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DEPARTMENT OF ENVIRONMENTAL PROTECTION



Bureau of Laboratories

Public and Private Environmental Laboratory Collaboration for a Standardized Methane Test Method

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National Environmental Monitoring
Conference

Virtual

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► Overview from the Public Regulatory Perspective

- ✔ Reasons for Methane Testing in PA and Need for Standardized Gas Testing Migration, Risk Assessment, Brief History Methane Analysis
- ✔ Techniques – Variability observed by PA DEP, O&G Advisory Committee, and O&G Industry
- ✔ The need for a standardized method
PA DEP Laboratory Sub-Sampling Study
Open vs. Closed Vial

Why Test for Methane?

Regulations:

- X** NO Federal Regulations or Advisory Levels

Possible Risk Factors:

- X** NOT listed as Toxic, Poisonous, Carcinogenic, Corrosive, Reactive

Why Test for Methane?

Possible Risk Factors:



Asphyxiation, Explosion



Fortunately Rare with O&G Regs

Other Reasons:

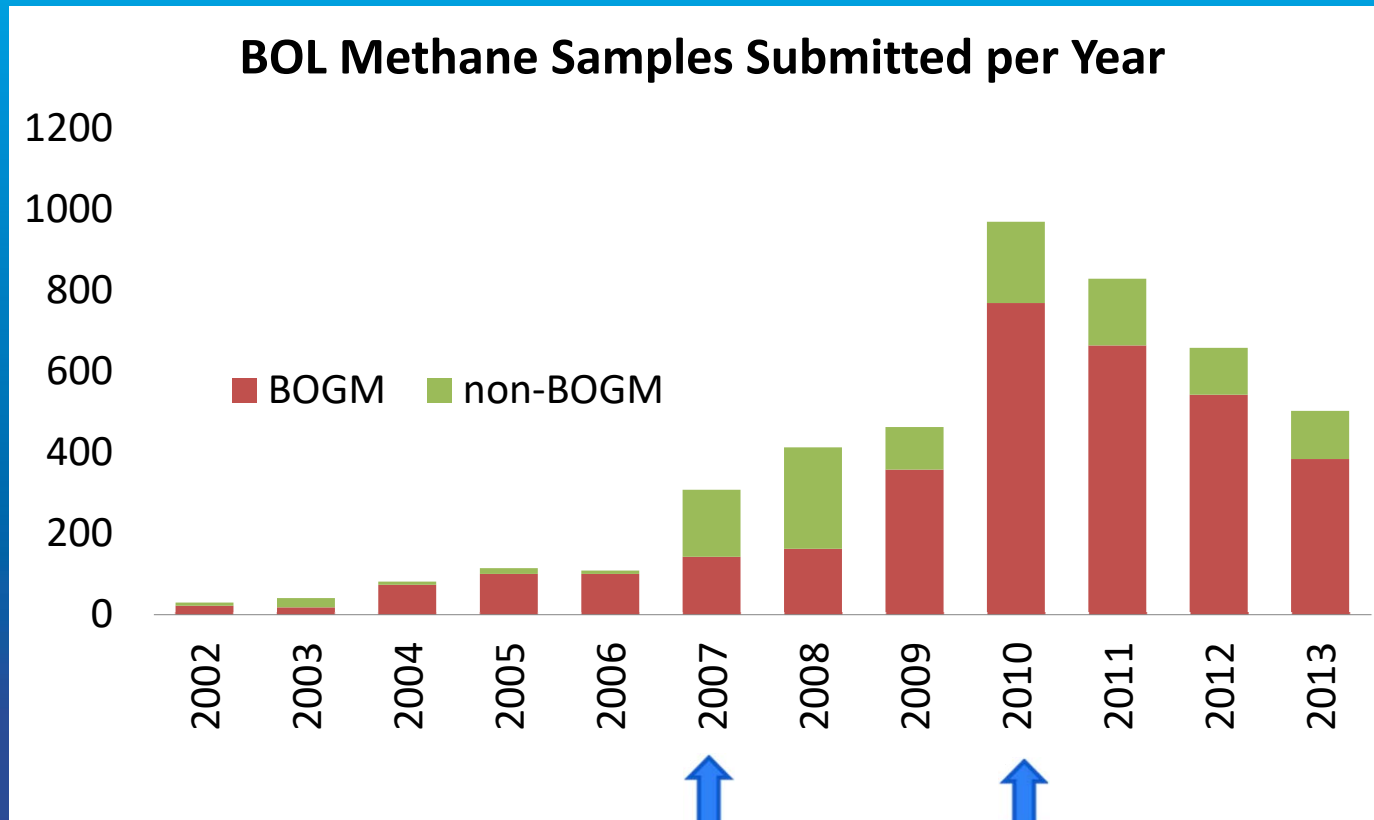


Indirect Effect on Water Quality

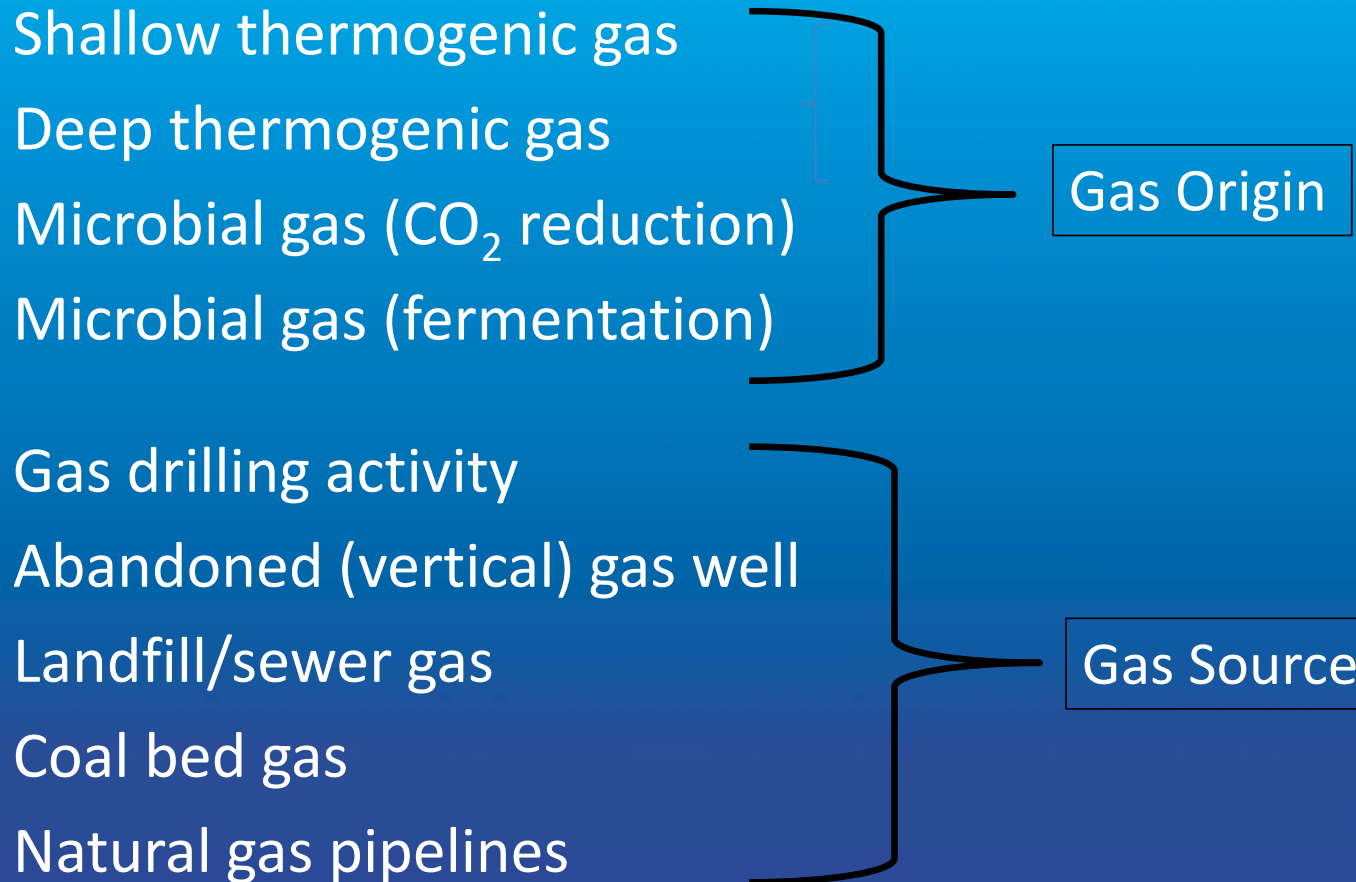


High methane concentration increases sulfides, iron, magnesium

Brief History of Methane Testing in PA



Origins & Sources of Methane



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)

Analytical Options

No Standardized Methods Available
and None Included in O&G Regulations

- ❖ RSK175

- ❖ PA DEP Method

(aka: RSK175 mod, BOL6019, EPA 5021 mod, PADEP 3686)

- ❖ Purge & Trap and PA DEP 9243

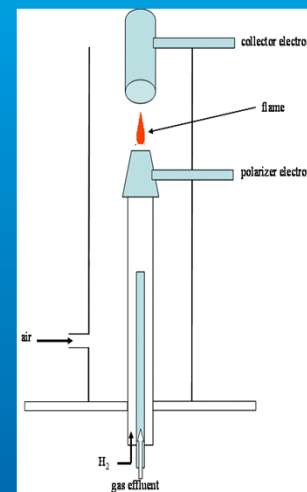
Analysis Techniques – Overview

Most Common is GC/FID:

- ❖ GC = Gas Chromatography
- ❖ FID = Flame Ionization Detection

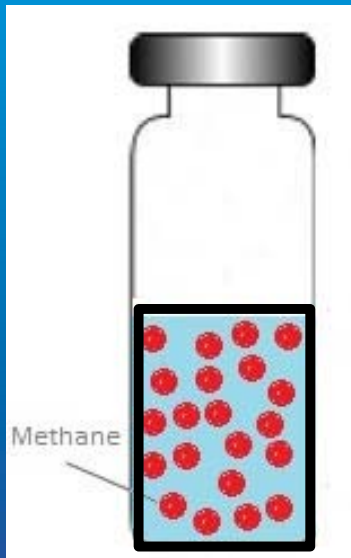
❖ Advantages of FID:

- ★ “Universal” Detector
- ★ Very Stable
- ★ Very Sensitive
- ★ Wide Linear Range



Sample Introduction: Headspace

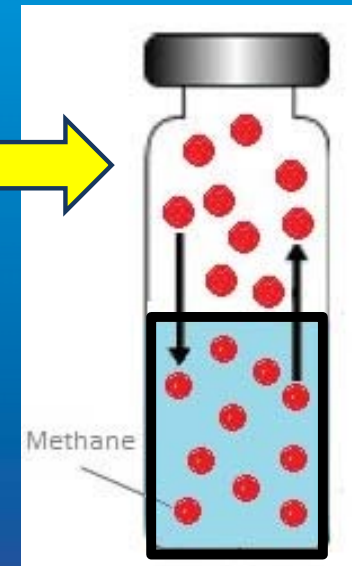
Static Equilibrium Technique



Before Equilibrium

Headspace GAS
Is Analyzed,
Not WATER

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



After Equilibrium

Gas vs. Aqueous Calibration

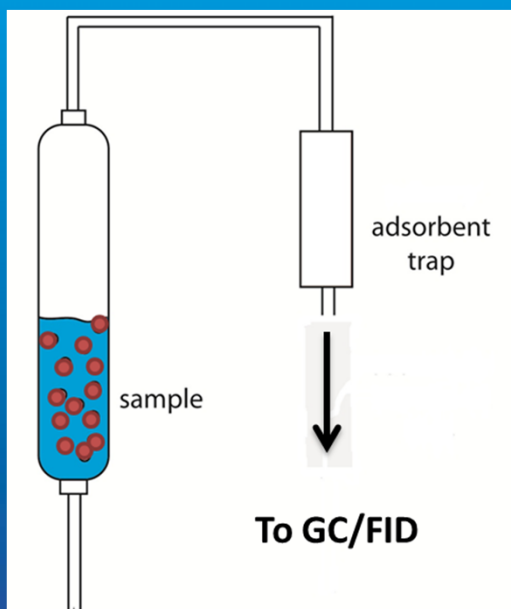
	Gaseous	Aqueous
Purchase Multiple Cylinders	Yes	Yes
Automated Prep	No	No
Automated Analysis	No	Yes
Upper Cal Limit	None	Saturation
Extensive Calculations	Yes	No
Direct Correlation with Sample Matrix	No	Yes

Headspace SOP Comparison

	RSK-175	PADEP
Automated Analysis	No	Yes
Automated Sample Prep	No	No
Gas or Aqueous Standards	Gas	Aqueous
Linear Range	Wide	Wide
Carryover Potential	Low	Low
Matrix Interferences	Low	Low
Open Sample Vial	No	Yes
Extensive Calculations	Yes	No
LCS/MS Possible	No/No	Yes/Yes

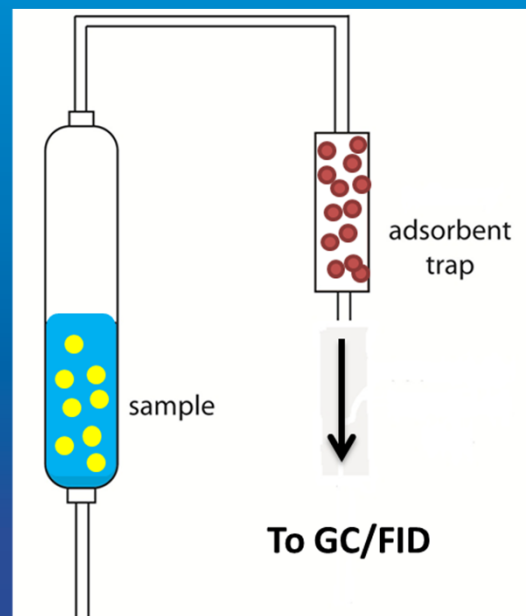
Sample Introduction: Purge & Trap

Dynamic Extraction Technique



Purge gas moves analytes from sample to trap

Direct determination of sample concentration



Purge gas

Overall Comparison of Analytical Options

	RSK-175	PADEP	P&T
Automated Analysis	No	Yes	Yes
Automated Sample Prep	No	No	Yes
Gas or Aqueous Standards	Gas	Aqueous	Aqueous
Linear Range	Wide	Wide	Moderate
Carryover Potential	Low	Low	High
Matrix Interferences	Low	Low	Moderate
Open Sample Vial	No	Yes	No
Extensive Calculations	Yes	No	No
LCS/MS Possible	No/No	Yes/Yes	Yes/No

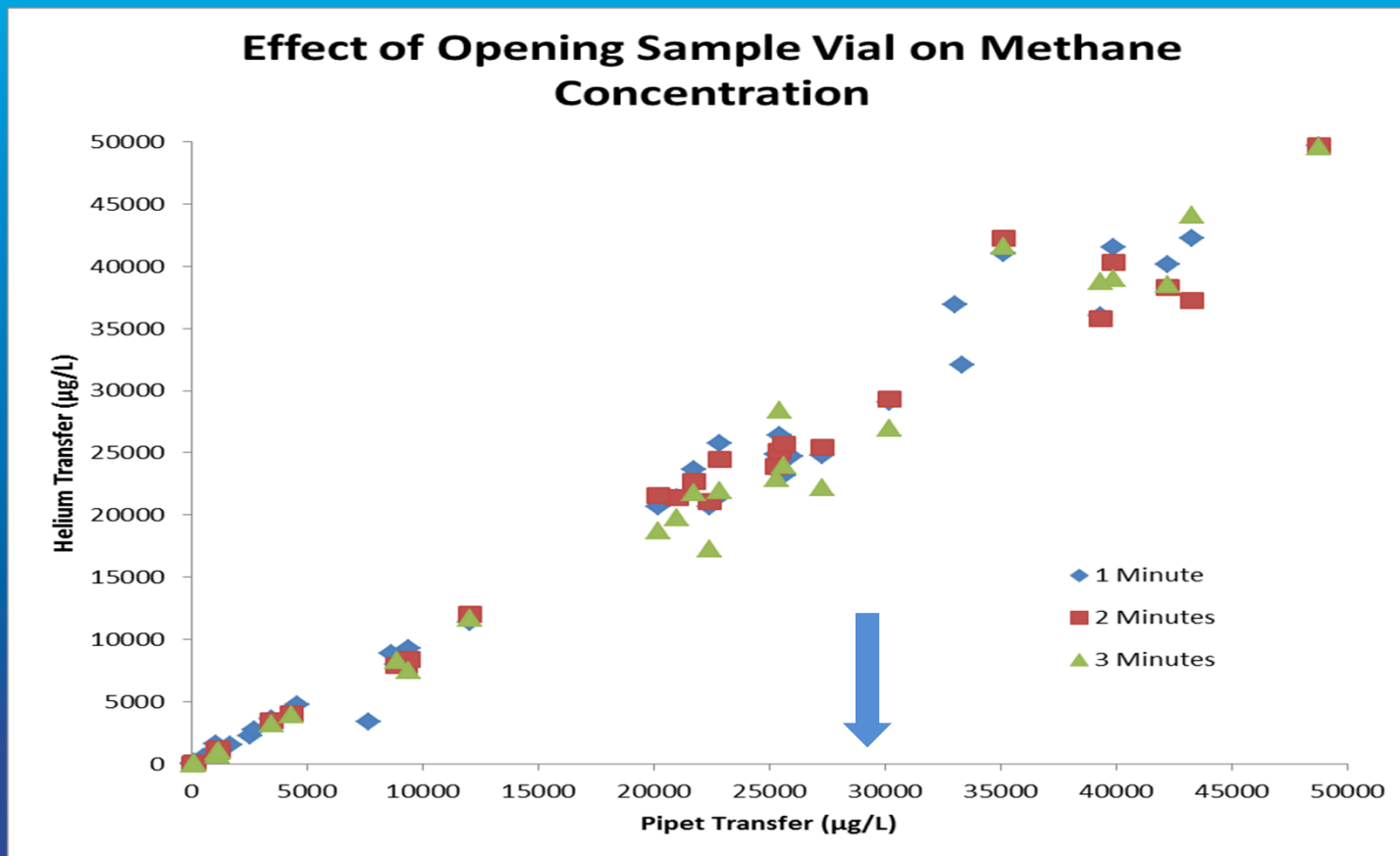
ASTM Method

- ❖ Headspace GC/FID Analysis
- ❖ Recommended: 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



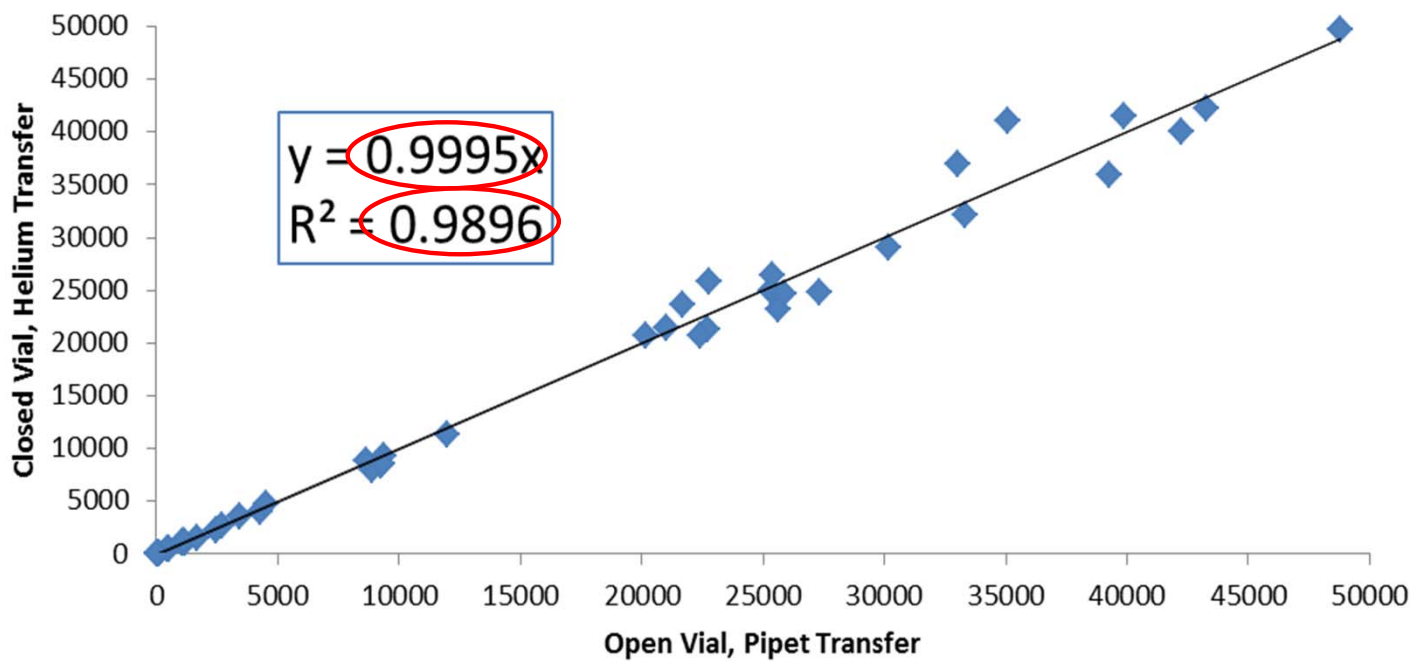
Good Laboratory Technique

❖ Analyst must be mindful of technique when working with volatile components

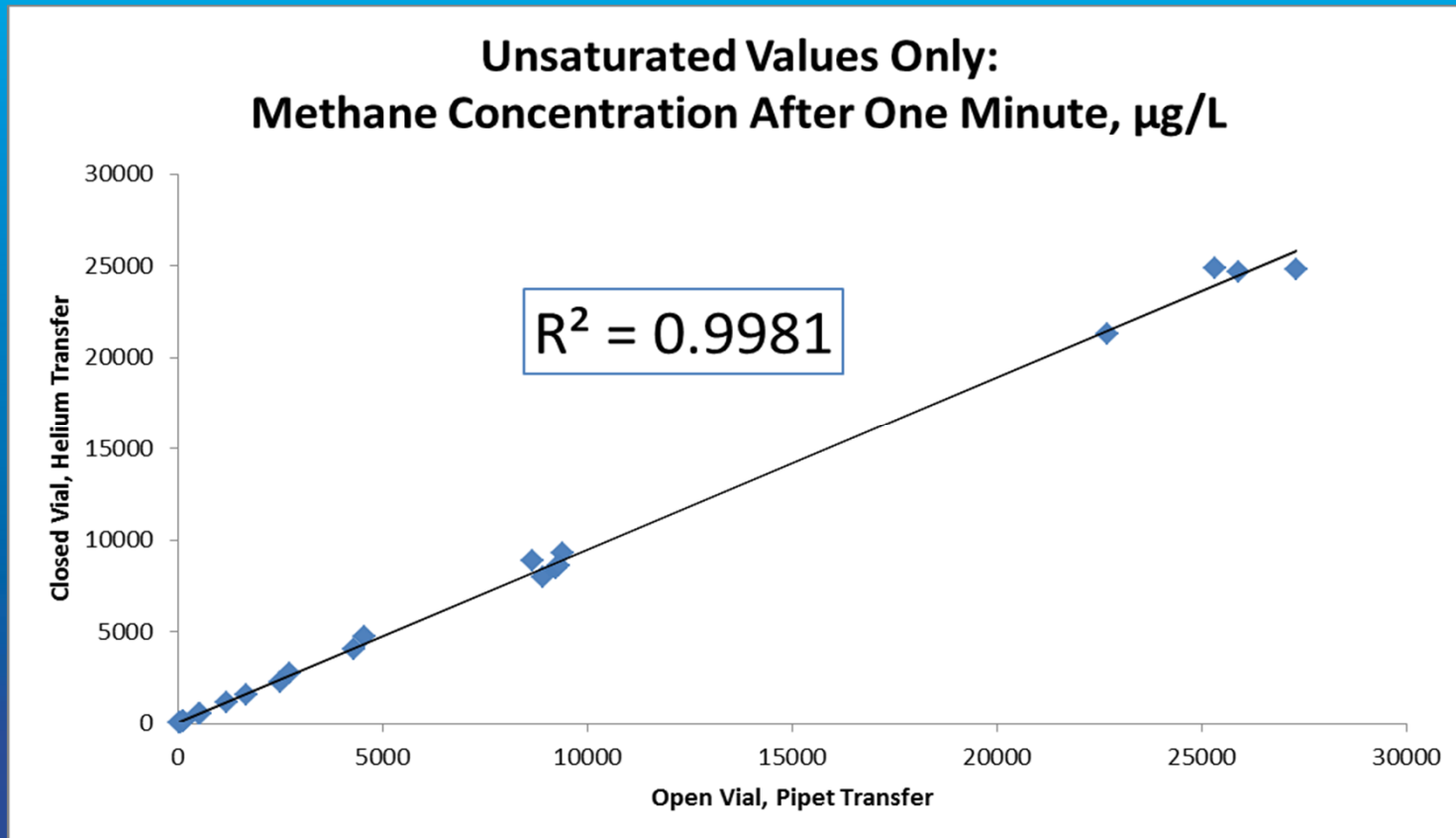
- ✅ Cold Sample (not room temp)
- ✅ One Sample At A Time
- ✅ Work Quickly
- ✅ Cap Immediately
- ✅ Should Take < 30 sec

Breakdown: 1 Minute

Effect of Opening Vial on Methane Concentration After One Minute, $\mu\text{g/L}$

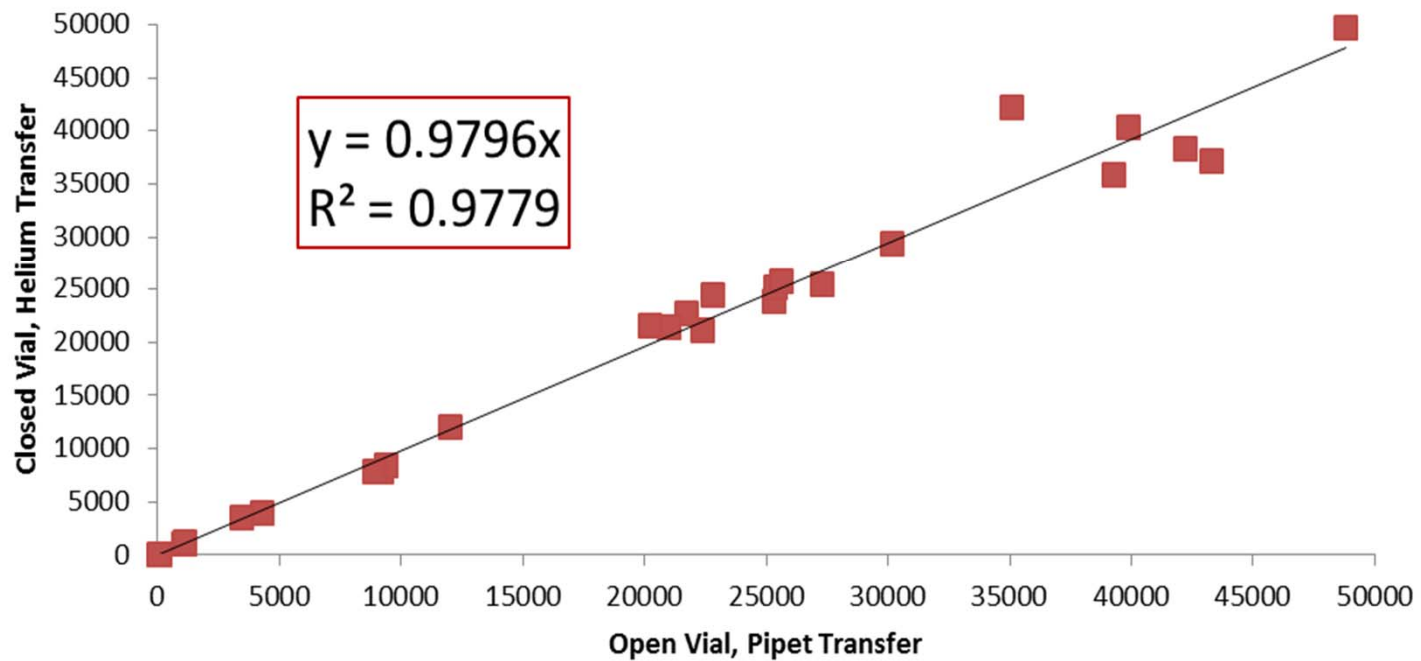


Breakdown: 1 Minute, Unsaturated



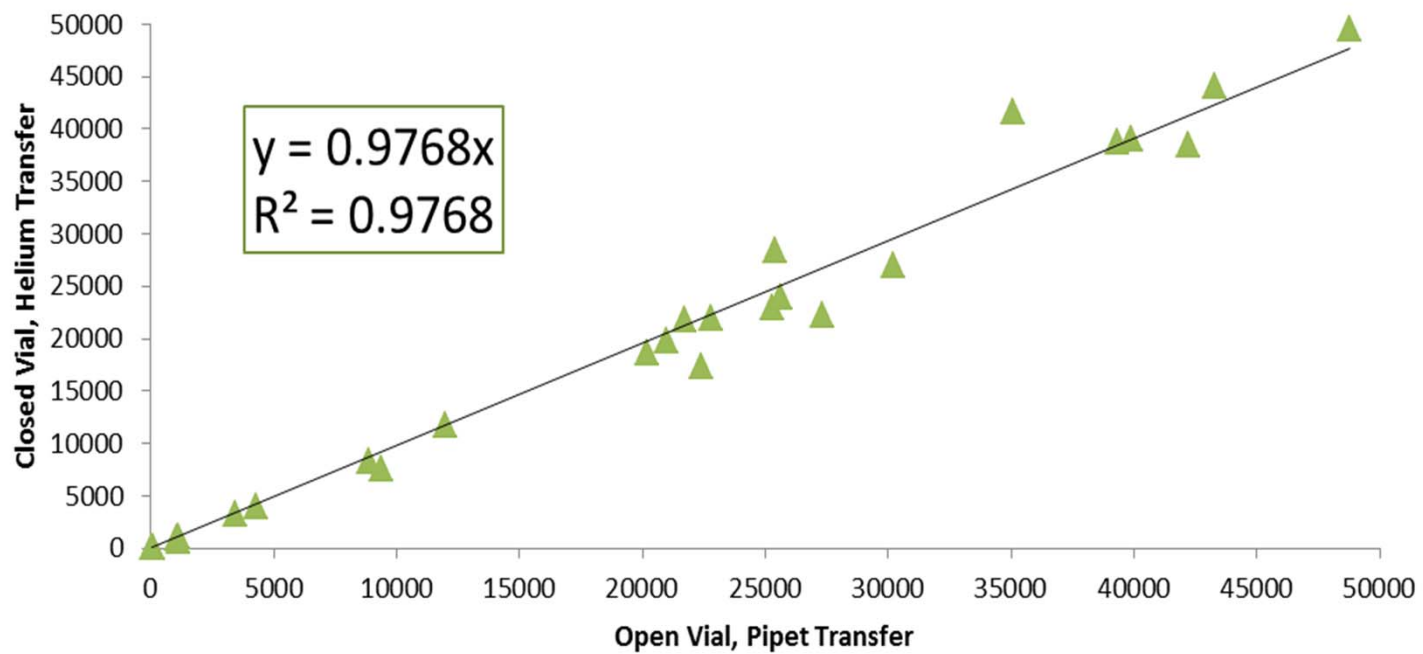
Breakdown: 2 Minutes

Effect of Opening Vial on Methane Concentration After Two Minutes, $\mu\text{g/L}$



Breakdown: 3 Minutes

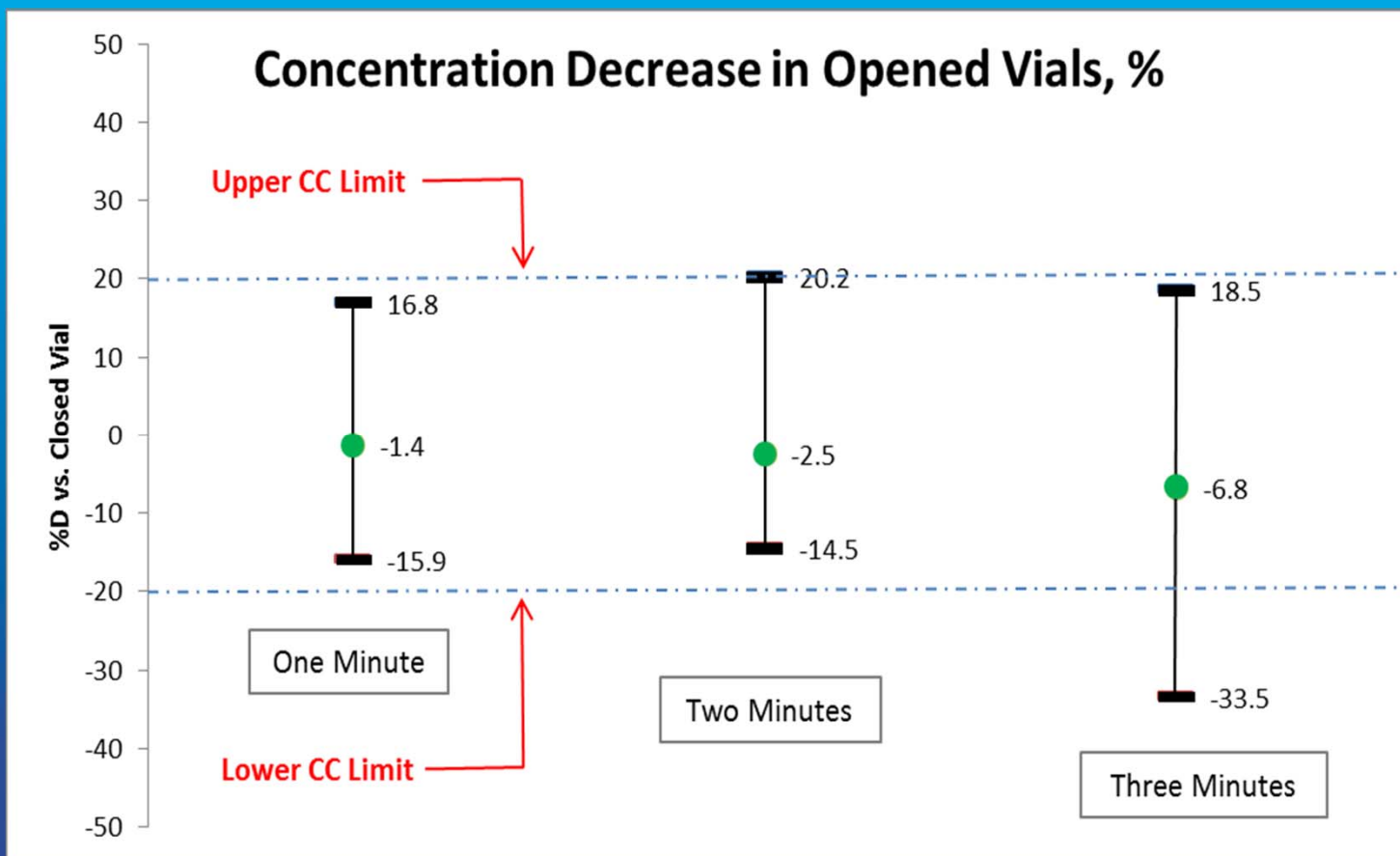
Effect of Opening Vial on Methane Concentration After Three Minutes, $\mu\text{g}/\text{L}$



Summary Statistics - Precision

- ❖ 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

Summary Statistics - Bias



Sub-Sampling Study Conclusions



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



A requirement to use a closed sampling system for methane analysis place may require unnecessary equipment purchase

Collaborative Summary

Through collaboration and discussions which began at NEMC the PA DEP, Marcellus Shale Coalition, Environmental Standards, Inc. and Environmental Services Laboratories (ESL) were able to develop a study and propose data for a standardized method as well as work with the development of certified reference materials. The study included multiple lab participation and multiple phases with a certified reference material developed



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Special Thank you to Acting Technical
Director, June Black



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Questions????

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