Challenges in the Measurement of Dissolved Gases in Water Samples from Shale Plays

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BACKGROUND

- Measurement of dissolved gases is a key component of predrill and ongoing monitoring activities in shale plays.
- Advent of shale plays circa 2008 utilized the only SOP, RSK-175, to determine dissolved gases (specifically methane).
- RSK-175 was developed by Robert S. Kerr Environmental Research Laboratory, EPA, Ada, OK.
- Primary focus of this method was to determine dissolved gas formation due to biodegradation of organic components in GW wells.
- **RSK-175 IS NOT A PROMULGATED EPA METHOD.**
- **There are no EPA promulgated methods as of this date.**
- In recent years, PA DEP developed additional methods, PA DEP 3686 and PA DEP 9243.
- ASTM workgroup under the D-19 committee has a single lab validated method, ASTM D8028.
- Many laboratories utilize RSK-175 for measuring dissolved gases. A few laboratories utilize the PADEP and ASTM 8028.
- RSK-175 employs headspace creation, equilibration of the headspace by utilization of a shaker followed by GC/FID analysis. (Figures 1 and 2)
- Variations in data from laboratory to laboratory as there is no standardized method.
- Standards utilized are typically gas phase standards.
- Water based standards are being validated by a commercial vendor (LGC) utilizing a commercial laboratory network (TestAmerica).
- No commercially available proficiency test samples in the industry.
- In order to understand the variations in measurements, the Marcellus Shale Coalition member group initiated a study to understand the variations from laboratories and to ultimately formulate a method; validate and seek approval by the USEPA.
- Three phases of the study have been completed. The phase 3 study results are forthcoming.
- This presentation examines the data for Laboratory Method Blanks and Laboratory Control Spike data from three laboratories (Lab A, Lab B and Lab C).
- All three laboratories utilized the RSK-175 method.
- Methane data is the focus of this presentation.

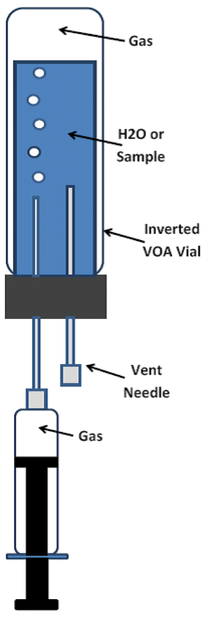


Figure 1 Headspace Creation

DISCUSSION AND DATA PRESENTATION

- Lab A – RSK-175 > Headspace creation > gas standards > manual injection of headspace gas > GC/FID analysis.
- Lab B – RSK-175 > Headspace creation > gas standards > manual injection of headspace gas > GC/FID analysis.
- Lab C – RSK-175 > Headspace creation > gas standards > headspace analyzer > GC/FID analysis.
- Techniques were slightly different in all three labs even though the same method is cited.
- GC Columns were different in all three labs. Lab C utilized a dual column approach.
- Headspace creation and equilibration techniques were slightly different.
- Data presented herein extends from November 1, 2017 through February 28, 2018.

Method Blank (MB) Data

- Method Blank data for Lab A, Lab B and Lab C is presented in Table 1.
- Lab A did not detect any methane in the blanks above MDL (method detection limit) or RL (reporting limit).
- Lab B detected methane in some blanks as noted in Table 1 below.
- Lab C detected methane in some blanks with the highest value detected at MDL as noted in Table 1 below.

Laboratory Control Spike (LCS) Data

- All labs performed Laboratory Control Spike and LCS Duplicate (LCSD) data.
- The LCS/LCSD recovery criteria for Lab A, Lab B and Lab C are 85-115%, 85-115% and 75-125% respectively. The RPD limits for all labs are +/- 20 %.
- Percent recovery data and relative percent difference (RPD) between the LCS/LCSD for methane are presented as histograms.
- The LCS/LCSD data for Lab A is presented in Table 2.
- The RPD data for Lab A is presented in Table 3.
- The LCS/LCSD data for Lab B is presented in Table 4.
- The RPD data for Lab B is presented in Table 5.
- The LCS data for Lab C is presented in Table 6.
- Lab C data was generated using the dual column approach and there were very few sets for of LCS/LCSD for RPD comparisons.

Figure 2 Equilibration of Samples

Table 1: Method Blank Data for Lab A, Lab B and Lab C

Laboratory	Conc. (mg/L)	MDL	RL	No. of data points
Lab A	None detected	0.0022	0.005	78
Lab B	Mean= - 0.00087 Max= 0.0035	0.0005	0.001	33
Lab C	Mean= 0.000033 Max= 0.0002	0.0002	0.005	152

Table 2: Lab A LCS/LCSD % Recovery for Methane

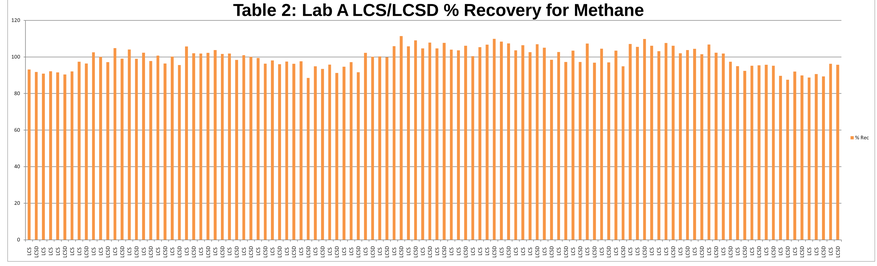


Table 3: Lab A LCS/LCSD %RPD

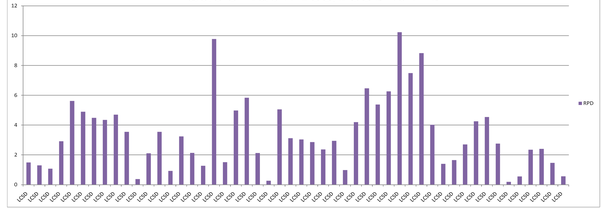


Table 4: Lab B LCS/LCSD % Recovery for Methane

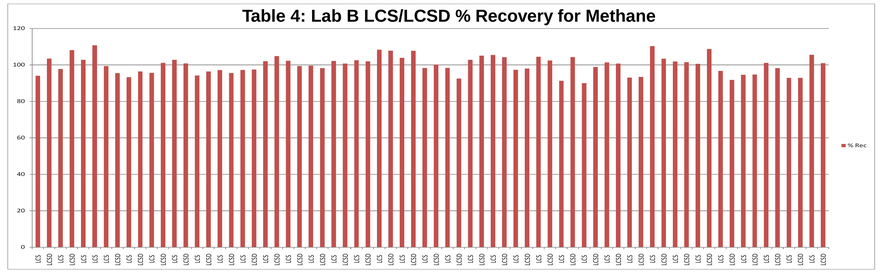


Table 5: Lab B LCS/LCSD % RPD for Methane

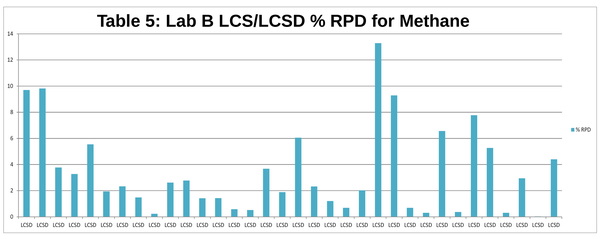
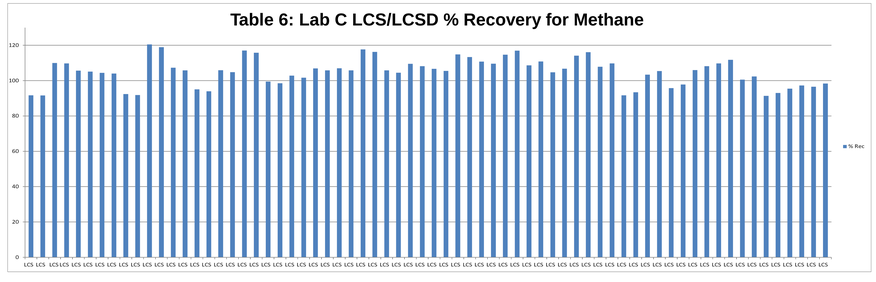


Table 6: Lab C LCS/LCSD % Recovery for Methane



Conclusion

- The data for Lab A and B show that, higher the recoveries the greater are the % RPD.
- Although there are technique variations between laboratories the LCS/LCSD recoveries meet QC limits established by each laboratory. The limits for Lab A and B are 85-115 %, whereas Lab C has a wider limit of 75-125%.
- Lab C data shows that the % recoveries for the pairs from the dual columns are very similar. Majority of the % recoveries are greater than 100%.
- The method blank data is relatively clean and below the RL's and in case of detects in Lab B and Lab C they are at the MDLs.
- There is a definite need for a validated method once the analytical variations are addressed.
- Once method variations are addressed, sampling variations can be tackled.

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