Dissolved Gas Determination Using the D-19 ASTM Method

Application Note

Environmental

Author

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Abstract

In recent years, there has been a marked increase in hydraulic fracturing or "fracking" in order to recover natural gas from deep beneath the earth's surface. As a result of this drilling, there has also been a rise in the concern of gases escaping during the "fracking" process and contaminating nearby water sources. In order to test for possible dissolved gas contamination, most laboratories refer to a standard operating procedure entitled "RSK-175". This procedure calls for static headspace sampling of the water samples and calculating the amount of dissolved gas using Henry's Constant. However, as RSK-175 is a standard operating procedure and not a formal method, interpretations can vary. In order to address this issue, a formal method is currently being written by American Society for Testing and Materials (ASTM) Committee D-19. This application will test for dissolved gases using the procedures established in the ASTM method.

Introduction:

The Robert S. Kerr (RSK) 175 Standard Operating Procedure (SOP) has been the primary reference for the sampling and analysis of dissolved gases. This procedure involves displacing ten percent of the sample volume, shaking the sample for five minutes and taking an aliquot of the headspace for injection onto the Gas Chromatograph (GC) column for separation. A Flame Ionization Detector (FID) is then used for analysis. The calibration curves are done using dilutions of a pure gas injected onto the GC column. Since the calibration curve is a gas standard and the samples are the headspace of a water matrix, the final dissolved gas concentration results must be calculated using the Henry's Constant.

The use of Henry's constant in order to determine the concentration of the gas in the water solution can sometimes be confusing. The calculation is complicated and if interpreted incorrectly, the concentration of the dissolved gas in the sample would be incorrect. In order to rectify this problem, the ASTM method removes the calculation from the analysis process. This is done by diluting a saturated gas solution in order to prepare the five point calibration curve. The sampling of the dissolved gases in the water is similar to what is described in the RSK-175 procedure. Thus, by performing the calibration this way, there is no need to calculate the sample concentration using the Henry's Constant as both the calibration and the field sample testing are achieved in the exact same manner.

EST Analytical has developed an autosampler, the LGX50, with a patented sampling process that automates the entire process of testing the headspace of dissolved gas samples. In automating this process, the sample integrity is ensured as there is no need to open the samples during the entire sampling procedure. Furthermore, the surrogate requirement of the ASTM method can be added during the sample transfer, thus ensuring accurate, reproducible surrogate recoveries. This examination will test for the four dissolved gases described in the ASTM method following the procedures required.

Experimental:

The instrumentation used for this analysis was an EST Analytical LGX50 Autosampler and an Agilent 7890 GC/FID. The LGX50 was affixed with a one milliliter headspace loop while the GC had a Restek QS Bond 30m x 0.53mm x 20μm column installed. A 500ppm standard of deuterated methyl tert-butyl ether was prepared and added to the internal standard vessel for automated surrogate spiking. The sampling and analysis parameters are listed in Tables 1 and 2 respectively.

LGX50 Autosampler Parameter	Dissolved Gas Settings
Sample Type	DGA
Sample Fill Mode	Loop
Sample Volume	20ml
Syringe Prime	3 sec.
Syringe Needle Rinse	20ml
Rinse Cycles	On/1
Sample Temperature	60°C
Stirrer	On/Medium
Sample Equilibration Time	10 min.
Vial Pressurization Time	5 sec.
Loop Fill Time	5 sec.
Loop Equilibration Time	5 sec.
Valve Temperature	65°C
GC Line Temperature	85°C
GC Cycle Time	15 min.
Rinse Water Temperature	65°C
IS	10μl

Table 1: LGX50 Autosampler 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

Table 2: GC/FID Experimental Parameters

High purity gases were procured from a local gas supplier. The saturated concentration of each gas was established at 20°C. Next, a 500ml volumetric flask was filled with de-ionized water and placed in a recirculating bath. The water was allowed to cool to 20°C and, once cooled, the pure gas was purged into the water for 30 minutes at a rate of 200ml/min using a flexible piece of Tygon tubing and a fritted water filter. Next, a serial dilution of the saturated gas solution was prepared in order to make the calibration standards. These steps were repeated for each gas being tested. Tables 3 through 6 describe the calibration curve preparation.

Saturated Methane Gas Solution Curve Preparation at 20°C		
Standard	Amount	Final Concentration
Saturated Solution	50ml	11.6ppm
Saturated Solution	25ml	5.8ppm
Saturated Solution	5ml	1.16ppm
Saturated Solution	1ml	232ppb
Saturated Solution	500ul	116ppb
Saturated Solution	100ul	23ppb
Saturated Solution	25ul	5.8ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 3: Methane Curve Preparation

Saturated Ethylene Gas Solution Curve Preparation at 20°C		
Standard	Amount	Final Concentration
Saturated Solution	4ml	5.96ppm
Saturated Solution	2ml	2.98ppm
Saturated Solution	800ul	1.19ppm
Saturated Solution	160ul	238ppb
Saturated Solution	40ul	60ppb
Saturated Solution	10ul	15ppb
Saturated Solution	4ul	6ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 4: Ethylene Curve Preparation

Saturated Ethane Gas Solution Curve Preparation at 20°C		
Standard	Amount	Final Concentration
Saturated Solution	8ml	5.0ppm
Saturated Solution	5ml	3.1ppm
Saturated Solution	2ml	1.25ppm
Saturated Solution	500ul	312ppb
Saturated Solution	100ul	62ppb
Saturated Solution	25ul	15ppb
Saturated Solution	10ul	6ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 5: Ethane Curve Preparation

Saturated Propane Gas Solution Curve Preparation at 20°C		
Standard	Amount	Final Concentration
Saturated Solution	7ml	5.5ppm
Saturated Solution	3ml	2.4ppm
Saturated Solution	1.5ml	1.2ppm
Saturated Solution	500ul	390ppb
Saturated Solution	200ul	156ppb
Saturated Solution	50ul	40ppb
Saturated Solution	10ul	8ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 6: Propane Curve Preparation

After a linear curve was established for each gas, Method Detection Limits (MDLs) and Demonstration of Capability (DOC) were performed in order to evaluate the limits and the precision and accuracy of the curves. The MDLs were done by preparing and sampling seven replicate low standards and calculated according to 40CFR Part 136, Appendix B. The DOCs were done by running four replicate standards and evaluating percent recovery and the percent relative standard deviation of the results. Table 7 lists the experimental results for each gas while Figure 1 displays a chromatographic overlay of each gas at the calibration curve mid-point. Finally, a series of 20 blank samples were run in order to test the surrogate addition precision and accuracy at 500ppb, see Figure 2.

Individual Gas Results							
Compound	Curve Range	Curve R²	MDL Spike Level (µg/L)	MDL (µg/L)	Precision Spike Level (µg/L)	Precision (% Recovery)	Accuracy (%RSD)
Methane	5.8 to 11600µg/L	0.997	5.80	2.68	1600.00	97.80	4.07
Ethane	6.0 to 5000µg/L	0.999	6.00	1.47	3100.00	94.56	6.64
Ethylene	6.0 to 6000µg/L	0.999	6.00	1.08	2980.00	89.66	4.61
Propane	8.0 to 5500µg/L	1.000	8.00	1.17	2400.00	96.82	7.69

Table 7: Dissolved Gas Results Summary

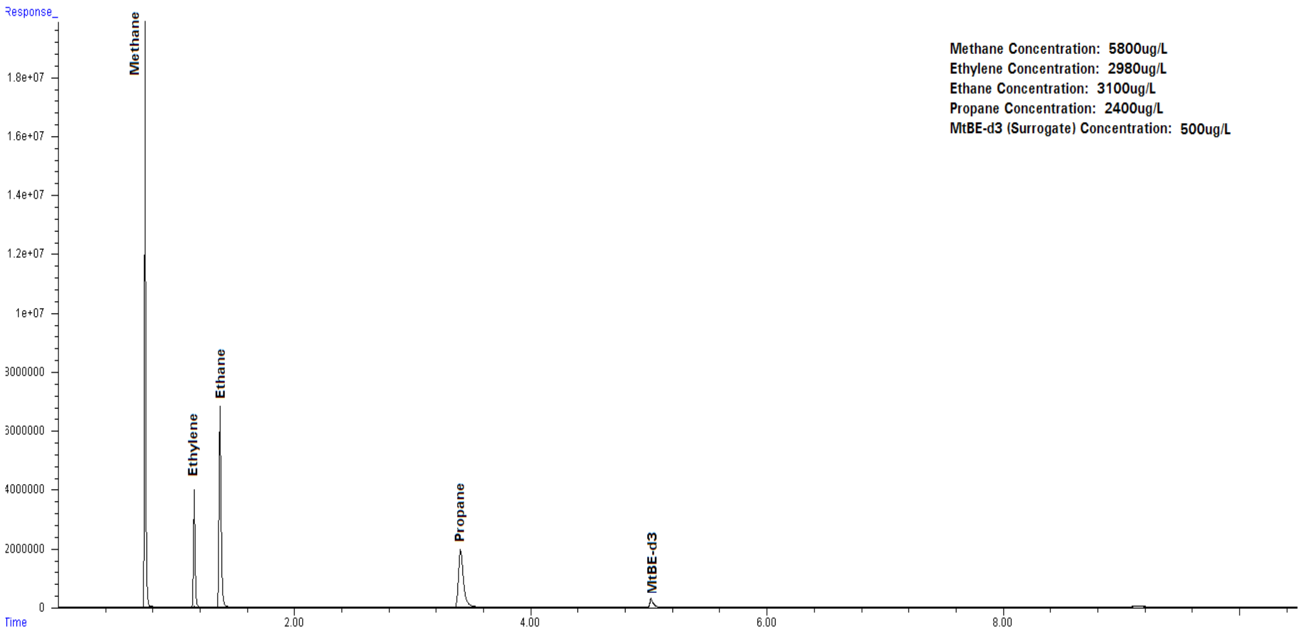

Figure 1: Overlay of Dissolve Gas Chromatograms

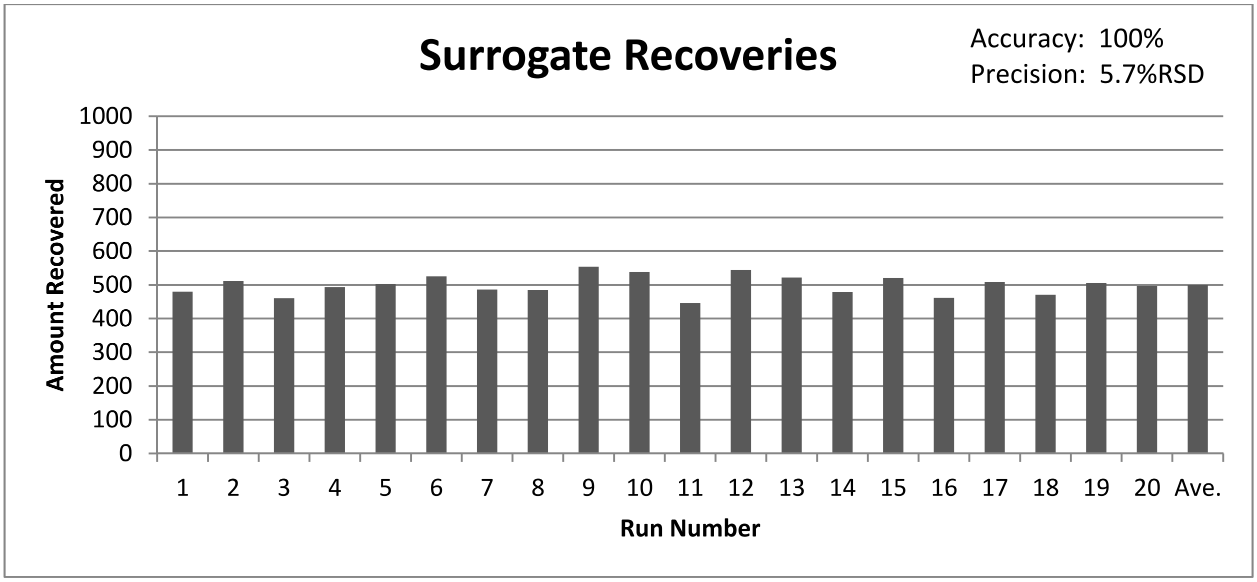

Figure 2: Surrogate Precision and Accuracy Results

Conclusions:

The LGX-50 automated the entire sampling process of the ASTM D-19 method. The dissolved gas curves were all linear with a regression of 0.997 or better. Furthermore, the system showed a 90% or better recovery for all of the gases at the mid-point of the curves and a precision of better than 8%. Finally, the surrogate addition over 20 blanks showed an average percent recovery of 100% with a better than 6% precision. The system met all of the ASTM method requirements and would provide any laboratory an excellent system for the sampling of dissolved gases.

For More Information

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