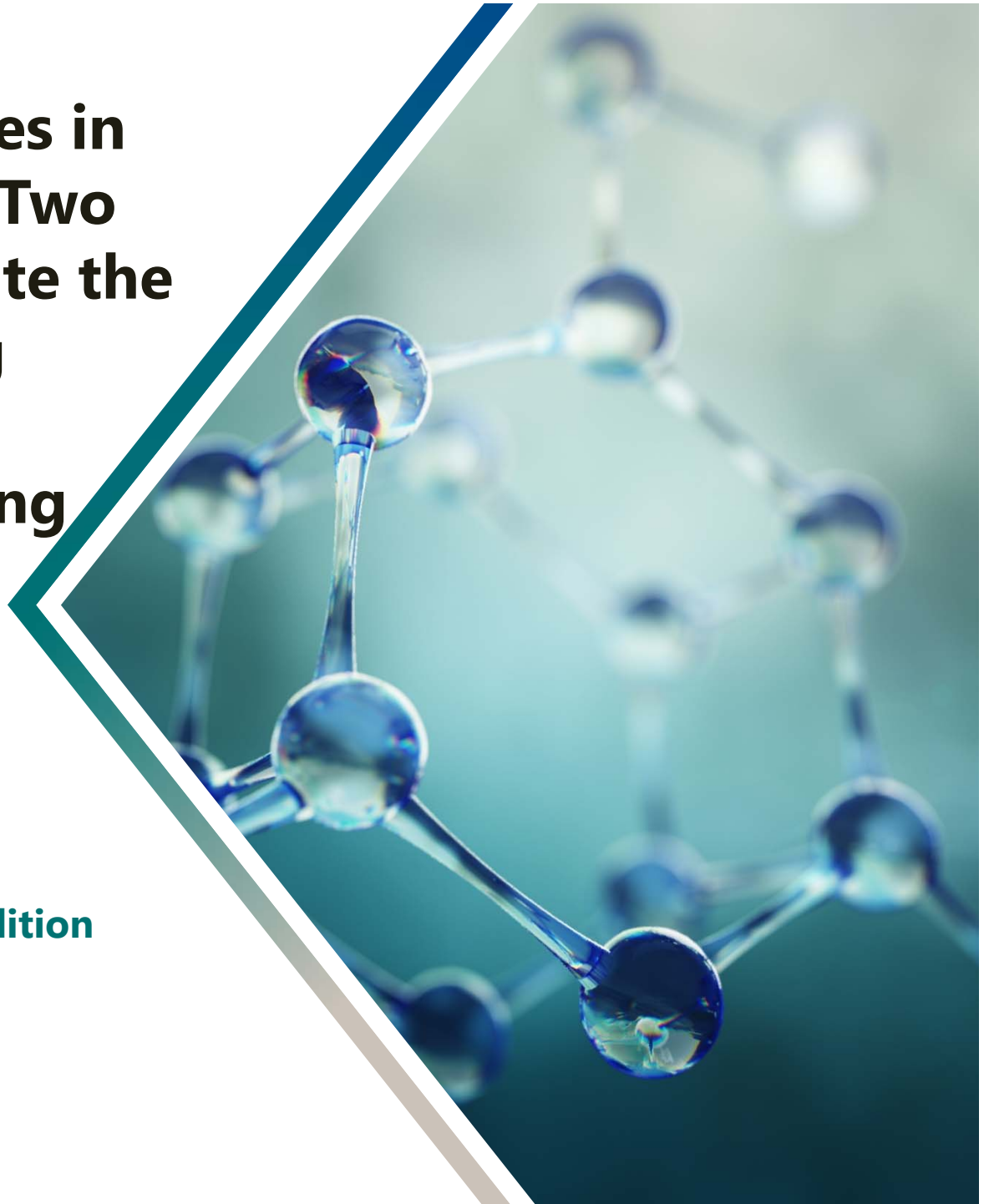


Alarming Differences in Commercial Data - Two Studies that Illustrate the Challenges in Using Methane Data for Regulatory Reporting

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Marcellus Shale Coalition Dissolve Methane Round Robin Studies

**Because significant error and
variability 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.**
 - Two groundwater samples across fifteen laboratories including one State Agency Laboratory.
 - **Phase 2 – Study Completed October, 2016.**
 - Four blind reference standards across fifteen laboratories including one State Agency Laboratory.
 - **Phase 3- Study Initiated January, 2018.**
 - Announced reference standard across 8 non-reference and 3 reference laboratories

Phase 1 Study Participants

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



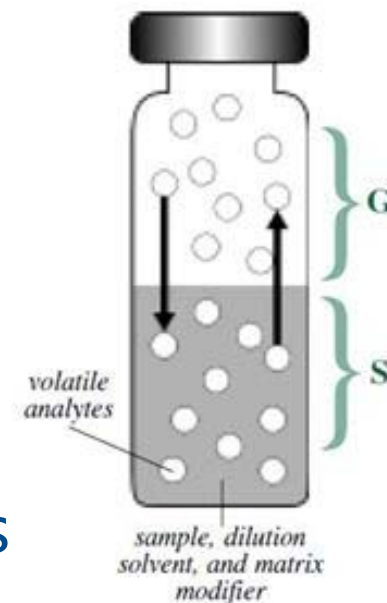
Phase 1 Design

- Infer issues that impact precision and bias.
 - Detailed Questionnaire and Review of Laboratory SOPs.
- Inter-laboratory study of two monitoring wells.
 - Groundwater wells known to be impacted with dissolved methane
- Evaluate sampling and analytical precision and bias.
 - 15 laboratories, 3 samples per well, 3 vials per sample.
 - Sampled vials number 1 through ~90 for each well.
 - Triplicates vials from each well analyzed within 48 hours.
 - Vials split across sampling so that each laboratory received vial across sampling period.
- Evaluate impact of preservation – both preserved and unpreserved submitted based on laboratory SOP (10 preserved, 5 unpreserved).

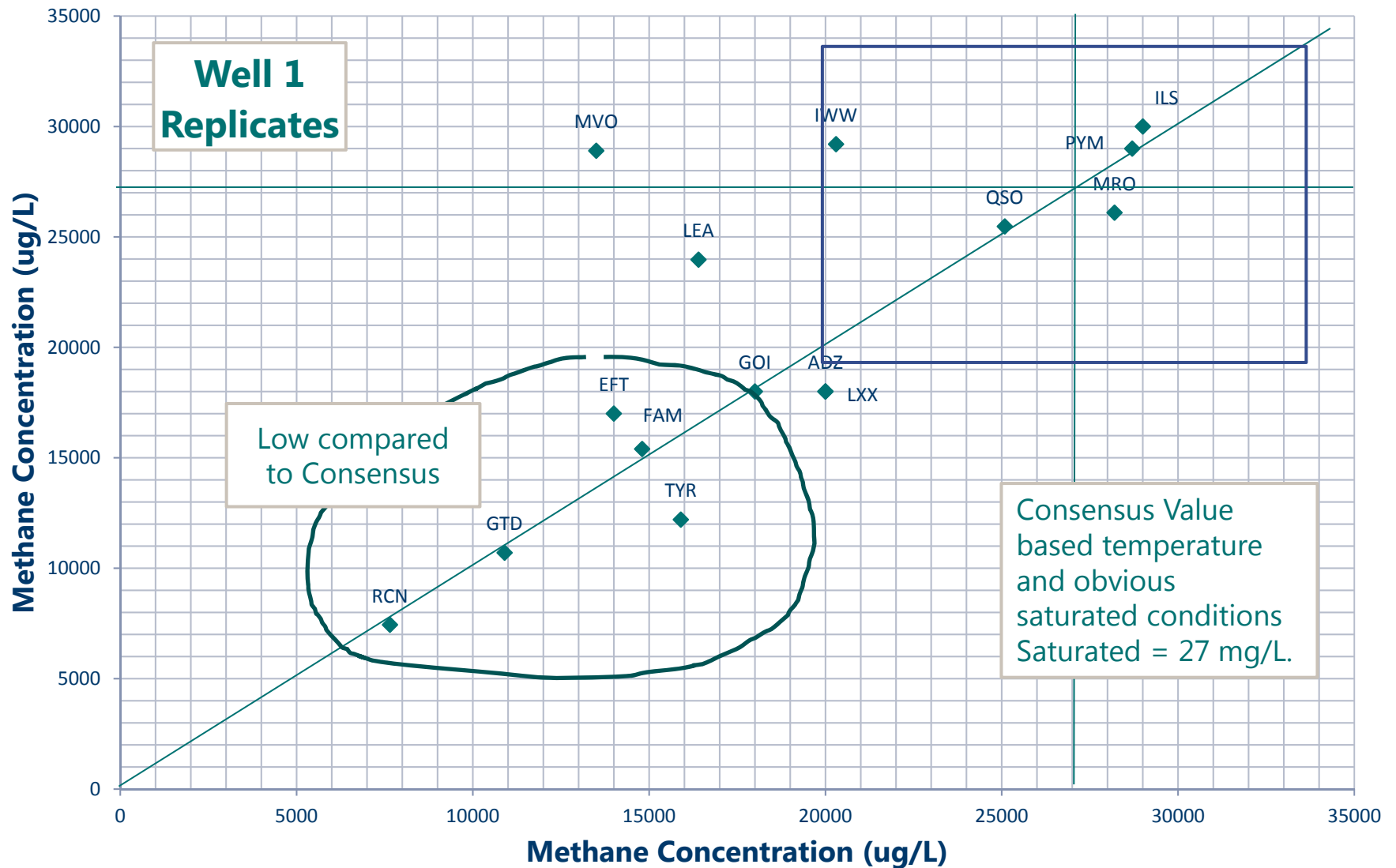
Phase 1 Results

Calibration Approaches

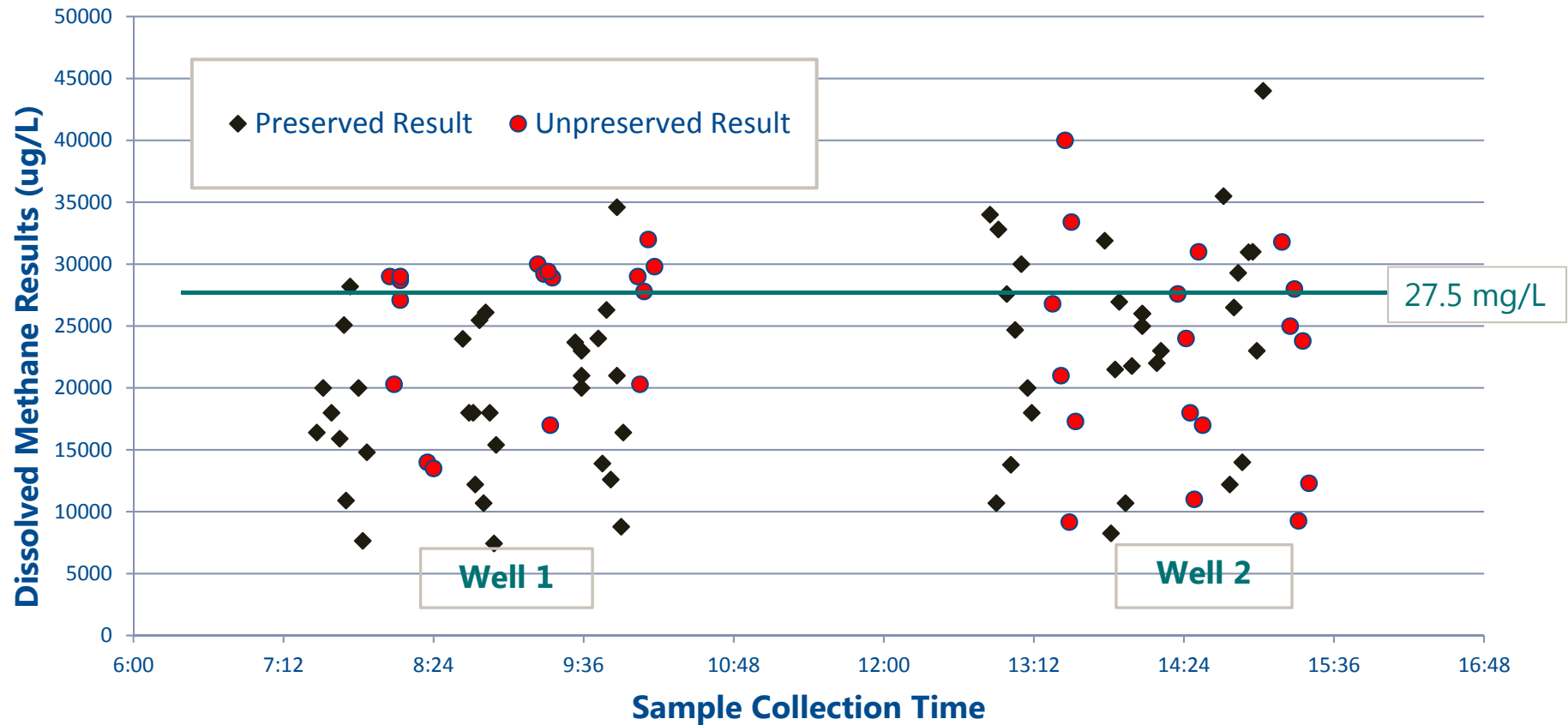
- Direct gas injection, Henry's Law
 - RSK-175
- Saturated aqueous solution, with dilutions
 - PA DEP 3685
 - ASTM WK43267
- Inject gas standard into headspace above aqueous phase, establish equilibrium. Inject gas phase from samples, calculate aqueous phase conc.



Phase 1 – Results Well 1



Phase 1 – Results, Preserved vs. Unpreserved



Phase 1 Conclusions

- Data showed large variations within pool, range of results from two wells:
 - Well 1 - 7.4 to 34.6 mg/L.
 - Well 1 Average Temperature 10.6 °C, theoretical saturation 27 mg/L
 - Well 2 - 8.3 to 44.0 mg/L (28 mg/L consensus).
 - Well 2 Average Temperature 9.4 °C, theoretical saturation 28 mg/L.
- No singular issue identified to explain spread and bias.
- Calibration varied, three general approaches.
- Propensity for dilution, especially at these levels.
- Additional testing at range of concentrations needed.

Phase 2

Study Participants

- Select members of the MSC Dissolved Methane Method Work Group.
- Environmental Standards, Inc., Valley Forge, PA.
- Environmental Services Laboratory, Indiana, PA. Reference Standard provider.
- 15 Participating Laboratories (14 commercial, one government).
 - One commercial laboratory reported two sets of data, using two different techniques.

Phase 2 Design

- Provide Blind Reference Standards (unpreserved) across concentration range and numbered each vial in order.
 - 0.27 mg/L, 1.08 mg/L, 2.70 mg/L, 7.01 mg/L
- Evaluate 4 different concentrations to allow response model evaluation.
- Each laboratory received 3 vials at each of the four concentrations. Report one at each level undiluted, duplicate analysis of remaining two vials. Only perform dilution if required.
- Control dilution affect by including at least one standard below calibration upper limit.

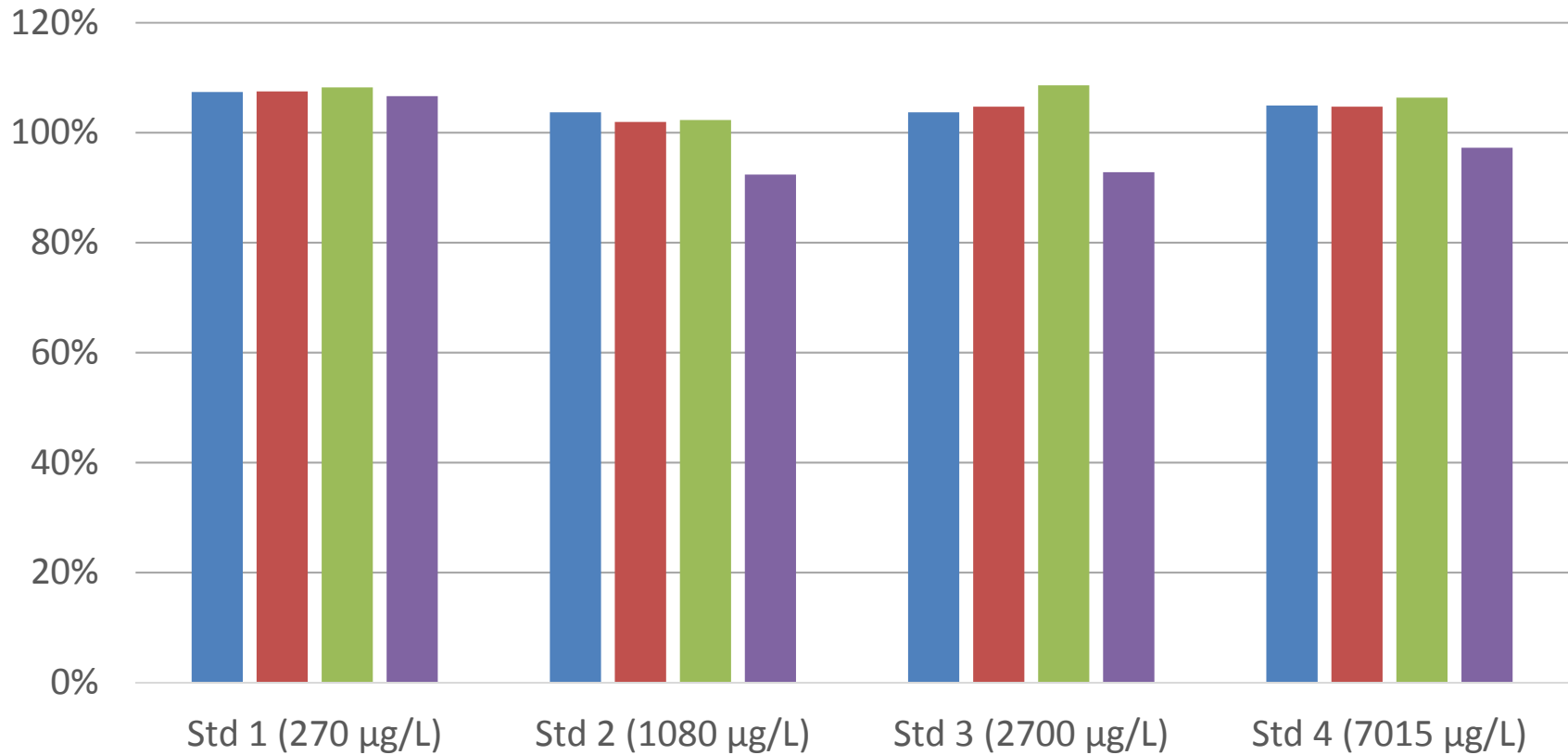
Phase 2

Calibration Approaches

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

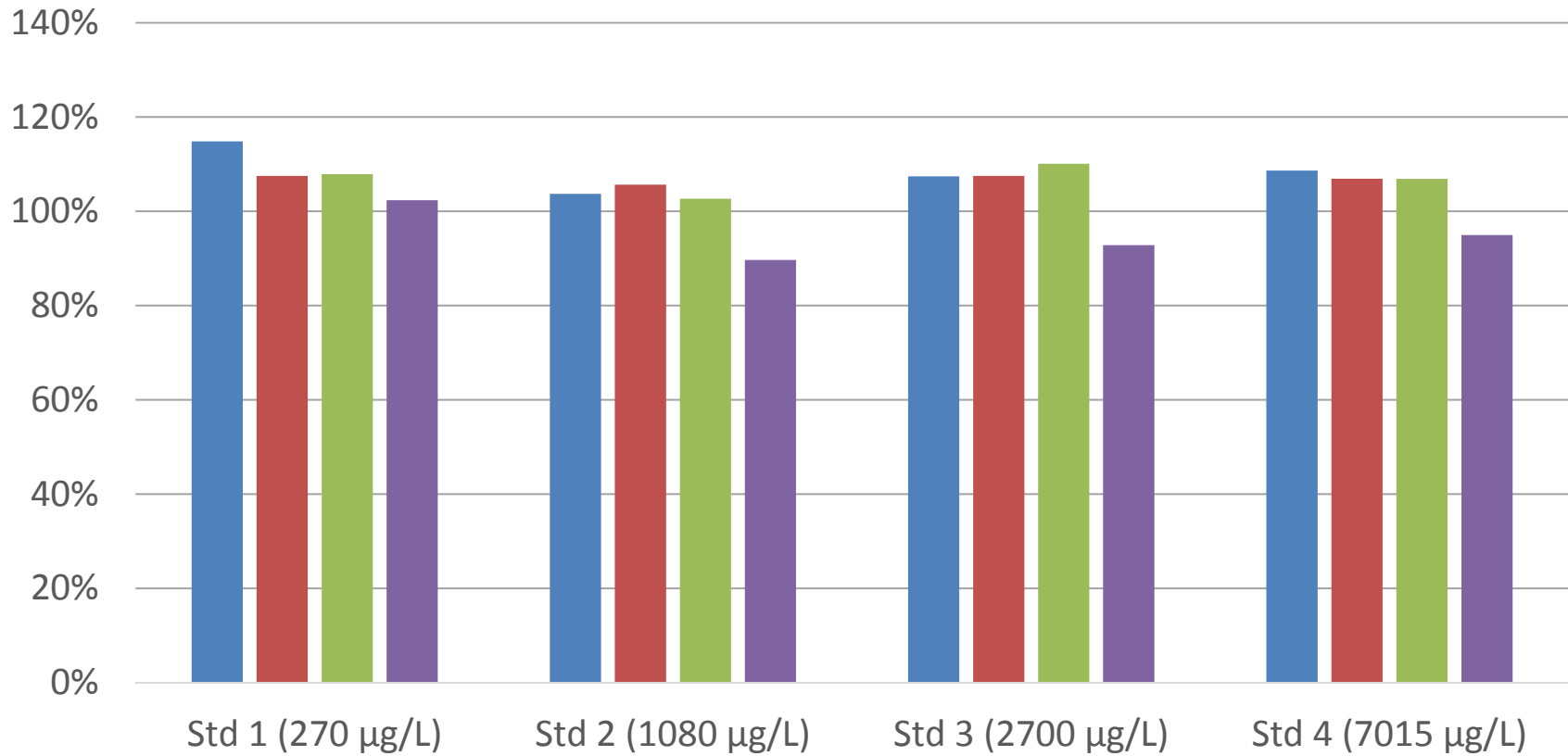
Phase 2: Reference Standard Provider Results

48-Hour Results

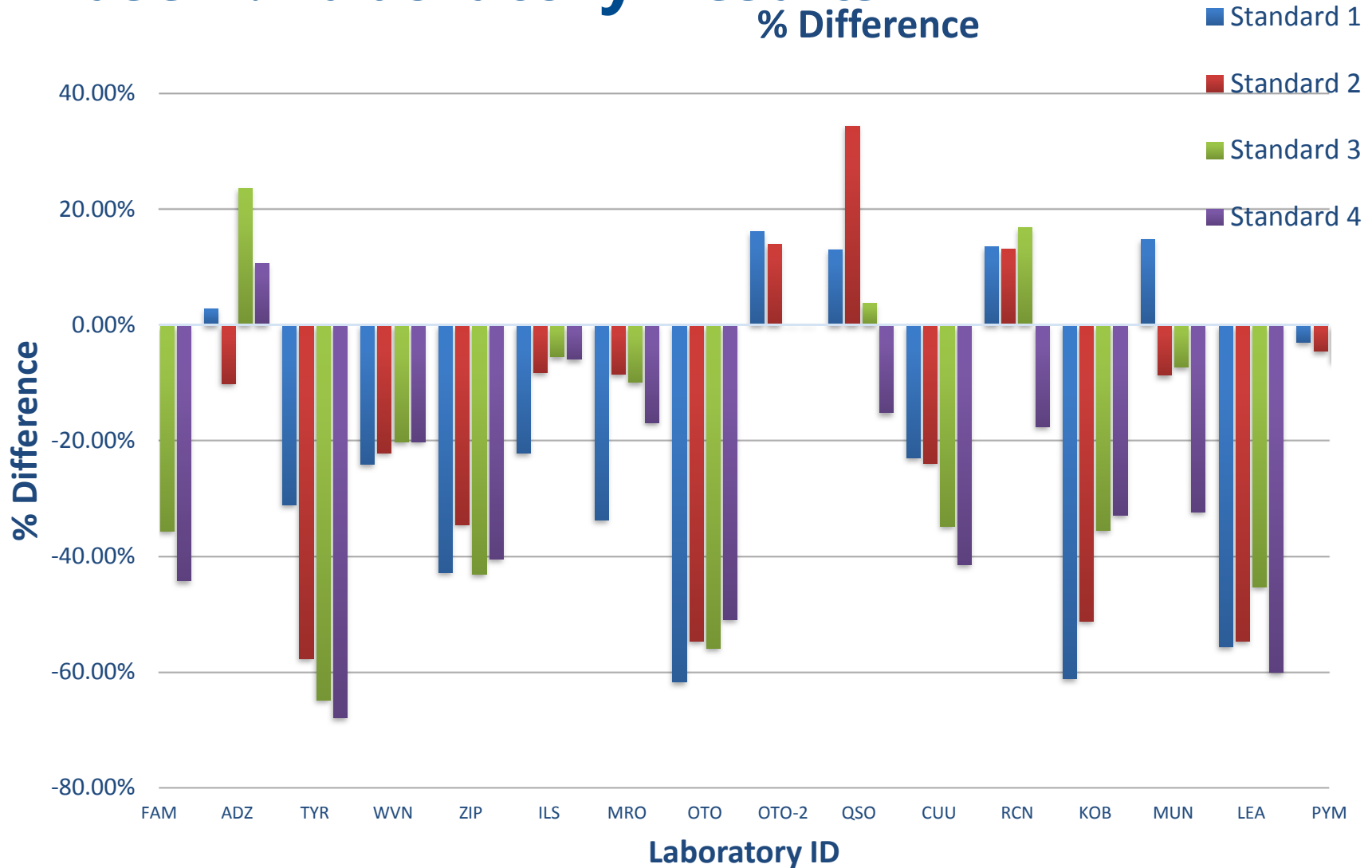


Phase 2: Reference Standard Provider Results

7-day Results

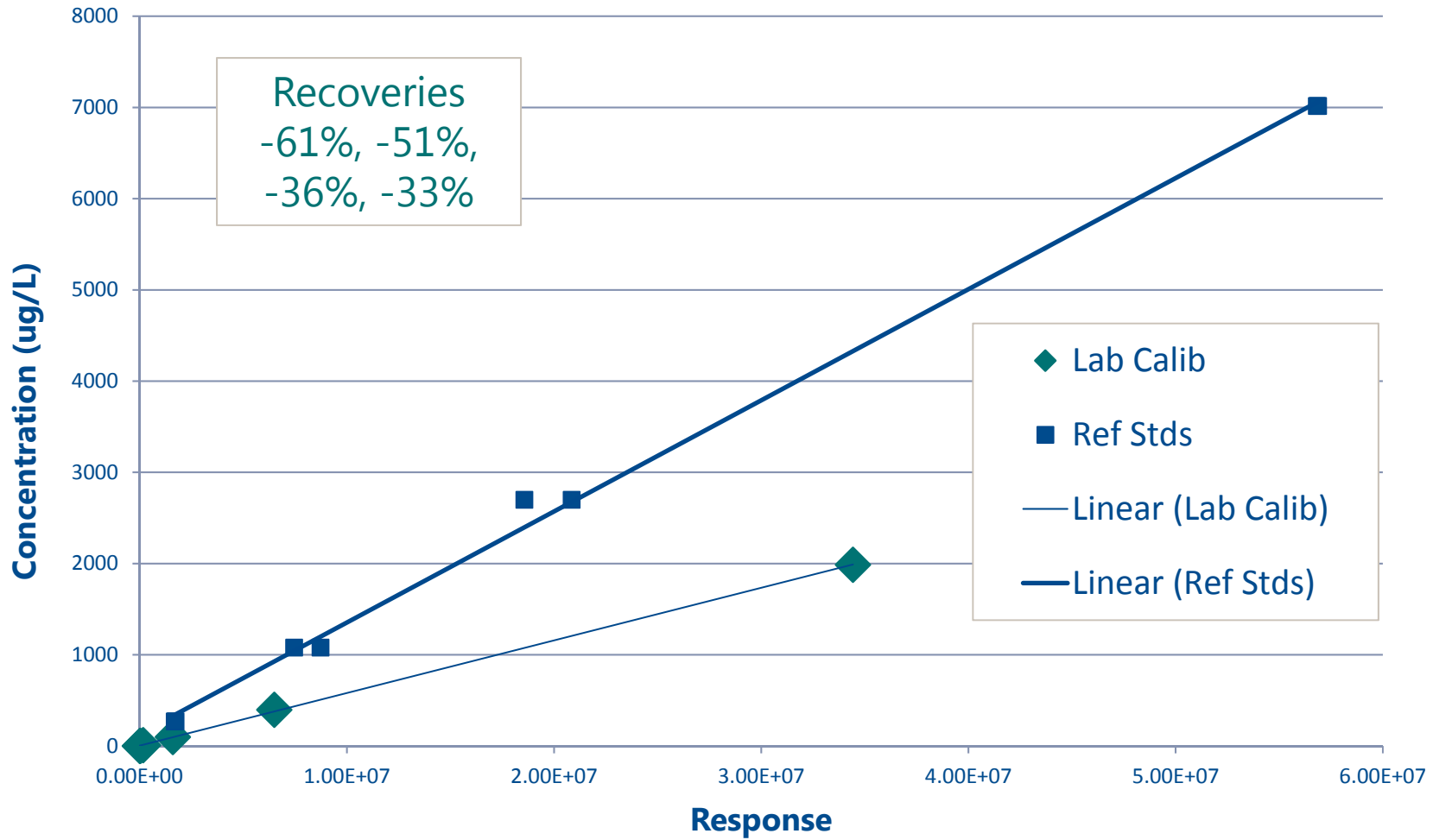


Phase 2: Laboratory Results



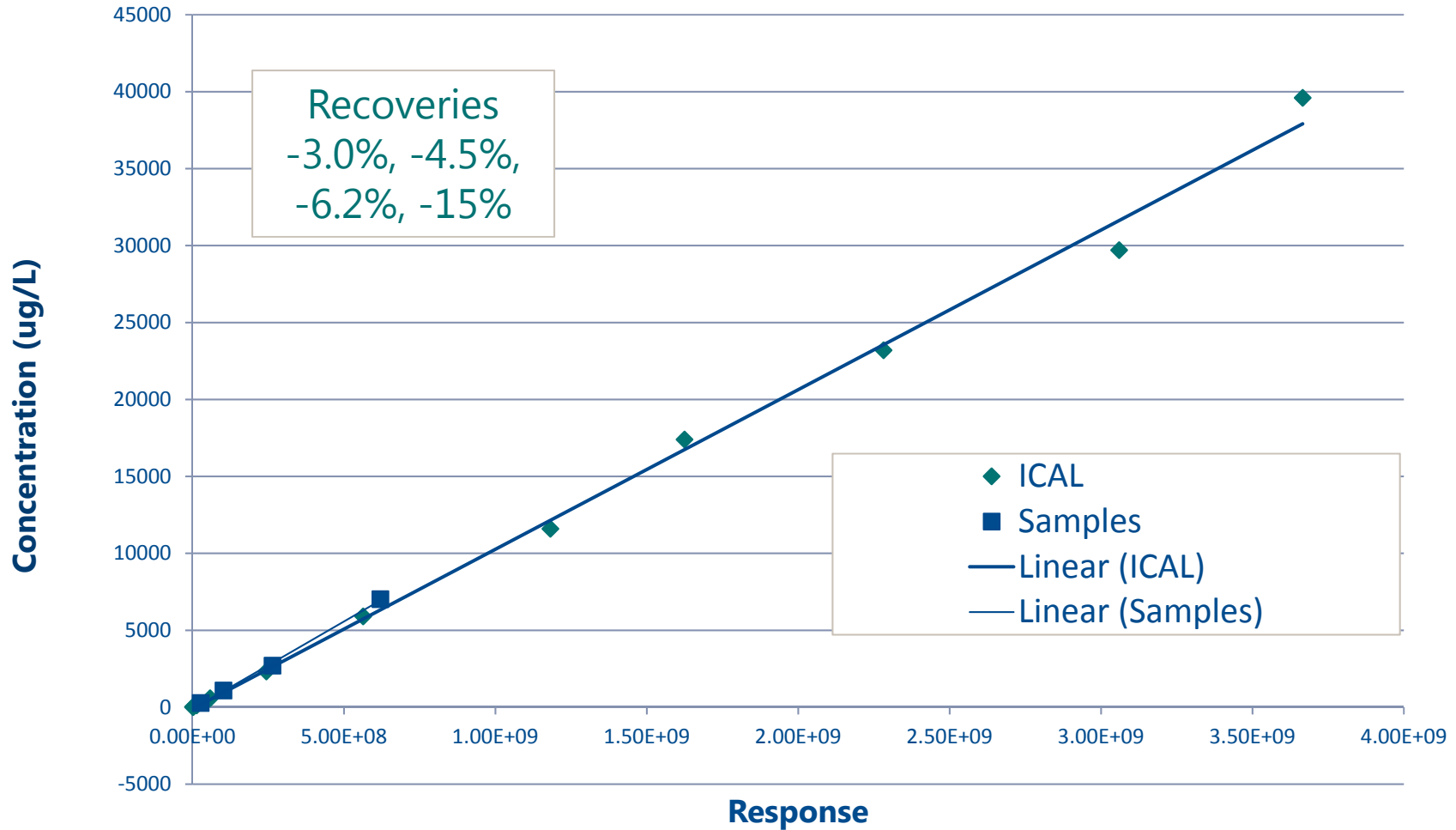
Phase 2: Calibration

Laboratory 13 Reference Samples vs. ICAL



Phase 2: Calibration

Laboratory 16 Reference Samples vs. ICAL



Phase 2 Conclusions & Recommendations

- 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 is critical.

Phase 3 Study Participants

- Select members of the MSC Dissolved Methane Method Work Group.
- Environmental Standards, Inc., Valley Forge, PA.
- Environmental Services Laboratory, Indiana, PA. Reference Standard provider.
- 8 Non-Reference Commercial Laboratories
 - Selected from those that failed Phase 1 or 2 at 30% difference mark.
- 3 Reference Laboratories (2 commercial and 1 government)

Phase 3 Design

- Send Laboratories known concentration standards.
 - ESL Prepared approximately 70 vials in two batches.
 - Self-diagnosis provided concentration, requested analyzed sequentially and review against known concentration. Make revisions to preparation, handling calibration, analysis and technique as needed.
- 3 Reference laboratories, analyzed samples over the course of 14 days (mini holding time study).

Phase 3 Results

Success with all participating laboratories achieving recoveries with 80-120%

Details to be published soon

Next Steps

- Publish/present Phase 3 report
- 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.

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 spread and bias.

Thank You



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