Collecting Water Samples for the Determination of Dissolved Gas Concentrations

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GWPC Annual Forum
September 2013
St. Louis, MO
Horizontal Drilling and Hydraulic Fracturing has created great concerns over dissolved gas in groundwater

1. Some early wells resulted in significant groundwater contamination
2. Hydraulic fracturing was accused of being the cause
3. Being able to adequately assess the concentration and geochemical fingerprint of dissolved gas, primarily methane, has become an area of great interest.
Henry’s Law

\[ X_a = K_a \cdot P_a \]

\( X_a \) = the mole fraction of gas “a” in the water

\( K_a \) = the Henry’s Law Constant for gas “a”

and is a function of solvent, solute, & T

\( P_a \) = the partial pressure of the gas “a”
Henry’s Law

\[ X_a = K_a \cdot P_a \]

The concentration of gas in solution can increase until the sum of the partial pressures of all dissolved gases exceeds the hydrostatic pressure. At that point a gas phase (i.e. bubbles) will form.

Because the hydrostatic pressure increases with depth, the amount of gas that can be dissolved can increase rapidly with depth.
Methane Solubility in mg/L (ppm) at 12 deg. C

Water Depth in Feet

Pressure in atmospheres (absolute)

Under Saturated
Completely dissolved, one phase

Solubility Limit (point at which gas phase will form)

27 ppm (41 cc/L)
Except under unusual circumstances, there is no significant danger if all of the gas is dissolved in water and there is no free gas space.
But if a gas phase develops in the aquifer and expands until it contacts a water well, gas could rapidly flow up the well and create a hazard.

Knowing the concentration of gas in the water allows evaluating whether a gas cap could exist in equilibrium with that water.
In most cases when sampling private water wells, our only option is to collect from a spigot. Samples for gas analysis should never be collected from the hot-water line, and if possible, water conditioners should be avoided.
Isotech specializes in gas analysis and we realize that:

1. You can’t get good interpretations from bad data
2. You can’t get good data from bad samples
3. You can’t get good samples using poor methods or inadequate containers
4. Your interpretation is only as good as the procedures and containers used to collect your samples.
Sampling Procedures

Headspace Equilibration

(Single Phase Sample)

- If the concentration of the gas is below the saturation limit, bubbles will not form and gas will leave solution only by diffusion, which is very slow.

- Water can be collected in a non-permeable bottle (not PE) by minimizing contact with air.

- Refrigeration or a preservative is needed to prevent bacterial activity during shipment to the laboratory.
The size of the bottle is really a function of the analytical method to be applied.

Glass bottles are fragile and make it difficult to know the internal pressure.

VOC vials can be used for determining dissolved gas concentrations, but they do not provide enough gas for isotope analysis in most cases.

Non-permeable plastic bottles work best.
A comparison of glass bottles and Isotech’s plastic bottles. Failure to add a bactericide to prevent bacterial oxidation can result in significant isotopic change.
Bactericide, with & without:

\[ \delta D (\text{‰}) \] vs. \[ \delta^{13}C (\text{‰}) \]

- Oxidized
- Unoxidized

- gls-with
- gls-without
- plstc-with
- plstc-without
- oxid trend
Failure to prevent oxidation can result in erroneous interpretations.
Addition of bactericide to prevent microbial degradation

A gelatin capsule is attached to the underside of the cap of Isotech’s water sampling bottles and slowly dissolves in the water, releasing bactericide.
Sampling Procedures

Headspace Equilibration

• In the laboratory, some of the water is withdrawn and replaced with a helium headspace

• The headspace and the water are equilibrated at constant temperature
Sampling Procedures

Headspace Equilibration

• The headspace is then analyzed
• The volume of water is measured by weighing
• The concentration of gas in the water is calculated based on the measurements made using Henry’s law.
Sampling Procedures

Headspace Equilibration
(Single Phase Sample)

This method is valid so long as

1. Accurate measurements are made
2. The sample was adequately preserved
3. No gas was lost during collection of the sample

4. The concentration of gas in the water was below the saturation limit when the sample was collected.
Methane Solubility in mg/L (ppm) at 12 deg. C

Pressure in atmospheres (absolute)

Water Depth in Feet

Under Saturated

27 ppm (41 cc/L)

Solubility Limit (point at which gas phase will form)
Sampling Procedures

Water Displacement

This method has been in use for over 50 years

50 years ago, there was no commercial interest in the concentration of methane in water, it was mostly an academic question, or when the problem was severe, a means of evaluating the extent of the problem

Measuring only the gas released from the water provided a means of evaluating the problem, and comparing one well to another
Sampling Procedures

Water Displacement
Sampling Procedures

**Water Displacement**

- Allows collecting large samples for multiple analyses
- Collects only the gas released from the water
- Provides only an estimate of the minimum amount of gas in the water
- Have to assume that all or a constant fraction of the gas in the water is collected
  - Affected by flow rate of water
  - Affected by size of orifice physical configuration (turbulence)
  - Affected by other gases in the water
Sampling Procedures

2 Phase Method

- To adequately assess the gas concentration in water that is saturated at depth, it is necessary to either maintain the water at pressure to prevent a gas phase from forming, or collect both the water and the gas phase.
- Bringing water to the surface while maintaining the pressure requires “pushing” rather than “pulling.” That is, it requires a submersible pump.
- The surface pressure “must” be maintained higher than the hydrostatic pressure until the sample is released into a container.
Sampling Procedures

2 Phase Method

• Evacuated gas bags can be used for collecting water by this method.
Sampling Procedures

2 Phase Method

- With transparent bags, in the laboratory, we can see if there is a separate gas phase, and if none exists, helium can be injected as with the headspace equilibration.
- The gas can be measured and analyzed and the gas concentration calculated with Henry’s Law.
- With gas bags, the pressure is easy to measure accurately because it is atmospheric pressure.
Sampling Procedures

Headspace method vs. 2 Phase Method

- Gas bags can be used even when only one phase is present, BUT
  - They are delicate and easily broken
  - They are more expensive than bottles
  - They do not allow collecting as much water and thus detection levels are higher than with large bottles
  - The bags are not totally impermeable and thus must be analyzed within a few days to prevent fractionation
Sampling Procedures

Headspace method vs. 2 Phase Method

• In our quest to make it easier to collect good samples, we have developed a container that we believe will be
  • easier to use in the laboratory,
  • easier to use in the field,
  • will allow one container to be used for multiple sampling methods
  • Will provide reliable data on dissolved gas concentrations while also providing sufficient sample for gas characterization
Introducing The IsoFlask™

• Collapsible like a gas bag, can be evacuated
• Will stand up like a bottle
• More rugged than a gas bag or a glass bottle
• Impermeable to hydrocarbon gases
• Multiple connection options
• Transparent
• Allows introduction of bactericide capsules
• ”One Size Fits All’
Sampling with the IsoFlask™
IsoFlask vs. IsoBag (above saturation, with headspace)

IsoFlask vs. Bottle (below saturation, with no headspace)

(Data is mathematically corrected for gas removed for analyses)
With IsoBags it was necessary to analyze them within a few days to prevent diffusive loss and isotopic fractionation of methane.

Different gas standards, which had different isotope compositions, were used for the two different comparisons.
CONCLUSIONS

1. The method necessary to collect samples for determining dissolved methane can depend on the gas concentration.

2. If no gas is present in the water in excess of the saturation limit at atmospheric pressure, head-space equilibration samples can be used.

3. If any gas is present in excess of the saturation limit at atmospheric pressure, bubbles will form and the 2-phase method must be used.

4. New containers, to become available within the next few weeks called IsoFlasks™, can be used for collection of samples by either method.