Topics in Shale Gas – Dissolved Gas Measurement

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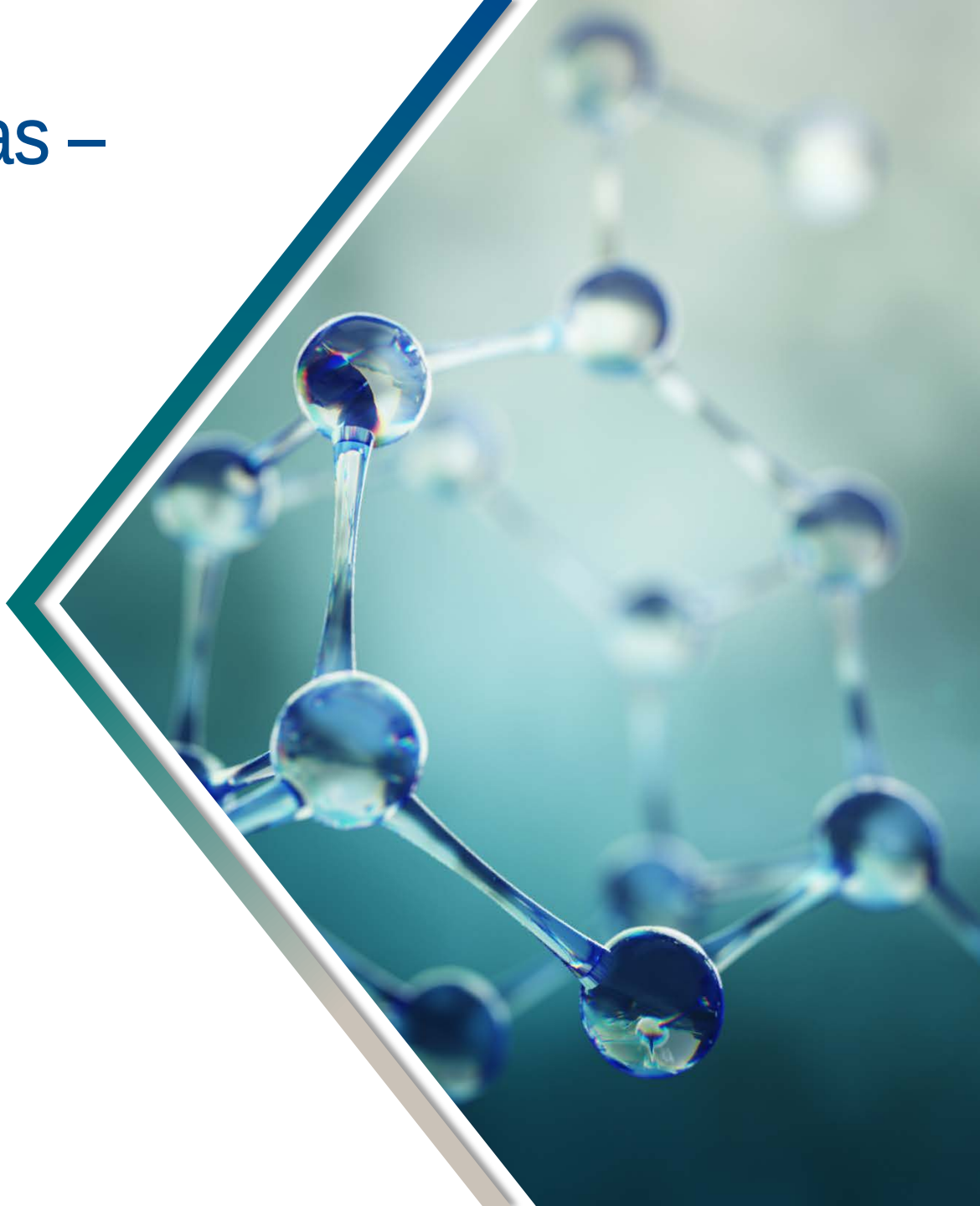

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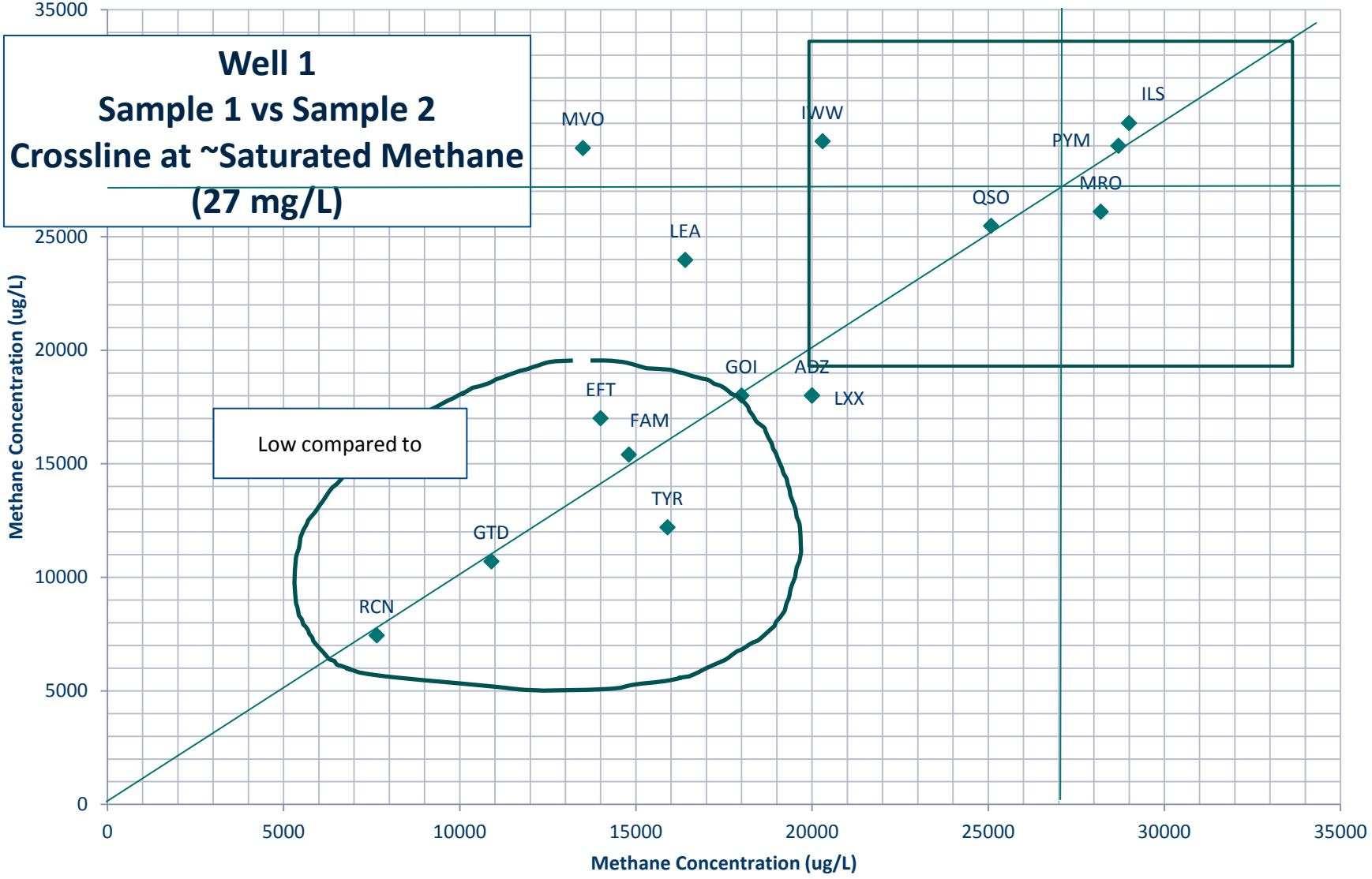
Marcellus Shale Coalition Dissolve Methane Round Robin Study Results- Phase 2

Because 40 - 60% error observed in Phase 1 is not acceptable

MSC Dissolved Methane Method Workgroup

- Formed to study this issue in early 2013
  - Compared notes and reviewed data/information:
    - Dissolved methane split sample data
    - Laboratory analytical protocols
  - Phase 1 Study Completed early 2015
  - Phase 1 – Groundwater samples across fifteen laboratories including one State Agency Laboratory

Phase 1



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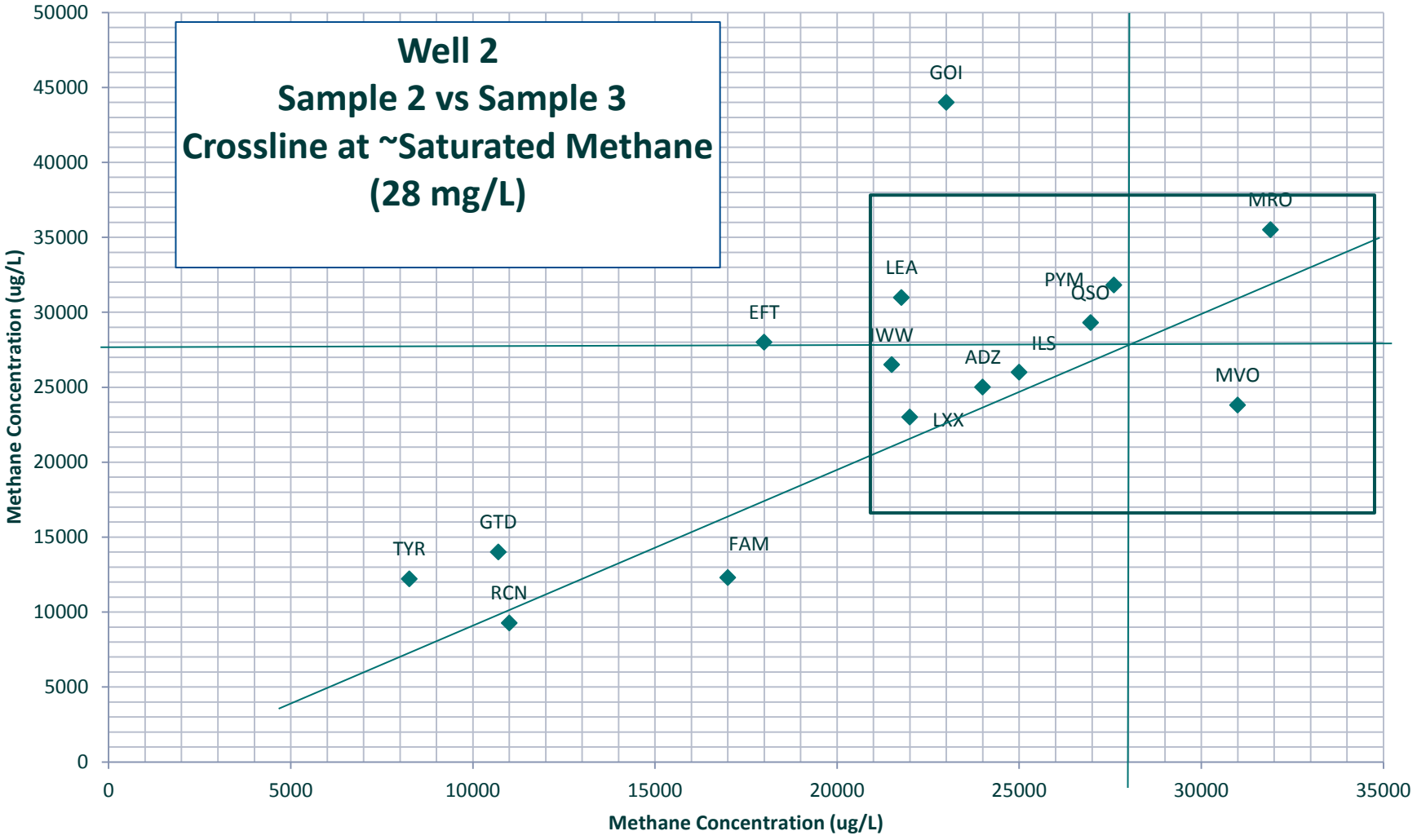
Phase 1



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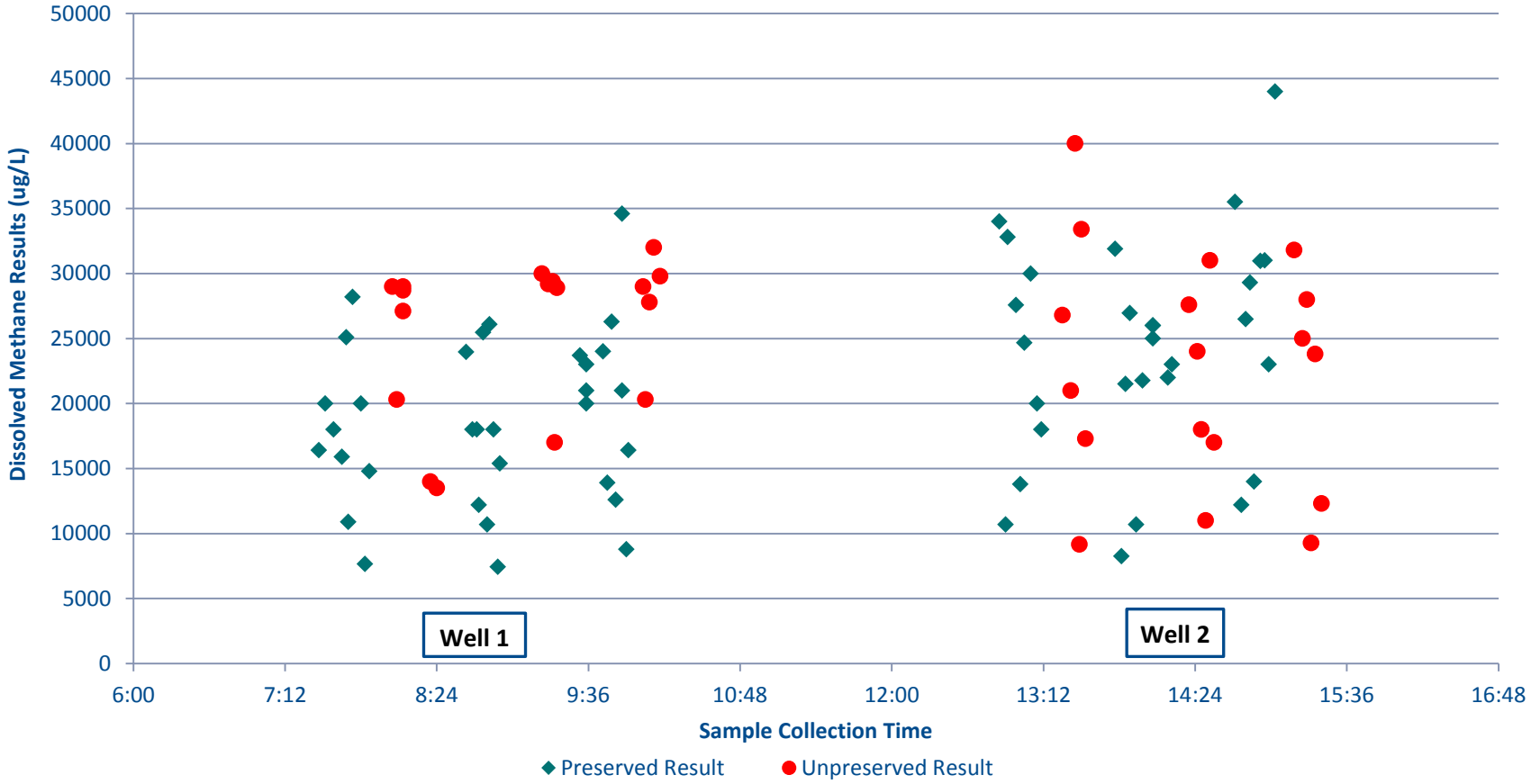
Phase 1 – Preserved vs. Unpreserved



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Phase 1

- Data showed large variations within pool, range of results from two wells:
  - 7,440 to 34,600 µg/L
  - 8,260 to 44,000 µg/L
- No singular issue identified to explain bias
- Calibration varied: direct gas injection>>gas injection into vial/equilibrium>>saturated solutions

Three Calibration Approaches

- 1. Direct gas injection, Henry's Law
  - RSK-175
- 2. Saturated aqueous solution, dilutions thereof
  - PA DEP 3685
  - ASTM WK43267
- 3. Inject gas standard into headspace above aqueous phase, establish equilibrium per Hc. Inject gas phase from samples, calculate aqueous phase conc.

- The Phase 1 study recommendations:
  - Procedures specific to instrument calibration
  - Sample handling/preparation
  - Analysis
  - Propensity for dilution
  - Calculations
- Of most importance is development of a certified performance sample that each laboratory can use to gauge their analysis

Phase 2 Q2 2016

- Select members of the MSC Dissolved Methane Method Work Group
- Environmental Standards, Inc.
- Environmental Services Laboratory (PT)
- 15 Participating Laboratories (14 commercial, one government)

Phase 2

- Reference Standards across lower concentration range
- Utilize 4 difference concentrations to allow response model evaluation
- Control dilution affect by including at least one standard below calibration upper limit

Phase 2 Design

- 15+1 laboratories
- Reference standards (PT) at 270 µg/L, 1,079 µg/L, 2,698 µg/L, and 7,015 µg/L
- Each laboratory received 3 vials at each of the four concentrations. Asked to report one at each level undiluted, duplicate analysis of remaining two vials. Only perform dilution if required

Phase 2 Design

- Analyze within 48-hours of receipt
- Provide raw results, including associated initial calibration data
  - Reference Standards across lower concentration range
  - Utilize 4 difference concentrations to allow response model evaluation
  - Control dilution affect by including at least one standard below calibration upper limit

Data Analysis

- Compiled analytical data
- Compiled data from key elements questionnaire, little change from Phase 1
- Evaluated SOPs
- Performed exploratory and statistical data analysis
- QA/QC review of all summary data
  - Few issues, none impacted data analysis

Phase 2

- Calibration:
  - 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

PT Provider Results

48-hour Results

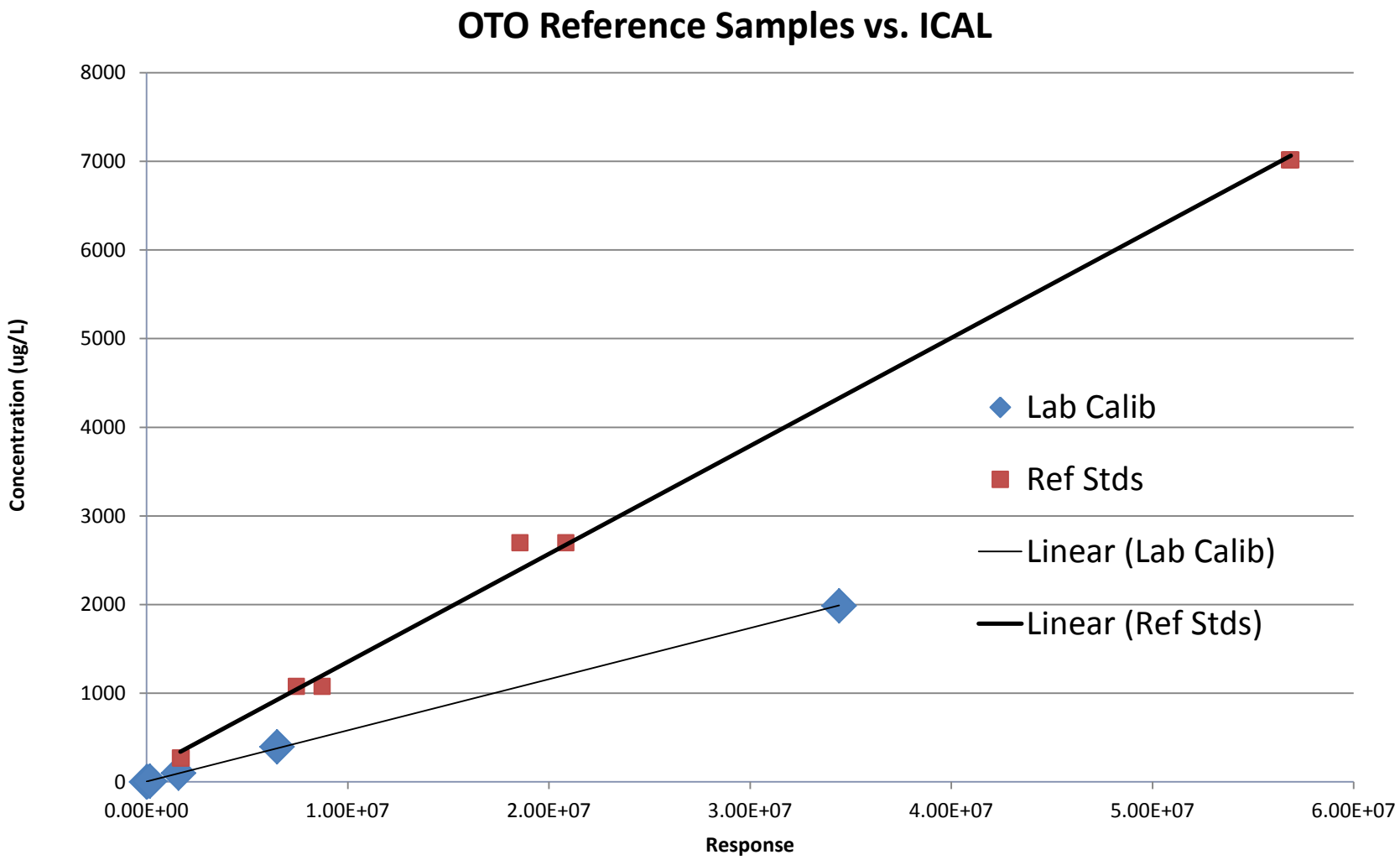
Assigned Concentration (µg/L)	Result A (vial 1)	Result B (vial 26)	Result C (vial 53)	Average	% Rec of Average	% RSD
270	290	280	280	283	**105%**	**2.04%**
1,079	1,160	1,100	1,130	1,130	**105%**	**2.65%**
2,698	2,920	2,760	2,930	2,870	**106%**	**3.32%**
7,015	7,480	6,480	6,510	6,823	**97%**	**8.34%**

7-day Results

Assigned Concentration (µg/L)	Result A (vial 2)	Result B (vial 27)	Result C (vial 54)	Average	% Rec of Average	% RSD
270	310	280	290	293	**109%**	**5.31%**
1,079	1,160	1,140	1,160	1,53	**107%**	**1.00%**
2,698	2,910	2,770	2,970	2,883	**107%**	**3.56%**
7,015	7,180	6,290	6,510	6,660	**95%**	**6.96%**

Laboratory ID	Average % Difference Standard 1 (270 µg/L)	Average % Difference Standard 2 (1079 µg/L)	Average % Difference Standard 3 (2698 µg/L)	Average % Difference Standard 4 (7015 µg/L)
FAM	-33.3%	-34.89%	-35.7%	-44.26%
ADZ	2.78%	-10.1%	23.6%	10.62%
TYR	-38.1%	-57.7%	-64.8%	-67.93%
WVN	-24.1%	-22.1%	-20.3%	-20.17%
ZIP	-42.8%	-34.5%	-43.1%	-40.48%
ILS	-22.2%	-8.2%	-5.49%	-5.92%
MRO	-33.7%	-8.48%	-9.93%	-16.89%
OTO	-61.7%	-54.6%	-55.9%	-50.96%
OTO-2	16.1%	14.0%	NR	NR
QSO	13.0%	34.4%	3.78%	-15.18%
CUU	-23.0%	-23.9%	-34.8%	-41.41%
RCN	13.5%	13.1%	16.8%	-17.61%
KOB	-61.1%	-51.2%	-35.51%	-32.93%
MUN	14.8%	-8.71%	-7.34%	-32.29%
LEA	-55.6%	-54.6%	-45.3%	-60.09%
PYM	-2.96%	-4.54%	-6.23%	-15.25%

Calibration



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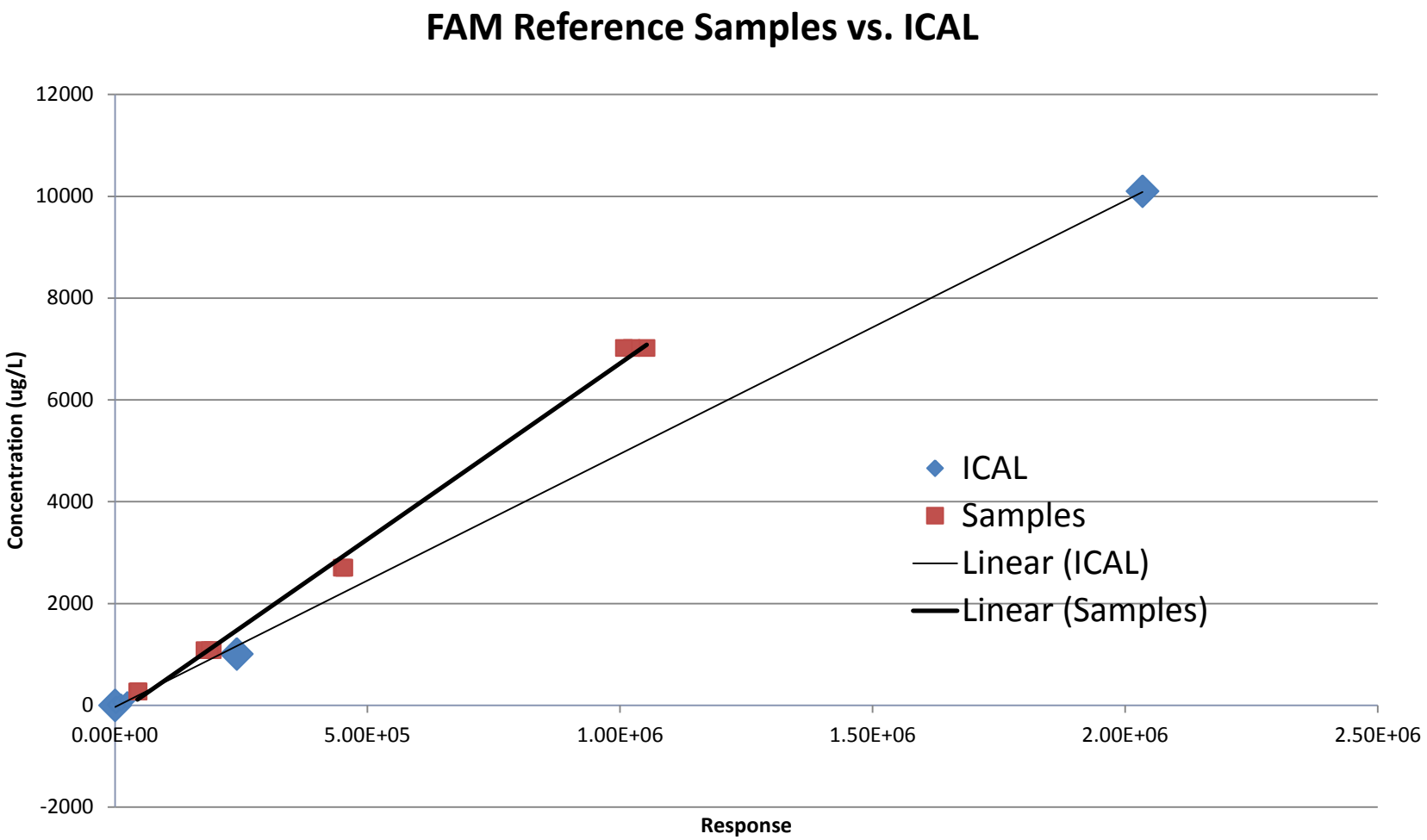
Calibration



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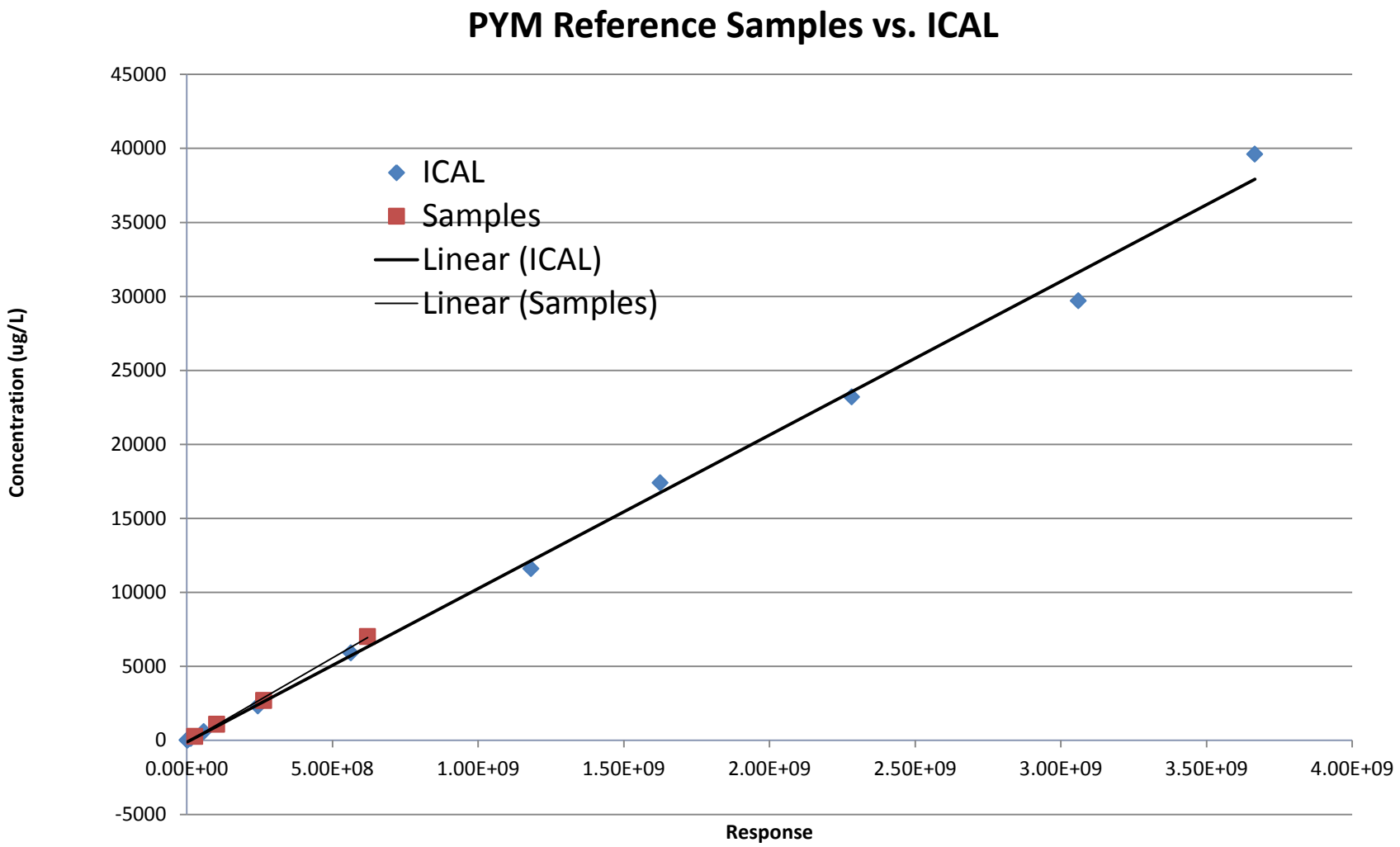

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Conclusions

- Dilution, in the majority of instances, did not appear to impact bias.
- Though large bias identified, at least one laboratory had acceptable results within each of the 3 calibration approaches.

Conclusions

- Calibration is the primary factor affecting bias
- This bias is the result of individual steps in the sample/standard preparation process
  - Sample and standard preparation differs.
  - Equilibrium must be reached.
  - Temperature control?
  - Combination of factors.

Next Steps

- Utilize PT Provider to identify sources of low bias with participating laboratories
- Standard Operating Procedure (SOP)/Work Instruction based on procedures, activities, and techniques from study
- SOP to guide final interlaboratory study to validate procedure

Recommendations

- A certified reference standard, developed under The NELAC Institute approach is paramount
  - Laboratories have no idea they are biased and thus no way to correct
- Develop a Test Method that includes three calibration approaches but controls sample and standard handling to minimize the potential for bias

Thank You

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