Assessing Analytical Issues and Improving/Remediating Those Issues

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contributed with support from the Marcellus Shale Coalition

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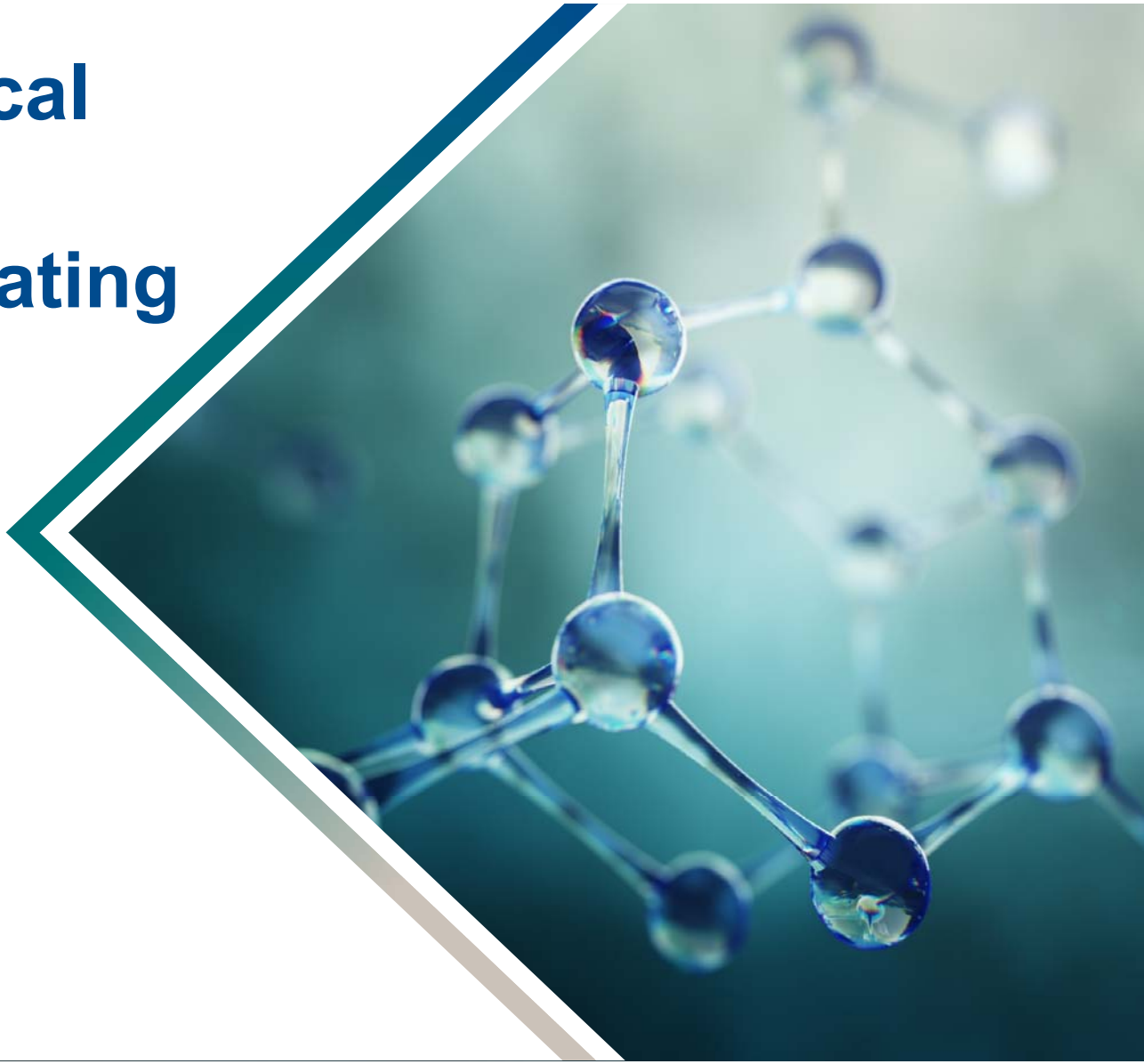

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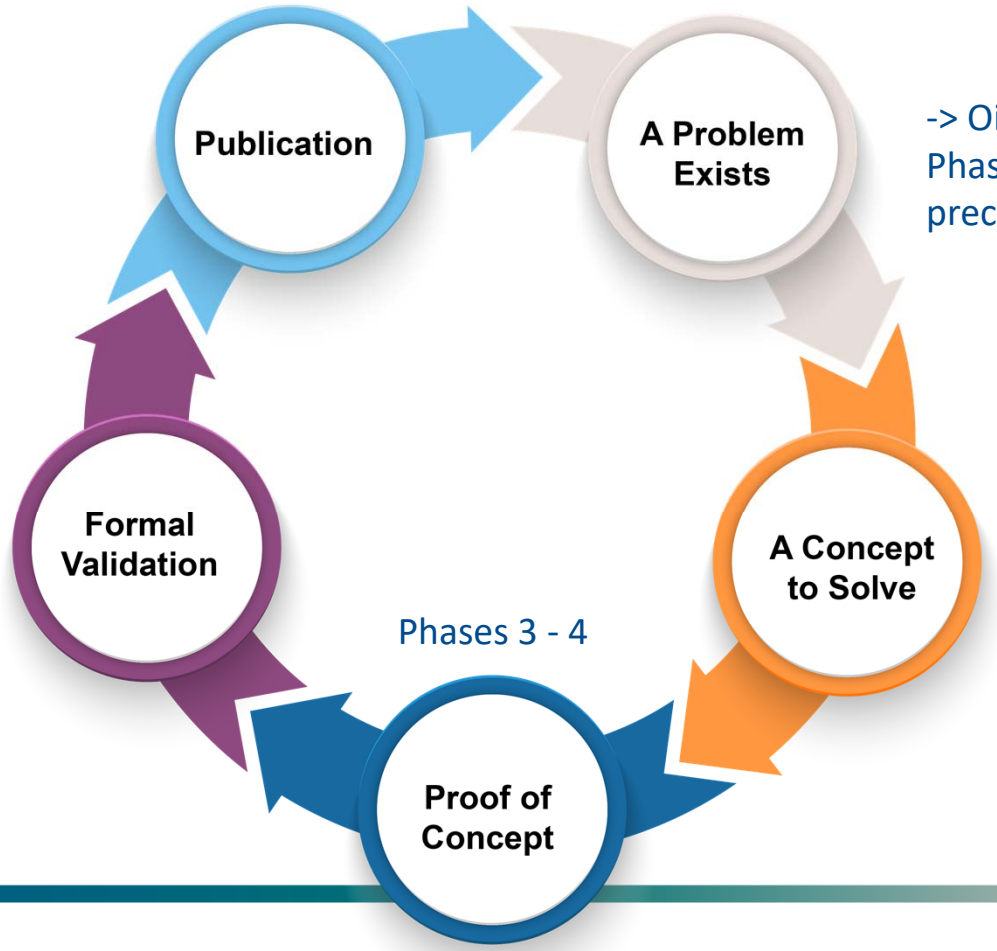
The Road to a Published Method



-> Oil & Gas & NMA Projects
Phase 1 & 2 – inaccurate, poor precision identified.

Phase 5 – Potable Water

Phase 6 - Groundwater

Phases 3 - 4

Build on RSK-175/ PA DEP 3686/ ASTM D8028 procedures with additional options per identified scope and laboratory community and capabilities.

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Formal Validation – Phases 5 & 6

- Demonstrate method to measure analytes in matrix of concern at concentrations of concern.
- Is there an anticipated need for this method?
    - Currently, approximately 35 commercial analytical laboratories in the U.S. provide measurement for dissolved light gases. Most reference US EPA SOP RSK 175, or PA DEP 3686.
- Is this “method” significantly different in principle or approach from existing published methods?
    - Static Headspace
        - US EPA 5021 does not have sufficient prescriptive steps; shaking for only 2 minutes has been shown to be insufficient (Phase 3). Insufficient to ensure equilibrium and static temperature and pressure.
    - GC/FID and/or TCD
        - US EPA 8015 is an assemblage - started as direct aqueous injection, then added volatile, extractables ...
    - Citing SOP RSK-175 has proven to be unreliable, need a single method with preparation and determination included.

Phase 1

- 15 laboratories
- 2 GW Sources
- 102 Question Survey – laboratory techniques associated with handling, storage, preparation, determination
  - Most laboratories open vial during preparation.
  - 6 of 15 included a surrogate compound, 1 of 15 included an internal standard compound.
- No apparent correlation of dilution factor to reported concentration and bias
- Holding Time Study
  - One laboratory - selected based on keeping vial closed during preparation
  - Preserved with HCl and unpreserved
  - No real difference between preserved and unpreserved

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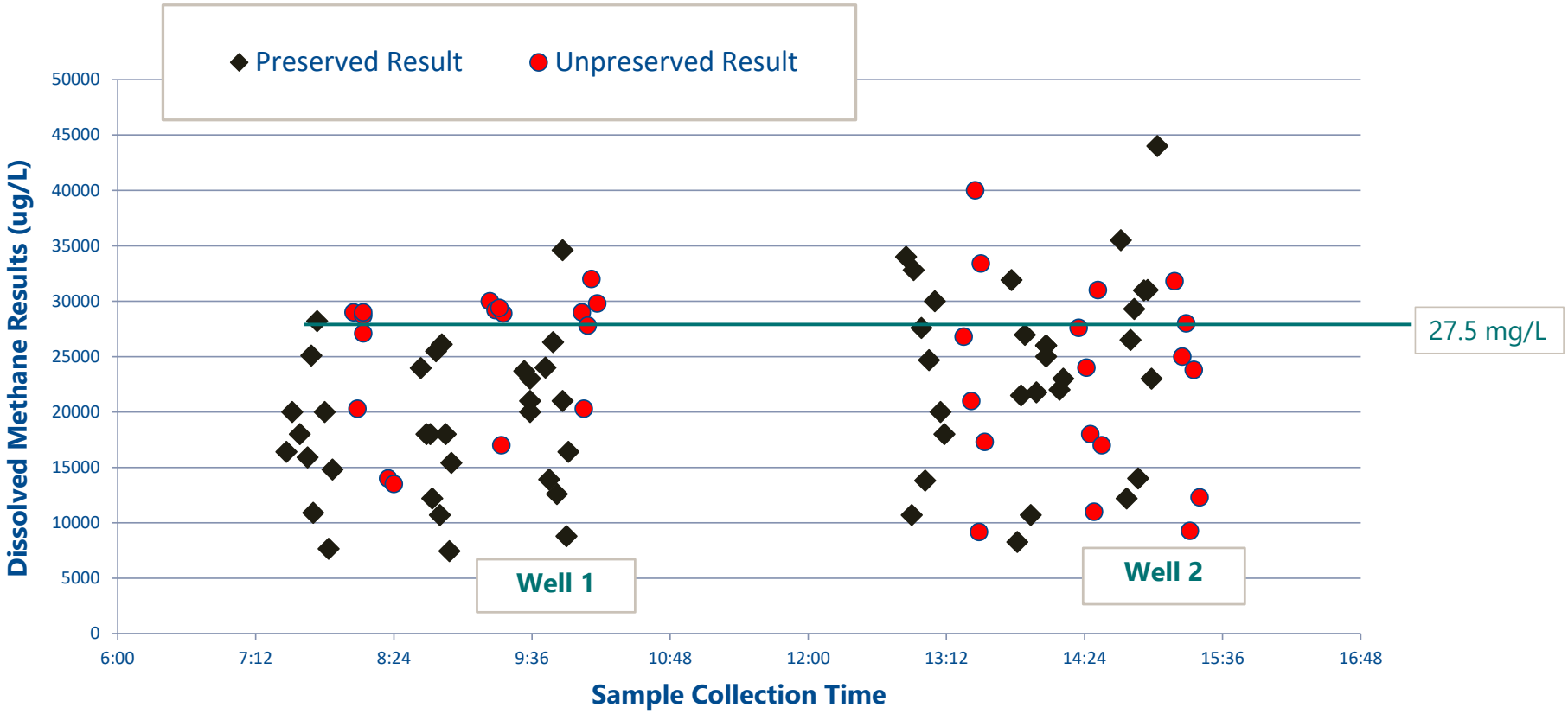
Phase 1 (Cont.)



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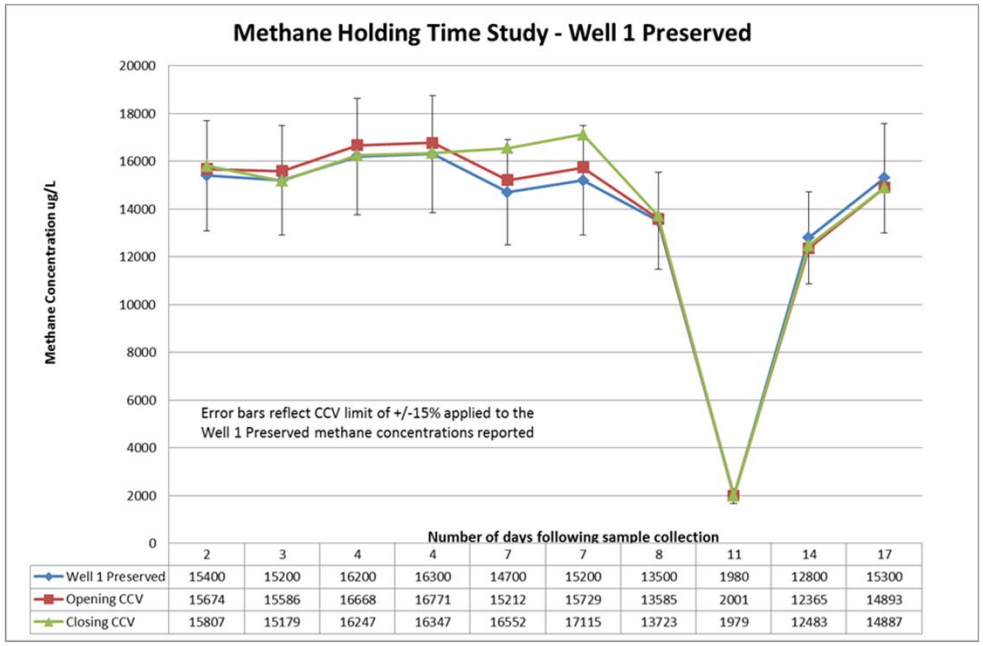
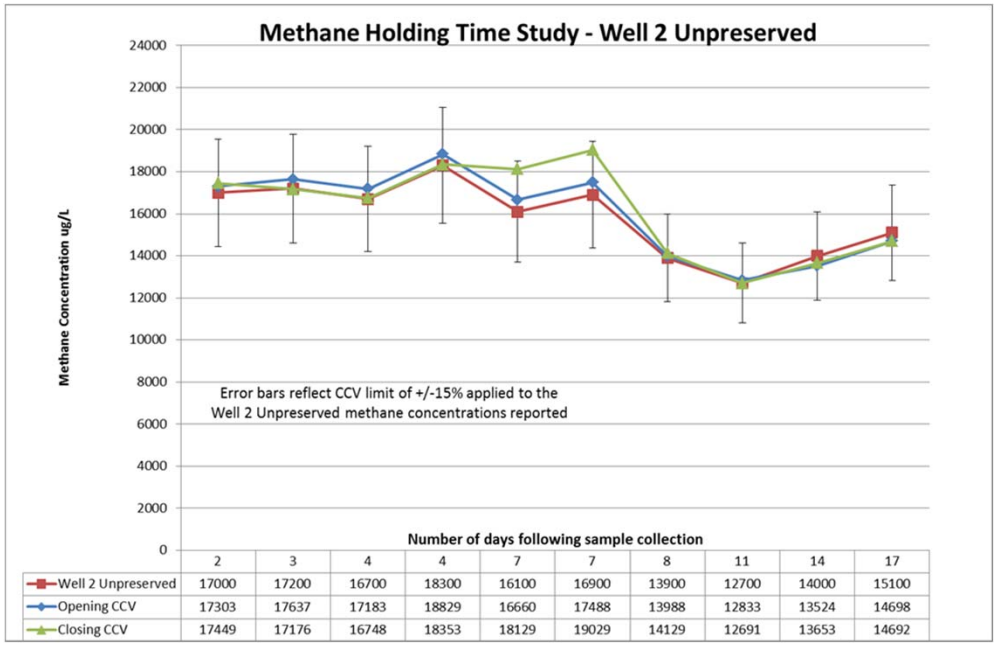
Holding Time Study



	2	3	4	4	7	7	8	11	14	17
Well 1 Preserved	15400	15200	16200	16300	14700	15200	13500	1980	12800	15300
Opening CCV	15674	15586	16668	16771	15212	15729	13585	2001	12365	14893
Closing CCV	15807	15179	16247	16347	16552	17115	13723	1979	12483	14887



	2	3	4	4	7	7	8	11	14	17
Well 2 Unpreserved	17000	17200	16700	18300	16100	16900	13900	12700	14000	15100
Opening CCV	17303	17637	17183	18829	16660	17488	13988	12833	13524	14698
Closing CCV	17449	17176	16748	18353	18129	19029	14129	12691	13653	14692

See also ASTM D8028-17 Appendix X1 study

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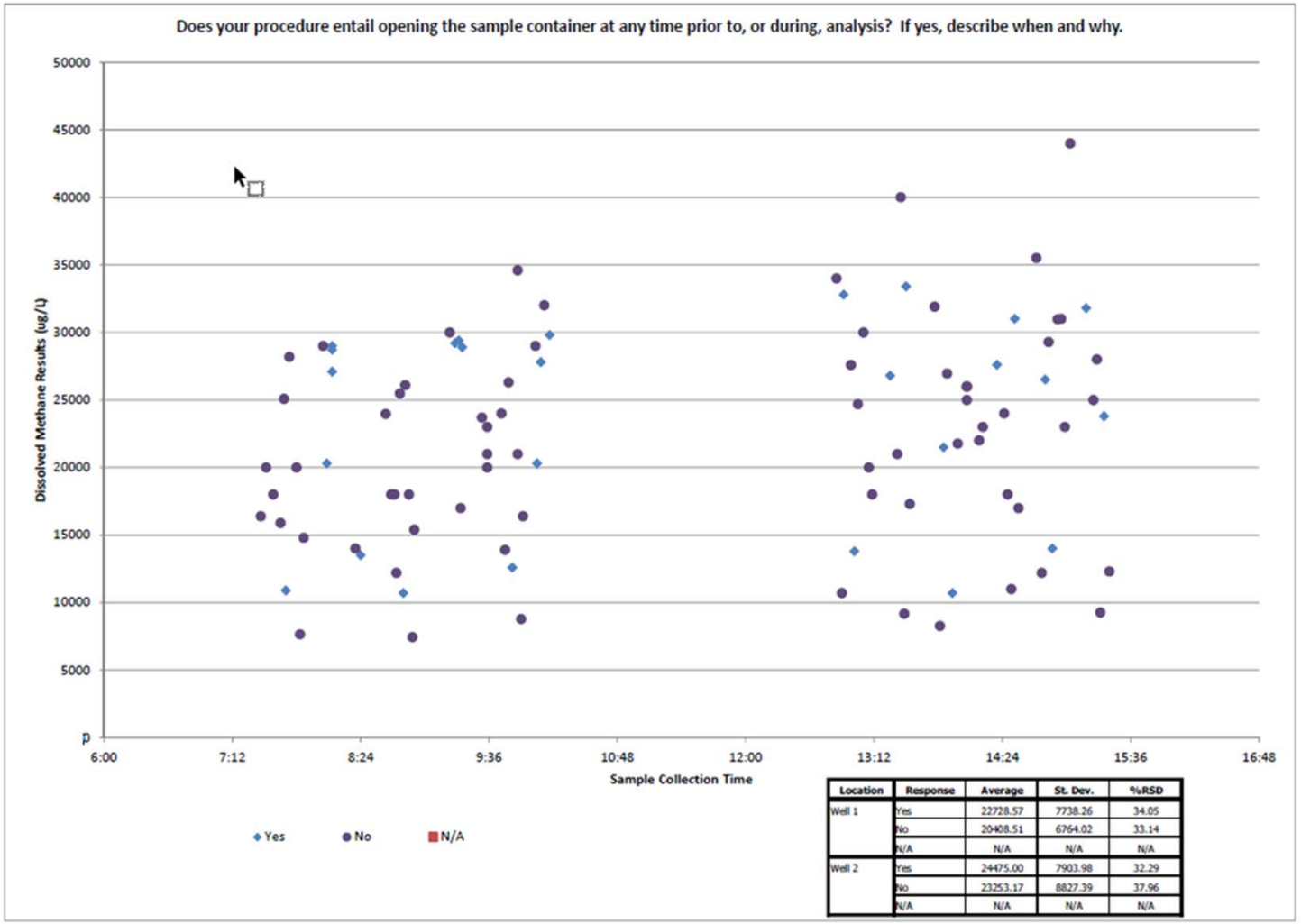
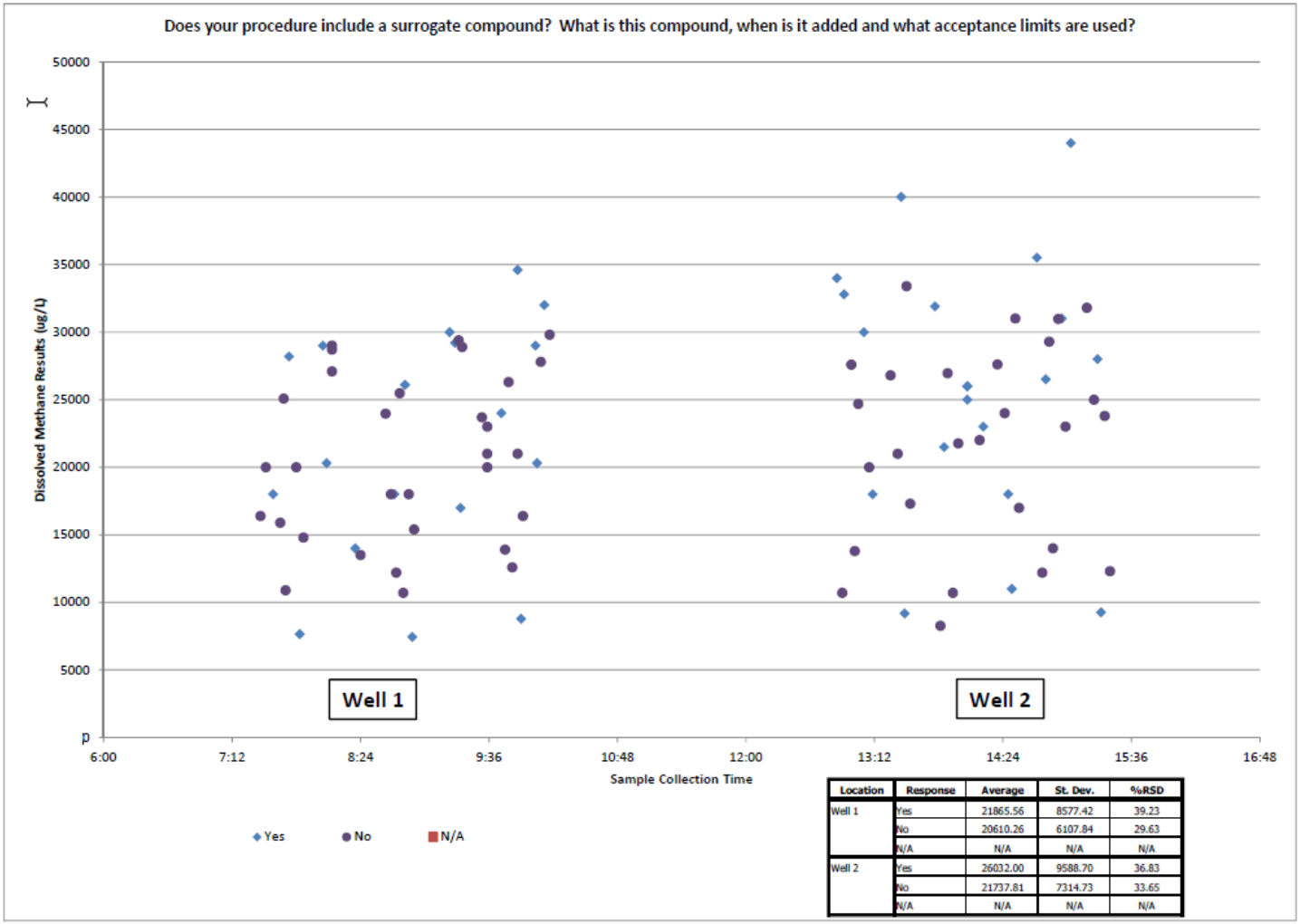


Location	Response	Average	St. Dev.	%RSD
Well 1	Yes	22728.57	7738.26	34.05
	No	20408.51	6764.02	33.14
	N/A	N/A	N/A	N/A
Well 2	Yes	24475.00	7903.98	32.29
	No	23253.17	8827.39	37.96
	N/A	N/A	N/A	N/A



Location	Response	Average	St. Dev.	%RSD
Well 1	Yes	21865.56	8577.42	39.23
	No	20610.26	6107.84	29.63
	N/A	N/A	N/A	N/A
Well 2	Yes	26032.00	9588.70	36.83
	No	21737.81	7314.73	33.65
	N/A	N/A	N/A	N/A

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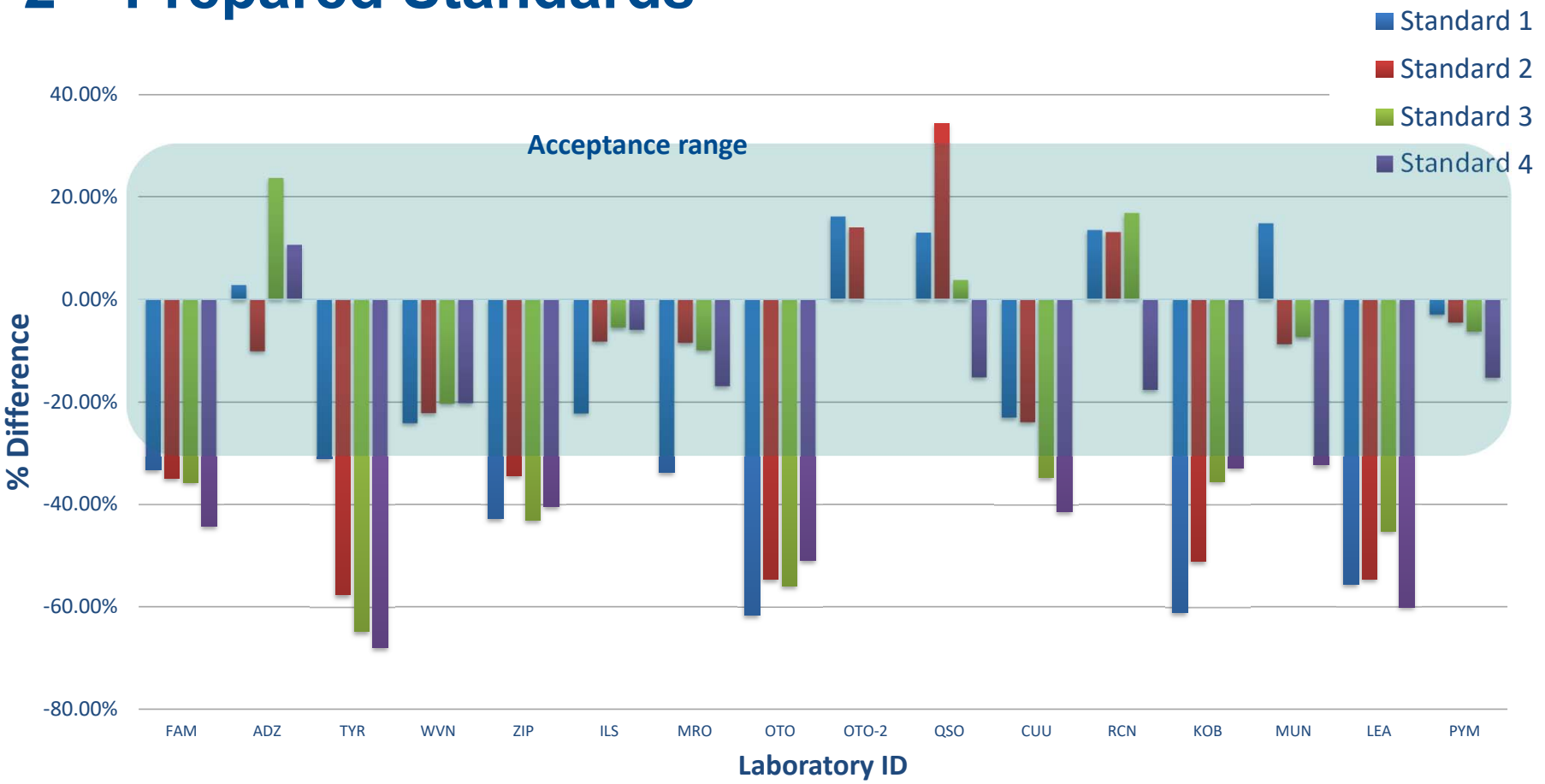
P2 – Prepared Standards



P2 – Statistical Analysis – Appendix to Report

- Normality and distribution assessment
- Analysis of variance heterogeneity (scedasticity)
- Assessment of difference between standard pair
- Evaluation of within and across laboratory precision

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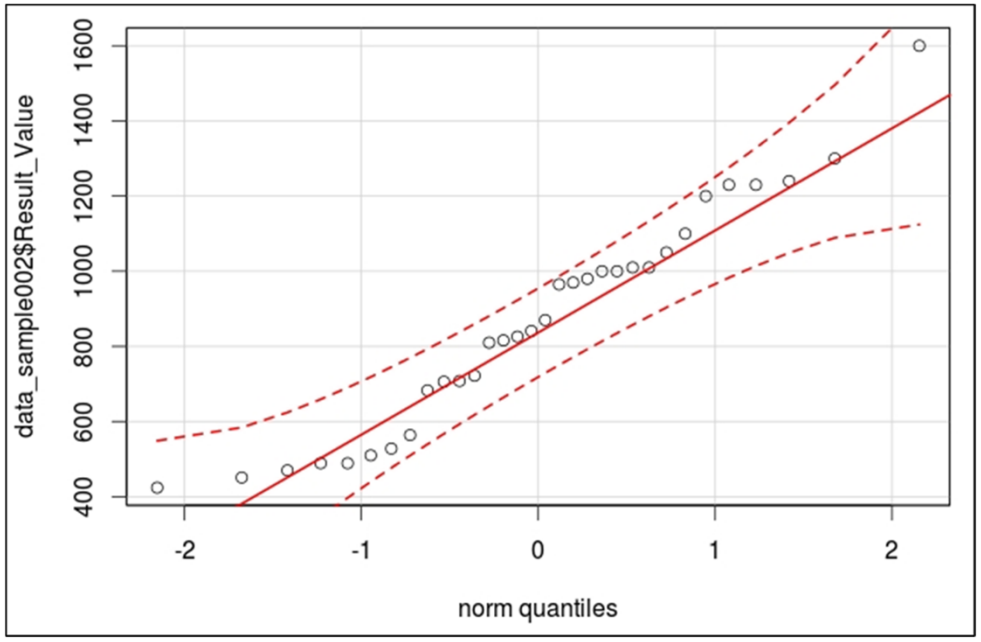
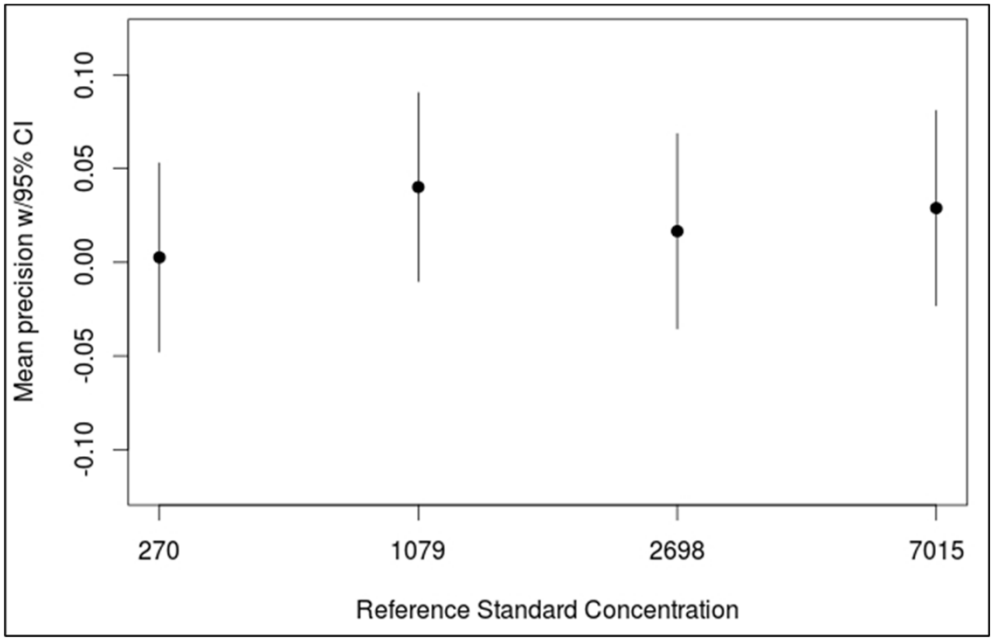
P2 – Statistical Analysis

Standard Concentration = 1,079 µg/L



- Normal distribution

Precision vs. Concentration



Mean variance consistent with concentration

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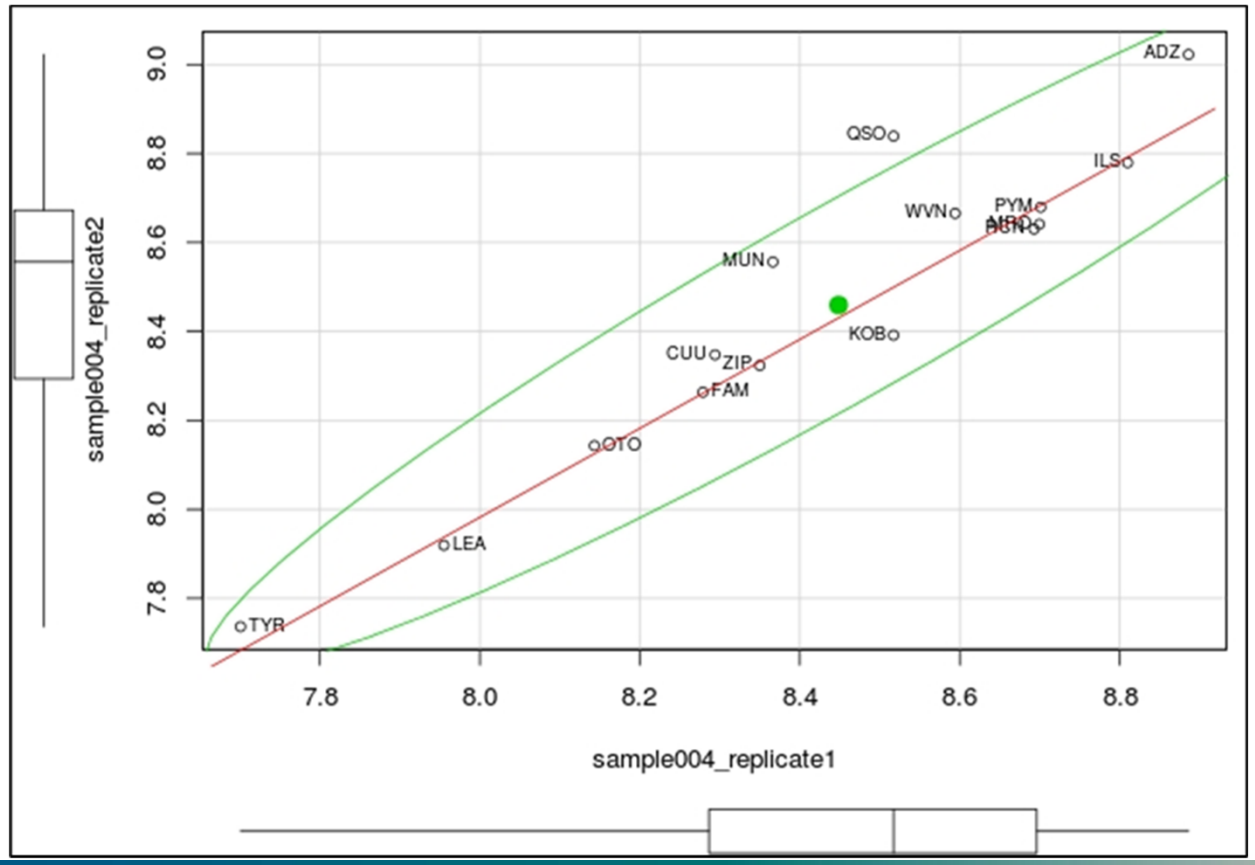
P2 – Statistical Analysis (Cont.)

The Youden-style plot for Reference Standard Concentration = 7,015 µg/L



A 45-degree reference line is shown in red, a 95% bivariate confidence ellipse (green lines) based on the actual results is shown to provide an approximate index as to the degree of expected spread, and a Tukey box plot of each duplicate pair member's distribution is shown on the corresponding axis.

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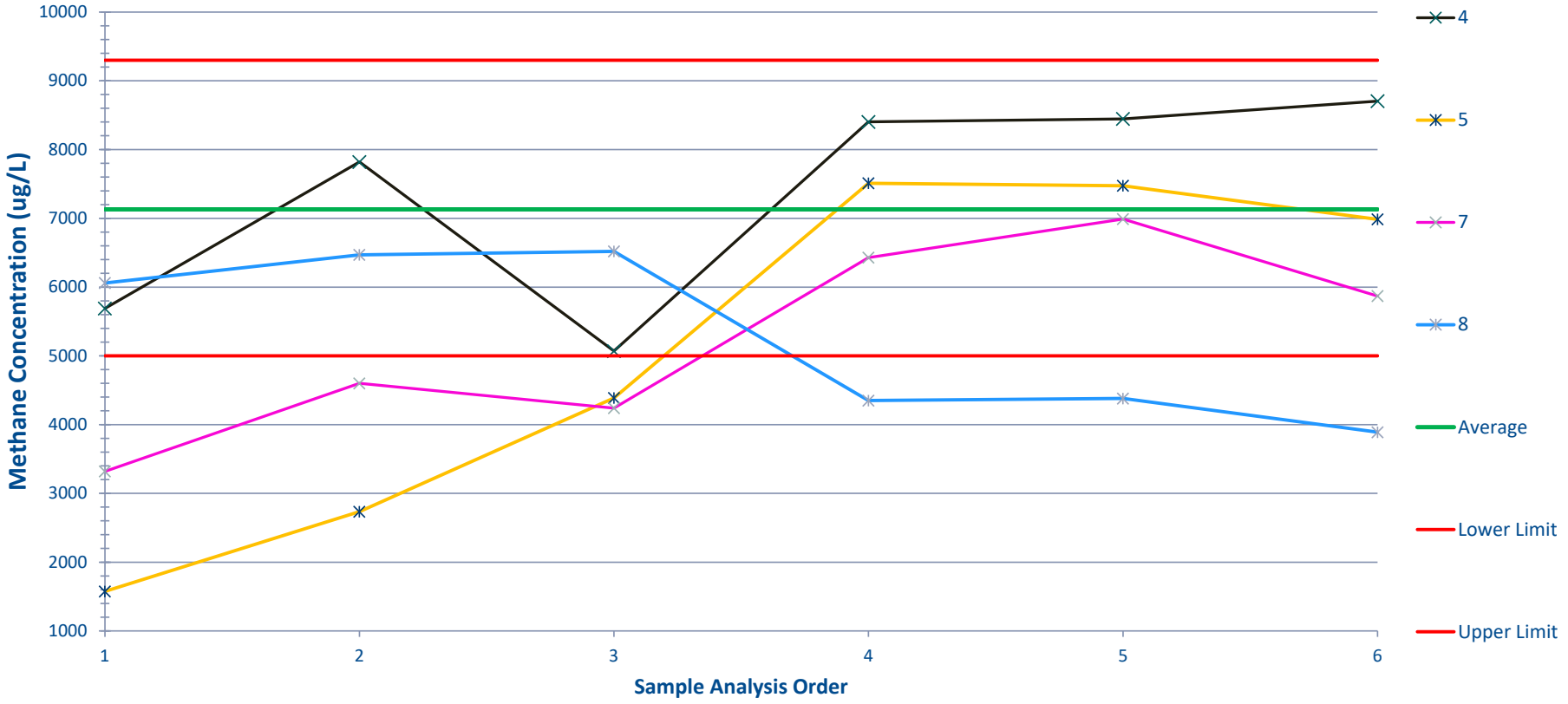
P3 – Self Diagnose – Proof of Concept



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P4 – Proof of Concept → Procedure

- Collect in chlorobutyl rubber septa (see ASTM D8028-17 App X1)
- Static headspace
- Three calibration options using GC and FID, TCD, or MS detector
  - Direct-gas injection*
  - Saturated aqueous standards
  - Prepare in vial with headspace (predominant)
- Initial Demonstration of Proficiency, Precision, Accuracy, Sensitivity (ongoing also - LLOQ)
- Equilibration time and steps prescriptive

* Limited use by laboratory community, removed from P6 procedure.

P4 – Proof of Concept → Procedure (Cont.)

- CRM provides accuracy assessment that allows for validation and accreditation.
- QC Requirements
  - ICAL – Average RF, or if linear regression or a quadratic model is used, the use of RE and RSE shall be employed.
  - ICV, CCV, LCS, LB, replicates.
  - Surrogates are optional, but highly recommended.
  - Matrix spikes are optional, but highly recommended.
  - Internal standards are optional.
  - GC resolution and retention time specifications.
  - Monitor for carryover.

Phase 5 – Potable Laboratory Water

CRM: Precision and Bias

Analyte	CRM #1				CRM #2			
	Number of Laboratories	Average Recovery (%)	Standard Deviation of Recovery	% recovery within 70-130%	Number of Laboratories	Average Recovery (%)	Standard Deviation of Recovery	% recovery within 70-130%
Methane	12	99.6%	16.9%	91.7%	12	99.5%	20.0%	91.7%
Ethane	9	92.2%	16.2%	77.8%	9	89.4%	14.9%	77.8%
Ethene	8	93.7%	22.9%	75.0%	8	92.6%	22.2%	75.0%
Propane	7	88.5%	12.6%	85.7%	7	84.5%	11.5%	85.7%

CRM from LGC Standards

CRM #1 in mg/L

Methane – 5.21±0.9 Ethane – 5.60±0.6 Ethene – 4.68±0.4 *n*-Propane – 6.11±0.5

CRM #2 in mg/L

Methane – 6.25±1 Ethane – 6.65±0.6 Ethene – 5.68±0.5 *n*-Propane – 6.92±0.5

Phase 5 – Potable Laboratory Water

PT Standards (methane only)

- Reproducibility - % Standard Deviation
- Estimated bias – percentage of laboratories within 70-130% recover

Analyte	200 ug/L			
	Number of Laboratories	Average Recovery (%)	Standard Deviation of Recovery	% recovery within 70-130%
Methane	12	96.4%	10.8%	100%

Analyte	5000 ug/L			
	Number of Laboratories	Average Recovery (%)	Standard Deviation of Recovery	% recovery within 70-130%
Methane	12	87.6%	17.5%	86.5%

Analyte	11000 ug/L			
	Number of Laboratories	Average Recovery (%)	Standard Deviation of Recovery	% recovery within 70-130%
Methane	12	92.5%	18.6%	88.9%

Analyte	23000 ug/L			
	Number of Laboratories	Average Recovery (%)	Standard Deviation of Recovery	% recovery within 70-130%
Methane	12	95.5%	27.7%	86.1%

Phase 6 – Groundwater Matrix Validation

- Design
  - 7+ laboratories including 2 government
  - Only saturated water and spiking headspace calibrations will be included – no direct gas injection
  - 2 Geochemically different groundwater sources
  - 2 Different concentrations of MEEP analytes
    - Triplicate analysis at each concentration and of each source
  - CRMs
  - MS/MSD vials available

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Phases 1 - 6

- Measurement of dissolved light gases applicable to natural monitored attenuation projects and oil and gas activities
- Identification of analytical problem – poor accuracy and precision
- Identification of analytical factors causing problems (P3)
- Prescriptive analytical procedure with QC requirements to address potential interferences
- Sensitivity from individual laboratories calibration and detection and reporting limits
  - Single-digit µg/L detection – meets NMA project requirements
  - Calibration up to saturation – meets oil and gas related project requirements
- Method optimized in P3, ruggedness tested via work in P1, P5 and in works via P6 with two groundwater sources
- Accuracy, precision, reproducibility data from P5 planned with P6 with replicates, two concentrations
- Suitable for potable (validated) and groundwater (in progress) matrices

Thank You

Questions?

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