas and the partial pressure of gases in the sampler, that can be used to determine the dissolved gas concentrations using Henry's Law. An important difference between this method and that of Jacinthe and Groffman (2001) is that the sample-holder is a part of the PTFE sampler, which minimizes the chance for user error when transferring the obtained gas sample into a storage vessel. A disadvantage of this method is that methane diffuses through PTFE very slowly (De Gregorio, personal communication) and hence long sampling periods are required.

Method summary: Diffusion sampler by De Gregorio et al. (2005)

Gases tested: CH_4 , CO_2 , O_2 , N_2

Type of results: Partial pressure (atm), also used for isotope ratios

Accuracy of the technique: No exact values given, CO₂ partial pressure compares favorably to theoretical value calculated using PHREEQC software
Reproducibility of the technique: Field duplicates generally vary by less than 5% for all gases
Detection limit: CH₄ = 0.02 atm CO₂, O₂, N₂ = 0.01 atm

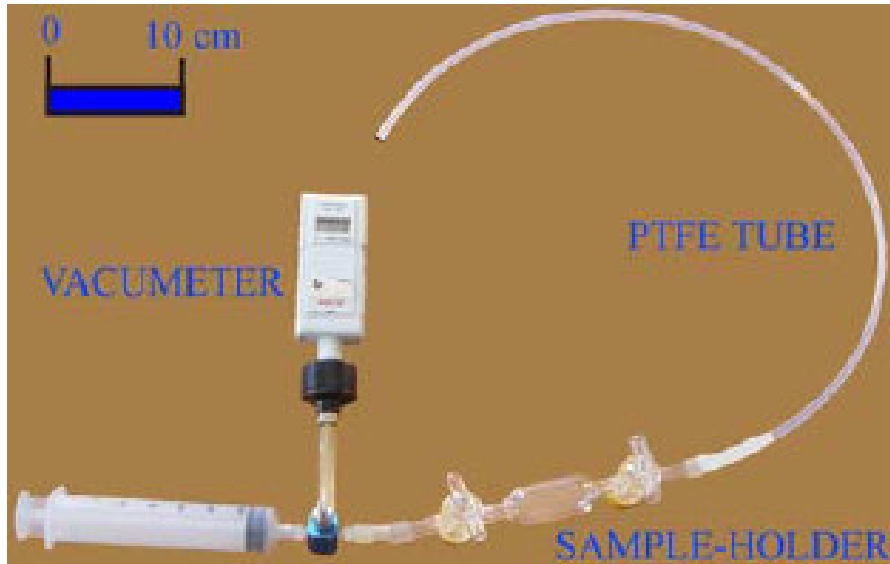


Figure 7: The PTFE sampling device and the vacuumeter that is used to control the evacuation process before the sampler is deployed into groundwater (De Gregorio et al., 2005).

3.2.2 *Non-Diffusion Downhole Samplers*

Not all downhole samplers rely on diffusion through a membrane to separate dissolved gases from the liquid phase. Some sampling devices use a system of valves controlled at the surface to trap water together with its dissolved gases once it has infiltrated the sampler (e.g., Lollar et al., 1994; Chapelle et al., 1997; Yager and Fountain, 2001; Van Stempvoort et al., 2005). Other samplers use a syringe that is lowered into the well to collect water and its dissolved gases (e.g., Simpkins and Parkin, 1993; Taylor et al., 1998). Once the water sample has been obtained, the gas must be separated from the liquid phase either in the field or in the laboratory (see section 3.3).

A downhole sampler designed for sampling from deep narrow boreholes was described by Nurmi and Kukkonen (1986). Their sampler consists of a long, narrow polyamide tube with a backpressure valve at the lower end (Figure 8). Water enters the sampler as it is lowered into the aquifer, theoretically preserving the vertical profile of the water in the borehole. The sampler comes in 50 m sections, each containing a shut off valve. The sections are added one at a time with the valves open as the sampler is lowered into the borehole. After the fluid in the borehole has been sampled, the tube is brought back to the surface. The shut off valve at the end of each pipe section is closed as it reaches the surface. If free gas is present, it rises to the top of the 50 m section, where it can be

sampled through a tube that is connected to the shut off valve. Once free gas has been sampled, aliquots of the groundwater with its dissolved gases are transferred from each 50 m section into storage containers for transportation back to the laboratory. This sampler was designed for very deep wells. It is not ideal for shallow groundwater wells since it is very bulky and difficult to transport. Also, during transfer of water samples to transport containers dissolved gas may be subject to atmospheric contamination.

Method Summary: Downhole sampler for deep wells by Nurmi and Kukkonen (1986):

Gases Analyzed: CH₄, Ar, N₂, H₂, O₂, CO₂, CO

Type of Results: Gas composition in percentage, not used for isotope ratios

Accuracy of the technique: Not stated

Reproducibility of the technique: Not stated

Detection Limit: Not stated

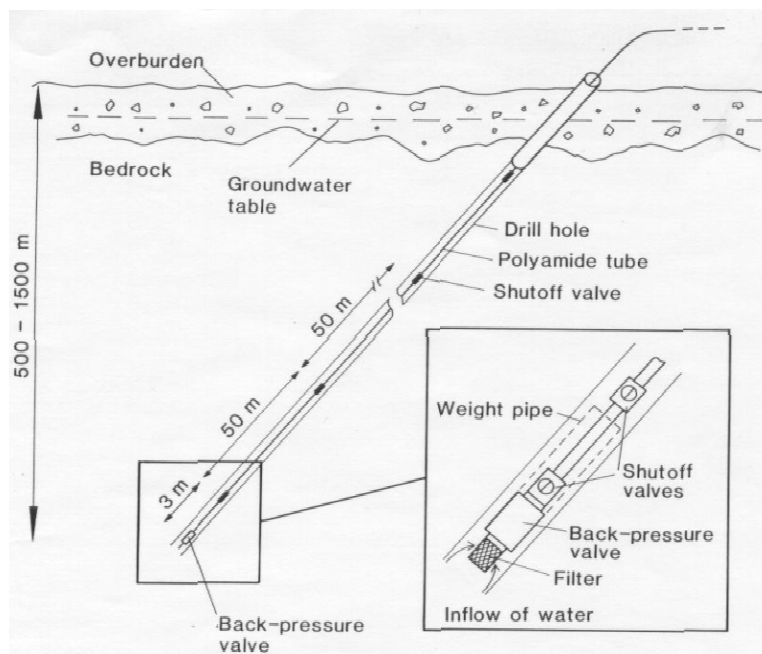


Figure 8: The downhole sampler used by the Finnish Geologic Survey for sampling deep groundwaters showing a close up of the bottom section of the sampler (Nurmi and Kukkonen, 1986).

Johnson et al. (1987) developed an alternate method for obtaining in situ samples from groundwater in narrow-diameter wells. Their sampler consists of five different sections that are silver-soldered together to form a single unit (Figure 9). At the bottom, the sampler contains a quartz pre-filter with a check valve attached to a sample container with a crimping section on each side. The sampler also contains an optional inflatable packer. A gas line that runs to the surface controls the pressure inside the sample reservoir. After the well has been purged, 1 mL of sample preservative is placed into the sample container and the sampler is lowered. Once the sampler has reached the desired sampling depth, a control on the surface is used to apply a slight vacuum to the sample container. This causes the groundwater sample to flow into the container. Once the

sampling volume is filled, positive pressure is applied forcing the check valve to close. The sampler is then returned to the surface where it is disconnected from the line, crimped shut, and capped for transport to the laboratory.

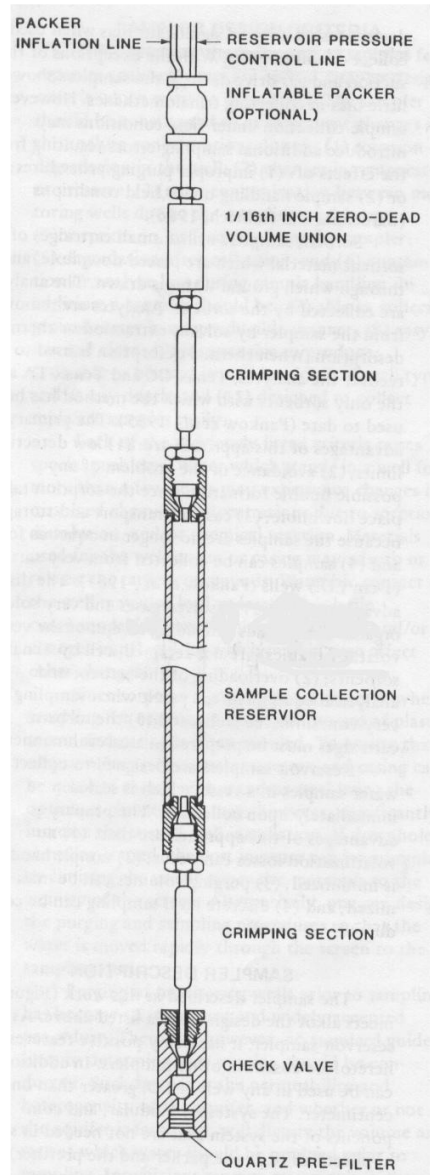


Figure 9: The various sections of the downhole sampler described in Johnson et al. (1987).

A major advantage of this sampler is that it traps the sample at depth in a proper storage container, which minimizes the probability of the sample being altered or contaminated during transfer to storage containers at the surface. Unfortunately, it is impossible to remove the sample container from the sampling unit itself. Hence, several samplers would be needed to sample multiple wells. It is also possible that the vacuum applied on the groundwater sample may cause it to degas, thereby reducing the accuracy of the

dissolved gas analyses. No data were reported describing any tests performed on this sampler.

Dubord (1992) designed a device to sample dissolved gases from deep boreholes while keeping the sample at formation pressure during its ascent to the surface. The sampler consists of an external casing covering a syringe and plunger assembly and a stainless steel tube with valves on each end to collect the groundwater. To obtain a sample, the apparatus is lowered down the borehole until it is about 5 m above the desired sampling depth. At this point, it is allowed to drop for the last 5 m. After the sampler has dropped to its final position, a chord is tightened causing the water sample to be drawn into the syringe. Once the syringe is full, the weight of the sampler activates the valves, causing them to shut. The sampler is subsequently brought back to the surface, and the sample container is removed. The sampler uses Nupro valves to prevent gas leakage under elevated pressures. The major strength of this sampler is that it can operate under high pressures while preventing gas from leaking. Unfortunately, the sampler is quite small and may not yield a large enough sample for isotopic analyses if methane concentrations are low. It may also be difficult to accurately sample a desired depth interval because it may be difficult to control how far the sampler falls before it snaps shut. No data on the precision, accuracy, or applications of the sampler were available.

A sampling apparatus used by Simpkins and Parkin (1993) consists of a 20 mL syringe connected to a vacuum line. Once the syringe is lowered into the groundwater, the sampler is purged and vacuum subsequently is applied, which causes the plunger in the syringe to rise, capturing the water sample. The filled syringe is immediately brought to the surface, and the collected water is injected into a crimped pre-evacuated glass vial for headspace analysis (see section 3.3.1). One advantage of this method is that the sample is rapidly transferred into a storage container in a way that minimizes chances for contamination. Disadvantages of this sampler are that it can only be used for small sample volumes, it may yield inaccurate results for high total suspended solids groundwater, and it has been shown to be inaccurate for sampling volatile organic compounds (EPA, 2006).

Method Summary: Downhole syringe sampler by Simpkins and Parkin (1993)

Gases tested: CH₄

Type of results: Chemical (mg/L) and isotopic composition

Accuracy of the technique: Not stated

Reproducibility of the technique: Not stated

Detection Limit: 0.001 mg/L

Taylor (1996) designed a downhole sampling device capable of working effectively in very low permeability aquifers. It consisted of a weighted outer cylinder with a flexible bottom end (the sampler foot) with a needle attached to it, and an evacuated sample container with a septum (Figure 10). A biocide was first added to the sample bottle to preserve the sample, and subsequently the sampler was lowered to the bottom of the piezometer with a winch. After reaching the bottom, the sampler foot is pushed towards the top of the sampler, forcing the needle to pierce the butyl septum of the sample

container. The difference in pressure between the inside of the evacuated sample container and the surrounding well water forces water and dissolved gas into the container. It takes 5-10 minutes to ensure that the sample container has been properly filled. Subsequently, the sampler is winched back to the surface. As the sampler leaves the bottom of the piezometer, a spring forces the needle out of the septum, thus sealing the sample in the container. At the surface, the sample container is removed for transport and storage prior to chemical and isotopic analyses, and replaced with a new container for the next sampling event. This sampler is easy to operate, relatively cheap, and has the advantage that it rapidly traps the sample in an appropriate storage container at formation pressure. The weight of the sampler and the fact that it needs at least one winch to operate make it somewhat difficult to transport.

Method summary: Downhole sampler by Taylor (1996)

Gases Tested: CH₄

Type of Results: Chemical composition (μmol/L), not tested for isotope ratios

Accuracy of the technique: Not stated

Reproducibility of the technique: Not stated

Detection Limit: On the order of 0.007 μmol/L

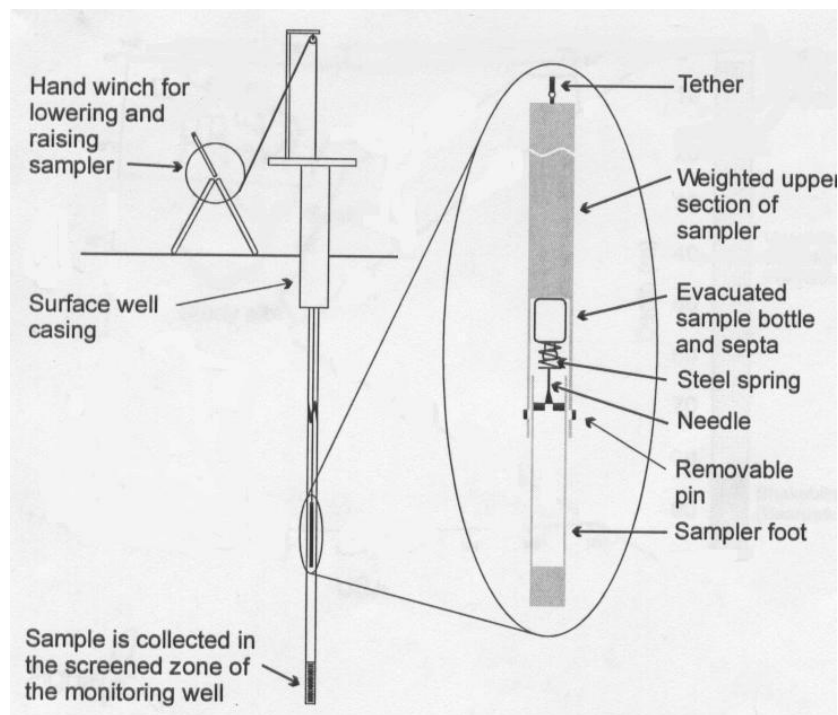


Figure 10: The downhole syringe sampler described by Taylor (1996), showing the internal structure of the sampler as well as the winch used to operate it.

Yager and Fountain (2001) described a simple in situ water sampling technique where water is collected in a stainless steel Westbay sampler under hydrostatic pressure. The sampler is evacuated at surface using a hand pump, and then lowered into the well. Once it reaches sampling depth, the sampler is opened from the surface to allow water to enter.

After the sample is collected, the sampler is closed from the surface to trap the sampled water and its free and dissolved gases, and brought back out of the well. At the surface, the sample container is attached to a Tedlar bag (see section 4) and opened. The drop in pressure forces the sample to degas rapidly into the bag. Advantages of this method are its simplicity and the speed at which samples can be collected. A disadvantage is the possibility of user error when transferring the gas sample into the Tedlar bag, which may lead to gas leakage or contamination.

Method summary: Downhole sampler by Yager and Fountain (2001)

Gases tested: CH₄, C₂H₆

Type of results: Chemical composition (mg/L), not tested for isotope ratios

Accuracy of the technique: Not stated

Reproducibility of the technique: Not stated

Detection Limit: ~1 mg/L CH₄, 0.1 mg/L C₂H₆

Lollar et al. (1994) developed a complex downhole gas sampler to obtain gas-containing water samples from narrow-diameter boreholes (Figure 11).

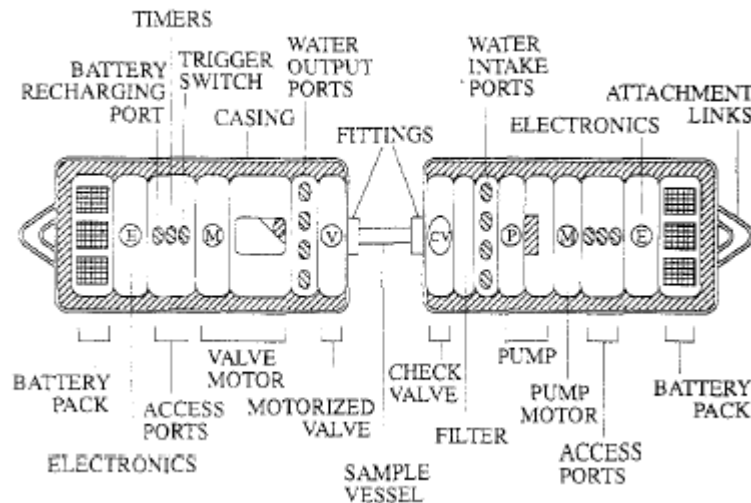


Figure 11: The Lollar et al. (1994) automated sampler, showing the complexity of the equipment.

The sampler is electronically controlled according to a timing sequence that is initiated from the surface. It is lowered to the groundwater with its valve open. Once it is in the water, a pump flushes the inside of the sample container with water eliminating any atmospheric contamination. Once the pump has stopped, a check valve closes automatically, trapping a 200 mL gas-containing water sample at the in-situ pressure. Subsequently, the valves on the sample container are shut, the container is brought back to the surface, and it is shipped to the laboratory for chemical and isotopic analyses. In the laboratory, a high vacuum extraction line is connected to the sample container to remove the gas, and the container is subjected to ultrasonic agitation to ensure complete

gas removal. The amount of gas removed from the sampler is measured, and the chemical composition of the gas is analyzed using a gas chromatograph (see section 5.1). This sampler is automated and hence relatively easy to operate, and obtains the sample at hydrostatic pressure while ensuring that degassing of the sample does not occur. The major disadvantage of this sampler is that it contains complex electronics that may be difficult to maintain in the field, and that it only allows to obtain one sample.

Method Summary: Downhole sampler by Lollar et al. (1994)

Gases tested: CH₄, N₂, O₂, H₂

Type of results: Total dissolved gas (mL gas/kg), isotopic composition

Accuracy of the technique: Not stated

Reproducibility of the technique: <5% volume gas/mass liquid

Detection Limit: Not stated

Another established sampling technique developed for isotopic analysis of dissolved noble gases is sampling groundwater with its dissolved gases downhole in a long narrow copper tube at aquifer pressure and to crimp the sampling tube using a valve operated from the surface (Andrews et al., 1985; Beyerle et al., 2000; Stute and Schlosser, 2000). After retrieving the copper tube from the aquifer, it is transported to the laboratory where it is directly connected to a gas line and ultra-pure helium is pumped through the sampler to initiate a gas-stripping process (e.g., Beyerle et al., 2000). The obtained gas is then used for chemical and isotopic analysis.

Method Summary: Copper Tube Sampling Technique

Gases tested: H₂, Kr, Ar, Xe, Ne, He

Type of results: Chemical composition

Accuracy of the technique: Mean % composition; Error – He = 0.5, Ne = 0.95, Ar = 0.77, Kr = 1.01, H₂ = 2.9

Mean % isotope ratio error - ³He/⁴He = 0.55, ²⁰Ne/²²Ne = 0.19, ⁴⁰Ar/³⁶Ar = 0.09

Reproducibility of the technique:

Composition: H₂ = 2.7%, He = 0.3%, Ne = 0.9%, Ar = 0.3%, Kr = 0.8%, and Xe 1.0 %

Isotope Ratios: ³He/⁴He = 0.7%, ²⁰Ne/²²Ne = 0.3%, and ⁴⁰Ar/³⁶Ar = 0.2%

Detection Limit: On the order of ppmv

3.2.3 *Inverted Bottle Method for Dissolved Gas*

In situations where lowering of sampling devices into a water well is not an option, groundwater samples for dissolved gas analyses must be obtained at above-ground access points. Depending on the aquifer pressure and the sampling setup this may cause alterations in the determined concentrations of dissolved gases, but is unlikely to affect its isotopic compositions. To obtain reproducible results in these situations, it is important to keep sampling procedures as consistent as possible.

A very simple approach for dissolved gas sampling is the inverted bottle method. The sampling apparatus for this method consists of an inverted bottle used for volatile organic analysis (VOA) that is filled with sample water while submerged in a pail full of the same

sample water. The bottle is lowered into the water-filled bucket and un-capped under water using gloved hands. A standpipe attached to a hose that leads to the well is inserted into the water-filled pail and inserted into the inverted bottle (Figure 12). The bottle is purged with a minimum of two bottle volumes. The bottle is then filled with groundwater and the standpipe is slowly removed from the inverted bottle. Subsequently, the bottle is closed without headspace using a septum or screw cap while it remains submerged in the bucket. For chemical analysis, 40 mL bottles are typically used. For isotope analyses bottle sizes between 125 and 1000 mL are more appropriate. This method is simple and does not require expensive equipment, but it is possible that samples may degas somewhat while they are pumped to the surface. After obtaining the sample, the static headspace equilibrium technique is used either in the field or in the laboratory to achieve equilibrium between gas dissolved in the water sample and an added inert headspace gas to determine the concentration and isotopic composition of dissolved gases in the groundwater sample (see section 3.3 for further details).



Figure 12: Sampling groundwater and its dissolved gases in an inverted 1-L Boston round bottle for subsequent extraction and chemical and isotopic analyses (photograph provided by Dr. A. W. Gorody, Universal Geoscience Consulting, Inc., Houston, Texas: from Gorody, 2006).

3.2.4 *Bubble strip method*

The bubble strip method is similar to flow-through cell methods for free gas sampling in that the water is pumped continuously through a sampler on the surface. The method relies on equilibrium between an inert gas phase in the sampler and the gas dissolved in the water sample. Well water is pumped through a 250 mL glass bulb with a rubber septum, usually at 200-600 mL per minute (Chapelle and McMahon, 1991). After thoroughly flushing the bulb with sample, a predefined volume of an inert gas is injected through the septum into the bulb to form a headspace (Figure 13). The agitation caused by the water being pumped through the bulb facilitates the achievement of equilibrium between the headspace gases and the dissolved gas in the sample. Equilibrium is achieved

more rapidly with a smaller gas bubble and a faster pumping rate (Chapelle and McMahon, 1991; Chapelle et al., 1995). Once equilibrium has been reached, a syringe is inserted through the septum and a portion of the headspace gas is removed for chemical and isotopic analysis. The concentrations of dissolved gases are subsequently calculated using Henry's law (see section 3.3.1). This method has commonly been used to sample hydrogen (Chapelle and McMahon, 1991; Vroblesky and Chapelle, 1994; Lovely et al., 1994; Chapelle et al., 1995; Chapelle et al., 1996). It has also been used to sample methane from groundwater (Kampbell et al., 1998; Skubal et al., 2001).

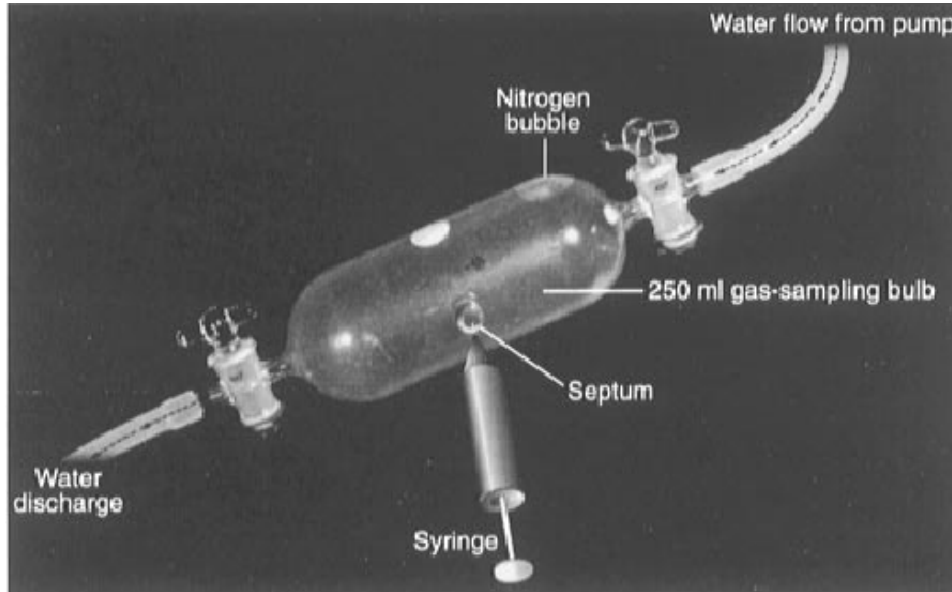


Figure 13: An example of a sampling bulb used in the bubble strip method with the syringe used for removing the gas sample (from Chapelle et al., 1997)

There are a number of variations on this method reported in the literature with respect to the type of headspace gas used, volume of headspace, and pumping rate. No specific information was given on the precision of this method, but Skubal et al. (2001) reported that methane concentrations as low as 75 micromoles/L were detectable. Kampbell et al. (1998) reported that methane equilibrates with a 20 mL headspace in about 10 minutes if a pumping rate of 400 mL/minute is used at 4°C.

Method Summary: Bubble Strip Method

Gases tested: CH₄, H₂, Vinyl Chloride

Type of results: Chemical composition (by volume, or mol/L)

Accuracy of the technique: Compared favorably to downhole sampler, no exact numbers given (Chapelle et al., 1997).

Reproducibility of the technique: Not stated

Detection Limit: ~0.1 nmoles/L H₂, 10 µmol/L CH₄

Microseeps Laboratories (Pittsburgh, Pennsylvania, USA) commercially manufactures a bubble strip sampling cell called the Gas Stripping Cell (Figure 14). The first step in operating the Gas Stripping Cell is to attach the cell's inflow tube to the wellhead. Water is then pumped through the cell and the flow rate through the cell is measured. Once the flow rate has been established, a syringe is used to inject 20 mL of an inert gas through the replaceable septum, creating a gas bubble in the sampler. The dissolved gas in the water sample is then allowed to equilibrate with the gas bubble for a period of time. The amount of time required for equilibration depends on the rate at which water is pumped through the sampling cell (Microseeps, 2006). Equilibrium is achieved in as little as 10 minutes if the sample is pumped through the cell at 300 mL/min, and as long as half an hour if the flow rate is between 100 and 120 mL/minute. Once the system has reached equilibrium, the syringe is used to collect a sample from the gas headspace. The gas sample is stored in a glass vial with a butyl septum for subsequent chemical and isotopic analysis. The concentrations of dissolved gases are subsequently calculated using Henry's law (see section 3.3.1). The sample cells are available from Microseeps (Pittsburgh, Pennsylvania, USA) at a price of circa US \$50 (Unrue, personal communication, 2006).

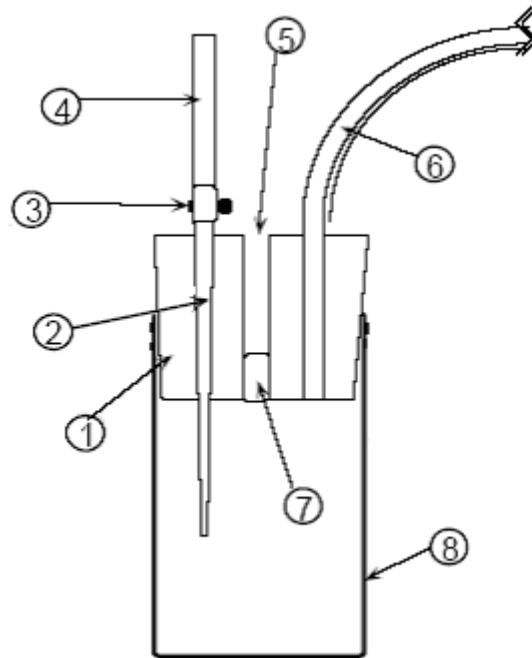


Figure 14: A cross-section of Microseeps Gas Stripping Cell. The parts of the cell are: 1. Housing Cover; 2. Jet spray nozzle; 3. Nylon tube; 4. Inlet Tube; 5. Needle guide port; 6. Drain tube; 7. Replaceable septum; 8. Glass housing (Microseeps, 2006).

Method Summary: Microseeps Gas Stripping Cell

Gases tested: CH₄, H₂, C₂H₆, Ethene, and CO₂

Type of results: Chemical composition (mass per volume)

Accuracy of the technique: Not Stated

Reproducibility of the technique: Not Stated

Detection Limit: Not Stated

3.3 Laboratory Techniques for Separating Dissolved Gas from Water Samples

Once groundwater samples with their dissolved gases are obtained, the dissolved gas must be separated from the water sample before chemical and isotopic analyses can be conducted. This is usually achieved with the static headspace equilibration technique.

3.3.1 Static Headspace Equilibrium Techniques

Water samples subject to the headspace equilibration technique are usually obtained either by pumping water directly into a sample bottle as described in section 3.2.3 (e.g., Murray and Beck, 1992; Chafin et al., 1996; Blicher-Mathiesen et al., 1998), or by using a downhole sampler as described in section 3.2.2 (e.g., Simpkins and Parkin, 1993; Taylor et al., 1998). Equilibrium between gas dissolved in a water sample and a headspace phase is a common method to remove dissolved gas from groundwater for chemical and isotopic analysis (e.g. Kampbell and Vandegrift, 1998; EPA, 2001; Amos et al., 2005). The gas separation can be performed either in the field or in the laboratory (Smith et al., 1991; Amos et al., 2005).

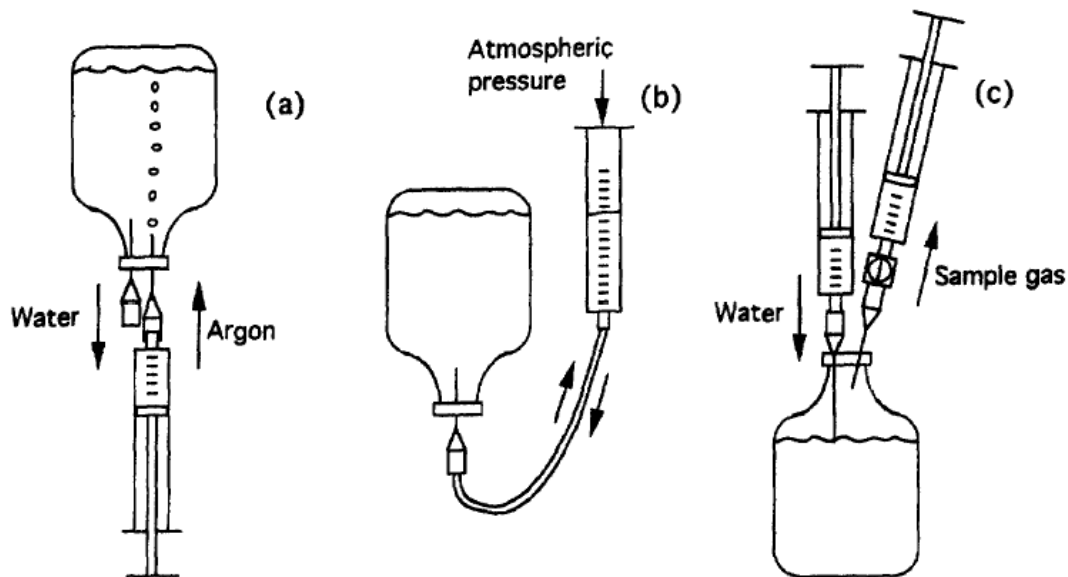


Figure 15: An example of a headspace equilibrium procedure showing a) the injection of the headspace gas, b) the restoration of atmospheric pressure in the sample container, c) the removal of the sample gas (from: Capasso and Iguaggiato, 1998).

The most widely used procedure for headspace extraction relies on equilibration of the dissolved gas in the water sample with an inert gas such as argon, nitrogen or helium (e.g., Revesz et al., 1995; Capasso and Iguaggiato, 1998; Kampbell and Vandegrift, 1998; EPA, 2001; Inguaggiato and Rizzo, 2004). First a sample is gathered with no headspace

in a glass container with a rubber septum (see section 3.2.3). Next, a syringe filled with inert gas is injected into the container, while an empty syringe is simultaneously injected to remove the water that is displaced by the gas, thereby keeping the sample at atmospheric pressure (Capasso and Iguaggiato, 1998; Figure 15). The sample container is then shaken typically between 5 and 60 minutes until equilibrium is reached between the headspace gas and the dissolved gas. Once equilibrium is achieved, a gas sample is extracted with a gas-tight syringe from the headspace and chemical and isotopic measurements are performed. The dissolved gas concentration in the water sample is calculated from the concentration in the gas phase using Henry's Law (EPA, 2001). There are many variations of this technique with different headspace gases, different ratios of headspace to liquid volume, and different equilibration times (Table 1). It is important that contamination with atmospheric gases is avoided (Iguaggiato and Rizzo, 2004), that sufficient time is allowed to achieve equilibrium between dissolved gases in the water sample and the headspace gas, that volumes of the gas and liquid phases are recorded precisely (Johnson et al., 1990), and that at least 4 appropriately spaced working standards are used (EPA, 2001). If these criteria are met, concentrations of dissolved methane of less than 1 mg/L can be determined with a reproducibility of less than $\pm 30\%$ (EPA, 2001).

Variations of the above described procedure include methods where the sample bottle is not completely filled with the water sample, thereby leaving headspace in the sample container, eliminating the need for inert gas injection (e.g., Heaton and Vogel, 1981; Smith et al., 1991; Murray and Beck, 1992; Chafin et al., 1996). The sample container is either pressurized with an inert gas prior to sampling and then connected to the wellhead and filled with the water sample until a desired volume of headspace remains (Murray and Beck, 1992), or evacuated before being partially filled with the water sample (Smith et al., 1991; Chafin et al., 1996). With these approaches it is, however, difficult to guarantee that the sample is kept at atmospheric pressure, and it is also problematic to measure the volumes of the liquid and the headspace accurately. This compromises the accuracy of the required calculations to determine concentrations of dissolved gases reliably.

Table 1: A summary of different types of static headspace analysis methods.

Paper	Sampling Method	Sample Container Volume (mL)	Ratio of Water Volume to Host Gas Volume	Detection Limit	Precision	Accuracy	Headspace Gas	Equilibration Time (Minutes)	Equilibration Method	Gases Sampled
Inguaggiato and Rizzo, 2004	N/A	N/A	121	He: 0.001 ppmv Ne: 0.01 ppmv	RSD He: 1.4% Ne: 1.75%	N/A	N/A	10	Ultrasonic Bath	He, Ne, I
Kampbell and Vandegrift, 1998	Pumped to surface	60	9	Methane 0.001 mg/L; Ethane 0.002 mg/L; Ethene 0.003 mg/L	RSD Methane: 3.25%; Ethene: 7.5%	N/A	He	5	Rotary Shaker	Methane, Ethane, Ethene
Capasso and Inguaggiato, 1998	N/A	122	11.2	CO, He: ~0.1 ppmv Methane: ~2 ppmv O ₂ , N ₂ , CO ₂ : ~0.1%	CO ₂ : 2-5%	N/A	Ar	5	Manual Shaking	Methane, CO ₂ , O ₂ , N ₂ , CO
Amos et al. 2005	Pumped to surface using positive displacement pump	500	32.33	Methane: 0.1 mg/L	RSD O ₂ : 3.4% N ₂ : 3.2% Ar: 2.1%	Ar: -2.1%, N ₂ : 3.4%, O ₂ : -3.2%	He	N/A	N/A	Methane, CO ₂ , N, O, Ar (only tested for last 3)
Smith et al. 1991	Pumped to surface using peristaltic pump	50	0.66	N/A	N/A	N/A	N/A	N/A	N/A	Methane
Revesz et al. 1995	N/A	500	9	0.0008 mg/L	N/A	N/A	N ₂	N/A	Shaking	Methane, I

Paper	Sampling Method	Sample Container Volume (mL)	Ratio of Water Volume to Host Gas Volume	Detection Limit	Precision	Accuracy	Headspace Gas	Equilibration Time (Minutes)	Equilibration Method	Gases Sampled
Murray and Beck, 1992	Pumped to Surface	18900	N/A	0.1 mg/L	N/A	N/A	N ₂	N/A	N/A	Methane
Chafin et al. 1996	Pumped to Surface	43	1.15	0.005 mg/L	N/A	N/A	Air	N/A	Shaking	Methane
Barker and Fritz, 1981b	Downhole Syringe Sampler	50	0.66	N/A	N/A	N/A	He	N/A	Shaking	Methane, CO ₂ , I
Heaton and Vogel, 1981	Pumped to surface	500	0.66	N/A	N/A	N/A	Vacuum	N/A	N/A	Ar, N ₂
Heaton et al. 2005	Pumped to surface	500	4	Methane: 0.05 parts per thousand (volume) O ₂ :0.01 ppthv	N/A	N/A	Vacuum	N/A	N/A	Methane, N ₂ , Ar, I
Walsh and McGlaughlin, 1999	Pumped to surface	5	19	0.1 mg/L	RSD 1.0%	2.90%	Air	780	Mixed, left at room temperature	Methane

Notes:

- N/A indicates that it was not mentioned in the literature, and the **bold I**, in the gases sampled column, indicates that it was used to analyze isotopic composition.
- RSD stands for relative standard deviation

3.3.2 Vacuum-Ultrasonic Method

The vacuum-ultrasonic method constitutes an alternative to gas stripping methods (3.2.4) or to the headspace equilibration technique (3.2.3 and 3.3.1). This method uses vacuum combined with ultrasonic agitation to separate dissolved gas from the water in which it was dissolved (Lammers and Suess, 1994). This method was originally designed by Schmitt et al. (1991) to sample methane gas dissolved in ocean water and was later modified slightly by Holt et al. (1995) to be used for groundwater sampling. In this method the sample bottle is placed in a water bath at room temperature (or slightly higher) and subject to ultrasonic agitation. The gas is released to the headspace of the sample bottle by ultrasound agitation while vacuum is applied to carry the released gas to a part of the apparatus where it can be removed via a syringe through a septum (Figure 16). An advantage of the vacuum-ultrasonic method is that it does not require the use of an ultrapure carrier gas. A disadvantage of this method is that ultrasonic agitation may break down C_2 to C_6 hydrocarbons if it is applied for an extended period of time (Schmitt et al., 1991).

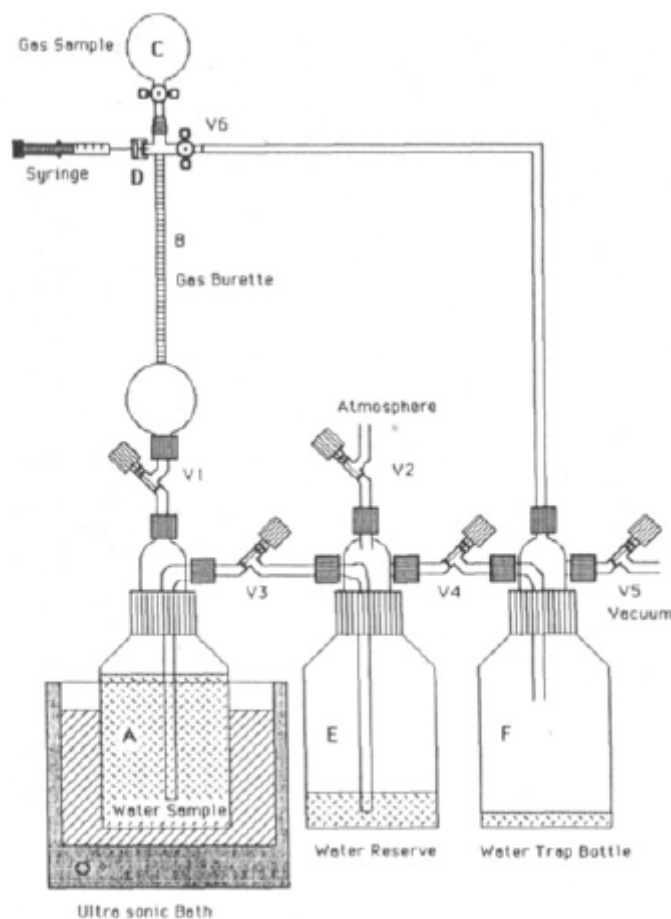


Figure 16: An example of a vacuum-ultrasonic apparatus from Schmitt et al. (1991), V1-V5 indicate the various valve positions.

Method Summary: Vacuum-ultrasonic method after Holt et al. (1995)

Gases tested: CH₄, CO₂

Type of results: Chemical composition (mol/L), stable isotope ratios

Accuracy: Not tested

Reproducibility of the technique: Relative standard deviations – CH₄ = 4.4%, CO₂ = 4.1%

Detection Limit: 0.1 micromoles for methane and CO₂

3.4 Applicability of Sampling Methods to the Baseline Water Well Testing Program

Sampling techniques and requirements for obtaining free gas, and possibly dissolved gas, for the Alberta Environment well water testing program must be comparatively simple while ensuring reliable and accurate results. Due to liability issues related to removing pump assemblies or other well installations, sampling is in most cases restricted to above-ground access points, essentially eliminating downhole sampling devices.

For sampling of free gas for chemical and isotopic analyses, the inverted bottle technique (3.1.1) and flow-through cells (3.1.3) appear to be two suitable methods. Flow-through cells are relatively simple to operate and they separate the gas from the water sample. They are easy to connect to a pump or a sampling hose and, therefore, represent a very practical approach to sampling free gas in groundwater wells. A matter of concern, however, is the lack of uniformity in their design (Magdich, personal communication 2006). Different sampling cells may yield different gas concentrations for the same groundwater because their shapes may be more or less conducive to degassing. Browne (2004) found that his flow-through design removed circa 15% of gases dissolved in water that had been equilibrated with the atmosphere at standard atmospheric temperature and pressure. The manufacturers of flow through cells in Alberta have not determined what percentage of the dissolved gas phase in a water sample remains in solution after the sample has passed through the cell. A further complication in the use of flow-through cells for free gas sampling is that the flow capacity of the cell is often insufficient to handle the discharge from pumping domestic water wells (Jones, personal communication, 2006). In these cases pumping from a well forces water into the cell faster than it can leave it, causing a pressure build-up inside the sampling cell. Some consultants deal with this situation by placing a constriction valve on the line from the well to the sampler to limit the flow rate going into the cell (Jones, personal communication, 2006). This eliminates the pressure build-up inside the cell and makes degassing more likely to occur. More commonly, consultants place a T-junction on the hose between the wellhead and the sampler. After the junction, one portion of the hose goes to the sampler, while the other portion by-passes the sampler. This also reduces pressure buildup inside the sampler, but may affect gas results (Blyth, personal communication, 2006; Jones, personal communication, 2006).

Sampling dissolved gases offers the opportunity to determine the isotope ratios of methane, higher alkanes, and CO₂ for water samples that do not yield a free gas sample. To determine the chemical and isotopic composition of dissolved gases in groundwater, the inverted bottle method

(3.2.3) followed by a headspace equilibrium technique (3.3.1) constitutes a simple and effective analytical method, as long as the analytical requirements are carefully observed (e.g. Gorody, 2007). The bubble strip method (3.2.4) offers an alternative technique for separating the dissolved gas phase from the liquid phase in the field. Sampling dissolved gases with the static headspace method, however, requires far less time and effort in the field than using the bubble strip method (e.g. Amos et al., 2005). Possible errors in the determination of the gas and liquid volumes in the bulb or changes in headspace volume due to excessive degassing of the sample may further limit the precision and accuracy of the bubble strip method (Chapelle, Personal Communication, 2006).

Pressure and temperature changes are known to affect gas solubility. If sampling is restricted to above-ground access points, pumping-induced pressure changes may affect the determined dissolved gas concentrations due to degassing during the pumping process (e.g., Yager and Fountain, 2001) partly due to agitation during the pumping process and partly due to pressure changes acting on the gas (e.g., Taylor, 1996; Browne, 2004). Although this effect is often assumed to be small for shallow groundwater, it is suggested that the effect of pumping-induced pressure changes on the concentration of dissolved gases in shallow groundwater in Alberta be evaluated by future research. This could be achieved by determining the concentrations of dissolved gases such as methane, ethane, and CO₂ in shallow groundwater sampled from selected wells using (a) downhole samplers and (b) groundwater obtained from above-ground access points using the inverted bottle method and the headspace equilibrium technique, followed by a comparison of the obtained results.

4.0 SAMPLE TRANSPORTATION AND STORAGE

After selecting a suitable method to reliably sample free or dissolved gases from groundwater, it is equally important to use transport and storage containers and procedures that ensure the integrity of the samples prior to analyses in the laboratory. Ideal storage methods will prevent gas leakage, chemical conversions of the compounds of interest, and degradation of the sample due to microbial processes.

4.1 Free Gas Samples

Since free gas samples are not usually in contact with a water sample during storage, the main criteria for such samples are leak-tight containers and prevention of chemical conversions of the gas components of interest. Commercially available electro-polished stainless steel air sampling canisters are highly suitable for this purpose (e.g. Restek, Bellefonte, PA, USA). Such evacuated canisters are easy to fill, they do not leak, and the electro-polished or otherwise treated surfaces make chemical reactions within the storage container highly unlikely. Repeated concentration measurements have shown excellent chemical stability of free gas samples over periods of a month or longer. Typically, analyses should be completed within a month of the sampling date, and within a week if H₂S is present (G. Prill, personal communication). The cost of these containers is significant (circa \$500 a piece), but they can be re-used almost indefinitely (unless the interior coating breaks down) thereby offsetting the initial costs with time.

An alternate option to store free gas for concentration and isotope analyses of methane and other compounds is the use of so-called Tedlar bags (e.g. Yager and Fountain, 2001). These bags made of 2 mil PVF (Tedlar) film with a sampling septum directly incorporated into the (polypropylene or stainless steel) valve are quite durable and considered inert to a wide range of compounds. They have gained widespread popularity, partially because of their comparatively low cost. Tedlar bags are designed for gas storage periods of the order of days, rather than months or years. Gas-filled Tedlar bags sometimes deflate somewhat during transport and storage, indicating that occasional leakage problems do occur, presumably due to the preferential loss of low molecular weight gases. FlexFoil grab bags are an alternate product for storing methane and other short-chain hydrocarbon samples. This foil material is stronger than Tedlar. The bags have strong evenly sealed seams and have been tested to keep methane concentrations constant for at least four days (Dowis and Coyne, 2005). FlexFoil bags and black Tedlar bags both protect against photodegradation of light-sensitive compounds. When Tedlar or FlexiFoil bags are used for sample transport and storage it is recommended to conduct the required chemical and isotopic analyses in the laboratory as soon as possible, and not to re-use the sampling bags.

Another option for transporting and storing of gas samples for subsequent chemical and isotopic analyses is to store the gas samples in glass vials capped with suitable septa (e.g. Jacinthe and Groffman, 2001; Browne, 2004). Care must be taken in choosing an appropriate septum since some types of rubber (e.g. Teflon-coated silicone) are permeable to light hydrocarbons (EPA 2001). The most commonly used stopper material is gray butyl rubber. According to the EPA (2001), short-chain hydrocarbon samples can be stored in vials with gray butyl stoppers for up to

two weeks, although Kiene and Capone (1985) found that within less than 24 hours small amounts of methane (~1.6%) may be absorbed by a butyl rubber stopper.

4.2 Dissolved Gas Samples

For analysis of the chemical and isotopic compositions of dissolved gases, water samples are typically stored in glass vials or bottles without headspace capped by a suitable septum (e.g. Johnson et al., 1990; Simpkins and Parkin, 1993; Revesz et al., 1995; Blicher-Mathiesen et al., 1998; Amos et al., 2005). Water samples may contain cultures of naturally occurring bacteria that have the potential to alter the chemical and isotopic composition of the water and gas sample. Since the dissolved gas is not separated from the water sample, it is therefore important to prevent microbial conversions that may have adverse effects on the chemical and isotopic composition of the original sample.

Refrigeration of the sample (e.g. Vroblesky and Chapelle, 1994) will slow down potential microbial activity, but not completely eliminate it. Hence, the addition of a bactericide to the sample has been recommended in the literature. The bactericide should be chosen carefully because some products may interfere with isotope analyses (Elt Schlager et al., 2001). Historically, bactericides such as CuCl_2 or HgCl_2 were recommended and widely used (e.g., Heaton and Vogel, 1981; Holt et al., 1995). More recently, Gorody (2007) suggested benzalkonium chloride (Alfa Aesar stock # 41339) as a more environmentally acceptable alternative. Gorody (2007) showed that the chemical and isotopic composition of dissolved gas samples preserved with benzalkonium chloride did not change over a period of 1 month.

5.1.1 *Free Gas Samples*

For free gas samples, a portion of the gas sample is admitted from the storage container into the gas chromatograph for analysis. The gas components are separated in the gas chromatograph and their concentrations are determined based on the resulting peak areas. Calibration gases with known gas compositions are used to ensure accuracy. In most cases, less than 1 mL of sample gas is injected into the gas chromatograph per analysis. Detection limits for methane and higher alkanes (C₂ to C₅) are as low as 0.05 ppmv, but considerably higher for CO₂ and N₂. Results for replicate injections from the same sample container agree typically within ±3% (G. Prill, personal communication). Therefore, error propagation suggests that a change of more than ±5% from a previously determined value for a repeatedly taken sample is outside of the uncertainty of the analytical equipment, not taking into account uncertainties introduced by the sampling procedure, sample transport and storage.

5.1.2 *Dissolved Gas Samples*

Water samples to be analyzed for dissolved gas components are often collected in duplicate in glass vials without headspace fitted with Teflon lined septa caps (see section 3.2.3). A portion of the water sample is replaced with helium or another inert gas, and allowed to equilibrate (3.3.1). An aliquot of the headspace is then analyzed by GC-FID and GC-TCD. Sample size requirements are typically below 1 mL per injection. Detection limits for dissolved methane and higher alkanes are in the range of 0.01 µg/L, 1 mg/L for CO₂ and 6 mg/L for N₂ (G. Prill, personal communication). Reproducibility of the obtained GC results for repeated injections from the same headspace sample are typically better than ±5%. Hence, the uncertainty introduced by the headspace equilibrium method (< ±30%) is significantly larger than that of the GC analysis.

5.2 **Isotope Analyses**

Carbon isotope ratio measurements on methane, ethane, propane, butane, pentane and CO₂ are typically conducted with isotope ratio mass spectrometers coupled to a gas chromatograph. The ¹³C/¹²C ratio is determined on CO₂ gas that is admitted to the mass spectrometer and results are expressed in the internationally accepted delta (δ) notation in per mil (‰) deviation from the internationally accepted standard Pee Dee Belemnite (V-PDB). The CO₂ in free or dissolved gas samples is separated from the other compounds using a gas chromatograph (GC) and the isolated and purified CO₂ is subsequently directly admitted to the mass spectrometer for isotope ratio determinations. Methane, ethane, propane, butane and pentane are also isolated by gas chromatography, but these compounds need to be converted to CO₂ in a combustion interface prior to admission to the mass spectrometer. Additional cryo-focusing devices may be desirable for small samples. A typical gas chromatograph (GC) combustion (C) isotope ratio mass spectrometer (IRMS) system in the Isotope Science Laboratory at the University of Calgary is shown in Figure 18. Note that the analysis of hydrogen isotope ratios of methane may provide supplementary information (see section 7), but determination of this parameter is currently not required by the Alberta Environment baseline water well testing program.

5.2.1 *Free Gas Samples*

For free gas samples, a portion of the gas sample is admitted from the storage container into the gas chromatograph. The gas compounds of interest are separated in the gas chromatograph, converted to CO₂ in the combustion interface where necessary, and admitted to the isotope ratio mass spectrometer for isotope ratio determinations. Calibration gases with known isotopic compositions are used to ensure accuracy. Sample injection volumes are typically less than 1 mL per compound and sample. The detection limits vary from 10 ppm for methane using a cryo-focusing device up to 500 ppm for ethane. The analytical reproducibility of the obtained $\delta^{13}\text{C}$ values for the various carbon-containing compounds is usually in the order of $\pm 0.5\text{‰}$ or better. Therefore, differences of more than 1 ‰ between samples are significant from an analytical viewpoint, not considering uncertainties introduced via sampling procedures, sample storage and transport.



Figure 18: Analytical setup for carbon isotope ratio determinations in the Isotope Science Laboratory at the University of Calgary showing a gas chromatograph (left) and a cryo-focusing system (top right) interfaced with an isotope ratio mass spectrometer (bottom right).

5.2.2 *Dissolved Gas Samples*

Water samples to be analyzed for dissolved gas components are usually collected in duplicate in glass vials without headspace fitted with Teflon lined septa caps (3.2.3). A portion of the water sample is replaced with helium, and allowed to equilibrate (3.3.1). An aliquot of the headspace is then removed from the headspace with a gas-tight syringe, injected into the gas chromatograph, and carbon isotope ratios are determined as described above. Sample requirements, detection limits, and analytical uncertainties are identical to those stated in section 5.2.1.

5.2.3 *Alternate Measurement Techniques*

Recently, analytical instruments based on laser absorption spectroscopy have become commercially available (e.g. Los Gatos Research, Mountain View, California, USA), offering an alternate method for rapid determination of carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$) of methane. These instruments are less complex, and therefore considerably cheaper, than gas source isotope ratio mass spectrometers. Their analytical range may be restricted to certain methane concentrations, and determination of carbon isotope ratios of higher alkanes (e.g. ethane, propane, butane) is currently not possible.

6.0 NATURAL TEMPORAL VARIABILITY OF METHANE IN GROUNDWATER

Concentrations of dissolved and free gases in groundwater can vary significantly for a variety of reasons. These include, but are not limited to changes in static and dynamic water level due to natural causes (e.g. drought, recharge events, etc.) or pumping, mixing of aquifer fluids containing different methane concentrations, bacterial methane oxidation, or sampling errors. There are hardly any studies reported in the peer-reviewed literature that have thoroughly investigated natural seasonal variations of methane concentrations and isotope ratios in dissolved or free gas in aquifers. The few studies on this topic have documented significant variations in dissolved methane concentrations in samples taken from the same wells during a season (e.g., Barker and Fritz, 1981a; Taylor, 1996), but none of these studies reported results for field duplicates. Hence it remains often unclear how much of the observed variation was due to the sampling technique, and how much was caused by natural variations in the methane concentrations or isotope ratios in the aquifers. Nevertheless, it appears that seasonal variations in methane concentrations in groundwater can be significantly higher than the analytical uncertainty associated with sampling, transport and storage, and analysis (Gorody et al., 2004; 2005).

Barker and Fritz (1981a) observed variations in dissolved methane concentrations in groundwater obtained from the same domestic well in southern Ontario ranging from 1.6 mg/L on June 2, 1976, to 3.04 mg/L 24 days later. In a nearby well they found the methane concentration to quadruple from 0.32 to 1.28 mg/L between April 20 and June 15, 1976. Barker and Fritz (1981a) attributed these changes to methane oxidation, since $\delta^{13}\text{C}$ values of methane varied between -37.0 and -28.8 ‰ with the higher carbon isotope values associated with the lower methane concentrations. Taylor (1996) also reported intra-seasonal variability in dissolved methane concentrations in groundwater from domestic wells near Warman, Saskatchewan. In two wells completed between 13-17 m depth, he observed a decrease in dissolved methane concentrations from 0.016 and 0.029 mg/L to 0.0090 and 0.0087 mg/L, respectively. At three wells completed in the same area between 20-30 m depth, however, he observed an increase in dissolved methane concentrations during the same time period from 0.024, 0.026 and 0.047 mg/L to 0.032, 0.040, and 0.048 mg/L, respectively. Taylor (1996) collected his samples using a bailer, and reasoned that the variation was likely due to degassing of the samples caused by the pressure change as they were brought to the surface, combined with agitation from the bailing process and the change in temperature. Based on the available literature, seasonal changes in concentrations of dissolved methane between 50 and 200% appear to be quite common, but changes approaching an order of magnitude or more are likely outside the normal natural range.

Significant seasonal changes in dissolved methane concentrations have also been reported for contaminated groundwater (e.g. Takeuchi et al., 2000). Spatial variations in methane concentrations in aquifers are also quite common, since methane may be unequally distributed in groundwater for a variety of reasons. These include potential methane contamination from a point source (e.g. borehole), or variations of microbially produced methane if the microorganisms are unevenly distributed in an aquifer.

Some attempts have recently been made to assess the variability of concentrations and isotope ratios of methane in groundwater sampled repeatedly throughout a single day. Employees at Gchem Ltd. (Lloydminster, Alberta, Canada) completed an unpublished study during which groundwater from the same well was sampled for dissolved methane with a downhole sampler known as the Shallow Aquifer Sampling Probe (copyright Gchem Ltd.) every hour for nine hours (Szatkowski, personal communication, 2006). The probe contains two 500 mL sampling bottles that are used to collect duplicate samples. The researchers observed a greater variation in the dissolved methane concentrations for samples taken at different times than they did for any duplicates taken at the same time (Szatkowski, personal communication, 2006). This indicates that the variability in the dissolved methane concentrations of the aquifer throughout the sampling day may exceed the uncertainty introduced by the sampling technique. The Applied Geochemistry group at the University of Calgary recently conducted a similar study in which they assessed the variability of carbon isotope ratios of methane, ethane and CO₂ in free gas samples obtained repeatedly throughout a four hour sampling campaign. Free gas was sampled with a flow-through cell (3.1.3) every 20 minutes yielding 13 samples throughout the sampling period. Methane (43.97±1.44 vol%), ethane (0.023±0.001 %) and CO₂ (0.30±0.04 %) contents in the free gas samples remained rather constant throughout the sampling period. The obtained δ¹³C values for methane (-76.7 ± 0.3‰, n = 13) and ethane (-36.3 ± 0.1 ‰; n= 13) varied by less than the analytical uncertainty, indicating no detectable natural variability in the carbon isotope ratios of methane and ethane throughout the four hour sampling period (Cheung and Mayer, 2007).

Knowledge of the extent of natural variability of concentrations and isotope ratios of dissolved and free methane, higher alkanes, and CO₂ in groundwater is a pre-requisite for a quantifiable assessment of potential contamination cases. Therefore, a systematic study assessing the natural variability of concentrations and isotope ratios of dissolved and free methane, higher alkanes, and CO₂ in selected groundwater wells completed in a variety of hydrogeological settings in the province of Alberta is strongly recommended. It is important that such a study makes an attempt to distinguish between uncertainties introduced by the sampling techniques versus natural variations in the concentrations and isotope ratios of dissolved and free gases.

7.0 ADDITIONAL CONSIDERATIONS

Stable carbon and hydrogen isotope ratios have been used to determine the origin of methane in groundwater for more than two decades (e.g. Schoell, 1980; Barker and Fritz, 1981a; Whiticar, 1999; Prinzhofer et al., 2000). Methane from different sources is characterized by different stable isotope ratios since biological and chemical reactions may partition heavy and light isotopes at different rates. The biogenic formation of methane by microorganisms tends to strongly favour light isotopes, thus producing methane that is strongly enriched in the light carbon (^{12}C) and hydrogen isotopes (^1H), resulting in very negative $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values. Thermogenic methane generation is associated with smaller isotope fractionation effects and hence results usually in methane with less negative $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values than microbially produced methane (e.g. Schoell, 1980; Whiticar, 1999; Breas et al., 2002).

The use of stable isotope ratio for source tracing of methane requires that the isotopic composition of pre-existing methane in groundwater is isotopically distinct from methane derived from a potential contaminant source. The “Standard for Baseline Water Well Testing for Coalbed Methane Operations” is designed to thoroughly assess the isotopic composition of free methane in groundwater. It is equally important to determine the isotopic composition of gases produced by coalbed methane operations to assess whether the isotopic compositions of methane and higher alkanes in coalbed-derived gases are distinct from those of dissolved and free gases in the sampled groundwater.

Even if there is a significant difference between the isotopic composition of natural methane in groundwater and methane produced by CBM operators it is possible that isotope effects during oxidation of methane may complicate the task of source apportionment using isotope techniques. Methane in groundwater may be subject to bacterial oxidation to CO_2 if appropriate redox conditions exist (e.g., Barker and Fritz, 1981a; Coleman et al., 1981). During this microbial process the light isotopes are preferential metabolized (Coleman et al., 1981), leaving the residual methane enriched in ^{13}C , thereby increasing its $\delta^{13}\text{C}$ value (e.g., Barker and Fritz, 1981a; Revesz et al., 1995; Grossman et al., 2002). Hence, partial oxidation of biogenic methane may result in remaining gas with an isotopic signature that is characteristic for thermogenic methane. Oxidation of methane can occur in anaerobic or aerobic conditions, and depending on the extent of the oxidation, can have a significant effect on the isotope ratios of the residual methane (e.g., Coleman et al., 1981; Grossman et al., 2002). For example, Grossman et al. (2002) found that microbially produced methane in a landfill leachate with an initial $\delta^{13}\text{C}$ value of -54‰ assumed a $\delta^{13}\text{C}$ value of -10‰ or higher after most of it had been oxidized at the plume margin. The analysis of hydrogen isotope ratios of methane and the determination of other geochemical groundwater parameters (e.g. $\delta^{13}\text{C}$ of dissolved inorganic carbon) are useful additional tools for assessing the occurrence of methane oxidation in aquifers. Gas composition data provide an additional tool to differentiate between biogenic and thermogenic gas even, if methane oxidation occurs. Microbial methane is generally associated with no or a very low abundance of ethane (e.g., Aravena et al., 1995; Yager and Fountain, 2001). Thermogenic gas samples may often contain propane, butane, and pentane in addition to methane and ethane (e.g., Coleman et al., 1981). Volumetric methane to ethane ratios of less than 100 and the occurrence of propane and butane are good indicators that a thermogenic gas component is present.

8.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

Collecting accurate baseline data on the chemical and isotopic composition of gases in shallow aquifers is an important first step in addressing concerns related to the potential for aquifer contamination with fluids or gases from coalbed methane (CBM) operations. Sampling and analysis of free gas obtained from selected well water samples has been mandatory in Alberta since May 1, 2006, consistent with the requirements of the “Standard for Baseline Water Well Testing for Coalbed Methane Operations” (AENV, 2006).

Sampling techniques and requirements for obtaining free gas samples, and possibly dissolved gas samples, for the Alberta Environment well-water testing program must be comparatively simple while ensuring reliable and accurate results. Because of the liability issues related to removing pump assemblies or other well installations, sampling is in most cases restricted to above-ground access points, essentially eliminating down-hole sampling devices. For sampling of free gas for chemical and isotopic analyses, the inverted bottle technique (3.1.1) and flow-through cells (3.1.3) are two suitable methods. Since the inception of the “Standard for Baseline Water Well Testing for Coalbed Methane Operations”, flow-through cells have been widely used to sample free gas for chemical and isotopic analyses from shallow groundwater in Alberta. So far, it has not been thoroughly tested whether the different designs of the flow-through cells and their operational setup in the field have a significant influence on the obtained gas volumes or the determined gas concentrations (3.4). Also, flow-through samplers for free gas may not yield a sample if gas concentrations are significantly below the saturation point of methane, e.g. if methane occurs only dissolved in groundwater (circa < 25 mg/L dependent on pressure and temperature). A simple and effective method to determine the chemical and isotopic composition of dissolved gases in groundwater is the inverted bottle method (3.2.3) followed by a headspace equilibrium technique (3.3.1). This approach has been successfully applied in coalbed methane producing regions in the United States of America, e.g. Colorado (Gorody et al., 2004). If consistent sampling procedures are carefully employed, this technique can yield reliable concentration and isotope data for samples containing dissolved methane at concentrations of less than 2 mg/L (e.g. Gorody et al., 2004; 2005).

It is important to use appropriate sample transport and storage containers, to adhere to the appropriate sample holding times, and the addition of a preservative is highly recommended for dissolved gas samples (section 4). The available analytical techniques to determine concentrations and isotope ratios of free and dissolved gas are highly sensitive and capable of generating highly accurate and reproducible results (section 5). Hence it appears that the highest potential to introduce large uncertainties in the obtained concentration and isotope data for free and dissolved methane in groundwater is in all likelihood associated with the sampling procedures in the field. It is suggested that future research should evaluate the influence of sampling procedures and sampler design on the obtained concentration and isotope data for free and dissolved methane in groundwater in Alberta (recommendation 1 and 2).

Knowledge of the extent of natural variability of concentrations and isotope ratios of dissolved methane, higher alkanes, and CO₂ in groundwater is an important pre-requisite for a quantifiable assessment of potential contamination cases (section 6). Therefore, a systematic study assessing

the natural variability of concentrations and isotope ratios of free and dissolved gas components in shallow groundwater in Alberta is highly desirable (recommendation 3).

The use of stable isotope ratios for source tracing of methane requires that the isotopic composition of pre-existing methane in groundwater is isotopically distinct from methane derived from a potential contaminant source (section 7). Therefore, it is also important to determine the isotopic composition of gases produced by coalbed methane operators to assess whether the isotopic compositions of methane and higher alkanes in coalbed-derived gases are distinct from those of dissolved and free gases in the sampled groundwater (recommendation 4).

The “Standard for Baseline Water Well Testing for Coalbed Methane Operations” is designed to assess the concentration and isotopic composition of methane, higher alkanes, and CO₂ in free gas of shallow groundwater. If these gases occur only in dissolved form in the groundwater, no concentration and isotope data may be obtained. However, sampling (3.2) and analytical procedures (3.3) exist to accurately determine concentration and isotope compositions of dissolved methane at levels of less than 2 mg/L. This approach allows the determination of chemical and isotopic baseline data in situations where free gas sampling devices may yield no sample. Based on concentration and isotope data obtained for free gas in the first year of the baseline water well testing program, it should be evaluated whether it is desirable to expand the testing program to dissolved gases in groundwater.

Recommendations for future research are summarized below:

Recommendation 1: It should be evaluated whether the different designs of the flow-through cells for sampling of free gas and their operational setup in the field have a significant influence on the obtained gas volumes or gas concentrations, particularly for water wells with low gas contents.

Recommendation 2: It is suggested to evaluate the magnitude of potential pumping-induced pressure changes on the concentration of dissolved gases in shallow groundwater in Alberta. This could be achieved by determining the concentrations of dissolved gases such as methane, ethane, and CO₂ in shallow groundwater obtained from selected wells using (a) downhole samplers, and (b) the inverted bottle method followed by a headspace equilibrium technique.

Recommendation 3: A systematic study assessing the natural variability of concentrations and isotope ratios of dissolved and free methane, higher alkanes, and CO₂ in selected groundwater wells completed in a variety of hydrogeological settings in the province of Alberta is strongly recommended. It is important that such a study makes an attempt to distinguish between uncertainties introduced by the sampling techniques and natural variations in the concentrations and isotope ratios of dissolved and free gases.

Recommendation 4: It is important to also determine the isotopic composition of gases produced by coalbed methane operations to assess whether the isotopic compositions of methane and higher alkanes in coalbed-derived gases are distinct from those of free or dissolved gases in shallow groundwater of Alberta.

9.0 LITERATURE CITED

Alberta Environment (2006). "Standard for baseline water-well testing for coalbed methane / natural gas in coal operations. Released April 2006.

Amos, R. T., K. U. Mayer, B. A. Bekins, G. N. Delin and R. L. Williams (2005). "Use of dissolved and vapor-phase gases to investigate methanogenic degradation of petroleum hydrocarbon contamination in the subsurface." *Water Resources Research* 41(2), W02001.

Andrews, J. N., J. E. Goldbrunner, W. G. Darling, P. J. Hooker, G. B. Wilson, M. J. Youngman, L. Eichinger, W. Rauert and W. Stichler (1985). "A radiochemical, hydrochemical and dissolved gas study of groundwaters in the Molasse Basin of Upper Austria." *Earth and Planetary Science Letters* 73(2-4): 317-332.

Aravena, R. and L. I. Wassenaar (1993). "Dissolved organic carbon and methane in a regional confined aquifer, southern Ontario, Canada; carbon isotope evidence for associated subsurface sources." *Applied Geochemistry* 8(5): 483-493.

Aravena, R., L. I. Wassenaar and J. F. Barker (1995). "Distribution and isotopic characterization of methane in a confined aquifer in southern Ontario, Canada." *Journal of Hydrology* 173(1-4): 51-70.

Barber, C. and D. Briegel (1987). "A method for the in-situ determination of dissolved methane in groundwater in shallow aquifers." *Journal of Contaminant Hydrology* 2(1): 51-60.

Barker, J. F. and P. Fritz (1981a). "Carbon isotope fractionation during microbial methane oxidation." *Nature* 293(5830): 289-291.

Barker, J. F. and P. Fritz (1981b). "The occurrence and origin of methane in some groundwater flow systems." *Canadian Journal of Earth Sciences* 18(12): 1802-1816.

Beyerle, U., W. Aeschbach-Hertig, D. M. Imboden, H. Baur, T. Graf and R. Kipfer (2000). "A mass spectrometric system for the analysis of noble gases and tritium from water samples." *Environmental Science & Technology* 34(10): 2042-2050.

Blicher-Mathiesen, G., G. W. McCarty and L. P. Nielsen (1998). "Denitrification and degassing in groundwater estimated from dissolved di-nitrogen and argon." *Journal of Hydrology* 208(1-2): 16-24.

Blyth, Alec. Personal Communication: Phone Conversation: 1:30-2:00 PM on July 25th, 2006.

Breas, O., C. Guillou, F. Reniero and E. Wada (2002). "The global methane cycle: isotopes and mixing ratios, sources and sinks." *Isotopes in Environmental and Health Studies* 37(4): 257-379.

Browne, B. A. (2004). "Pumping-Induced Ebullition: A Unified and Simplified Method for Measuring Multiple Dissolved Gases." *Environmental Science and Technology* 38 (21), 5729 - 5736.

Capasso, G. and S. Inguaggiato (1998). "A simple method for the determination of dissolved gases in natural waters: an application to thermal waters from Volcano Island". *Applied Geochemistry* 13(5): 631-642.

Chafin, D. T., D. M. Swanson and D. Grey (1996). Methane-concentration and methane-isotope data for ground water and soil gas in the Animas River Valley, Colorado and New Mexico, 1990-1991. *Water Resources Investigations Reports United States Geological Survey*.

Chapelle, F. 2006. Personal Communication: Email: Re: Effects of degassing on the bubblestrip method. Received at 11:02 AM on Friday, August 24th, 2006.

Chapelle, F. H. and P. B. McMahon (1991). "Geochemistry of dissolved inorganic carbon in a coastal plain aquifer; 1, Sulfate from confining beds as an oxidant in microbial CO₂ production." *Journal of Hydrology* 127(1-4): 85-108.

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): 359-371.

Chapelle, F. H., P. M. Bradley, D. R. Lovley and D. A. Vroblesky (1996). "Measuring rates of biodegradation in a contaminated aquifer using field and laboratory methods." *Ground Water* 34(4): 691-698.

Chapelle, F. H., D. A. Vroblesky, J. C. Woodward and D. R. Lovley (1997). "Practical considerations for measuring hydrogen concentrations in groundwater." *Environmental Science & Technology* 31(10): 2873-2877.

Cheung, K. and Mayer, B. (2007). Chemical and Isotopic Characterization of Shallow Groundwater from Selected Monitoring Wells. Report submitted to Alberta Environment, March 31, 2007.

Clark, I. and P. Fritz (1997). *Environmental Isotopes in Hydrogeology*. Boca Raton New York, Lewis Publishers.

Coleman, D. D., Risatti, J. B. and Schoell, M. (1981). Fractionation of carbon and hydrogen isotopes by methane-oxidizing bacteria. *Geochim. Cosmochim. Acta* 45: 1033-1037.

Coleman, D. D., C.-L. Liu and K. M. Riley (1988). Microbial methane in the shallow Paleozoic sediments and glacial deposits of Illinois, U.S.A. *Chemical Geology* 71: 23-40.

De Gregorio, S. Personal Communication: Email to Trevor Hirsche: Re: PTFE Gas Sampler. Received at 7:20 AM on June 20, 2006. Sofia De Gregorio is a Researcher at the Istituto

Nazionale di Geofisica e Vulcanologia Sezione di Palermo, Via Ugo La Malfa 153, 90146 Palermo, Italy

De Gregorio, S., S. Gurrieri and M. Valenza (2005). "A PTFE membrane for the in situ extraction of dissolved gases in natural waters; theory and applications." *Geochemistry, Geophysics, Geosystems* 6(9):13.

Dowis, D. and Coyne, L. 2005. Stability of FlexiFoil Bags with Methane. SKC Publication Number 1707, Issue 0509. Accessed Online from <http://www.skcinc.com/instructions/1707.pdf> on July 11, 2006.

Drimmie, R. J., R. Aravena, L. I. Wassenaar, P. Fritz, M. J. Hendry and G. Hut (1991). Radiocarbon and stable isotopes in water and dissolved constituents, Milk River Aquifer, Alberta, Canada. *Applied Geochemistry* 6: 381-392.

Dubord, M. P. (1992). Design and Field Testing of Deep Borehole Water and Dissolved Gas Samplers. Earth Science. Waterloo, Ontario, University of Waterloo. M.Sc.: 104.

Eltschlager, K. K., J. W. Hawkens, W. C. Ehler and F. Baldassare (2001). Technical Measures for the Investigation and Mitigation of Fugitive Methane Hazards in Areas of Coal Mining. Pittsburgh, PA, U.S. Department of the Interior - Office of Surface Mining Reclamation and Enforcement 124.

EPA (2001). Technical Guidance for the Natural Attenuation Indicators: Methane, Ethane, and Ethene. U. E. P. Agency and R.-N. England, US EPA: 18.

EPA (2006). Koenig, L., D. Tjoelker, S. Poole and J. Patzke. Chapter 10: Ground Water Sampling. Technical Guide for Ground Water Investigations. J. Patzke, US Environmental Protection Agency - Ohio Branch.

EUB Directive 035 "Baseline Water Well Testing Requirement for Coalbed Methane Wells Completed Above the Base of Groundwater Protection."
www.eub.ca/docs/Documents/directives/Directive035.pdf

Gorody, A. W., D., Baldwin and C. Scott (2004). Methane in Ground Water, San Juan Basin, La Plata County Colorado: Analysis of Data Submitted in Response to COGCC Orders 112-156 and 112-157. COGCC-Library-San Juan Basin...link-> <http://oil-gas.state.co.us/>

Gorody, A. W., D., Baldwin and C. Scott (2005). Methane in water wells, San Juan Basin, Colorado: Analysis of data submitted in response to COGCC orders 112-156 and 112-157, IPEC 12th Ann. Symp. Proc., <http://ipec.utulsa.edu/Conf2005/Papers/Gorody>
[DISSOLVED METHANE IN GROUNDWATER.pdf](http://ipec.utulsa.edu/Conf2005/Papers/Gorody)

Gorody, A. W. (2007). "Recommended sampling, analysis, and reporting protocols to comply with groundwater baseline sampling as required by the COGCC under rule 318A." Report

prepared for the Colorado Oil and Gas Association, Universal Geoscience Consulting Inc. Houston, Texas.

Grossman, E. L., L. A. Cifuentes and I. M. Cozzarrelli (2002). "Anaerobic methane oxidation in a landfill-leachate plume." *Environmental Science & Technology* 36(11): 2436-2442.

Heaton, T. H. E. and J. C. Vogel (1981). "'Excess air' in groundwater." *Journal of Hydrology* 50(1-4): 201-216.

Heaton, T. H. E., J. K. Trick and G. M. Williams (2005). "Isotope and dissolved gas evidence for nitrogen attenuation in landfill leachate dispersing into a chalk aquifer." *Applied Geochemistry* 20(5): 933-945.

Hesslein, R. H. (1976). "An in situ sampler for close interval pore water studies." *Limnology and Oceanography* 21(6): 912-914.

Holt, B. D., N. C. Sturchio, G. B. Arehart and A. J. Bakel (1995). "Ultrasonic vacuum extraction of gases from water for chemical and isotopic analysis." *Chemical Geology* 122(1-4): 275-284.

Inguaggiato, S. and A. Rizzo (2004). "Dissolved helium isotope ratios in ground-waters; a new technique based on gas-water re-equilibration and its application to Stromboli volcanic system." *Applied Geochemistry* 19(5): 665-673.

Jacinthe, Pierre-Andre. Personal Communication: Email to Trevor Hirsche. Re: Applications of the silicone rubber gas sampler. Received at 12:03 PM on June 22, 2006. Dr. Jacinthe is an associate professor at the Department of Earth Sciences in Indiana Univ. - Purdue Univ. at Indianapolis (IUPUI). 723 W. Michigan Street, SL 122 Indianapolis, IN 46202

Jacinthe, P. A. and P. M. Groffman (2001). "Silicone rubber sampler to measure dissolved gases in saturated soils and waters." *Soil Biology & Biochemistry* 33(7-8): 907-912.

Jones, D. Personal Communication: Phone Conversation on August 24, 2006.

Johnson, R. L., J. F. Pankow and J. A. Cherry (1987). "Design of a ground-water sampler for collecting volatile organics and dissolved gases in small-diameter wells." *Ground Water* 25(4): 448-454.

Johnson, K. M., J. E. Hughes, P. L. Donaghay and J. M. Sieburth (1990). "Bottle calibration static head space method for the determination of methane dissolved in seawater." *Analytical Chemistry* 62(21): 2408-2412.

Kampbell, D. H. and S. A. Vandegrift (1998). "Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique." *Journal of Chromatographic Science* 36: 253-256.

Kampbell, D. H., J. T. Wilson and D. M. McInnes (1998). Determining dissolved hydrogen, methane, and vinyl chloride concentrations in aqueous solution on a nanomolar scale with the bubble strip method. The 1998 Conference on Hazardous Waste Research.

Keech, D. K. and M. S. Gaber (1982). "Methane in Water Wells." *Water Well Journal* 36(22): 33-36.

Kennedy, Peter. Manager, Technical Support Group, Edmonton Operations for Maxxam Analytics Inc. Personal Communication: Phone Conversation at 10:00-10:15 AM, July 17, 2006.

Kiene, R. P. and D. G. Capone (1985). "Degassing of pore water methane during sediment incubations." *Applied and Environmental Microbiology* 49(1): 143-147.

Lammers, S. and E. Suess (1994). "An improved head-space analysis method for methane in seawater." *Marine Chemistry* 47(2): 115-125.

Lollar, B. S., S. K. Frape and S. M. Weise (1994). New sampling devices for environmental characterization of groundwater and dissolved gas chemistry (CH₄, N₂, He)." *Environmental Science & Technology* 28(13): 2423-2427.

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." *Environmental Science & Technology* 28(7): 1205-1210.

Magdich, Frank. Technician at Oak Environmental Ltd. Personal Communication: Phone Conversation at 1:20-2:30 PM on July 14, 2006.

Maxxam Analytics (2006). Coalbed Methane Operations Baseline Water-well Testing. Environmental Services Solutions. Sol-050e. 2pp. Accessed online from: [http://www.maxxam.ca/solutions/sol_ind_Coalbed_Methane_0606\(1\).pdf](http://www.maxxam.ca/solutions/sol_ind_Coalbed_Methane_0606(1).pdf) on August 17, 2006.

Microseeps (2006). Gas Stripping Cell Instructions – Technical Guidance from Microseeps. Accessed online from: <http://www.microseeps.com/pdf/gasstripcell.pdf> on August 17, 2006.

Murray, H. E. and J. N. Beck (1992). "Methane in well water from Lake Charles, Louisiana." *Bulletin of Environmental Contamination and Toxicology* 48(5): 768-771.

Nurmi, P. A. and I. T. Kukkonen (1986). "A new technique for sampling water and gas from deep drill holes." *Canadian Journal of Earth Sciences* 23(9): 1450-1454.

Prill, G. Personal Communication: Email to Bernhard Mayer. Re: gas sampling canisters. Received at 12:03 PM on June 12, 2007.

Prinzhofer, A., Mello, M. R. and Takaki, T. (2000). Geochemical characterization of natural gas: a physical multivariable approach and its application in maturity and migration estimates. *AAPG Bull.* V. 84: 1152-1172.

Revesz, K., T. B. Coplen, M. J. Baedeker, P. D. Glynn and M. Hult (1995). "Methane production and consumption monitored by stable H and C isotope ratios at a crude oil spill site, Bemidji, Minnesota." *Applied Geochemistry* 10(5): 505-516.

Sanford, W. E., R. G. Shropshire and D. K. Solomon (1996). "Dissolved gas tracers in groundwater; simplified injection, sampling, and analysis." *Water Resources Research* 32(6): 1635-1642.

Schmitt, M., E. Faber, R. Botz and P. Stoffers (1991). "Extraction of methane from seawater using ultrasonic vacuum degassing." *Analytical Chemistry* 63(5): 529-532.

Schoell, M. (1980). "The hydrogen and carbon isotopic composition of methane from natural gases of various origins." *Geochimica et Cosmochimica Acta* 44(5): 649-662.

Simpkins, W. W. and T. B. Parkin (1993). "Hydrogeology and redox geochemistry of CH₄ in a late Wisconsinan till and loess sequence in central Iowa." *Water Resources Research* 29(11): 3643-3657.

Skubal, K. L., M. J. Barcelona and P. Adriaens (2001). "An assessment of natural biotransformation of petroleum hydrocarbons and chlorinated solvents at an aquifer plume transect." *Journal of Contaminant Hydrology* 49(1-2): 151-169.

Smith, R. L., B. L. Howes and S. P. Garabedian (1991). "In situ measurement of methane oxidation in groundwater by using natural-gradient tracer tests." *Applied and Environmental Microbiology* 57(7): 1997-2004.

Stute, M. and P. Schlosser (2000). *Atmospheric Noble Gases. Environmental Tracers in Subsurface Hydrology*. P. G. Cook and A. L. Herczeg, Springer: 552.

Szatkowski, Bryan. Employee at GCHEM. Personal Communication: Phone Conversation: 3:30-4:10 PM, August 3rd, 2006

Takahata, N., G. Igarashi and Y. Sano (1997). "Continuous monitoring of dissolved gas concentrations in groundwater using a quadrupole mass spectrometer." *Applied Geochemistry* 12(4): 377-382.

Takeuchi, M., Nanba, K., Iwamoto, H., Nirei, H., Kazaoka, O. and Furuya, K. (2000). "Distribution and seasonal variation of methanotrophs in trichloroethylene contaminated groundwater." *Water Research* 34(15): 3717-3724.

Taylor, S. W. (1996). *Bacterial hydrocarbon gases in surficial aquitards and shallow bedrock aquifers in the Western Canadian Sedimentary Basin*. Geology. Toronto, University of Toronto. M.Sc. Pages: 114.

Taylor, S. W., L. I. Wassenaar and M. J. Hendry (1998). A down hole dissolved gas sampler for use in aquitards, Environment Canada. Pages: 13.

Unrue, Dave. Technical Support for Microseeps. Personal Communication: Phone conversation: 1:45-2:10 PM, August 4, 2006.

Van Stempvoort, D., H. Maathuis, E. Jaworski, B. Mayer and K. Rich (2005). "Oxidation of fugitive methane in ground water linked to bacterial sulfate reduction." *Ground Water* 43(2): 187-199.

Vroblecky, D. A. and F. H. Chapelle (1994). "Temporal and spatial changes of terminal electron-accepting processes in a petroleum hydrocarbon contaminated aquifer and the significance for contaminant biodegradation." *Water Resources Research* 30(5): 1561-1570.

Walsh, K. P. and R. G. McLaughlin (1999). "Bubble extraction of dissolved gases from groundwater samples." *Water, Air and Soil Pollution* 115(1-4): 525-534.

Whiticar, M. J. (1999). Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chemical Geology* 161: 291-314.

Yager, R. M. and J. C. Fountain (2001). "Effect of natural gas exsolution on specific storage in a confined aquifer undergoing water level decline." *Ground Water* 39(4): 517-525.

Yalowsky, S. H. and Y. He (2003). *Handbook of Aqueous Solubility*. Boca Raton, London, New York, Washington, D.C., CRC.