ASTM WK 43267
Standard Test Method for Dissolved Gases

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Rationale

- Hydraulic Fracturing is becoming more and more common.
- Nearby water well can be affected during the “fracking” process.
- There is no standardized method for the determination of dissolved gases in water.

Rationale

- The most common method for testing for dissolved gases is RSK-175.
- The RSK-175 procedure is a standard operating procedure, not a formal method.
- There have been assorted interpretations and modifications of RSK-175 in order to determine the amount of gas dissolved in the water.

RSK-175 Summary

- Displace 10% of the sample volume with high purity helium
- Shake the sample for 5 minutes
- Inject the headspace of the sample onto the GC
- Detection performed by a Thermal Conductivity Detector (TCD) or Flame Ionization Detector (FID).
- Concentration calculated using the Henry's Constant, the headspace volume versus the sample vial volume, and the temperature of the sample

WK 43267

Standardizes the method for the determination of dissolved gases in water.

Gases:

- Methane
- Ethane
- Ethylene
- Propane

Calibration Approach

- Saturate water with the gas to be analyzed
- Perform a serial dilution of the saturated water in order to establish a calibration curve.
- Note: By saturating the water with the gas, there is no need to back calculate the gas concentration using the Henry's constant.

Dissolved Gas Solution Preparation

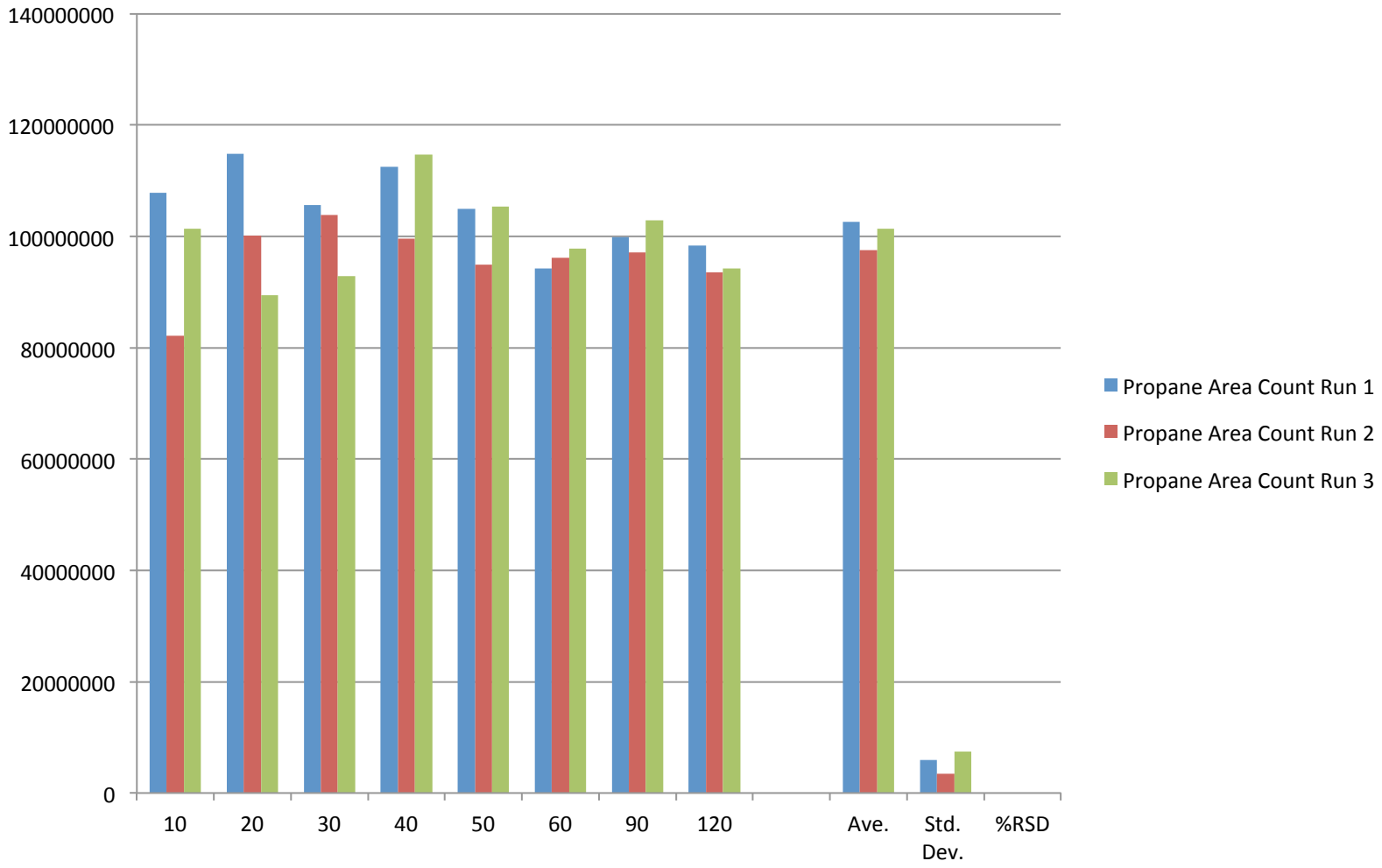
- Order high purity gases from gas supplier
- Fill 500ml volumetric flask with DI water
- Prepare 20°C recirculating water bath
- Place volumetric flask in water bath and let the DI water come to the 20°C temperature.
- Purge water at 200 to 250ml/min gas flow in volumetric flask with the high purity gas for 30 minutes for full saturation

Saturation Time Study

Using the procedure outlined previously

- Deionized water was purged with the designated gas for two hours at 20°C with samples taken from the solution every 10 minutes for the first hour and every 30 minutes for the second hour.
- The samples were then sampled and analyzed for the respective compound area counts to determine when the gas had saturated the water solution.

Propane Saturation Time Results



Dissolved Gas Solution Concentrations

Saturated Gas Concentrations:

- Methane 23.2 mg/L at 20°C
- Ethane 62.0 mg/L at 20°C
- Ethylene 149.0 mg/L at 20°C
- Propane 76.7 mg/L at 20°C

Concentrations Referenced from Lange's Handbook of Chemistry, 14th edition and encyclopedia.airliquide.com

Dissolved Methane Curve Preparation

Saturated Methane Gas Solution Curve Preparation at 20°C		
Standard	**Amount**	**Final Concentration**
Saturated Solution	50ml	11600µg/L
Saturated Solution	25ml	5800µg/L
Saturated Solution	5ml	1160µg/L
Saturated Solution	1ml	232µg/L
Saturated Solution	500ul	116µg/L
Saturated Solution	100ul	23µg/L
Saturated Solution	25ul	6µg/L

*Samples Prepared in a 100ml Volumetric Flask

Curve Ranges

- Methane 6 to 11600 µg/L
- Ethane 6 to 5000 µg/L
- Ethylene 6 to 5960 µg/L
- Propane 8 to 5500 µg/L

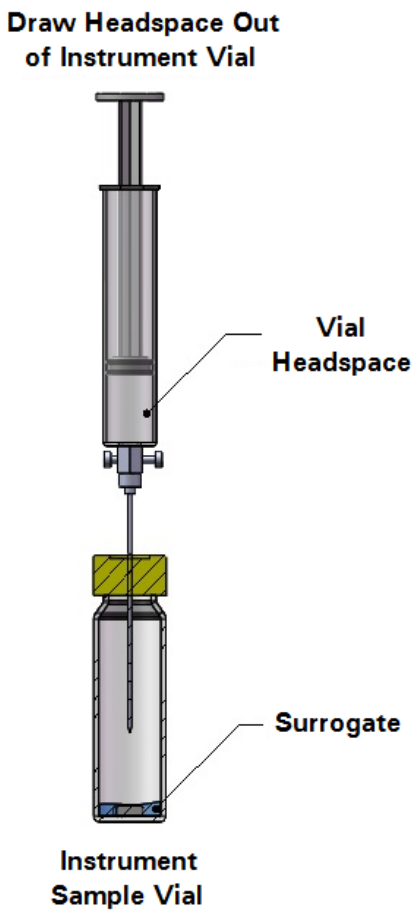
GC/FID Experimental Parameters

GC/FID	Agilent 5890
Inlet Temperature	250°C
Inlet Pressure	9psi
Gas	Helium
Inlet	Split/Splitless
Split Ratio	20:1
Column Flow	14.33ml/min
Column	Restek RT Q-bond 30m x 0.53mm x 20µm
Oven Program	45°C hold for 1 minute, ramp 16°C/min to 180°C hold for 1.06 min, 10.5 min total runtime
FID Temperature	250°C

Sampling Process

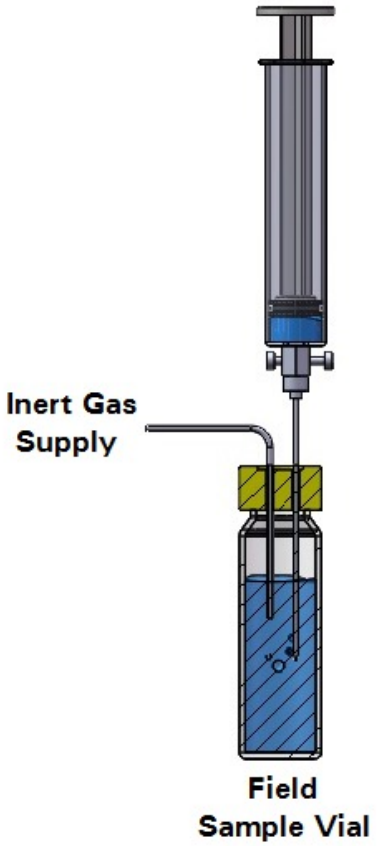
- Saturated gas calibration standards or dissolved gas samples
- Displace a volume of saturated gas standard
- Heat and mix the standard
- Inject an aliquot of the headspace on GC/FID for separation and analysis.

Step 1– Instrument Vial Preparation



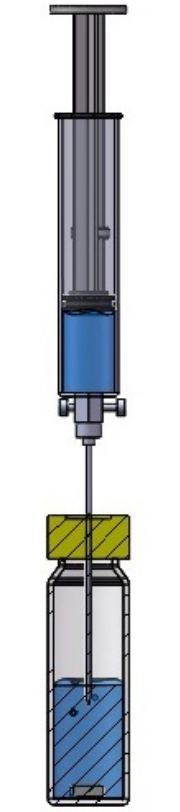
- Place a stir bar into an empty sampling vial.
- Sweep vial with nitrogen gas.
- Using a gas tight syringe spike the vial with surrogate and cap vial.
- Pull a volume of air from the sampling vial with 25ml syringe fitted with a luer lock needle leaving the luer lock needle in the vial septa and removing only the syringe thus insuring the integrity of the sample vial. Note: Volume of air removed to be the equivalent of volume of sample to be added

Step 2—Sampling from Vial



- Bring sample or standard vial to room temperature.
- Insert gas tight syringe with luer lock needle into the sample vial.
- Purge vial with an inert gas in order to pull a volume of sample into the syringe.

Step 3—Transferring Sample for Headspace Analysis



Instrument
Sample Vial

- Transfer sample into the prepared vial for sample agitation and headspace sampling.
- Take a 1ml aliquot of the headspace and inject it into the GC/FID for separation and analysis.

Sample/Standard Storage

- Samples collected in clean 40ml vials with butyl rubber septa
- Filled to volume with no headspace
- Stored at approximately 6°C
- Expire after 7 days with no preservative or 14 days if preserved with sulfuric acid
- Samples collected in duplicate
- Careful to minimize sample agitation during sampling and transport

Preservation Study

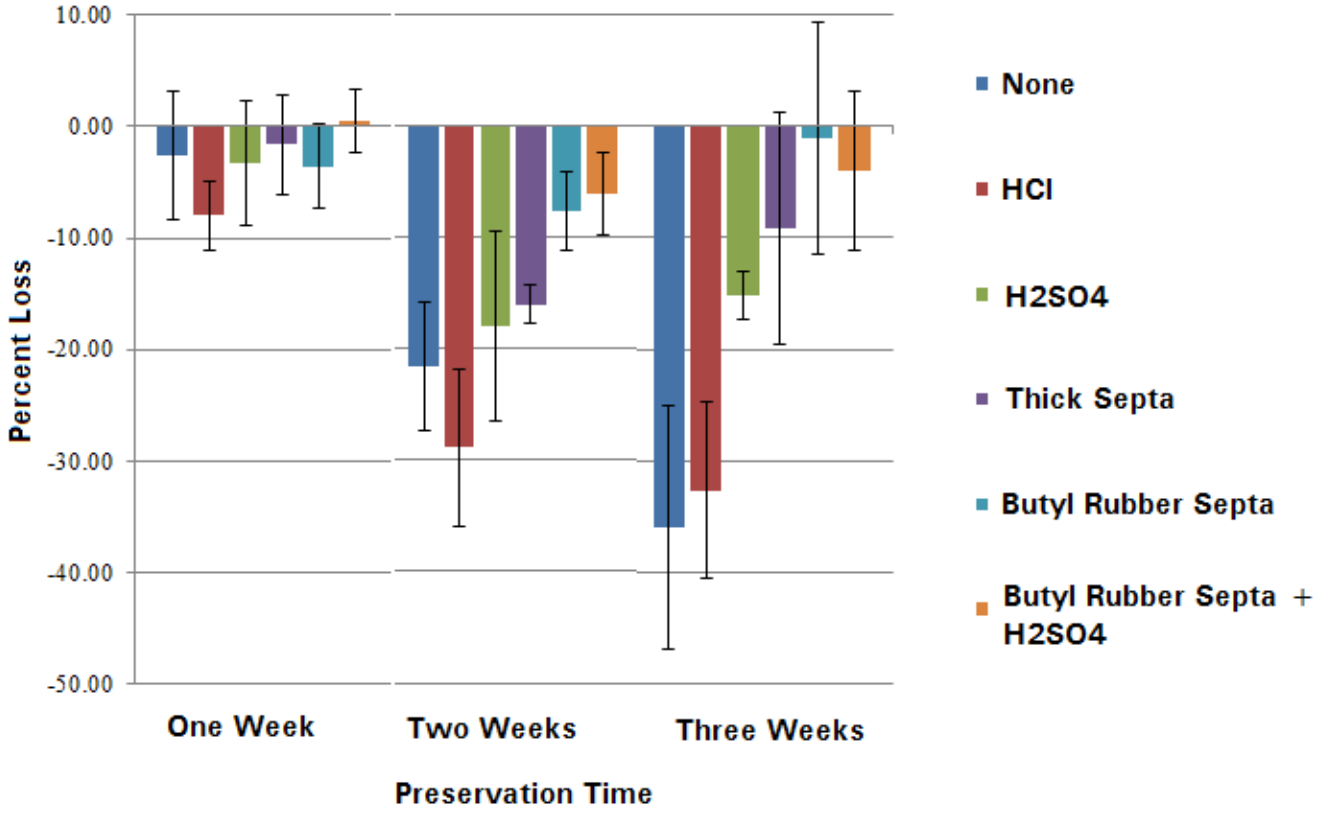
- Methane Standards Prepared at 5800ug/L in replicates of five
- Each set of replicates was preserved differently
- Preserved samples were run for initial results and then stored for 4 weeks with a standard run once a week to account for analyte loss

Preservation Study Results

Preservation Scheme	Ave. % Lost in One Week	Std. Dev. One Week	Ave. % Lost in Two Weeks	Std. Dev. Two Weeks	Ave. % Lost in Three Weeks	Std. Dev. Three Weeks
None	-2.59	5.68	-21.59	5.77	-35.94	10.93
HCl	-8.01	3.06	-28.88	7.09	-32.59	7.81
H2SO4	-3.32	5.56	-18.02	8.53	-15.16	2.19
Thick Septa	-1.61	4.47	-16.07	1.72	-9.14	10.42
Butyl Rubber Septa	-3.55	3.75	-7.60	3.53	-1.10	10.36
Butyl Rubber Septa + H2SO4	0.55	2.86	-6.10	3.71	-4.01	7.19

EST analytical

Preservation Study Results



Curve Requirements

- Curves to be 5 points minimum
- Low point on the curve needs to be at or below laboratory quantitation limit
- Curve should bracket the linear range of the instrument
- Curve should be linear with better than 0.995 linear regression

Quality Control

- Initial demonstration of low system background must be done before any samples are analyzed
- Background subtraction may be done, if it is proven that a consistent amount of background contamination exists in the method blanks

Quality Control

- Method Blank for compound analyzed
- Calibration verification every 12 hours, alternating a mid-range standard and a low range standard, calibration standard to pass, +/-30% for mid range and +/-50% for low range, verification needs to be done for every compound to be analyzed
- Surrogate needs to pass +/-30% of expected for standards, blanks and samples

Quality Control

- LCS/LCSD used in lieu of MS/MSD
- LCS/LCSD should be at or around the mid-point of the curve with recoveries to be +/-30% of expected
- LCS/LCSD needs to be demonstrated for each analyte tested
- LCS/LCSD needs to be done for every 20 samples tested or one batch

Precision and Bias

- A single lab participated in the study
- Tested six levels of each compound
- Ten replicates of each level
- All samples spiked with surrogate

Precision and Bias

- At the time of the study, there was no accepted reference material, for determining the bias for the dissolved gases in the method.
- Bias for the surrogate was less than 10% for the single lab study.
- The single lab study produced an approximate 95% probability of correct results.

Repeatability Limit Methane

Analyte	Average	Repeatability Standard Deviation	Repeatability Limit	Percent Relative Standard Deviation	Percent Recovery
Methane-46	36.53	3.40	9.52	8.83	79.41
Methane-116	100.68	5.97	16.72	5.63	86.79
Methane-232	204.88	15.88	44.47	18.25	93.63
Methane-1160	1026.22	65.77	184.15	6.08	88.47
Methane-5800	4676.24	298.39	835.48	6.05	80.62
Methane-9280	7563.47	521.05	1458.93	6.54	81.50
Surrogate-500	489.99	25.19	70.53	4.88	98.00

Repeatability Limit Ethane

Analyte	Average	Repeatability Standard Deviation	Repeatability Limit	Percent Relative Standard Deviation	Percent Recovery
Ethane-32	32.30	1.16	3.25	3.41	100.94
Ethane-64	75.20	7.32	20.48	9.23	121.29
Ethane-310	284.00	23.34	65.36	7.80	91.61
Ethane-1250	1063.40	98.96	277.09	8.83	85.07
Ethane-3100	3224.50	342.81	959.87	10.09	104.02
Ethane-4380	4198.40	201.00	562.81	4.54	95.85
Surrogate-500	462.70	32.97	91.49	6.70	92.54

Repeatability Limit Ethylene

Analyte	Average	Repeatability Standard Deviation	Repeatability Limit	Percent Relative Standard Deviation	Percent Recovery
Ethylene-30	25.80	4.50	12.70	16.54	85.93
Ethylene-60	59.20	4.60	13.00	7.43	98.67
Ethylene-238	227.80	25.90	72.50	10.78	95.71
Ethylene-1190	1036.80	138.80	388.80	12.70	87.13
Ethylene-2980	2337.60	155.00	434.00	15.67	88.39
Ethylene-4470	3857.90	494.00	1383.20	12.15	86.31
Surrogate-500	537.50	57.30	160.50	10.12	107.50

Repeatability Limit Propane

Analyte	Average	Repeatability Standard Deviation	Repeatability Limit	Percent Relative Standard Deviation	Percent Recovery
Propane-40	32.70	4.81	13.46	13.95	81.75
Propane-196	188.90	32.58	91.21	16.36	96.38
Propane-790	753.60	108.31	303.28	13.64	95.39
Propane-1200	1180.40	123.51	345.82	9.93	98.37
Propane-2400	2211.00	216.01	604.83	9.27	92.13
Propane-4700	5007.90	285.11	798.30	5.40	106.55
Surrogate-500	525.90	42.04	117.71	7.58	105.18

Current Status

- Work Item has been submitted to Subcommittee Ballot for approval
- New revision to be re-balloted
- Working with Commercial Company to try and develop Certified Reference Materials

References

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3. ConocoPhillips Company, *Drilling and Completion,* Retrieved January 20, 2012, from http://www.powerincooperation.com/en/pages/drilling-and-completion.html

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5. EPA New England, *Technical Guidance for the Natural Attenuation Indicators: Methane, Ethane, and Ethene.* Revision 1, July, 2001.

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THANK YOU . . . QUESTIONS

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