Dissolved Methane Round Robin Case Study – Regulations Without a Robust Analytical Method

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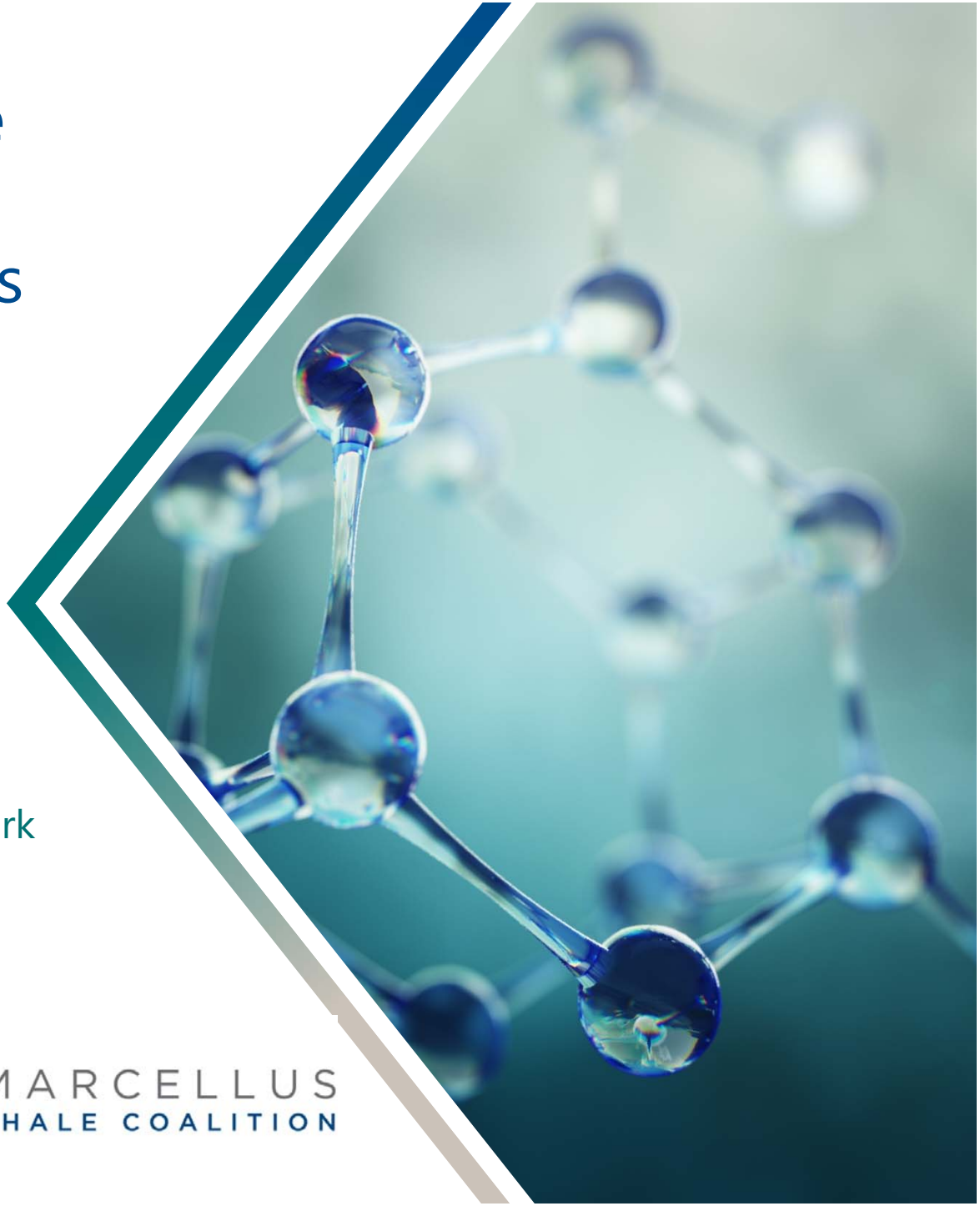
Work sponsored by the MSC Dissolved Methane Method Work Group



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MARCELLUS SHALE COALITION

Phases 1 and 2

- Phase 1: Analysis of two groundwater wells, concentrations at saturation
  - Well 1 – 7,400 to 34,600 µg/L.
    - Well 1 Average Temperature 10.6°C
  - Well 2 – 8,300 to 44,000 µg/L .
    - Well 2 Average Temperature 9.4°C.
- Phase 2 Blind Reference Standards
  - 270 µg/L; 1,080 µg/L; 2,700 µg/L; 7,015 µg/L

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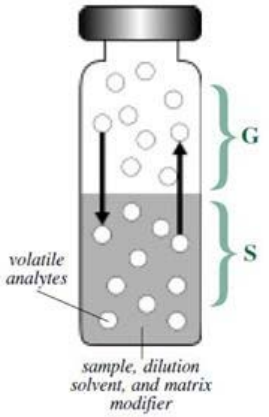
Calibration Approaches



- Phase 2:
  - 4 Laboratories perform via direct gas injection, Henry's Constant calculation
  - 2 Laboratories prepared a saturated solution
  - 10 Laboratories prepared via injection of concentrated standards into vial with headspace above aqueous phase

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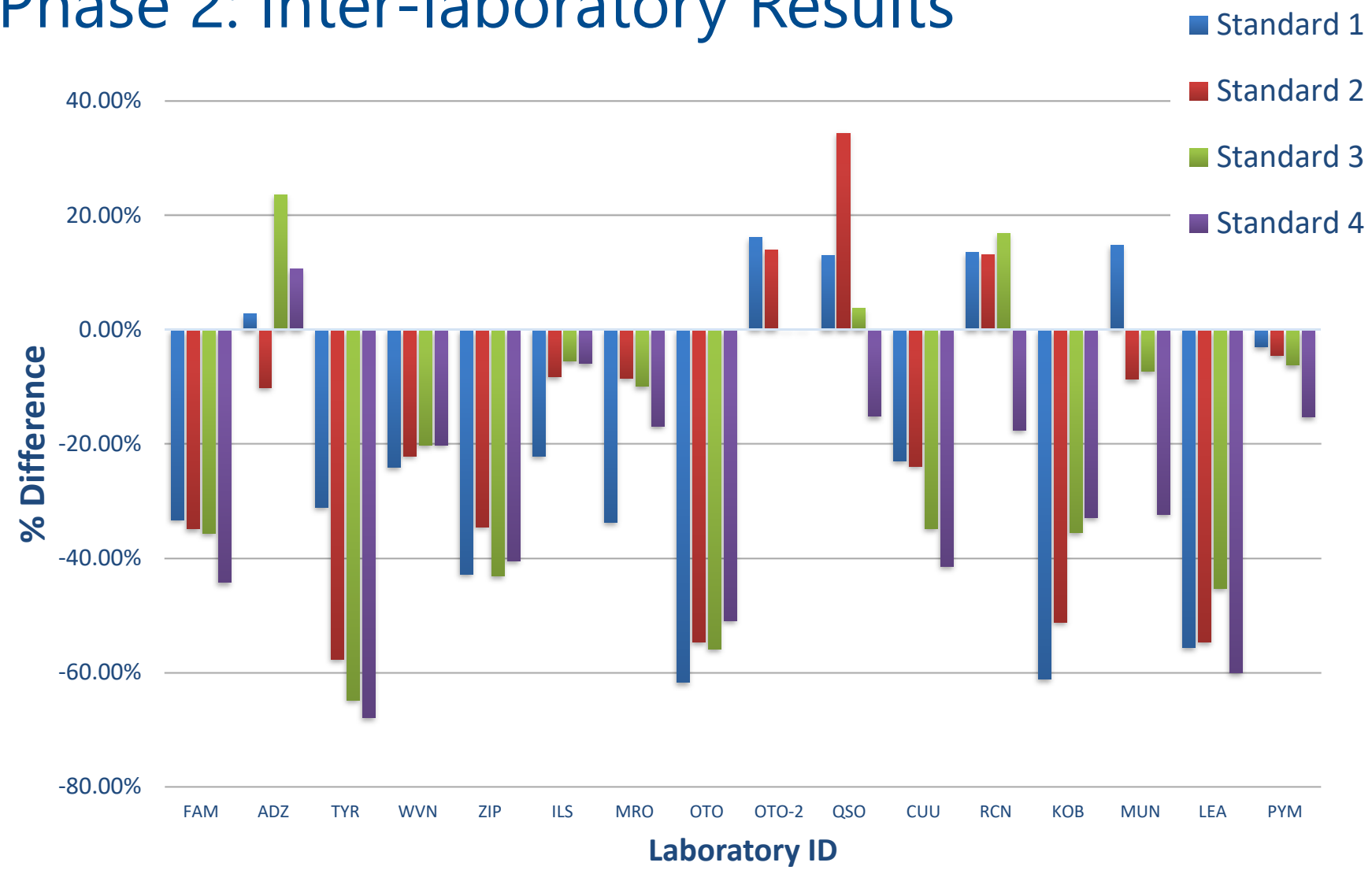
Phase 2: Inter-laboratory Results



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Phase 3 Study Participants

- Select members of the Marcellus Shale Coalition Dissolved Methane Method Work Group
- Environmental Standards, Inc., Valley Forge, Pennsylvania
- Environmental Services Laboratory (ESL), Indiana, Pennsylvania. Reference Standard provider
- Eight Non-Reference Laboratories
- Three Reference Laboratories (selected from prior phases)

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Phase 3 Design

- Send laboratories known concentration standards.
  - ESL Prepared approximately 70 vials in two batches, all at a single final concentration.
- Assess results sequentially and review against known concentration. Make revisions to preparation, handling, calibration, analysis and technique as needed.
- Include three Reference Laboratories for comparison, analyze samples over the course of ~14 days.
- Goal was acceptable analyses with self diagnosis of 70-130% of reference concentration (~7000µg/L).

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As-made Concentration

	ESL Reported Concentration (µg/L)	Reference Laboratory 1 (µg/L)	Reference Laboratory 2 (µg/L)	Reference Laboratory 3 (µg/L)
	8490	6600	7560	7880
	8640	7000	7190	**7440**
	8570	**6500**	**6490**	**7490**
	8750	**7100**	**7465**	6820
	8460			
	8150			
Average	**8510**	**6800**	**7176**	**7408**
Standard Deviation	**205**	**294**	**484**	**438**
%RSD	**2.4%**	**4.3%**	**6.7%**	**5.9%**
Duplicate Analysis RPD		**8.8%**	**14%**	**0.7%**

Average of Reference Laboratories	**7130**
Standard Deviation of Reference Laboratories	**456**
%RSD of Reference Laboratories	**6.4%**

Bold are replicate analyses.
ESL analyzed overnight.
Reference Laboratories analyzed over ~14 days.

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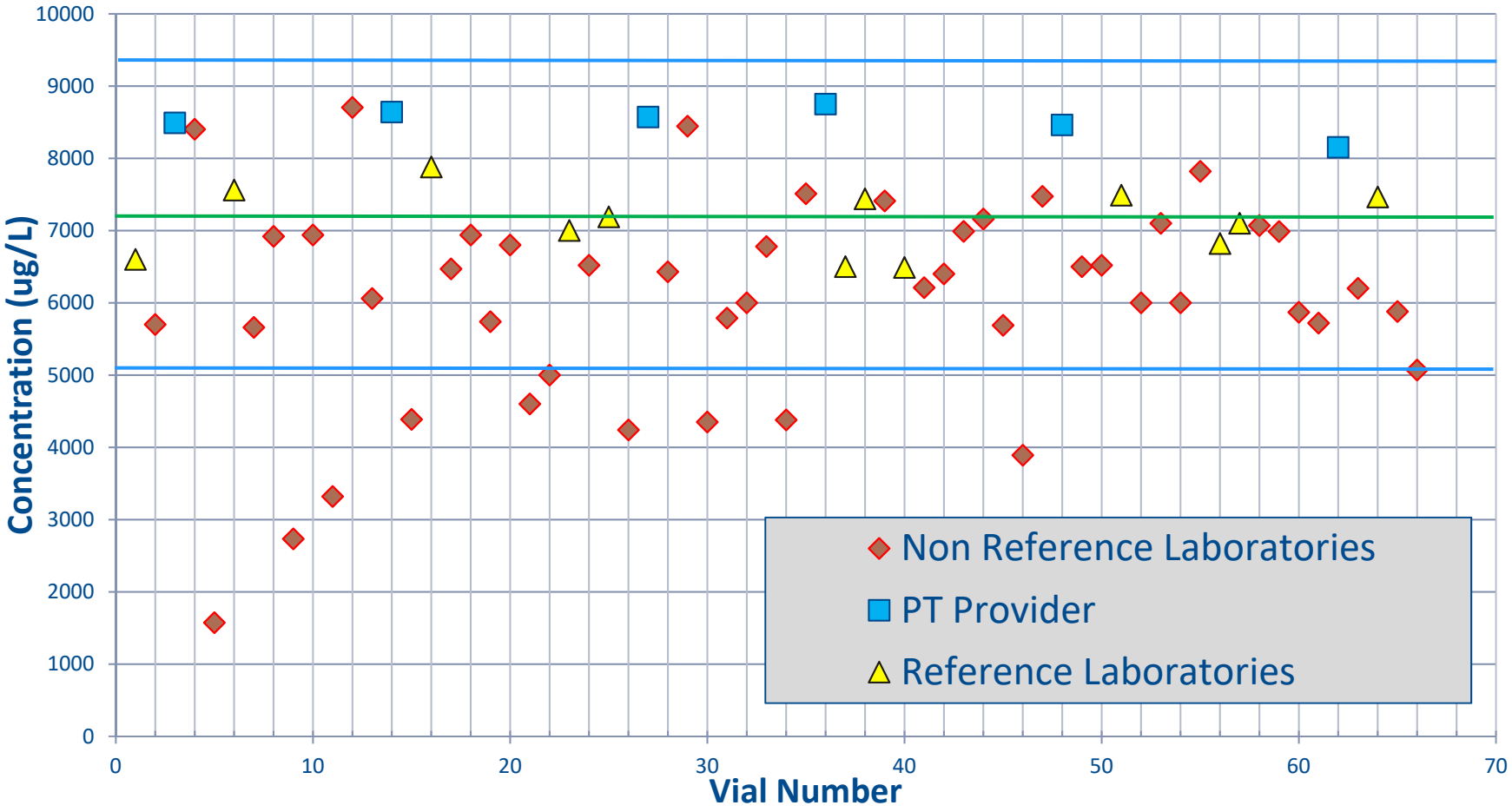
All Laboratories: Methane Concentration by Vial Number



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Reference Laboratories vs Standard Provider

- Possible Reasons
  - Normal analytical uncertainty
  - Calibration gas source differences
  - Initial loss of methane within 48 hours, static thereafter

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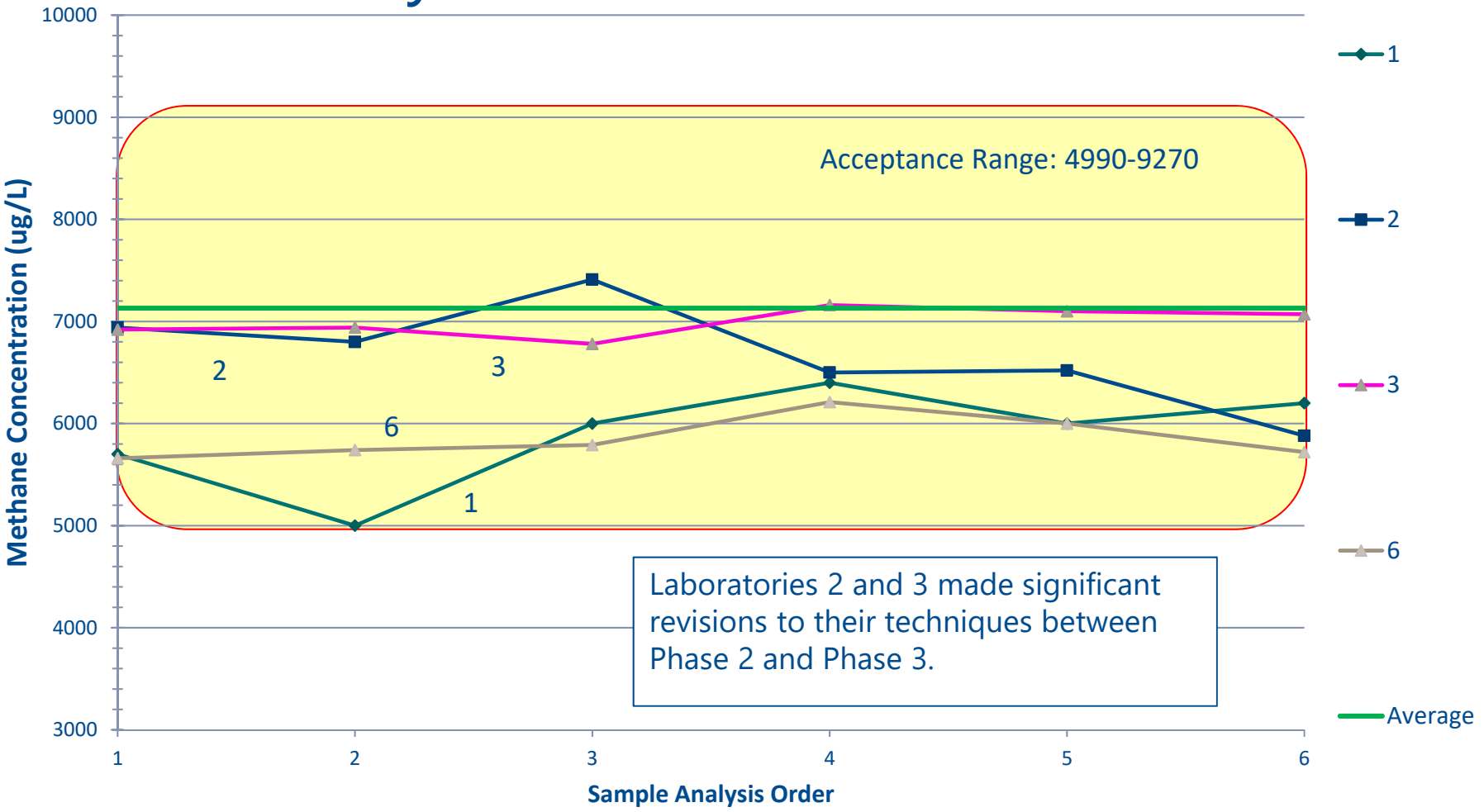
Non-Reference Laboratories (1, 2, 3, and 6) in Order of Analysis



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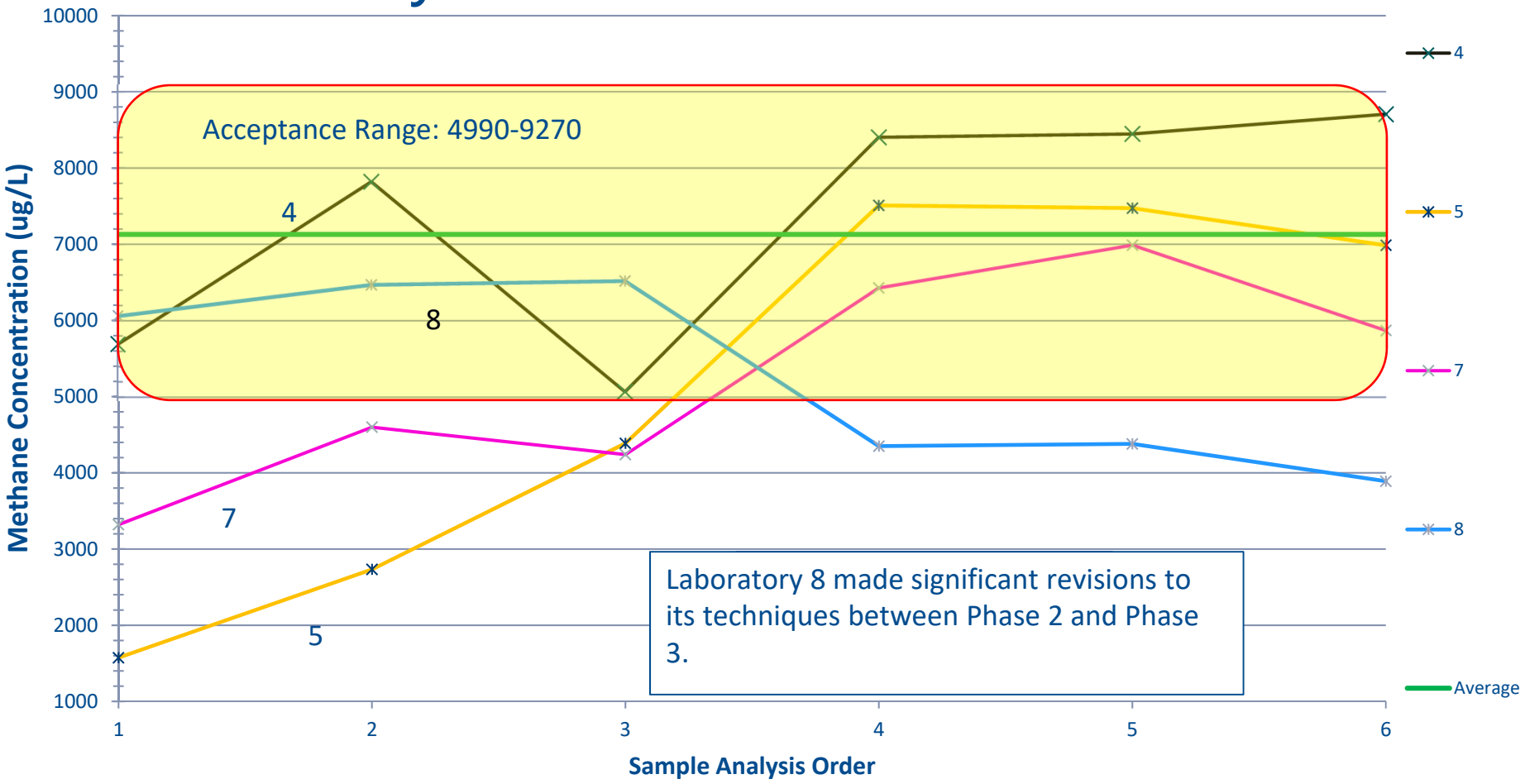
Non-Reference Laboratories (4, 5, 7, and 8) in Order of Analysis



Dissolved Methane Results (µg/L)
Non-Reference Laboratories

Vial Order	Laboratory ID Number							
	1	2	3	4	5	6	7	8
Vial 1	5700	6940	6920	5690	**1574**	5660	**3320**	6060
Vial 2	5000	6800	6940	7820	**2733**	5740	**4600**	6470
Vial 3	6000	7410	6780	5070	**4387**	5790	**4240**	6520
Vial 4	6400	6500	7160	8402	7510	6210	6430	**4350**
Vial 5	6000	6520	7100	8446	7474	6000	6990	**4380**
Vial 6	6200	5880	7070	8705	6987	5720	5870	**3890**

Lower recovery limit: 4990, upper recovery limit: 9270. Limits are based upon the average concentration from the three Reference Laboratories and the acceptance limits of 70-130% recovery established in Work Plan. Values outside these limits are highlighted in bold.

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Self Diagnosis: Calibration

Observation/Original Approach	Adjustments Made	Impact of Adjustments
Original calibration entailed direct gas injection.	Prepared saturated solution standards following procedure in PA DEP 3686.	A 60% increase was observed by using saturated solution standards for the initial calibration. This combined with extended sample warm up (2 hours) to reach equilibrium, resulted in a total increase of 260%.
Original calibration entailed direct gas injection.	Prepared standards using vials with headspace, allowing equilibrium (time) conditions. Extended equilibrium conditions for laboratory control samples (LCSs).	Combined changes resulted in approximately 150% increase in reported concentration. The results then were within the recovery limits.

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Self Diagnosis: Dilution

Observation	Adjustments Made	Impact of Adjustments
Poor recovery for 10-fold dilution performed via removal of liquid phase into volumetric flask.	Sample and volumetric flask with reagent water placed in ice bath to cool prior to removal of aqueous phase for dilution.	Approximately 75% increase in concentration with change, provided improved accuracy, relative to Reference Laboratories.
Comparing impact on concentration when range of 10 µL - 200 µL gas volume is removed from 4 mL of headspace.	Varying volume of headspace removed.	No impact on results.

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Self Diagnosis: Sample Pressure

Observation	Adjustments Made	Impact of Adjustments
Adjusting helium volume during preparation steps affected headspace pressure.	Attempted to optimize volume of helium added so that headspace was at nominal atmospheric pressure, or above, after sample was removed. Volume injected varied with sample concentration. Measured actual headspace pressure.	All improved accuracy. Headspace pressure measurement was determined to be critical, directly proportional to improved accuracy. A 10% increase was observed by incorporating the measured headspace pressure *versus* assuming it was at ambient.

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Self Diagnosis: Sample Pressure

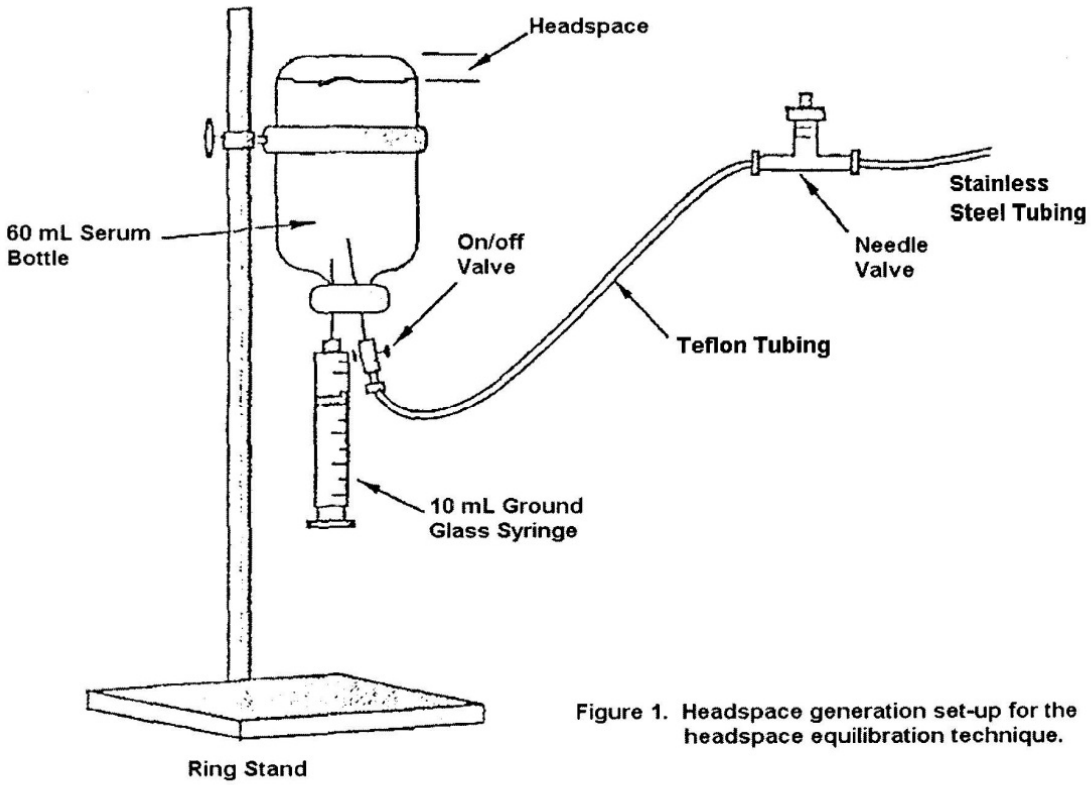

Figure 1. Headspace generation set-up for the headspace equilibration technique.

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Self Diagnosis: Temperature and Equilibrium

Observation	Adjustments Made	Impact of Adjustments
Low bias in prior studies.	Vortex time, once headspace was created, increased from 2 minutes to 5 minutes. Time and mixing adjusted.	The two techniques combined, results in approximately 35% increase in reported concentration. These were sufficient to eliminate the low bias and meet the acceptance limits of the study.
Low bias in prior studies.	Shaking table time was extended to 5 minutes. Time and mixing adjusted.	A 20-30% increase in reported value was achieved by extending the time for shaking the samples. This eliminated the low bias and met the acceptance limits of the study.

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Self Diagnosis: Sample Transfer

Observation	Adjustments Made	Impact of Adjustments
Noted small gas bubbles at times when removing aqueous phase sample from original vial for dilution or transfer to autosampler vial.	Reduced the speed of plunger withdrawal to prevent vacuum and bubble formation.	When bubbles formed, approximately 30% of methane was lost.

Self Diagnosis: Other

Observation	Adjustments Made	Impact of Adjustments
Leaking noted with multiple piercing of Septum. Operation included addition of helium to create headspace pressure.	Minimized piercing as much as possible.	Noted source of leaking and low bias. Approximate 25% increase in reported value was achieved by eliminating leakage via septa.
Time needles left in septum increased potential for leaks.	Punctured septum immediately prior to analysis.	Reduced leakage, and less bias observed. Approximate 25% increase in reported value was achieved by eliminating leakage via septa.
Use of average response factor (RF) resulted in large residuals at high concentration range of calibration.	Linear regression calibration reduced residuals in model.	No significant change for this study.

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Statistical Summary: All Phases

Results by Phase	N	Mean (µg/L)	% RSD
Phase 1, Well 1	53	21070	33%
Phase 1, Well 2	50	23565	36%
Phase 2, Standard 1 (lowest concentration)	45	212	33%
Phase 2, Standard 2	43	861	32%
Phase 2, Standard 3	40	2121	32%
Phase 2, Standard 4 (highest concentration)	35	4900	30%
Phase 3 All/Accepted Values	39	6050/6590	24%/13%

RSD = relative standard deviation, N = number of samples

Phase 2: Standard 1 @ 270 µg/L, Standard 2 @ 1081 µg/L, Standard 3 @ 2,700 µg/L, Standard 4 @ 7,015 µg/L

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Phase 3 Results

- Success with all participating laboratories achieving multiple recoveries within 80-120% of Reference Laboratories average value (exceeded goal)
- Techniques causing bias identified
- Reduced variance
- Difference between Standard provider and Reference Laboratories not confirmed

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Phase 3 Results

Next Steps

- Develop SOP/Work Instruction based on procedures, activities, and techniques learned from Phases 3 study.
- SOP to guide final inter-laboratory study to validate procedure.
- Develop a Test Method that includes three calibration approaches, but controls sample and standard handling to minimize the potential for spread and bias.

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Thank You

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