Determination of Dissolved Gases in Ground Waters

By
Ray Martrano
Laboratory Director
Seewald Laboratories Inc.

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LABORATORIES, INC.

Overview of Presentation

What is a dissolved gas?

Why do we want to study dissolved gases?

Methods used for dissolved gases

Limitations

Thoughts for the future

What is a Dissolved Gas?

Any Gas that can be found in solution

Has significant vapor pressure at room temperature

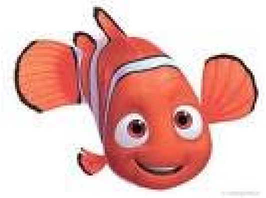
Difference between gases and liquids are functions of temperature and pressure

VOCs and Dissolved Gases

- VOCs are dissolved gases
  - Most commonly identified as volatile liquids
  - Elemental gases and low MW compounds
  - Permanent gases
- Many methods are available for VOCs
- Many methods for gases

Reasons for Studying Dissolved Gases

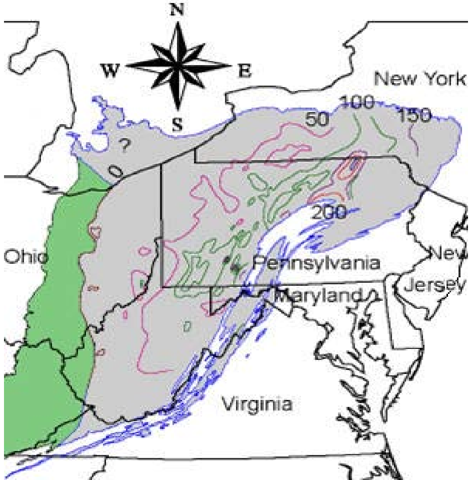
Dissolved Oxygen, BOD



Energy related issues

Identification of hazards

Bioremediation



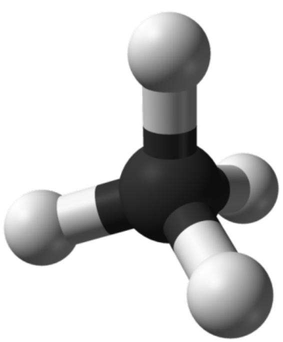
Marcellus Shale

What is Marcellus Shale

One of the largest natural gas formations recently found.

Enough energy to supply U.S. for several years

Methane is recovered by hydraulic fracking



Growing need to monitor methane in groundwater

House Explosions in Bradford, Pennsylvania tied to Migrating Methane Gas from Drilling Activity

March 24, 2011

A home in Bradford PA where apparent gas migration caused it to explode

Common methods for dissolved gases

RSK 175

PA DEP Method

Headspace methods

ASTM Method

TO-XX air methods

Background on Gas Laws

Equilibrium

Vapor-liquid equilibrium (**VLE**) is a condition where a liquid and its vapor (gas phase) are in equilibrium with each other, a condition or state where the rate of evaporation (liquid changing to vapor) equals the rate of condensation (vapor changing to liquid) on a molecular level such that there is no net (overall) vapor-liquid interconversion.

Ideal Gas Law

The state of an amount of gas is determined by its pressure, volume, and temperature. The modern form of the equation is:

$$PV = nRT$$

where *P* is the absolute pressure of the gas; *V* is the volume; *n* is the amount of substance of gas and *R* is the ideal, or universal, gas constant, and *T* is the absolute temperature.

Dalton's Law

Dalton's law (also called **Dalton's law of partial pressures**) states that the total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures of each individual component in a gas mixture.

$$P_{total} = \sum_{i=1}^{n} p_i \qquad P_{total} = p_1 + p_2 + \cdots + p_n$$

where $p_1, p_2, \ldots, p_n$ represent the partial pressure of each component.

It is assumed that the gases do not react with each other.

$$p_i = P_{total} y_i$$

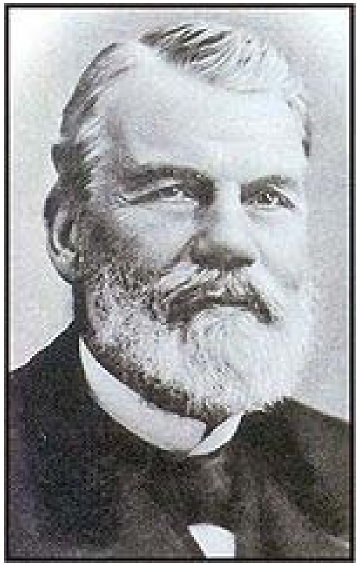
Where: $y_i =$ the mole fraction of the i-th component in the total mixture of *n* components

Raoult's Law

Raoult's Law: *the vapor pressure of an ideal solution is dependent on the vapor pressure of each chemical component and the mole fraction of the component present in the solution*.

Once the components in the solution have reached equilibrium, the total vapor pressure *p* of the solution is:

$$p = p_A^\star x_A + p_B^\star x_B + \cdots$$



and the individual vapor pressure for each component:

$$p_i = p_i^\star x_i$$

p_i is the partial pressure of the component i in the mixture (in the solution)
p^*_i is the vapor pressure of the pure component i
x_i is the mole fraction of the component i in the mixture (in the solution)

Henry's Law

With a little work for ideal systems:

$$p_i = p_i^* x_i = P_{total}\, y_i$$

For real systems we have Henry's Law

At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

$$P_i = x_i H_i$$

H_i = Henry's law constant for i th component

RSK 175

Founded on Henry's Law

Developed at EPA's Robert S. Kerr Laboratory

Standard Operating Procedure 175

RSK 175
Procedure

GC/FID; Calibrated by injecting gas standards

Collected in headspace free containers

Headspace generated in laboratory

Concentration of headspace determined

Concentration of liquid is calculated

RSK 175
Advantages

Gives good approximation of liquid concentrations

Accounts for vapor and liquid

Easy, quick chromatographic method

Can be used for other applications

RSK 175
Disadvantages

Manual method

Standards are expensive

Limited QA procedures

Dilutions done manually

PA DEP Method

- Described as an in-house method
- Uses headspace sampling device
- Calibration done on saturated solutions and subsequent dilutions
- Pure response factor method
- Does not use Henry's Law

PA DEP Method Advantages

Automated

No complex calculations

Reduced standard cost (for methane)

Quick GC/FID method

PA DEP Method Disadvantages

Handling of standards

Limited application

Multi component analysis complicated

Diluting samples

The Future

Field Sampling

Containers

Preservation

Holding times

Standardization of methods

No formal method

Lack of certification

Lack of knowledge

Lack of maximum contaminant levels (MCLs)

Lack of certified reference materials, PE samples

THANK YOU

Ray Martrano
Laboratory Director
Seewald Laboratories Inc.
2829 Reach Road
Williamsport Pa 17701
570-326-4001
rmartrano@seewaldlabs.com
www.seewaldlabs.com

SEEWALD LABORATORIES, INC.