Laboratory Sub-Sampling & Analysis for Methane in Water

National Environmental Monitoring Conference
Washington, DC
August 7, 2014
Overview

- Reasons for Methane Testing in PA
  - Gas Migration, Risk Assessment

- Methane Analysis Techniques
  - Headspace vs. Purge & Trap

- Laboratory Sub-Sampling Study
  - Open vs. Closed Vial
Why Test for Methane?

Regulations:

- NO Federal Regulations or Advisory Levels

Possible Risk Factors:

- NOT Toxic, Poisonous, Carcinogenic, Corrosive, Reactive
Why Test for Methane?

Possible Risk Factors:
- Asphyxiation, Explosion
  - Rare & unlikely

Other Reasons:
- Indirect Effect on Water Quality
  - High methane concentration increases sulfides, iron, magnesium
Perceived Risk

Calculated Risk = Hazard \times Exposure

Perceived Risk = Calculated Risk \times Outrage

Outrage: Everything that is relevant to our perception of a risk except how likely it is to actually be harmful

Sensationalized Media Coverage = Increased Outrage
Origins & Sources of Methane

Gas Origin

- Shallow thermogenic gas
- Deep thermogenic gas
- Microbial gas (CO₂ reduction)
- Microbial gas (fermentation)

Gas Source

- Gas drilling activity
- Abandoned (vertical) gas well
- Landfill/sewer gas
- Coal bed gas
- Natural gas pipelines
Brief History of Methane Testing in PA

BOL Methane Samples Submitted per Year

- BOGM
- non-BOGM

Years:
- 2002
- 2003
- 2004
- 2005
- 2006
- 2007
- 2008
- 2009
- 2010
- 2011
- 2012
- 2013

Sample Numbers:
- 0
- 100
- 200
- 300
- 400
- 500
- 600
- 700
- 800
- 900
- 1000
- 1100
- 1200
Why Does BOL Test for Methane?

Drilling-Related:
Gas Migration Investigations
Pre-Screen for Isotopic Analysis (> 2 mg/L)

Non-Drilling Related:
Monitor Landfill Gases
Chlorinated Solvent Remediation (Ethene)
No Published Methods Available!

- RSK175
- PA DEP Method
  (aka: RSK175 mod, BOL6019, EPA 5021 mod, PADEP 3686)
- Purge & Trap
  (aka: PADEP 9243, EPA 5030C)
Analysis Techniques – Overview

Most Common is GC/FID:

- GC = Gas Chromatography
- FID = Flame Ionization Detection

Advantages of FID:

- "Universal" Detector
- Very Sensitive
- Very Stable
- Wide Linear Range
Sample Introduction: Headspace

Static Equilibrium Technique

Headspace GAS Is Analyzed, Not WATER

IMPORTANT
Initial Sample Conc. 
*Does Not Equal* !
Equilibrated Gas Conc.

Before Equilibrium

After Equilibrium
## Gas vs. Aqueous Calibration

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<tr>
<th>Feature</th>
<th>Gaseous</th>
<th>Aqueous</th>
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</thead>
<tbody>
<tr>
<td>Purchase Multiple Cylinders</td>
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<td>Yes</td>
</tr>
<tr>
<td>Automated Prep</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Automated Analysis</td>
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<td>Yes</td>
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<tr>
<td>Upper Cal Limit</td>
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<td>Saturation</td>
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<tr>
<td>Extensive Calculations</td>
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<td>Direct Correlation with Sample Matrix</td>
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# Headspace SOP Comparison

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<tr>
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<th>RSK-175</th>
<th>PADEP</th>
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<tbody>
<tr>
<td>Automated Analysis</td>
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<tr>
<td>Automated Sample Prep</td>
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<td>Gas or Aqueous Standards</td>
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<tr>
<td>Carryover Potential</td>
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<td>Low</td>
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<tr>
<td>Matrix Interferences</td>
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<tr>
<td>Open Sample Vial</td>
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<tr>
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<td>No/No</td>
<td>Yes/Yes</td>
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Sample Introduction: Purge & Trap

Dynamic Extraction Technique

Purge gas moves analytes from sample to trap

Direct determination of sample concentration

To GC/FID

Purge gas
## Overall Comparison of Analytical Options

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<th>P&amp;T</th>
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Proposed ASTM Method

- Headspace GC/FID Analysis
- **Requirement:** Closed Sampling System
- Can only be achieved using manual prep or a vendor-specific, modified P&T autosampler
- Will increase the cost and/or time burden on labs that do not own the correct P&T

- Is it actually necessary?
Laboratory Sub-Sampling Study

- Side-by-side analysis:
  - All aliquots taken from same sample bottle
  - H0: Transfer to HS vial using He (closed system)
  - P1: Remove cap, use pipet (~ 1 minute)
  - P2: Leave open 60 sec, use pipet (~ 2 minutes)
  - P3: Leave open 60 sec, use pipet (~ 3 minutes)
Study Results

Effect of Opening Sample Vial on Methane Concentration

- Helium Transfer (µg/L)
- Pipet Transfer (µg/L)

Legend:
- Diamond: 1 Minute
- Square: 2 Minutes
- Triangle: 3 Minutes

Data points for each time interval show the effect on methane concentration.
Good Laboratory Technique

- Analyst must be mindful of technique when working with volatile components
  - Cold Sample (not room temp)
  - One Sample At A Time
  - Work Quickly
  - Cap Immediately
  - Should Take < 30 sec
Breakdown: 1 Minute

Effect of Opening Vial on Methane Concentration After One Minute, μg/L

\[ y = 0.9995x \]

\[ R^2 = 0.9896 \]
Breakdown: 1 Minute, Unsaturated

Unsaturated Values Only:
Methane Concentration After One Minute, µg/L

$R^2 = 0.9981$
Breakdown: 2 Minutes

Effect of Opening Vial on Methane Concentration
After Two Minutes, μg/L

\[ y = 0.9796x \]
\[ R^2 = 0.9779 \]
Effect of Opening Vial on Methane Concentration After Three Minutes, μg/L

\[ y = 0.9768x \]

\[ R^2 = 0.9768 \]
Precision may be quantified using %RSD => Calculate %RSD for H0/P1/P2/P3 data set

Hypothesis: IF opening vial introduces bias, THEN expect elevated %RSD values

Observation: Average %RSD = 5.9%
%RSD Range = 0.9 to 18.9%

Conclusion: Bias from opening vial not significant compared to accepted control limits
Sub-Sampling Study Conclusions

Opening the sample bottle does not significantly affect the results as long as the analyst uses Good Laboratory Technique.

Codifying a requirement to use a closed sampling system for methane analysis places an unnecessary burden on the analytical laboratory.
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